

Tetrachalcogenafulvalenes, Metal 1,2-Dichalcogenolenes and Their Conducting Salts

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CHAPTER 3

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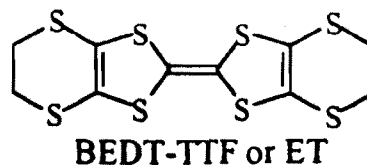
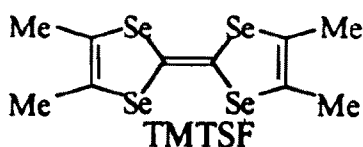
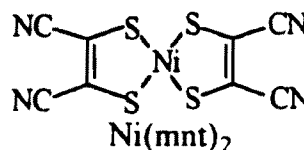
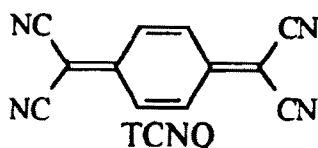
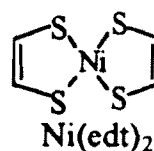
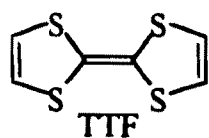
1 INTRODUCTION

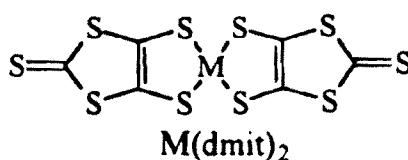
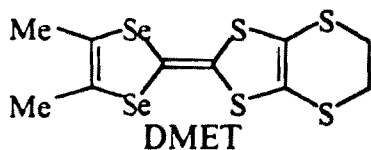
Tetrathiafulvalene (TTF) is one of the simplest symmetrical tetrachalcogenafulvalenes. It was synthesized for the first time in 1970 [1]. However, some substituted derivatives, such as dibenzotetrathiafulvalene had been synthesized some years before [2]. The Se analog, i.e., tetraselenafulvalene (TSF) [3], and the Te analog, i.e., tetratellurafulvalene (TTeF) [4], are two other of the simplest symmetrical tetrachalcogenafulvalenes that have also been prepared. Nickel, bis[1,2-ethylenedithiolate (2-)-*S,S'*]-, abbreviated as Ni(edt)₂, is one of the simplest (symmetrical) metal 1,2-dichalcogenolenes. The difference, in comparison to TTF, is that the double central bond of TTF is replaced by Ni. It was synthesized for the first time in 1964 [5]. However, some substituted derivatives had been known some years before [6,7]. A number of tetrachalcogenafulvalenes and metal 1,2-dichalcogenolenes had been prepared after the discovery of electrical conductivity in charge-transfer complexes (CTCs) [8] of some polycyclic aromatic compounds (π -donors) with bromine or iodine [9,10] and after the suggestions from the authors of refs. [10] that CTCs of sulfur containing aromatic systems could be good conductors. Indeed, CTCs of TTF with bromine, chlorine etc. were found to be good conductors [11]. Also, CTCs of TTF with organic π -acceptors, such as 7,7',8,8'-tetracyanoquinodimethane (TCNQ), or metal 1,2-dichalcogenolenes, such as Ni(mnt)₂, where mnt is maleonitriledithiolate were found to be good room temperature conductors (see [12] and [13], respectively).

Some of these salts are metallic and undergo metal to insulator transition at low temperatures. Also, the symmetrical π -donor molecules, tetramethyltetraselenafulvalene (TMTSF) and bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF or ET) were found to give a large number of conducting materials, i.e., radical cation salts [8] and CTCs, some of which undergo metal to superconducting transition (T_c) at low temperatures [14,15].

The first organic superconductor, (TMTSF)₂PF₆ [14], with critical temperature $T_c = 1.4$ K under a pressure of 6.5 kbar, was discovered in 1980. The first organic superconductor based on ET, i.e., (ET)₂ ReO₄ [15], with $T_c = 2$ K under 4 kbar pressure was discovered in 1982. The salts based on TMTSF (Bechgaard salts) are quasi-1-dimensional (q-1D) conductors, while salts based on ET are quasi-2-dimensional (q-2D) conductors, because of the strong in-plane intermolecular interactions due to S...S contacts. Some unsymmetrical molecules, such as 3,4-dimethyl-3',4'-ethylenedithio-2,5-diselena-2',5'-dithiafulvalene (DMET) and methylenedithiotetrathiafulvalene (MDTTTF) give superconducting salts (see [16] and [17], respectively).

In the early 1980s, salts based on M(dmit)₂ complexes, with M = Ni, Pd, Pt and dimercaptoisotrithione (dmit) as ligand (charge-transfer or cation deficient complexes), such as (TTF)Ni(dmit)₂ and (Bu₄N)_{0.25}Ni(dmit)₂ were found to be conducting materials [18] and some of them such as TTF[Ni(dmit)₂]₂ found to be superconductors at low temperatures [19]. However, since 1990, κ -(ET)₂Cu[N(CN)₂]Cl remains the highest T_c superconducting material based

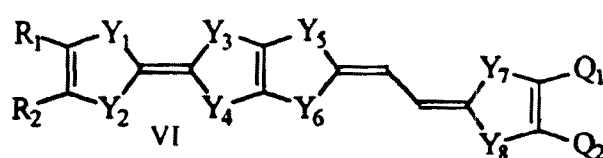
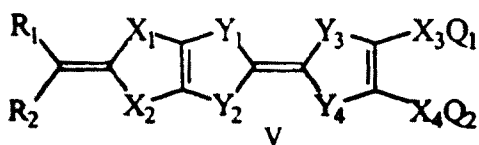
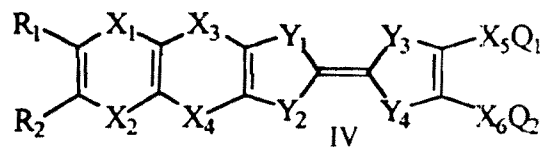
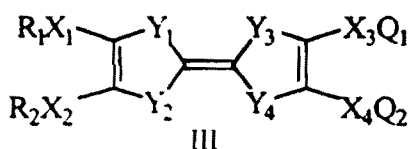
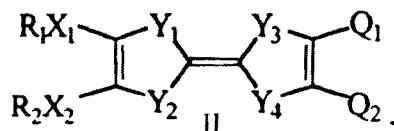
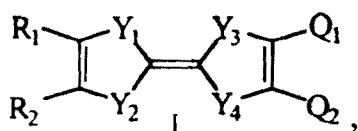




on organic molecules (ET), with $T_c = 12.8$ K under 0.3 kbar [20].

During the last 25 years a number of tetrachalcogen-fulvalenes and metal 1,2-dichalcogenolenes as well as a large number of their conducting salts have been prepared and studied. In our attempts to obtain new 2D conductors and superconductors, a number of these compounds have been prepared and studied at our Institutes. The field of tetrachalcogen-fulvalenes, metal 1,2-dichalcogenolene and their conducting salts has been well covered by books and review articles [21–38] through the 1970s and early 1990s. Also, a number of brief review articles have appeared in conference proceedings [39–46]. Because of the number of works in this area through the literature of 1970–1990, this paper will concentrate on more recent advances on new compounds. Where necessary, for reasons of completeness or historical importance, earlier works are cited. The coverage of the last sections of this paper is limited to conducting materials based on simple tetrachalco-

gen-fulvalenes and metal 1,2-dichalcogenolenes with O, S, Se, Te, N as additional heteroatoms, namely in compounds of the formulae I–IV where $X_i = O, S, Se, Te, N$; $Y_i = S, Se$; $R_i, Q_i =$ alkyl groups, as well as on the corresponding (symmetrical) metal 1,2-dichalcogenolenes, where the central C=C bond of tetrachalcogen-fulvalenes is replaced by Ni, Pd, Pt etc. Also, some information is given for materials based on larger molecules, such as V, VI and the corresponding metal 1,2-dichalcogenolenes as well as the metal complexes, including the Ni, Pd etc. atoms, are coordinated with the edge heteroatoms of the above molecules. It should be noticed that some related review articles appearing in this volume give mainly information on the physical properties of the individual materials: The structural and physical properties of conducting and superconducting metal 1,2-dithiolenes are reported by Kobayashi and Kobayashi [47a]. Nakamura [47b] surveys electrically conducting Langmuir–Blodgett films, some of which are based on tetrathiafulvalenes



and metal 1,2-dithiolenes. Finally, the properties of some perylene-metal 1,2-dithiolenes are reviewed by Almeida and Henriques [47c].

2 PREPARATION AND PROPERTIES OF PRECURSORS

In this section the preparation and the chemical and physicochemical properties of tetrachalcogenafulvalenes and metal 1,2-dichalcogenolenes, which are molecular precursors (or components) of conducting materials, are described.

2.1 Starting and intermediate materials

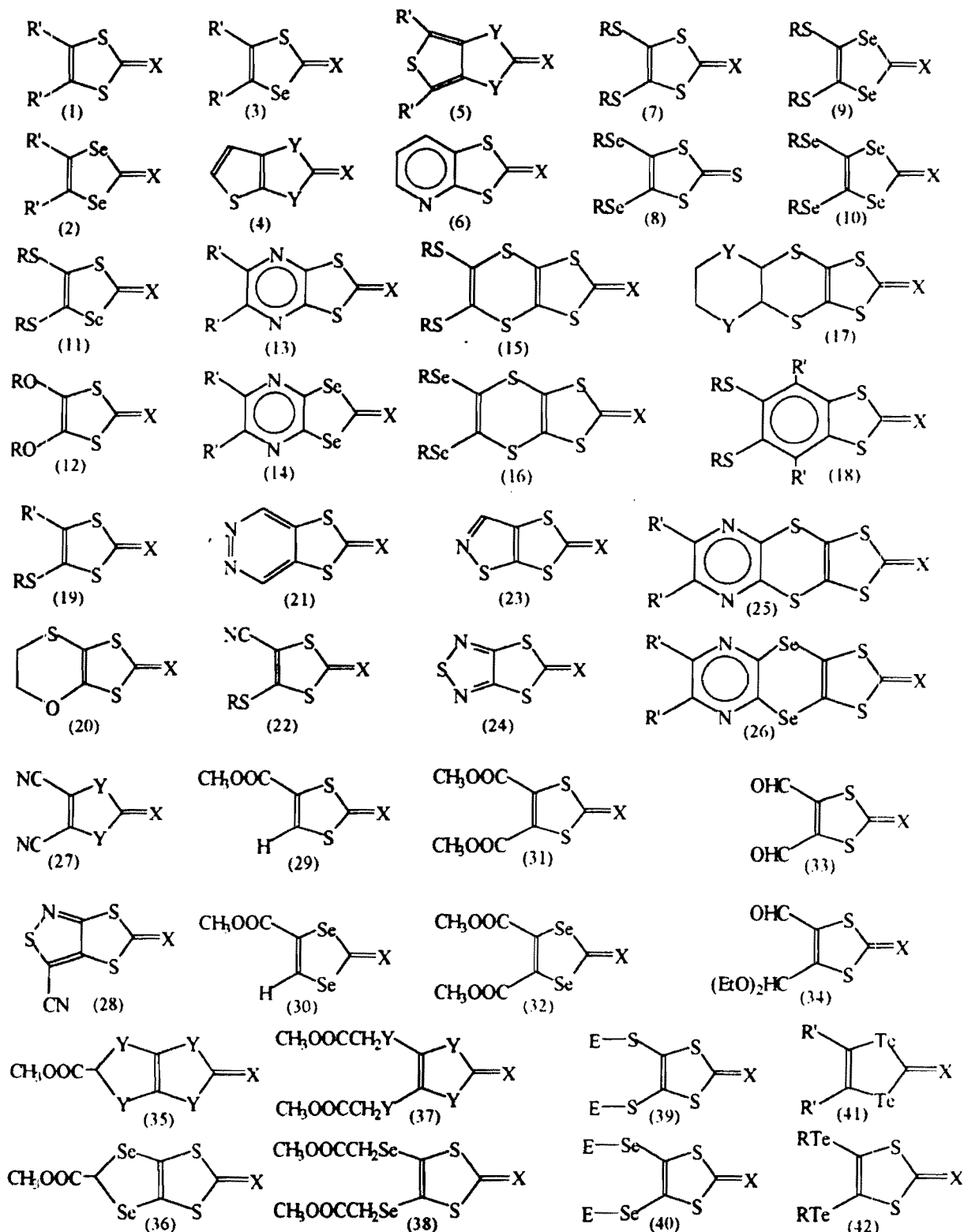
Elemental S, Se, Te and some simple sulfur containing and selenium containing compounds such as CS₂, CSe₂, H₂Se, HSCH₂CH₂SH, (Me₂N)₂C=S are used as starting materials for the preparation of tetrachalcogenafulvalenes and metal 1,2-dichalcogenolenes. Most of these starting materials are commercially available. In most preparations, the intermediate compounds, 2-oxo-1,3-dithioles, 2-oxo-1,3-diselenoles and similar compounds are obtained by several methods (see [1,3,7,16,17,25–300] and refs. cited therein). Most of the intermediate compounds contain more than one additional heteroatom (O, S, Se, Te, N). The simplest intermediate compounds are listed in Table 3.1 (where X = O, S, Se). However, (23) and Te containing compounds (41), (42) are not known. Compounds (1g'), (2g'), (1h'), (2h') (7g), (7h), (7l), (22) and (27)–(40) contain functional groups such as CN, CHO, SCH₂CH₂CN which can be transformed to other groups: a CN group can be transformed to COOH [57], a CHO group can be transformed to CH₂OH [127,130], SCH₂CH₂CN can be transformed to S[−] and then to SR [218] etc. (for details see below and [283]). Some of the intermediate compounds, such as vinylene trithiocarbonate (1a', X = S) and 4,5-dimethyl-1,3-diselenole-2-selenone (2b', X = Se), precursors of TTF and TMTSF, respectively, are commercially available. Also, some tetrachalcogenafulvalenes, such as TTF, TMTSF and ET, are commercially available.

Compounds (1), (2) and (3) have been prepared by several cyclization procedures (see [1–3,25,28,35,37,73,75,77,216,246] and refs. therein). Vinylene trithiocarbonate (1a') can be obtained in a good yield by treating potassium trithiocarbonate, KS–C(=S)–SK, with 1,2-dichloroethyl ethyl ester, ClCH₂CHCl(OEt), followed by elimination of ethanol with *p*-toluenesulfonic acid. Vinylene trithiocarbonate

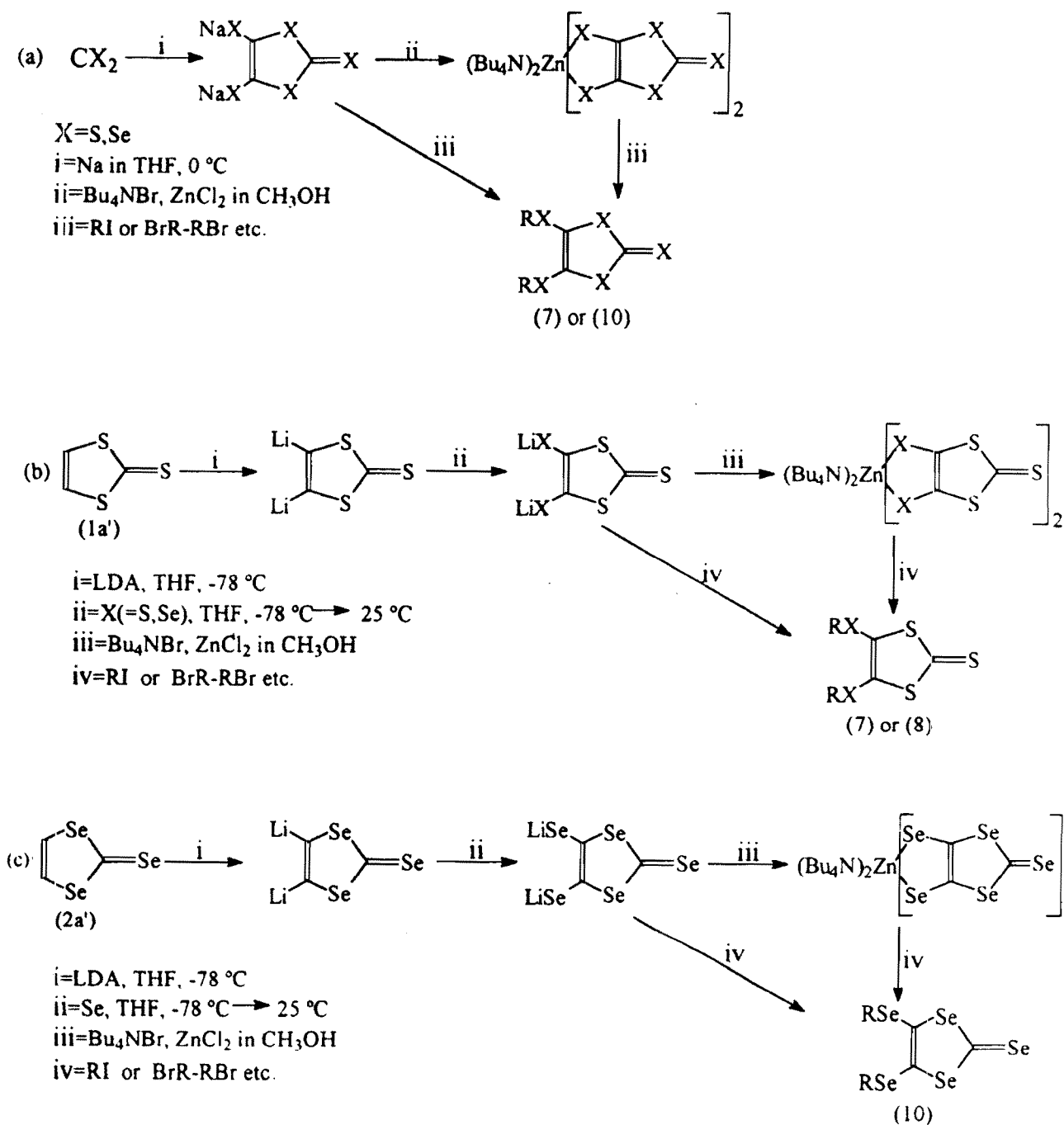
(1a') and the Se analog (2a') can be obtained in high yields from (27), (29), (30), (31) and (32) by hydrolysis and decarboxylation. Also, they can be obtained by thermolysis of 1,2,3-thiadiazoles or 1,2,3-selenathiazoles in the presence of CS₂ or CSe₂. Substituted derivatives of (1a'), (2a') and (3a') can be prepared from the corresponding β -keto-*N,N*-dialkylthiocarbonates, β -keto-*S*-alkyltrithiocarbonates and Se analogs by several different cyclization procedures, depending on the nature of R and the heteroatom, etc. Similar methods are applied for preparation of (4) [80,251] and (5) [49,251]. Compound (6) has been prepared by reaction of 1,2,3-pyrido[−4,5-*b*]thiadiazole with carbon disulfide [50,58]. Compounds (7), (8) and (10) have been prepared by treating the corresponding metal 1,2-dichalcogenolates with alkyl halides such as CH₃I, or dibromoalkanes such as BrCH₂Br or BrCH₂CH₂Br (see for example [48,53, 61, 64, 66,68,71, 76, 79, 87, 95, 100, 101, 109, 110, 118, 125, 136, 140, 157, 179, 180, 189, 194, 198, 202, 212, 237, 243,244,249]). (Bu₄N)₂Zn(dmit)₂ and (Et₄N)₂Zn(dmit)₂ are commercially available, or can be obtained by chemical reduction of carbon disulfide with Na (see for example [53,66,68]). The Se analog can be obtained by a similar method from CSe₂ [66,68]. (Bu₄N)₂Hg(dmit)₂ is obtained by electrochemical reduction of CS₂ [66,68]. They are useful materials for preparation of larger molecules (see below). Also, vinylene trithiocarbonate and the Se analog can be used for preparation of the corresponding zinc 1,2-dichalcogenolenes. Scheme 3.1 outlines the procedures for preparation of (7), (8) and (10) [64,68]. Dilithiation of materials containing a vinylene group (in which acidic hydrogen atoms are substituted by lithium) can be achieved with lithium diisopropylamide (LDA) at low temperature (−78°C). To the resulting product S or Se can be added on going from −78°C to room temperature. Then, the solid zinc 1,2-dichalcogenolates are isolated by reaction with ZnCl₂. An alternative method is used for preparation of (7c) (see [170] and refs. therein). Compounds containing vinylene group, such as (7g), are obtained in good yield from the dilithium or disodium chalcogenolates are purification through 4,5-bis(benzoylthio)-1,3-dithiole-2-thione or through oligo(1,3-dithiole-2,4,5-trithione) and Se analogs (see [68]). Details of the preparation of (7e) and (7f) are given in [93,138,249] and refs. therein. Compound (7f) can be obtained as a chiral (*S,S*-7f) or as a racemic modification.

Compounds similar to (7), (8) and (10) with 2R = Ti(Cp)₂ or 2R = SnBu₂ are prepared by reaction of metal 1,2-dichalcogenolates or disodium 1,2-dichal-

Table 3.1. Selected 1,3-dithiole-2-ones (-2-thiones, -2-selenones) and Se and Te analogs



X = O, S, Se; (a') R' = H, (b') R' = CH₃, (c') 2R' = CH₂CH₂, (d') 2R' = CH=CH-CH=CH, (e') R' = OCH₃, (f') R' = SCH₃, (g') R' = CH₂OH, (h') R' = Cl etc.; (a) R = CH₃, (b) 2R = CH₂, (c) 2R = CH₂CH₂, (d) 2R = CH₂CH₂CH₂, (e) 2R = CH(CH₃)CH₂, (f) 2R = CH(CH₃)CH(CH₃), (g) 2R = CH=CH, (h) 2R = C=O, (i) R = C₁₈H₃₇, (j) 2R = CH₂OCH₂, (k) 2R = CH₂SCH₂, (l) R = CH₂CH₂Cl, (m) 2R = CH₂CH₂CH₂CH₂, (n) 2R = CH₃C=CCH₃; (a) E = CH₂O(CH₂)₂Si(CH₃)₃, (b) E = CH₂C₆H₄Ac, (c) E = CH₂CH₂CN⁻, (d) E = COPh; (a) Y = O, (b) Y = S, for (17); (a) Y = S, (b) Y = Se, for (4), (5), (27), (35) and (37), (c) Y = Te for (5).



Scheme 3.1

cogenolates with titanocene dichloride, Ti(Cp)₂Cl₂, [78,117,125,153,252] and dibutyltin dichloride, Bu₂SnCl₂ [275,288,291], respectively. Similar materials can be prepared from the other compounds of Table 3.1. Organotin thiolates and selenolates, such as (Sn1), (Sn2), (Sn7) (Sn9) and (Sn15e) can be prepared by reaction of the corresponding 1,3-dithiole-2-ones and 1,3-diselenole-2-ones with MeMgBr (3.3 equivalents) in tetrahydrofuran (THF), followed by trapping with

Cl₂SnBu₂ at -78 °C [291]. Transmetalation of (Sn1), (Sn2), (Sn7), (Sn9) with *n*-butyllithium (2 eqv) at -78 °C, followed by treatment with methyl dichloroacetate, Cl₂HCCOOMe, affords the corresponding esters (E1), (E2), (E7), (E9) [275,291]. For the preparation of similar compounds (35) and (36) see below. These compounds can be considered as intermediate materials for preparation of larger precursors or tetrachalcogen-fulvalenes. Scheme 3.2 illustrates the preparation of

(9c, X = O) from 2,3-dihydro-1,4-dithiin through the corresponding $Ti(cp)_2$ intermediate [78], which reacts with triphosgene $(CCl_3O)_2CO$ to give (9c). A similar procedure has been applied for the preparation of (2c') [178]. Compound (11c, X = Se) can be prepared by application of well known ring-closure methods [36,37,48] as illustrated in Scheme 3.3. A similar procedure has been applied for the preparation of (3).

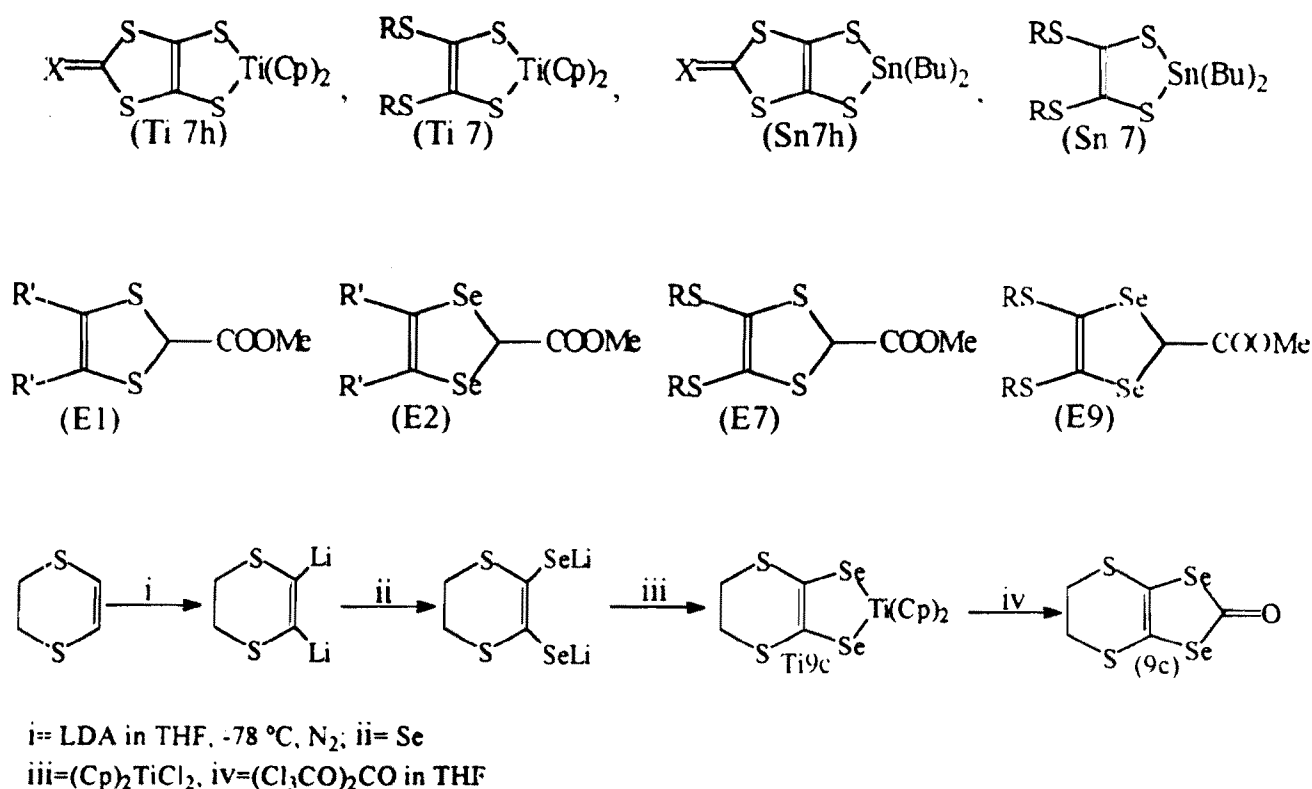
Similar ring-closure procedures have been applied for the preparation of (12a, X = S) from 1,2-dichloro-1,2-dimethoxyethane [124] and (12c) from 2,3-dichlorodioxane (see [68-70,81,124] and refs. cited therein). Also, the preparation of (20) from 2,3-dichloro-*p*-thioxane by a similar method has been reported very recently [265]. Scheme 3.4 outlines the preparation procedure of (12c) and (20) [68,265]. Compound (20) has also been prepared by a ring-closure procedure [111] starting from mercaptoethanol and methyl bromoacetate [235]. The derivative with X = O has limited shelf-life, even in the freezer, and it is used immediately after preparation [235].

A number of alternate, simple procedures have been applied for the preparation of (13) and (14) (see [51-54,59-61]): (13a', X = S), for example, can be obtained by treatment of 2,3-dichloropyrazine with

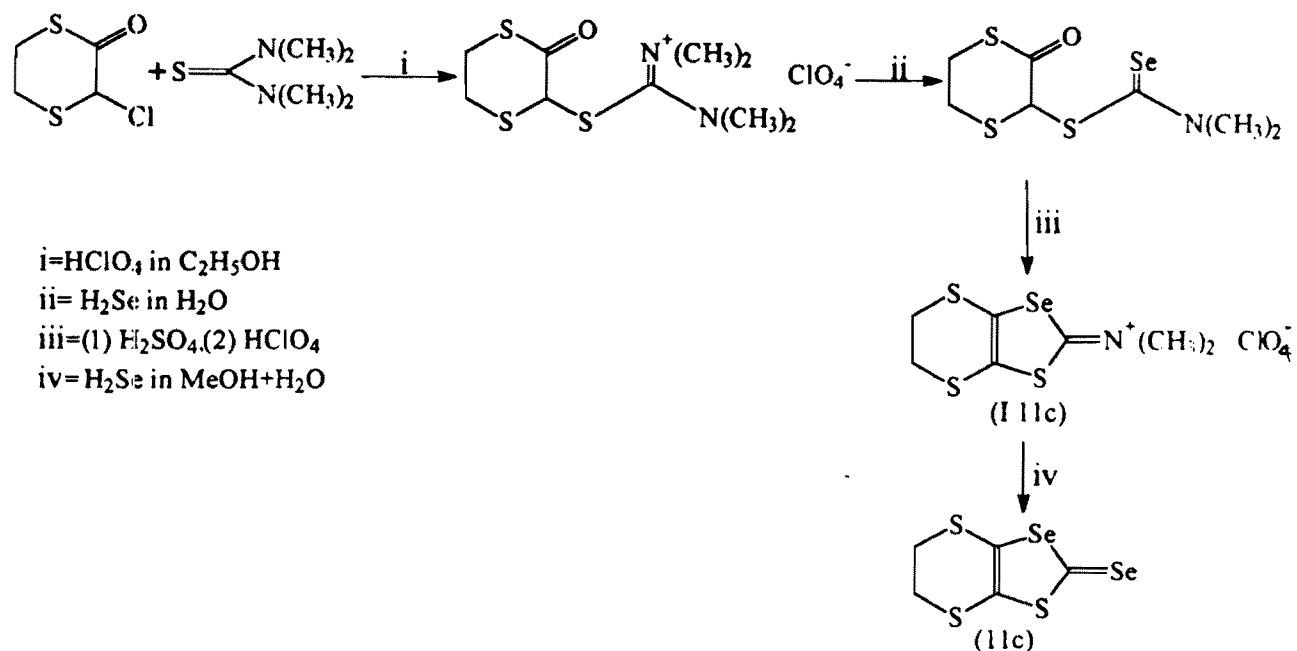
potassium trithiocarbonate. Compounds (16c) can be easily separated from byproducts (7c) by silica gel column chromatography using CS_2 as eluent. Compounds (15) can be obtained by the same procedure, but the yields are low. An alternate method, via the BF_3 -mediated reaction, is applied for the preparation of (15c) from (17b) according to Scheme 3.5(a) [275]. A simpler procedure is applied for the preparation of (17a) (Scheme 3.5b) [275,267,288].

Starting from 4,5-vinylenedithio-1,3-dithiole-2-thione, (7g), larger molecules, namely compounds (16), have been obtained by the procedure illustrated in Scheme 3.6 [72,275]. For the preparation of (18) and similar compounds see [98,197,119,165,197,205,218,257] and refs. cited therein. For the preparation of (19) see [74,88,91,94,119,151,223,227,231,255] and refs. cited therein. Compound (21) can be prepared by the same methods as for (13) and (14) from the dichloropyridazine [50]. An improved procedure is described below, starting from (34). The preparation of compounds (22) and (24) are described in [56] and [156,279], respectively.

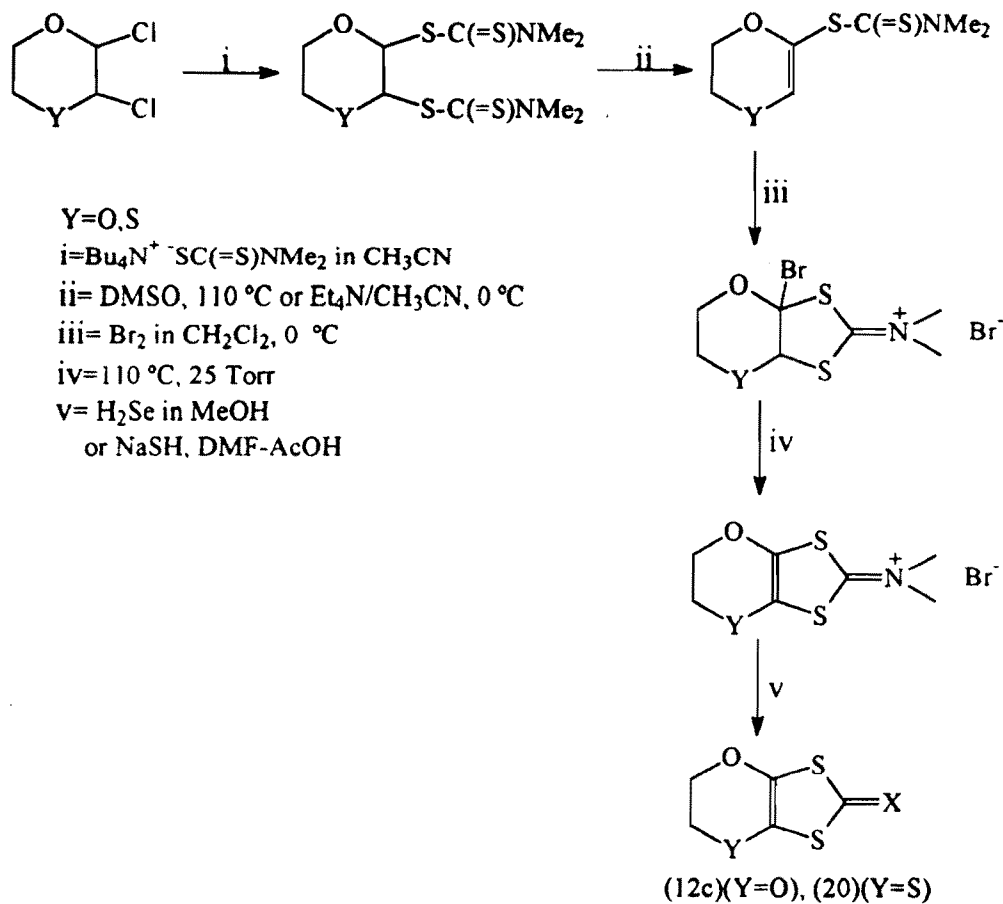
Compounds (25) and (26) can be prepared from the corresponding dichloropyrazines and the corresponding



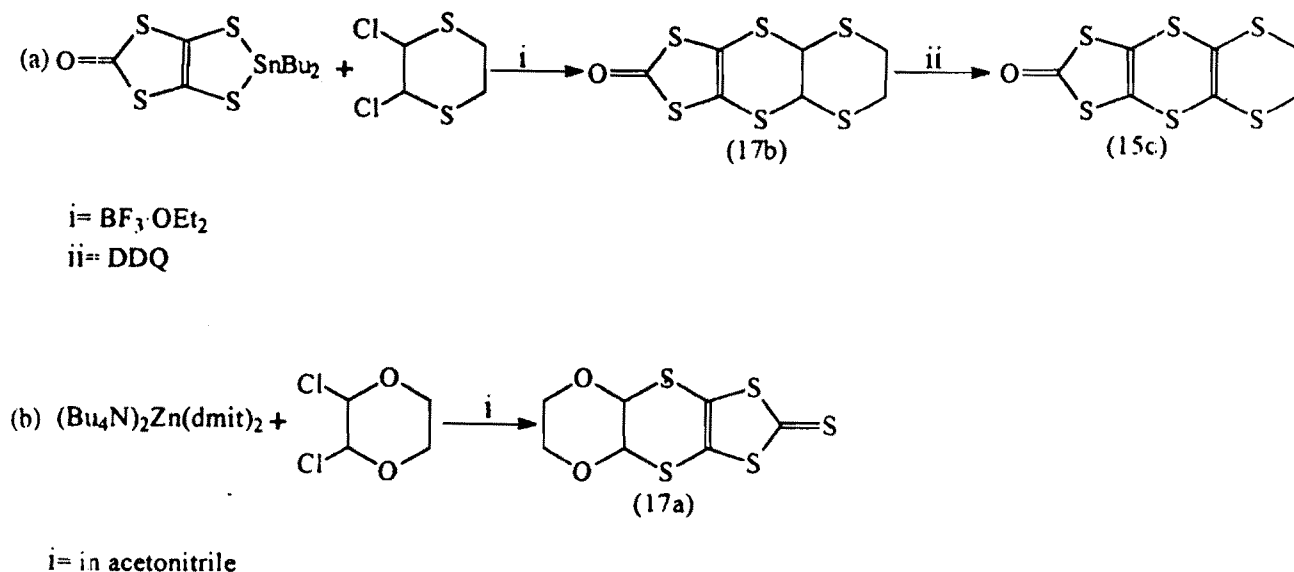
Scheme 3.2



Scheme 3.3



Scheme 3.4



Scheme 3.5

disodium dichalcogenolates. Methods for preparation of (27) and (28) are reported in [37,6,7] and [55,57], respectively. Compounds (27), (29) and (30)–(33) can be obtained by reaction of acetylenes containing electron-withdrawing groups (CN, COOR, CHO etc.) with ethylenetrithiocarbonate or ethylenetriselecocarbonate (see [28,68] and refs. therein). Compound (34) can be obtained by a similar procedure as illustrated in Scheme 3.7. It can be transformed to (21) by treatment with hydrazine, H_2NNH_2 [130].

Compounds (35), (36) as well as (37), (38) have been prepared from the corresponding zinc 1,2-dichalcogenolates by treatment with dichloroacetate ($\text{CH}_3\text{OOCCHCl}_2$) [62] and bromoacetate ($\text{CH}_3\text{OOCCH}_2\text{Br}$) [63] respectively. Also, (39), (40) are prepared by a similar method, using $\text{Si}(\text{CH}_3)_3\text{-(CH}_2)_2\text{OCH}_2\text{Cl}$, $\text{Ac-}p\text{C}_6\text{H}_4\text{CH}_2\text{Cl}$, $\text{NCCH}_2\text{CH}_2\text{Cl}$ and PhCOCl as reagents [93,131,134,225,231].

Compounds (1)–(40) can be transformed into the corresponding phosphoranes (Wittig reagents) or into the corresponding phosphonate esters (Wittig–Horner reagents [241]); these last reagents give better results. Scheme 3.8 illustrates the procedures of their preparation [53,105,108,122,129,181,215,241,277,290,300].

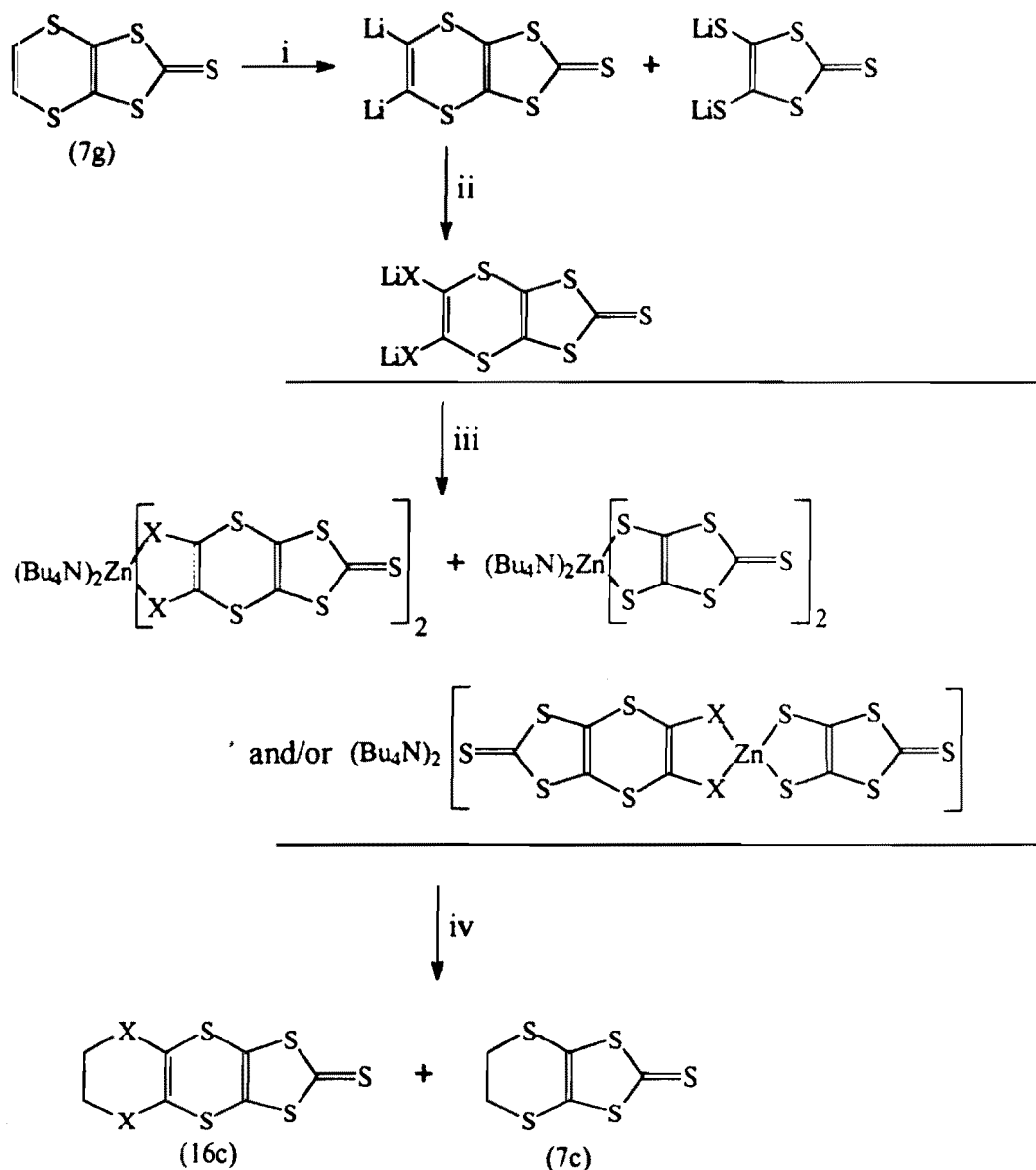
Phosphonates based on (1), i.e., (P1), can be prepared simply by heating 1,3-dithiole-2-thiones with a trialkyl phosphite at high dilution [215]. They react with aldehydes, ketones, 2-iminium-1,3-dithioles or dithiolium salts and selenium analogs to give larger molecules, precursors of extended tetrachalcogenafulvalenes (see below). The reactions take place in the presence of a base, such as butyllithium (BuLi) or LDA. Some aldehydes and ketones, which have

recently been used for preparation of large molecular precursors, are listed in Table 3.2. Information on the preparation and properties of some compounds of type (43) [108,123,129,161,171], (44) [37,240,247], (45) [292], (46) [292], (47) [184,262], (48) [184,262], (49) [230,246,276], (50) [99,108,188,228,246], (51), (52) [186,268,273,274], (53) [292] (54) [133,246], (55) [116,154,187,203], (56) [121,233], (57) [122], (58) [102,104,105,122,127], (59) [191] and (60) [183,241] is given in the recent literature.

2.2 Preparation of tetrachalcogenafulvalenes

One can design a large number of tetrachalcogenafulvalenes by making (binary, ternary etc.) combinations of compounds (1)–(60). However, few of these materials have been actually prepared and studied. In this section some methods applied over the years for the preparation of tetrachalcogenafulvalenes are described. Most of the symmetrical tetrachalcogenafulvalenes have been prepared by self-coupling reactions of the corresponding precursors (1)–(40), via triethyl phosphite, $(\text{EtO})_3\text{P}$, or other trivalent derivatives of phosphorous (e.g., Ph_3P), as shown in Scheme 3.9 (see for example [53,62,48]). In the following paragraphs the simple notation based on the numbers, which are referred to the labels of the corresponding precursors (1)–(60) or the corresponding singles, are used, e.g., (7c-7c), ET or BEDT-TTF for bis(ethylenedithio)tetrathiafulvalene.

In some cases, e.g. coupling of (1) ($\text{R}' = \text{H, Me, Ph}$; $2\text{R}' = \text{CH}_2\text{CH}_2\text{CH}_2, \text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2$) with (33) and



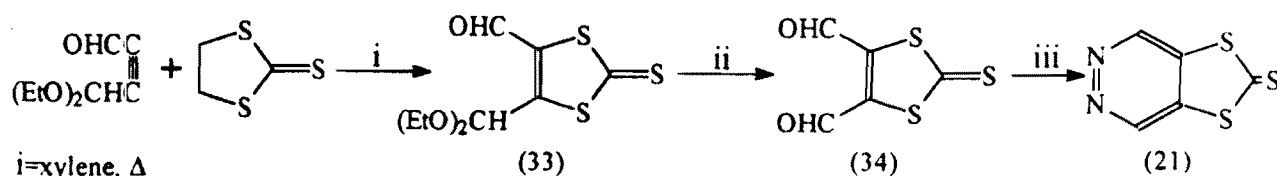
i=LDA, THF at $-72\text{ }^\circ\text{C}$

ii= X(=Se) at $-72\text{ }^\circ\text{C} \rightarrow 25\text{ }^\circ\text{C}$

iii= Bu_4NBr , ZnCl_2 in CH_3OH ;

iv= $\text{BrCH}_2\text{CH}_2\text{Br}$ in acetone

Scheme 3.6

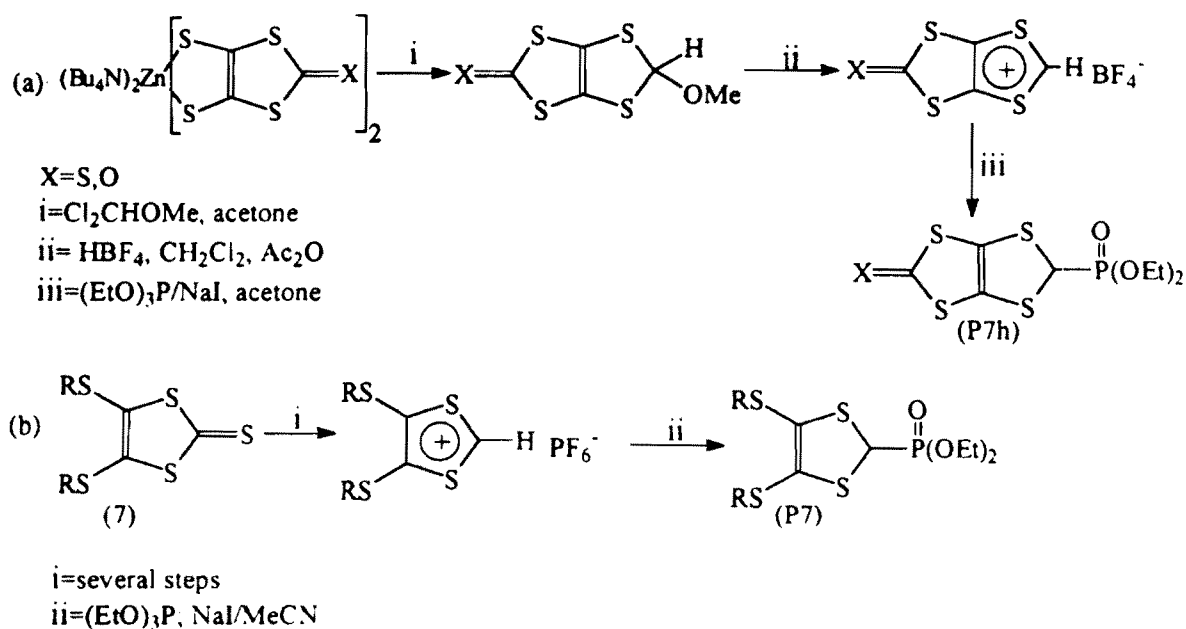


i=xylene, Δ

ii= HCO_2H , CH_2Cl_2

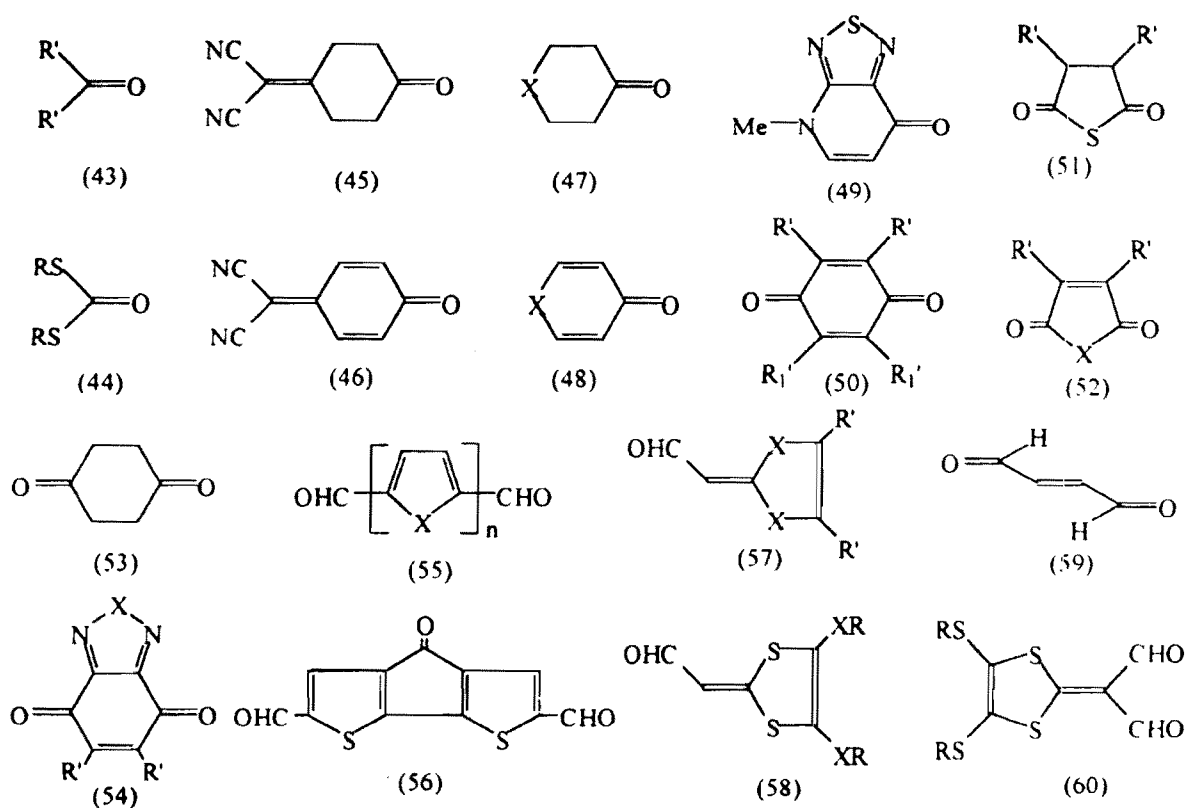
iii= H_2NNH_2 , DMF

Scheme 3.7

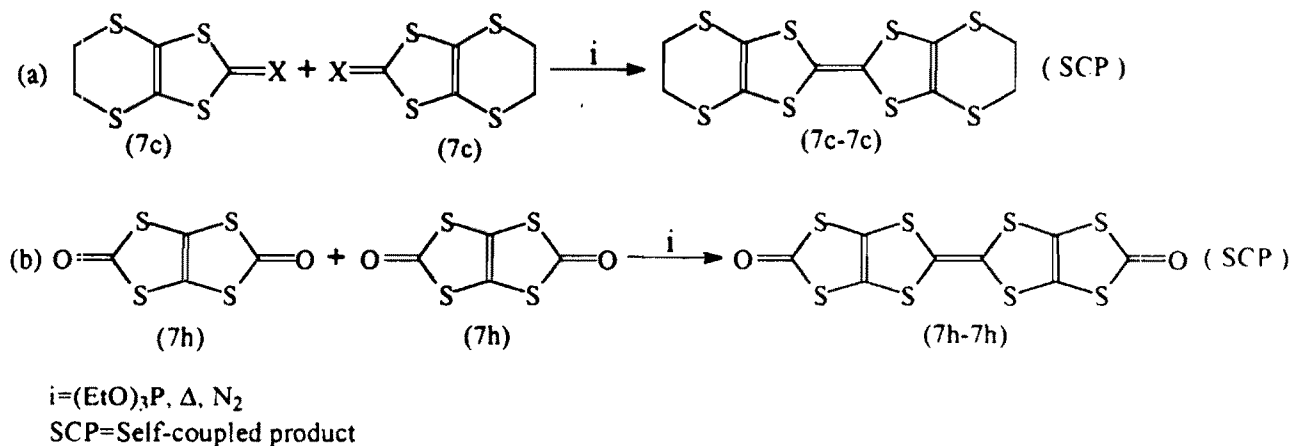


Scheme 3.8

Table 3.2. Selected aldehydes and ketones



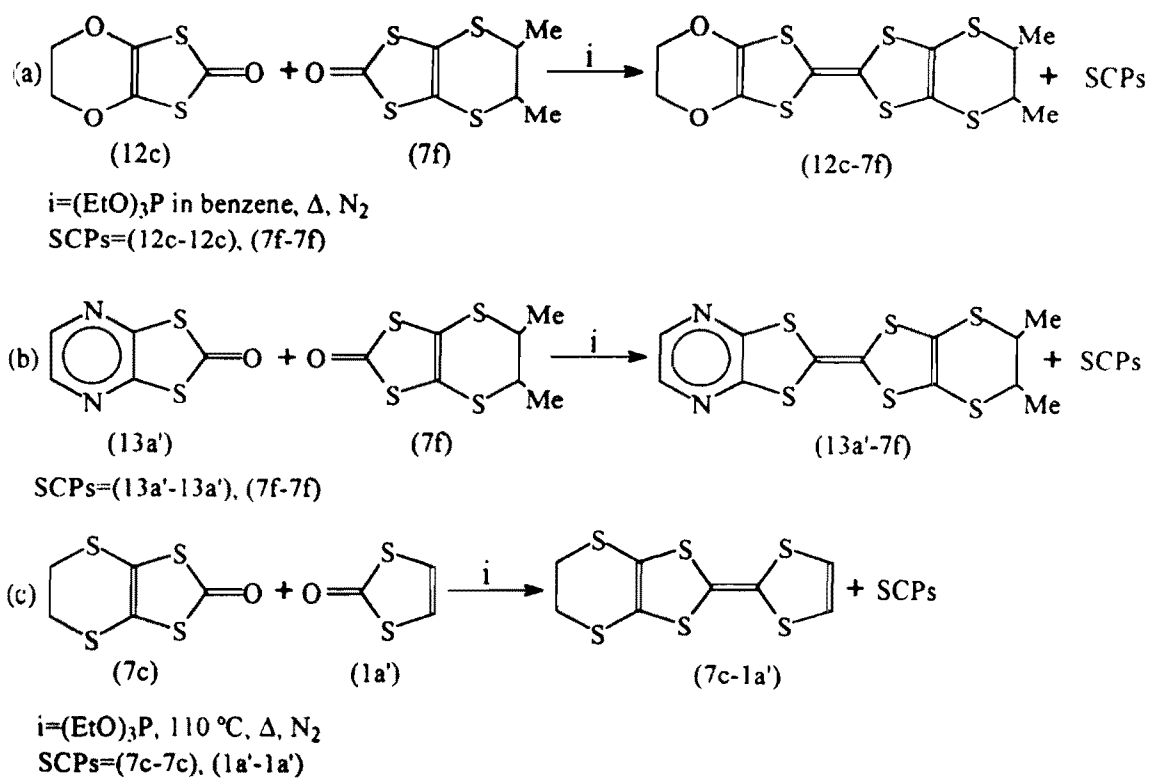
X = O, S for (47), (48), (52); X = S, Se for (54), (55), (57); also X = NMe for (55); R, R' as in Table 1 and ref. [28]; n = 1, 2, 3, ...



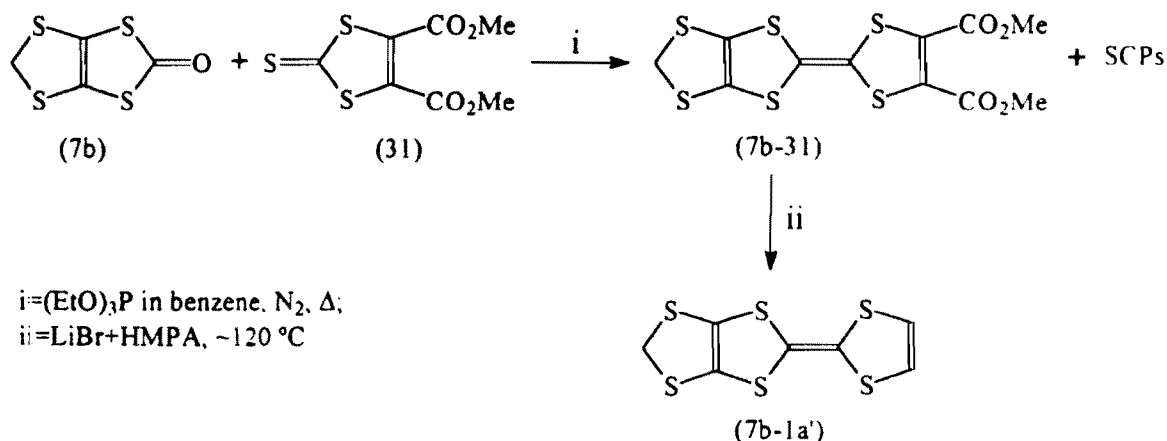
Scheme 3.9

(34), dicobaltoctacarbonyl ($\text{Co}_2(\text{CO})_8$) in benzene or toluene is used instead of $(\text{EtO})_3\text{P}$ [30,37,130]. In most cases, the best yield of self-coupled product (SCP) is obtained by using 2-oxo-1,3-dithioles [180] and 2-oxo-1,3-diselenoles ($\text{X} = \text{O}$) instead of the corresponding 2-thio- ($\text{X} = \text{S}$) or 2-selenoxo- ($\text{X} = \text{Se}$) compounds. One can transform the 2-thio- or 2-selenoxo-compounds to the corresponding 2-oxo compound by using, for example, mercury acetate, $\text{Hg}(\text{OAc})_2$, in a $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{COOH}$ (1:1) mixture. The opposite

transformations $\text{C}=\text{O} \rightarrow \text{C}=\text{S}$, $\text{C}=\text{O} \rightarrow \text{C}=\text{Se}$, $\text{C}=\text{S} \rightarrow \text{C}=\text{O}$ are also possible. They can be performed directly with B_2S_3 or P_2S_5 [48,35] or through the 1,3-dithiolium salts or 2-imino-1,3-dithioles with H_2Se [35,112] or NaHSe [126]. In some cases, selenones give high yields in tetrathiafulvalenes after treatment with Ph_3P [75b]. The coupling sometimes can be achieved through the 1,3-dithiolium salts (Scheme 3.8) by treatment with triethylamine (see [37,204,226,277]). A large number of unsymmetrical tetrachalcogenaful-



Scheme 3.10

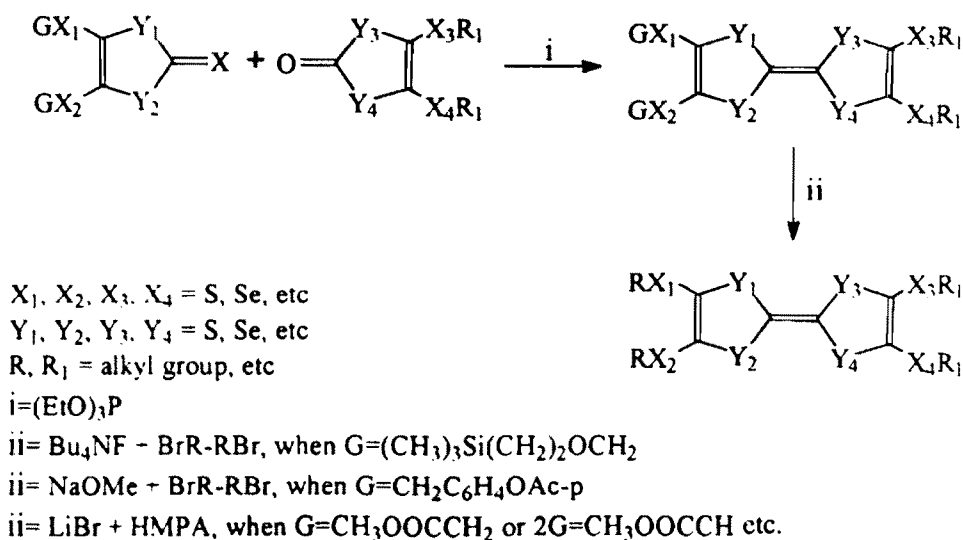


Scheme 3.12

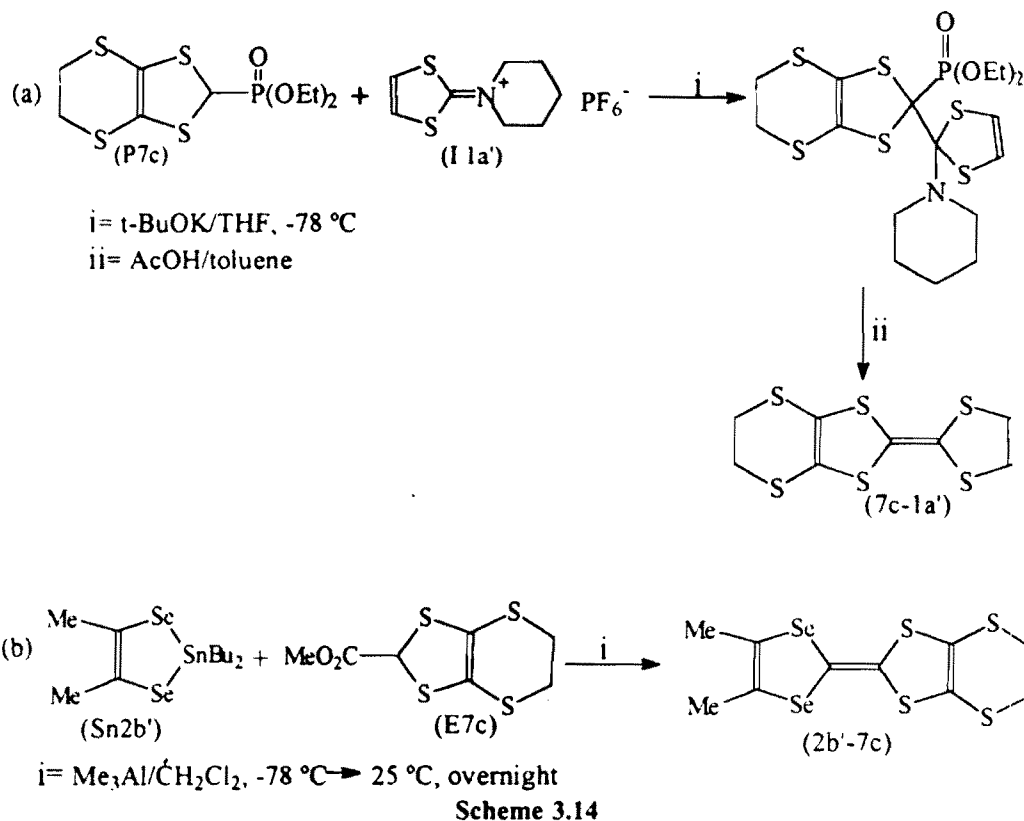
halides to give S, Se, and Te containing tetrachalcogenafulvalenes. Isolation of the intermediate zinc 1,2-dichalcogenolates followed by reaction with alkyl halides (Scheme 3.16) gives pure products [71]. An alternative mechanism is the formation, first, of the monolithiation-product, in which then Se is added and so on [269].

Larger molecules can be obtained from small molecules containing several other functional groups, such as CHO [130,217,283], as outlined in Scheme 3.17 [127,130]. The aldehyde-functionalized compounds lead to the preparation of different products, such as (1g'-1g'), (7c-21) (see also [266]). Moreover, a four-fold olefination with the Wittig reagents $\text{Ph}_3\text{P}=\text{CR}'\text{R}'$ (instead of H_2NNH_2) allows the preparation of tetraolefinated tetrathiafulvalenes [89,130,271]. For the preparation of some new tetrathiafulvalenes

from (71-71), (39c-39c), which contain the $\text{CH}_2\text{CH}_2\text{Cl}$ and $\text{CH}_2\text{CH}_2\text{CN}$ functional groups, see [95] and [218], respectively. Bis- and tritetrathiafulvalene amphiphiles have been prepared by using simple functionalized tetrathiafulvalenes, such as (7c-29) [219,264,283]. The preparation of some extended (fused) tetrachalcogenafulvalenes, which are ternary, quaternary etc. combinations of some compounds listed in Tables 3.1 and 3.2, has already been described (Scheme 3.11). However, some improved procedures, which give the required product in a pure form and in high yield, have been proposed recently. In these cases materials with functional groups are used for the preparation of extended systems. Scheme 3.18 outlines the preparation of (7a-7h-7a) from (7a-39b) [134,172,176,117,236]. Compound (7a-39b) contains the $\text{SCH}_2\text{C}_6\text{H}_4\text{-}p\text{Ac}$ functional group. It can be obtained easily by a cross-



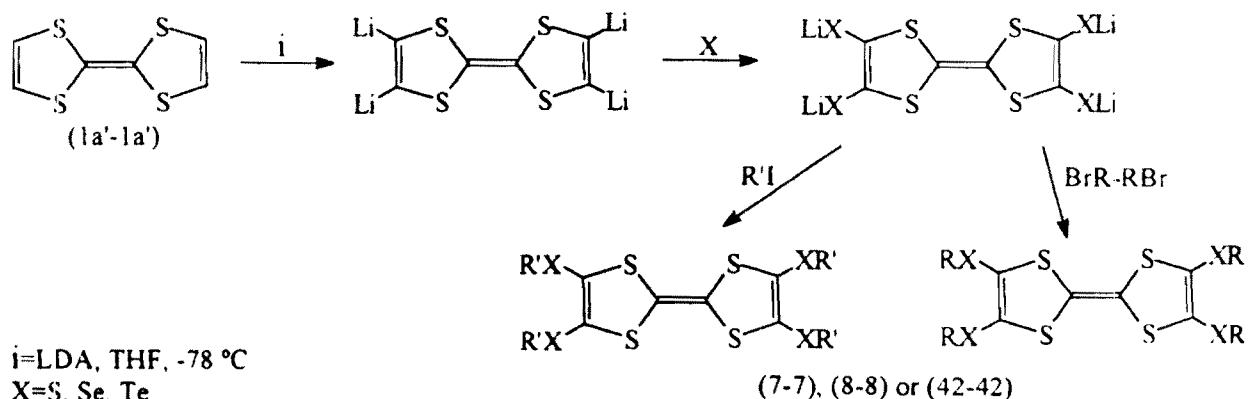
Scheme 3.13

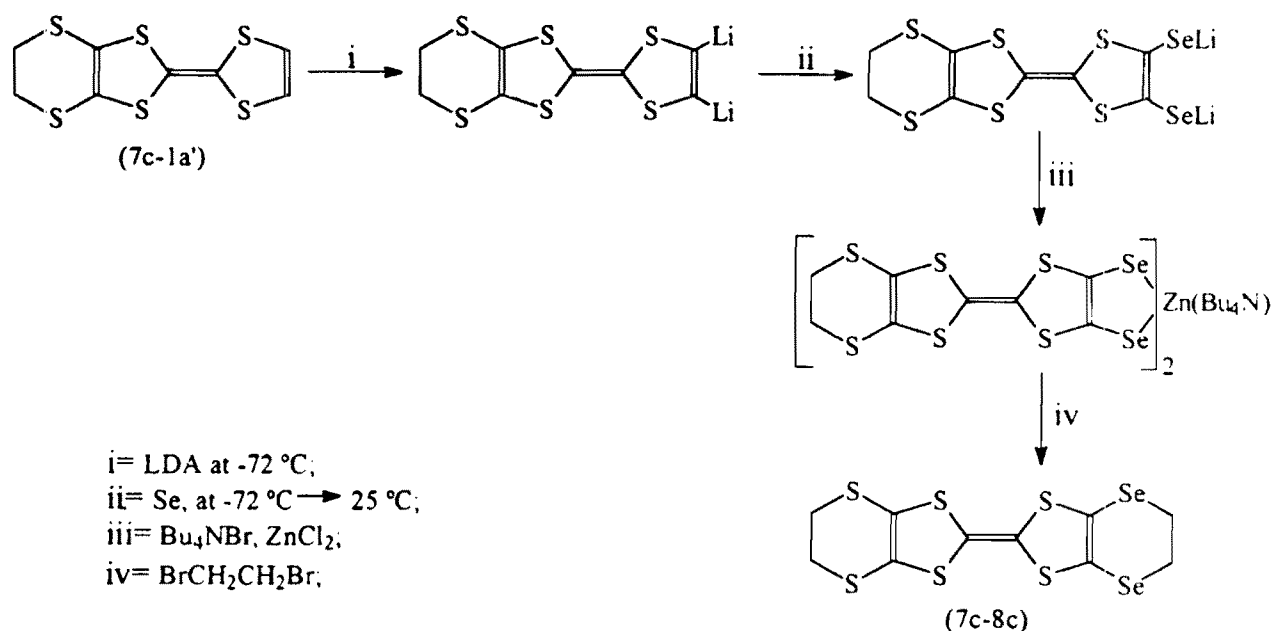


coupling reaction of (7a) and (39b) via (EtO)₃P. The intermediate zinc 1,2-dithiolate (as in Scheme 3.16) and compound (7a-7h) are isolated in pure form. Coupling of (7a-7h) with (7a) gives the required extended system (7a-7h-7a); this is (7a-7a) in which a tetrathiaphene (TTP) unit is inserted into its central double bond. The same method has been applied for the preparation of (7a-7h-13) from (7a-7h) and (13) [288] as well as of some ethylenedioxy containing compounds from (7-7h) and (12c) [174,175]. For the preparation of (7-18h-18h-7) by a similar procedure, see [221]. Scheme 3.19 outlines the preparation of

some other extended systems [123,134,176,236,263]. Also in these cases, compound (1a'-3b) is firstly prepared by a cross-coupling reaction of (1a') and (3b) via (EtO)₃P.

The same method has been applied for the preparation of (1a'-7h-13) from (1a'-7h) and (13) [289], and (1b'-7h-7) from (1b'-7h) and (7) [236]. For the preparation of similar compounds see [171,173,186,273,292]. Compounds (1-51a'-7) prepared with the same method can be transformed into the corresponding (1-52a'-7) via 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ), which is a dehy-

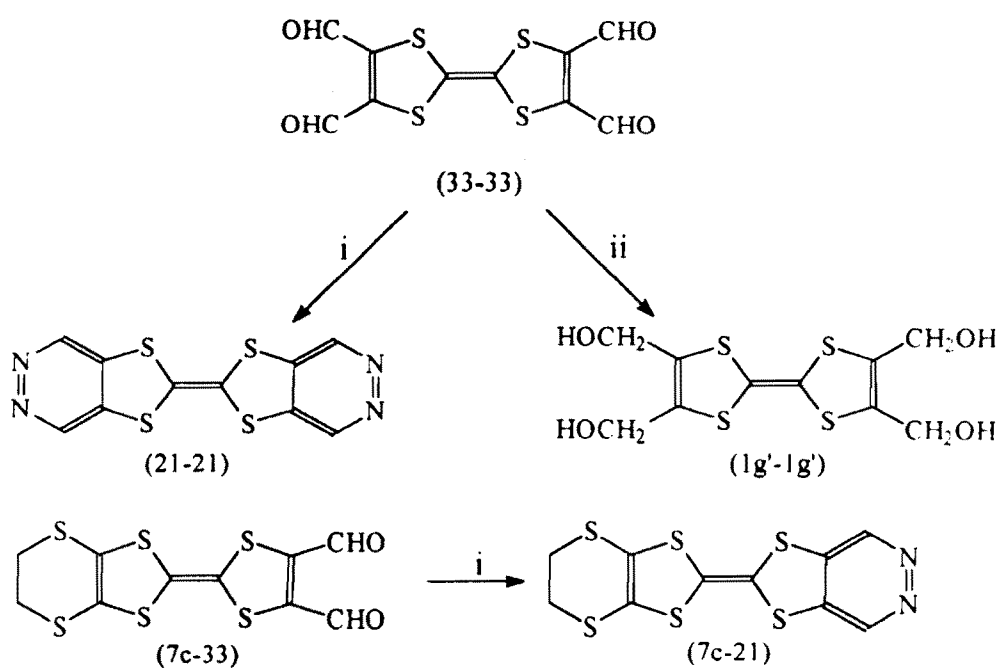




Scheme 3.16

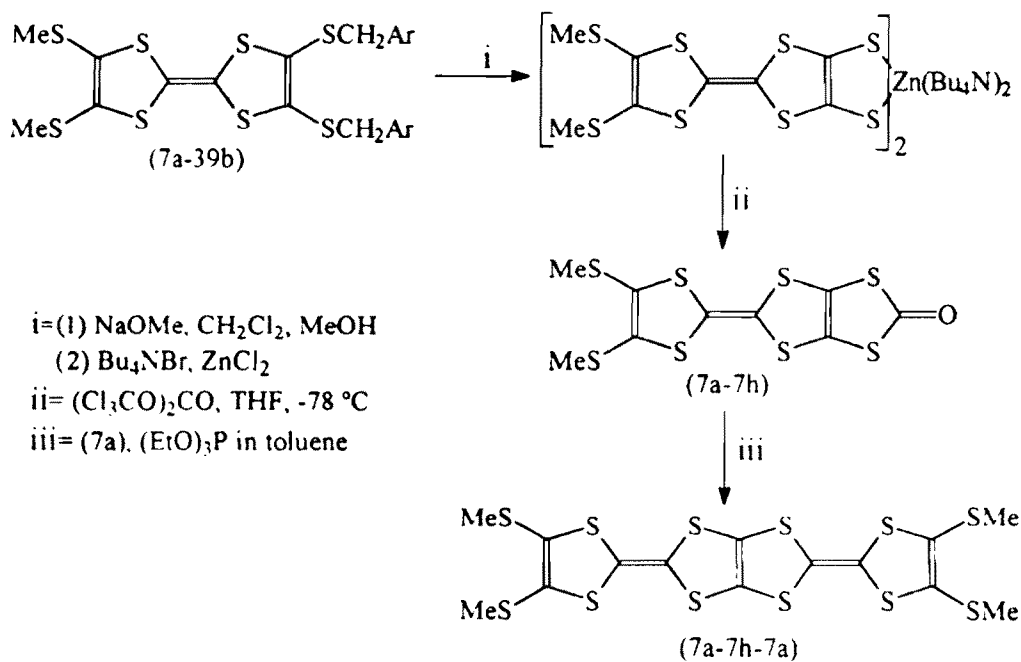
drogenation reagent [186]. Some intermediate functionalized compounds, obtained by reactions of Wittig-Horner reagents, such as those of Scheme 3.8, with ketones (compounds of Table 3.2) are used for preparation of extended π -donor molecules. In

Scheme 3.20 an example of the preparation of these new materials is outlined [129]. The same method has been applied for the preparation of (47-7h-7). They can be transformed into (48-7h-7) with DDQ [184,262]

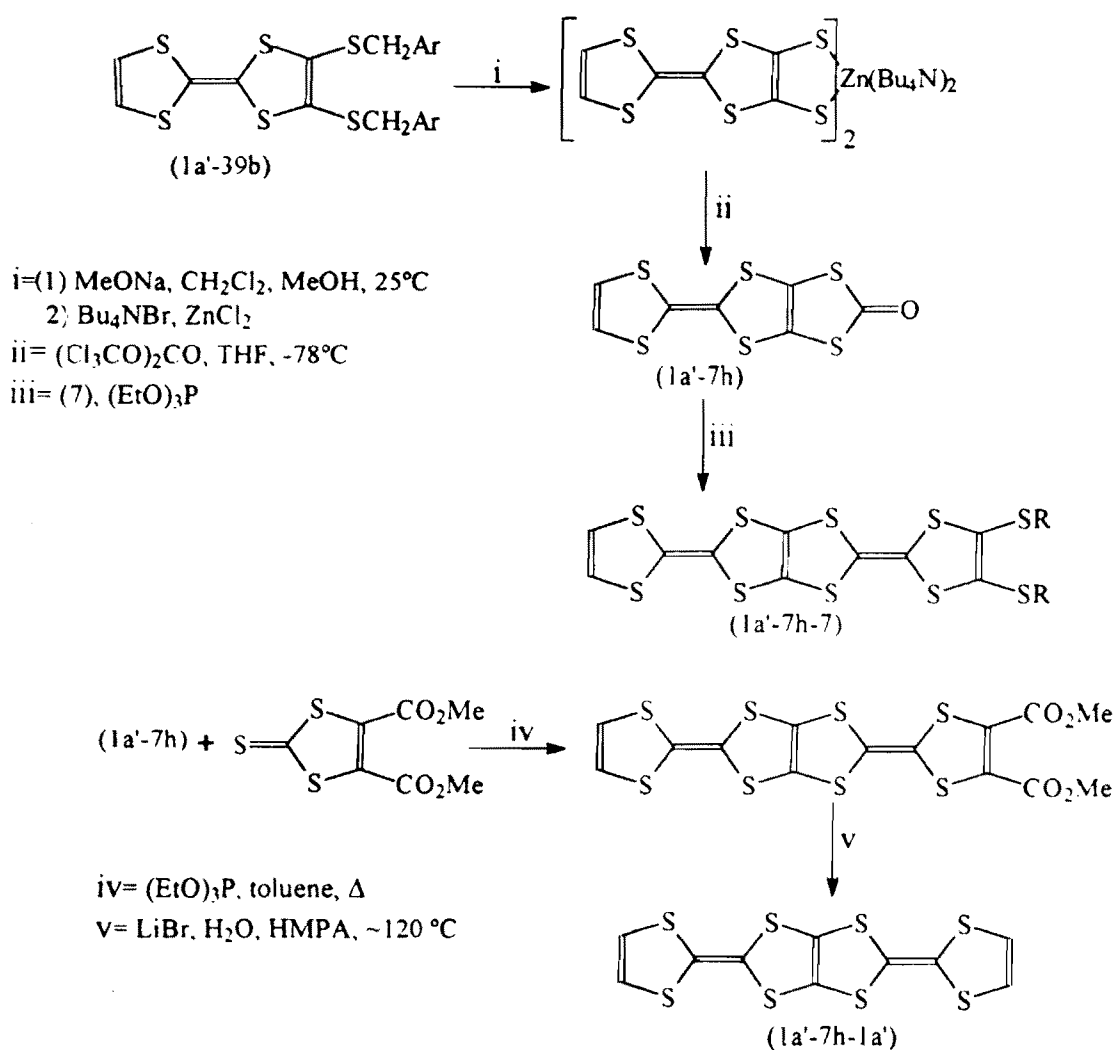


i = H_2NNH_2 , DMF
 ii = NaBH_4 , THF, MeOH

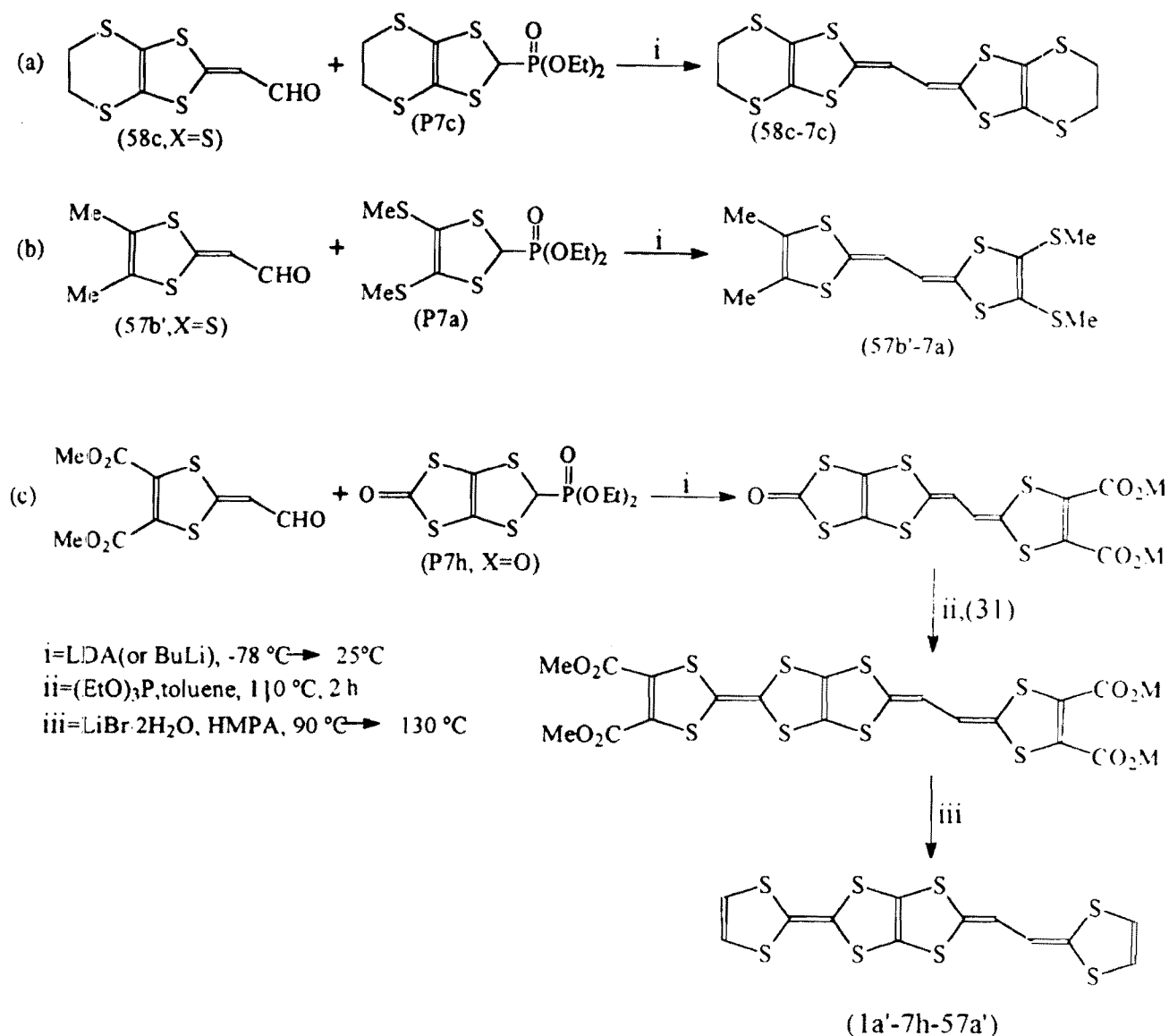
Scheme 3.17



Scheme 3.18



Scheme 3.19



Scheme 3.22

2.3 Electrochemical behavior of tetrachalcogenafulvalenes

The electrochemical parameters, i.e., the half-wave redox potentials ($E_{1/2}^1$, $E_{1/2}^2$, $E_{1/2}^3$ etc.), of tetrachalcogenafulvalenes play an important role in the preparation, stability etc. of CTCs and radical cation salts (RCSs) (see below). They depend on the temperature and the nature of the surrounding medium (solvent, electrolyte), etc. The first redox potential, ($E_{1/2}^1$) value, is a measure of the ability of the donor (D) to give an electron, i.e., it is related with the reaction $\text{D}^0 \rightleftharpoons \text{D}^{+\cdot}$. The difference $\Delta E (= E_{1/2}^2 - E_{1/2}^1)$ is related with the reaction $\text{D}^{+\cdot} \rightleftharpoons \text{D}^{2+}$ (or $2\text{D}^{+\cdot} \rightleftharpoons \text{D}^0 + \text{D}^{2+}$) (see [1,26,268] and refs. cited therein); it is a measure of the on-site Coulomb repulsion in the dicationic state (see

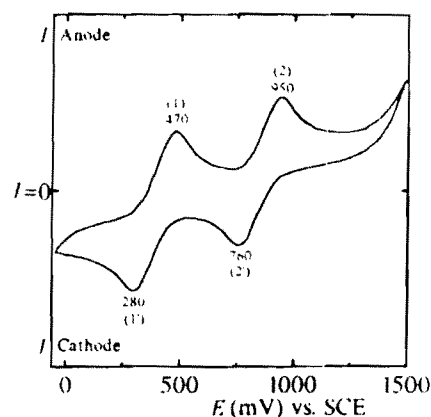


Figure 3.1. Cyclic voltammogram of TTF at a Pt electrode (7×10^{-4} M TTF and 0.025 M Bu_4NPF_6 in $\text{C}_6\text{H}_5\text{CN}$ at $23\text{ }^{\circ}\text{C}$); scan rate 10 mV/s; sensitivity 200 μA FS.

below). Figure 3.1 shows the two reversible redox couples (peaks 1,1' and 2,2') of TTF in Bu_4NPF_6 vs. a standard calomel electrode (SCE). The electrochemical parameters of an unsymmetrical donor (AB) can be calculated from the parameters of the corresponding symmetrical donors (AA, BB) by the equation

$$E'(AB) = \frac{1}{2}[E'(AA) + E'(BB)] \quad (3.2)$$

In Tables 3.3, 3.4 and 3.5 the experimental values of $E_{1/2}^1$, $E_{1/2}^2$, and ΔE of selected tetrachalcogenafulvalenes, and in some cases the calculated values via equation (3.2) under a variety of conditions are listed [28,70,117,123,129,164,184,186,268,290]. In some cases a third ($i = 3$), fourth ($i = 4$) and so on redox wave is observed, for example in the compounds (7c-18a'-7c), (2d'-7h-43b'), (43b'-7h-7h-43b') [117,164], (43b'-7h-1) [123], (7a-7h-1), (7a-7h-7) [177], (48-7h-1a') [184], (1-15h-1), (7-15h-7) [239] etc. [129,154,155,183,187,195,192c,205a,221,228,233]. These waves are due to higher oxidation stages (see [26] and review [13] and refs. cited therein).

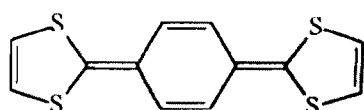
2.4 Role of additional edge groups and spacer groups in the properties of tetrachalcogenafulvalenes

Of course, there are two ways to obtain extended tetrachalcogenafulvalenes: One is the substitution of the H-atoms of TTF (Se and Te analogs) by several (hetero) groups (i.e. edge groups) and the other is the substitution of the intercyclic C=C bond of TTF by several π -linking (hetero) groups (i.e. spacer groups). For example, substitution of the H-atoms of TTF (1a'-1a') on both sides by CH_3 , $\text{CH}=\text{CH}-\text{CH}=\text{CH}$, $\text{SCH}_2\text{CH}_2\text{S}$, $\text{N}=\text{CH}-\text{CH}=\text{N}$ gives respectively the

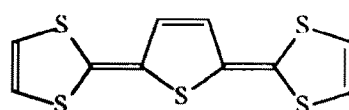
symmetrical tetramethyl tetrathiafulvalene (1b'-1b'), dibenzotetrathiafulvalene (1d'-1d'), bis(ethylenedithio)tetrathiafulvalene (7c-7c) and bis(pyrazino)tetrathiafulvalene (13a'-13a'), while substitution of the 2H atoms of TTF on one only side by these groups gives respectively the unsymmetrical compounds dimethyl tetrathiafulvalene (1b'-1a'), benzotetrathiafulvalene (1d'-1a'), ethylenedithiotetrathiafulvalene (7c-1a') and pyrazinotetrathiafulvalene (13a'-1a'). Also, two tetrachalcogenafulvalene units could be linked directly or by an alkyl or thioalkyl, aromatic, ethenylene, ethynylene and other spacer groups (see for example [121,214,119,139,148,187,199,205,219,220,231,250]). The other case is the substitution of the central C=C bond of TTF by several π -linking spacer synthons, based on (50a') and (51a'), for example, giving respectively the compounds (1a'-50a'-1a') and (1a'-51a'-1a').

These kinds of substitutions affect on the polarity, solubility, oxidation potentials and other physical and chemical properties of tetrachalcogenafulvalenes. Some examples are given in the following.

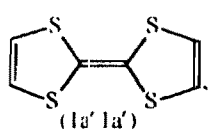
It has already been described that a number of unsymmetrical tetrachalcogenafulvalenes can be prepared by a cross-coupling reaction of the corresponding 1,3-dithiole-2-ones or 1,3-diselenole-2-ones, via triethyl phosphite, followed by column chromatography separation of the cross-coupled product (CCP) from the self-coupled byproducts (SCPs), if there is a considerable difference in the R_F values of the CCP and SCPs. For example, the R_F values of compounds (1a'-1a'), (7b-7b), (8c-8c), (10c-10c), (12c-12c), (13a'-13a') and (29-29) are 0.75, 0.77, 0.55, 0.49, 0.25, 0.08, 0.05, respectively, on a silica gel plate using CH_2Cl_2 as eluent, i.e., the polarity of the latter compounds is larger



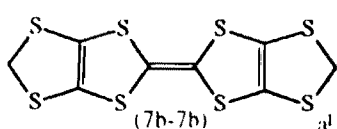
(1a'-50a'-1a')



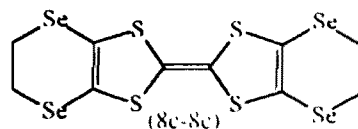
(1a'-51a'-1a')



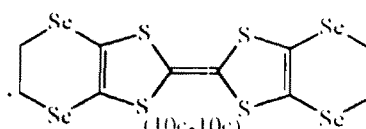
(1a'-1a')



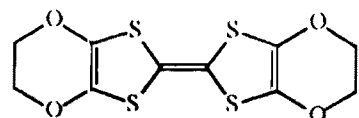
(7b-7b)



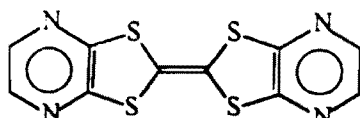
(8c-8c)



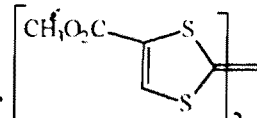
(10c-10c)



(12c-12c)

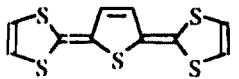
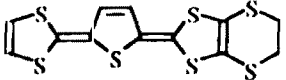
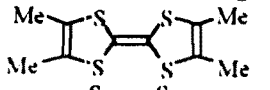
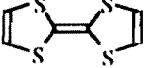
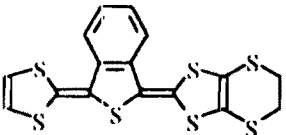
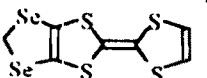
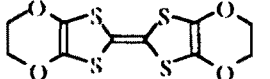
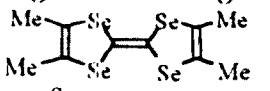
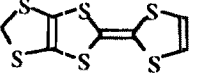
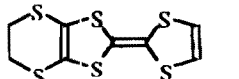
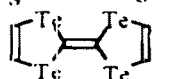
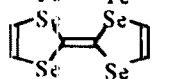
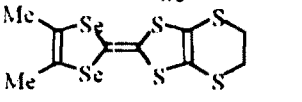
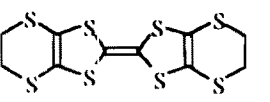
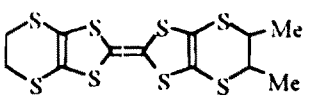
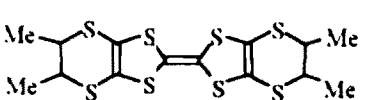


(13a'-13a')



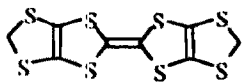
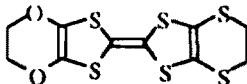
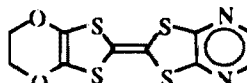
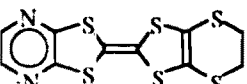
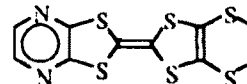
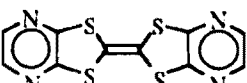
(29-29)

Table 3.3. Room temperature half-wave redox potentials and peak potentials (in mV) of selected tetrachalcogenafulvalenes under different conditions [28,70,186,268]; calculated values via equation (2.2) are given in parentheses

Compound	$E_{1/2}^1$	$E_{1/2}^2$	ΔE	E_{ox}^1	E_{ox}^2	E_{rd}^1	E_{rd}^2
 (1a'-52a'-1a')	110 ^c	340 ^c	230 ^c				
 (1a'-52a'-7c)	180 ^c 290 ^a	380 ^c 650 ^q	200 ^c 360 ^a				
 (1b'-1b')	360 ^d 375 ^b 367 ^a	840 ^d 845 ^b 748 ^a	480 ^d 470 ^b 381 ^a	470 ^b 370 ^c	940 ^b 750 ^c	280 ^b 380 ^c	750 ^b
 (1a'-1a')	319 ^c 470 ^d	701 ^c 810 ^d	382 ^c 340 ^d				
 (1a'-52d'-7c)	370 ^c	580 ^e	210 ^c				
 (8b-1a')	405 ^b	790 ^b	385 ^b	490 ^b	870 ^b	320 ^b	710 ^b
 (12c-12c)	435 ^a 440 ^a	699 ^a 720 ^a	264 ^a 280 ^a				
 (2b'-2b')	550 ^d 455 ^b	940 ^d 832 ^b	390 ^d 377 ^b	535 ^b	915 ^b	375 ^b	750 ^b
 (7b-1a')	(451) ^b 460 ^b (467) ^a 390 ^c	(829) ^b 885 ^b (788) ^a 690 ^c	(378) ^b 425 ^b (321) ^a 300 ^c	545 ^b	970 ^b	375 ^b	800 ^b
 (7c-1a')	(402) ^c	(720) ^c	(318) ^c				
 (41a'-41a')	590 ^d 480 ^a	840 ^d 760 ^a	250 ^d 280 ^a				
 (2a'-2a')	(620?) ^d	(900?) ^d	(280?) ^d				
 (2b'-7c)	(503) ^a 520 ^b 567 ^a 486 ^c	(774) ^a 907 ^b 829 ^a 739 ^c	(271) ^a 387 ^b 262 ^a 253 ^{cb}	600 ^b	980 ^b	440 ^b	835 ^b
 (7c-7c)							
 (7c-7f)	(521) ^b	(902) ^b	(381) ^b				
 (7f-7f)	522 ^b	897 ^b	375 ^b	595 ^b	970 ^b	450 ^b	825 ^b

(continued)

Table 3.3 (continued)

Compound	$E_{1/2}^1$	$E_{1/2}^2$	ΔE	E_{ox}^1	E_{ox}^2	E_{rd}^1	E_{rd}^2
 (7b-7b)	527 ^b	812 ^b	285 ^b	595 ^b	880 ^b	460 ^b	745 ^b
 (12c-7g)				620 ^b	1000 ^b		
 (12c-13a')	630 ^b	1105 ^b	475 ^b	700 ^b	1190 ^b	560 ^b	1020 ^b
	720 ^b	1135 ^b	415 ^b	790 ^b	1220 ^b	650 ^b	1050 ^b
	680 ^c	1020 ^c	340 ^c				
 (13a'-7c)	(688) ^c	(955) ^c	(266) ^c				
 (13a'-7f)	(721) ^b	(1130) ^b	*(409) ^b				
	(920) ^b	(1363) ^b	(443) ^b				
 (13a'-13a')	890 ^c	1170 ^c	280 ^c				

^a 0.1 M Bu₄NPF₆ in CH₃CN vs. Ag/AgCl electrode; ^b 0.025 M Bu₄NPF₆ in C₆H₅CN vs. SCE; ^c 0.1 M Et₄NClO₄ in CH₃CN vs. SCE; ^d 0.2 M Bu₄NBF₄ vs. SCE (see [28,70]); ^e 0.1 M Bu₄NClO₄ in C₆H₅CN vs. see [186,268].

than that of the former compounds. This means that the additional groups (=SCH₂S, SCH₂CH₂S etc.) considerably influence the R_F values. Consequently, unsymmetrical compounds (CCPs), such as (1a'-29), (7c-13a') and (12c-8c) can be easily separated from the corresponding symmetrical SCPs, because of the large difference in the R_F values. Instead, unsymmetrical compounds (CCPs), such as (1a'-7b) and (7c-8c) cannot be easily separated from the corresponding symmetrical SCPs, even using CS₂ as eluent. Some indirect methods are applied in these cases (Schemes 3.12, 3.13, 3.16, etc.).

For preparation of CTCs and RCSs from solutions (see below) the precursors (i.e., tetrachalcogenafulvalenes) should be soluble in organic solvents. Substitution of H-atoms of TTF (and Se or Te analogs) by CH₃,

CH₃(CH₂)_n, CN, COOCH₃, CH₂O(CH₂)₂Si(CH₃)₃ increases the solubility. TTF and ET are soluble enough in CH₂Cl₂ or C₆H₅CN, but bis(ethylenediseleno)tetraselenafulvalene [28] and uracil containing tetrathiafulvalene [270] are less soluble. Also, substitution of SeCH₂CH₂Se and SCH₂CHS by OCH₂CH₂O and substitution of N=CH-CH=N or SCH=CHS groups by SCH₂CH₂S and OCH₂CH₂O groups increases the solubility.

It has been established that the solutions of tetrachalcogenafulvalenes (π -donors) with $E_{1/2}^1$ values smaller than those of TTF (see Table 3.3) are oxidized in air [268]. On the other hand, π -donors based on (4)-(6), (13), (14) (17), (21), (23), (24) and (26)-(28) have high $E_{1/2}^1$ values and do not give stable CTCs or RCSs. Salts of bis(pyrazino)tetrathiafulvalene (13a'-13a'), for

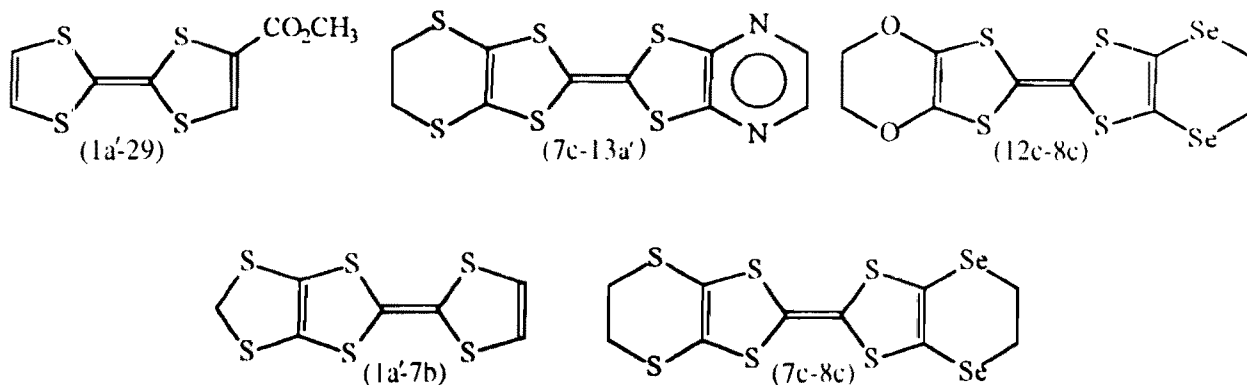


Table 3.4. Room temperature half-wave redox potentials (in mV) of selected tetrachalcogenafulvalenes under conditions given below [117,164]^a; calculated values via equation (2.2) are given in parentheses

Compound	$E_{1/2}^1$	$E_{1/2}^2$	ΔE	
	(1a'-1a')	-50	360	410
	(2b'-2b')	40	380	340
	(2b'-7c)	(70)	(395)	(325)
	(2b'-7h-43b')	70	360	290
	(2a'-2a')	90	400	310
	(7b-7b)	100	330	230
	(7b-7d)	100	410	310
	(43b'-7h-7h-43b')	110 150	320 440	210 290
	(2b'-9c)	(155) 170	(435) 410	(280) 240
	(9c-7h-43b')	(190)	(405)	(215)
	(9c-7b)	180	410	230
	(7c-9c)	(185)	(450)	(265)
	(9c-9c)	270	490	220
	(9d-9d)	270	510	240

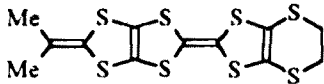
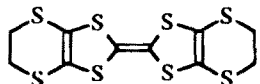
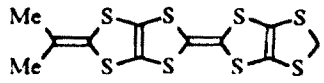
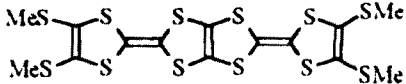
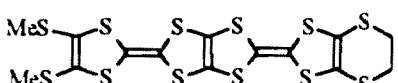
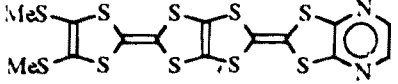
^a 0.1 M Bu₄NPF₆ in C₆H₅CN vs. Ag/AgNO₃ electrode.

Table 3.5. Room temperature half-wave redox potentials (in mV) of some selected multiheterotetrathiafulvalenes; the corresponding values of some simple compounds are given for comparison [123,129,184,290]^a

Compound	$E_{1/2}^1$	$E_{1/2}^2$	ΔE	
	(1a'-1a')	350	770	420
	(1a'-7h-57a') X = S	370	500	130
	(48-7h-1a') X = s	370	600	230
	(1a'-7h-1a')	440	620	180
	(43b'-7h-1b')	450	760	370
	(7a-7h-7a)	490	710	220
	(43b'-7h-7a)	500	750	250
	(7b-7b)	500	720	220
	(43b'-7h-7d)	500	780	280
	(7a-7h-7b)	510	700	190
	(7a-7h-12c)	510	720	210
	(7a-7h-7d)	510	730	230
	(7a-7a)	510	780	270

(continued)

Table 3.5. (continued)

Compound		$E_{1/2}^1$	$E_{1/2}^2$	ΔE
	(43b'-7h-7c)	510	790	180
	(7c-7c)	510	820	280
	(43b-7h-7b)	510	830	310
	(7a-7h-7b0)	530	710	210
	(7a-7h-7c)	530	740	210
	(7a-7h-13a')	(> 530)	(> 740)	(> 210)

^a 0.1 M Bu₄NClO₄ in C₆H₅CN vs. SCE.

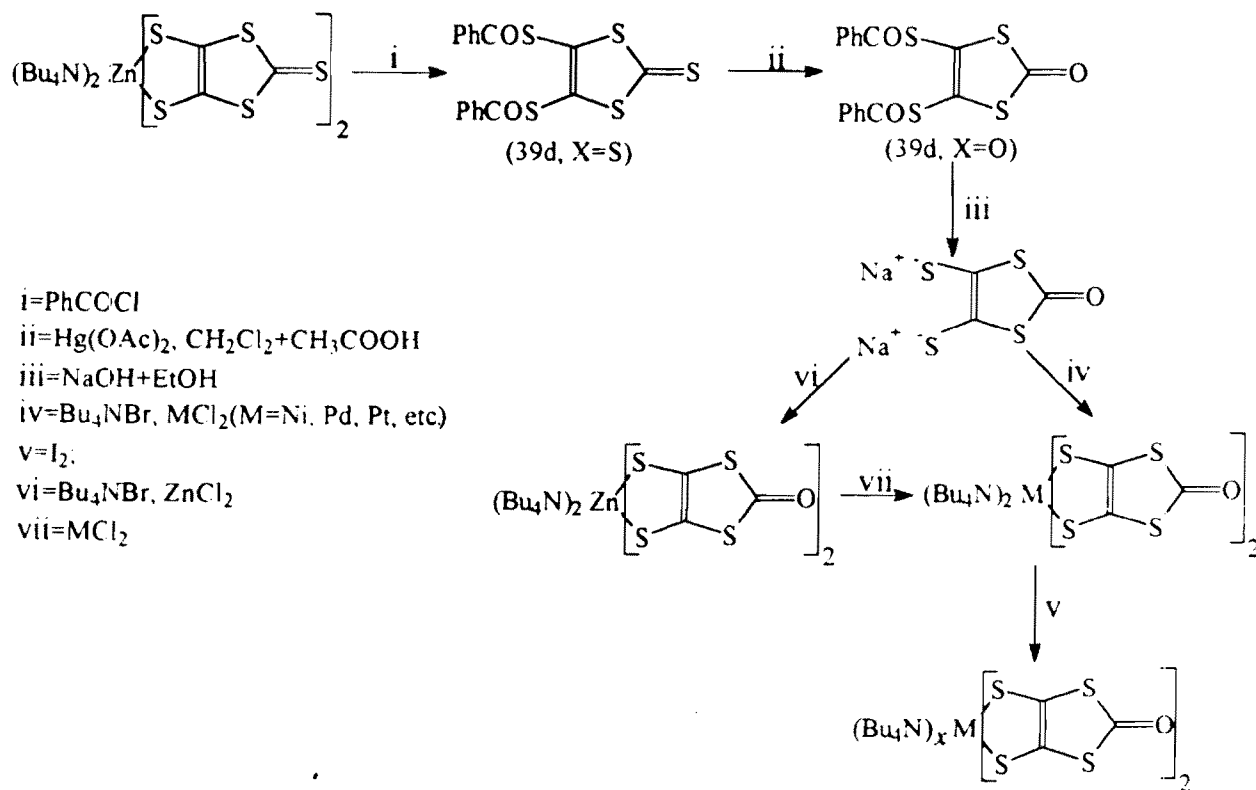
example, are not stable in moist air [52]; the reason is the weak donating ability of (13a'-13a'). In other words, for preparation of stable conducting materials, the precursors (π -donors) should have $E_{1/2}^1$ values smaller than that of (13a'-13a') (see Table 3.3). Substitution of H-atoms of TTF by alkyl (e.g. Me), cycloalkyl etc. (electron donating) groups decreases the $E_{1/2}^1$ value, while substitution by CF₃, CN, MeO₂C, etc. (electron-withdrawing) groups increases the $E_{1/2}^1$ value. Substitutions of H-atoms by S and O containing groups increases the $E_{1/2}^1$ values but decreases the ΔE value, an important result for decreasing the on-site Coulomb repulsion in the dication state. Also, substitution by S, Se and N containing groups increases the intermolecular interaction in the CTCs and RCSs, but increases the $E_{1/2}^1$ value (Tables 3.3 and 3.4). Moreover, the extension of tetrachalcogenafulvalenes by π -linking groups changes $E_{1/2}^1$ and ΔE values, as is shown in Tables 3.3-3.5. The compounds which are listed in Tables 3.3, 3.4 and 3.5 are good π -donors for the preparation of CTCs and RCSs.

Taking into account the above described and other similar empirical rules, as well as equations (3.1) and (3.2), one can design and prepare new π -donors, for instance by binary, ternary etc. combinations of (1)-(60), with the required polarity, solubility, π -donating ability, etc.

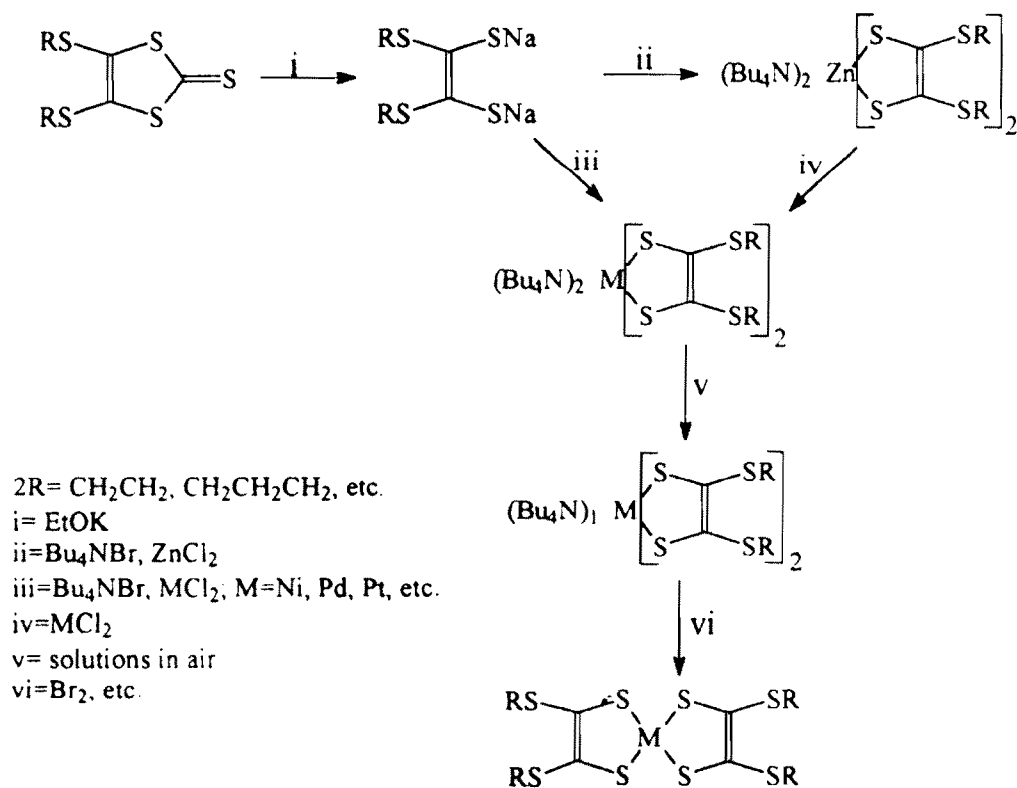
2.5 Preparation and properties of metal 1,2-dichalcogenolenes

The most important metal 1,2-dichalcogenolenes, which are precursors or components of conducting materials are prepared by using CS₂, CSe₂ and similar simple compounds as starting materials (see for example [29,30,36,66,68]). For some recent preparations see [301-320]. Rich-cation metal 1,2-dichalcogenolenes are used in some cases for the preparation of tetrachalcogenafulvalenes, as has already been described above (see Schemes 3.4, 3.8, 3.16, 3.18 and 3.19). Moreover, some compounds, (1)-(40), and some compounds obtained from combinations of (1)-(60) are used for the preparation of metal 1,2-dichalcogenolates in several oxidation states. Some examples are given in Schemes 3.23-3.25.

Starting from vinylenetrithiocarbonate (1a') and vinylenetriselenocarbonate (2a') some cation-rich and cation-deficient metal 1,2-dichalcogenolates can be prepared as outlined in Scheme 3.23 [18,64,66,68]. Also, using S instead of Se in route (c), Scheme 3.1, or using CSSe, 1,3-dithiole-2-selenone or 1,3-thiasele-2-selenone as starting materials, some 'alloys' of metal 1,2-dichalcogenolates, containing both S and Se, are obtained [66,68]. In refs. [301-303] the preparation of compounds (Bu₄N)_xM(dmise)₂ from 1,3-dithiole-2-

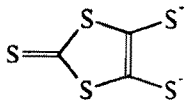
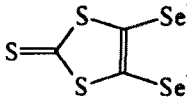
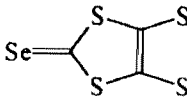
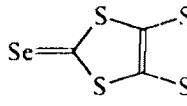
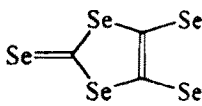
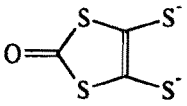
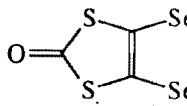
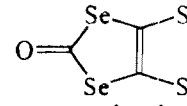
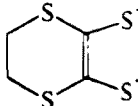
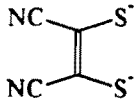
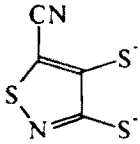
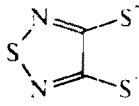


Scheme 3.24



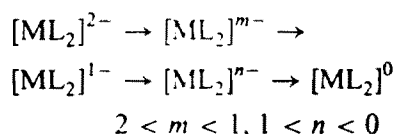
Scheme 3.25

Table 3.6. Selected ligands of metal complexes

			
dmit	dsit	dmise	dsise
			
dsis	dmio or dmio	dtods	dsods
			
dddt	mnt	dcit	tdas

by similar procedures have been described. However, a large number of studies have been done recently on metal complexes based on the ligand (L) molecules of Table 3.6 [301–320] (see also [66,67]). The unsymmetrical complexes $(\text{Bu}_4\text{N})_x\text{Ni}(\text{dmit})(\text{dsis})$ have been reported in [304].

Zinc 1,2-dichalcogenolenes with ligands larger than those of Table 3.6 have been obtained as intermediate materials during the preparation of extended tetrachalcogenafulvalenes (see Schemes 3.4 [72], 3.16 [71], 3.18 [134] and 3.19 [176,263]). The corresponding Ni, Pd, etc. complexes have not yet been prepared. However, some complexes of Ni with more complicated ligands are reported in [53b,305,307,308,311,316,317]. After oxidation of cation-rich metal (M) 1,2-dichalcogenolates (where M = Ni, Pd, Pt, etc.) by several methods [18,31,315] the corresponding cation-deficient ($2 < x < 1$, $x = 1$ and $1 < x < 0$) complexes and in some cases the neutral ($x = 0$) complexes are obtained, according to the following reactions

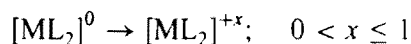


(for some examples see Schemes 3.23–3.25). The electrochemical redox potentials of complexes based on some of ligands in Table 3.6 are reported in refs. [294,301,303,304,314,320]. In all cases (ligands) the oxidation of monoanions $[\text{ML}_2]^{1-}$ to $[\text{ML}_2]^0$ occurs irreversibly. The effects of the ligand on the redox potentials are shown in the following examples [314]:

- The redox potentials of $[\text{ML}_2]^{2-} \rightleftharpoons [\text{ML}_2]^{1-}$ increase in the order $\text{dsis} < \text{dmit} < \text{dmise} < \text{dsit} < \text{dsise}$.
- The irreversible electrochemical oxidation potentials of $[\text{ML}_2]^{1-} \rightarrow [\text{ML}_2]^0$ decrease in the order $\text{dmit} > \text{dmise} > \text{dsit} > \text{dsise} > \text{dsis}$.

This means that the nature of the chalcogene coordinated to the metal as well as the nature of additional groups play an important role in the properties of the complexes.

In some cases, such as in complexes based on dddt and the methylenedithio analog [319], a third reversible or quasi-reversible oxidation wave is observed [312b,319]. This is due to oxidation of the neutral species to the cation, according to the reaction

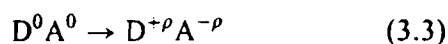


3 CHARGE-TRANSFER COMPLEXES AND RADICAL ION SALTS

3.1 Definitions and chemical classification

As was mentioned in the previous sections, tetrachalcogenafulvalenes and metal 1,2-dichalcogenolenes could give rise to precursors of CTCs (and/or radical ion salts), which are conducting materials. The origins of molecular conductors started at the beginning of this century with the empirical discovery of molecular association and complexes. It is currently accepted that,

when these associations give rise to a stable solid compound with a definite stoichiometry, thanks to an electron transfer between an electron donor and electron acceptor a stable complex association is created. The first theory, which has rationalized the experiments, was the intermolecular charge transfer (CT) resonance theory presented by Mülliken in 1951–1952 (see [8] and refs. cited therein). This dimer model explains, on the one hand, the presence of either an almost neutral or an almost ionic ground state, and on the other hand, the presence of a new, intense CT optical absorption band in the visible or near infrared range. Indeed, this color change is the first experimental signature of CT salts [8]. On a more general note, the resulting organization in the solid state is very sensitive to the choice of the donors and acceptors, the compound stoichiometry and the synthesis route. As pointed out in the early works the most interesting properties can be observed in compounds with strong CT interactions, which result from π -type orbitals and involve the formation of homomolecular stacks [321]. These systems are usually divided in two different series labeled either as a CTC or as a radical ion salt (RIS). In the former case the neutral molecules tend to associate into stable complexes with partial charge transfer from the donor (D) to the acceptor (A):



where ρ denotes the amount of charge transfer in the DA complex; its value depends mainly on the ionization potential of the donor and electron affinity of the acceptor, quantities which are related to the redox potentials in solution [268,322,323]. In radical salts, donors or acceptors should be at first chemically transformed into ions by an oxidation or a reduction process and then these ions have to be spatially organized, whereby a molecular association is realized between a radical ion and a counterion, which in some cases is a 'closed shell' system [321]. Compound with $0 < \rho < 1$ (mixed valence systems), which are conducting materials, are obtained by reaction of donors and acceptors with moderate redox potentials or by reaction of a strong donor (acceptor) and a weak acceptor (donor). Strong donor and strong acceptor gives anionic (single valence) complex ($\rho = 1$), while weak donor and weak acceptor gives a neutral (molecular) complex, where no charge transfer occurs [322]. A simple chemical classification of the salts obtained from tetrachalcogenafulvalenes and metal 1,2-dichalcogenolenes is as follows: Tetrachalcogenafulvalenes give radical cation salts (RCSs) with (diamagnetic) anions such as Cl^- , ClO_4^- , PF_6^- and

$AuBr_2^-$, as well as CTCs with π -acceptors such as TCNQ. Also some metal 1,2-dithiolenes such as $Ni(ddd)_2$ give RCSs with $AuBr_2^-$, IBr_2^- , ClO_4^- etc. Alkali metals, ammonium, tetramethylammonium and similar (diamagnetic) cations form radical anions salts with metal 1,2-dichalcogenolenes. Last, salts are similar to those obtained from diamagnetic cations with π -acceptors such as TCNQ. Also, there is another type of salts, i.e., metal 1,2-dichalcogenolenes with tetrachalcogenafulvalenes or other 'open-shell' organic cations such as the perylene cation, which is not well classified.

3.2 Preparation of compounds

Charge transfer complexes and radical ion salts can be prepared either as single crystals and polycrystalline powder or as thin films. Single crystals can be obtained by the following methods:

- (a) Chemical methods: In one of the methods, the two compounds (e.g. a donor and an acceptor) are dissolved in a solvent and the resulting (saturated) solution is either cooled at low temperature or is warmed at higher temperature (for evaporation of the solvent) to obtain a crystallization. If these processes are performed slowly, the obtained crystals are large and of good quality. In the cases where one or both the components are not soluble in solvents they are mixed together in a stoppered flask containing a small portion of solvent, and the mixture remains to react for several months [113]. If the reaction is achieved by heating or ultrasound agitation (in an open flask), it gives large yields in a short time [324a]. In the diffusion methods the two components are placed in two separate tubes, for example in two coaxial tubes, which are filled with a solvent. If one of the components can be easily evaporated (e.g. I_2), only the tube which contains the other component is filled with a solvent.
- (b) Electrochemical method: This is also a slow method. The reaction takes place in an H-shaped cell with a porosity frit, for example, where the anodic compartment of the cell contains a solution of donor or acceptor and a solution of supporting electrolyte, while the other (cathodic) compartment contains only a solution of electrolyte (see for example [25]). A low density current is applied ($0.2-1 \mu A cm^{-2}$) and the crystals are obtained after several days or

months depending on the nature of the materials, the concentration and the current density. The reaction should take place under neutral atmosphere and/or in the dark, in the cases of sensitive components. For the preparation of RIS crystals by this method, supporting electrolytes with various anions have been used. These anions are: (i) monovalent: simple halide (Cl^- , Br^- , etc.), pseudohalide (CN^- , SCN^- , etc.), linear polyhalide (I_3^- , IBr_2^- , etc.), linear metal halide or pseudohalide (AuBr_2^- , AuI_2^- , AgBr_2^- , $\text{Ag}(\text{CN})_2^-$, etc.), trigonal (NO_3^-), tetrahedral (ClO_4^- , InI_4^- , GaCl_4^- , etc.), square planar (AuEt_4^-), trigonal pyramidal (TeF_6^-), octahedral (PF_6^- , SbCl_6^- , etc.); (ii) bivalent ($\text{Pt}(\text{CN})_4^{2-}$, SO_4^{2-} , $\text{Hg}_2\text{I}_8^{2-}$, CuCl_4^{2-}); (iii) polyoxometalates such as $\text{MW}_{12}\text{O}_{40}$ ($\text{M} = \text{Co}, \text{Cu}$, etc.); (iv) chelate complexes, such as metal 1,2-dithiole-nes, $\text{Fe}(\text{C}_2\text{O}_4)_3$, $\text{Ni}(\text{C}_2\text{S}_2\text{O}_2)_2$; or (v) organo-

metallic, such as $\text{Cu}(\text{CF}_3)_4$; (vi) organic, such as $\text{C}(\text{CN})_3$, $\text{N}(\text{CN})_2$. In some cases, the anion in the RCS is different from that of the supported electrolyte. For example, $\text{Hg}_2\text{Br}_3^{2-}$ gives salts with $\text{Hg}_{2.89}\text{Br}_8^{2-}$ (polyanion) [325a], $\text{N}(\text{CN})_2^-$ and CuBr give $\text{CuN}(\text{CN})_2\text{Br}^-$ (polyanion) [325b], and SeCN^- and CuI give I_3^- (simple anion) [113,326]. By changing the experimental conditions or the method of preparation often several different phases are obtained. Video microscopic studies of electrochemical crystal growth have been described recently [329]. This monitoring of crystal growth *in situ*, allows us to adjust external parameters such as temperature, voltage and current density, in order to obtain high quality crystals.

Chemical oxidation or electrochemical oxidation of rich metal 1,2-dichalcogenolates give cation-deficient conducting materials, but in the presence of a π -donor

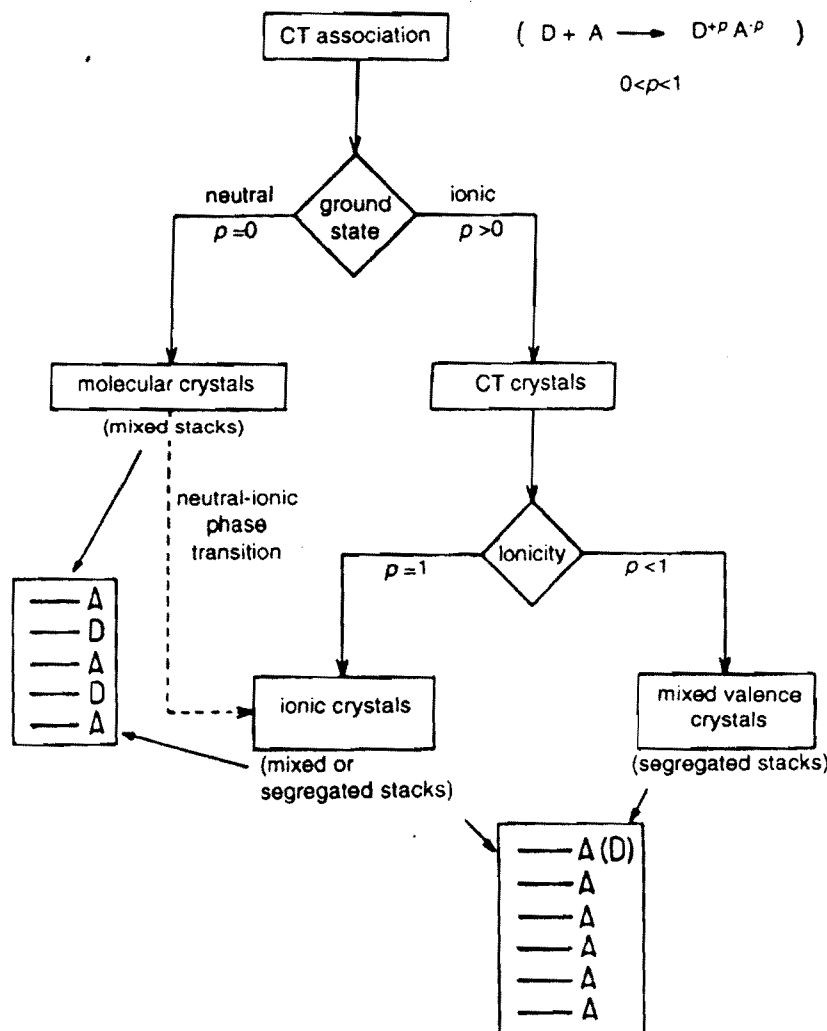
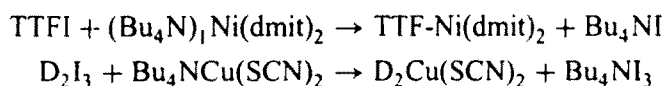


Figure 3.2. Schematic structural organization of π -molecular CT complexes [331].

(e.g., tetrachalcogenafulvalene, perylene) give the corresponding metal 1,2-dichalcogenolene-'open shell' system.

Mutual substitution or metathesis, instead of a direct oxidation reaction, is also applied as shown in the following examples [18a,66]



Thin films of CTC or RIS deposited on several substrates (e.g. glass, polymer, metal) can be prepared by the evaporation-deposition method [327,328], or the Langmuir-Blodgett technique [330,47b].

3.3 Some common general features

Up to now several hundred CTCs and RISs have been synthesized with a wide range of stoichiometries, crystal structures and physical properties, and some common features have been identified [331]:

- (a) Donor or acceptor molecules are organized to form homomolecular blocks $(\text{D})_n$ or $(\text{A})_n$ as dimers, trimers or tetramers, and not heteromolecular blocks of the (AD) type, as expected formerly. These molecular blocks can form segregated or mixed stacks as shown in Figure 3.2 [331].
- (b) The degree of charge transfer in a CTC or the degree of ionicity of a radical ion (ρ) in the salt is a crucial parameter, and is controlled in the former case by the redox potentials in solution and in the latter case through the compound stoichiometry [322,332]. It can be either an integer or a fractional number. In the latter case, we have mixed-valence molecular blocks, e.g. $(\text{D}_2)^+$, $(\text{D}_3)^{2+}$, $(\text{D}_4)^{2+}$, or even a uniform stack $(\text{D}_x)^{n+}$. A direct analogy with the Robin-Day classification for inorganic mixed-valence compounds has been proposed whereby all kinds of molecular compounds may be classified [333]. If all lattice sites are equivalent, each molecule may be regarded as carrying a fractional charge due to delocalization of radical electrons: in other words we consider mainly the following homogeneous mixed-valence states.
- (c) π -molecular orbitals occupied by radical electrons can overlap, forming a continuous path in one direction (stacked or planar molecules) or creating 2-dimensional sheets. In both cases the

transfer integral, t , can be calculated from the extended Hückel approximation [334], which predicts very narrow electronic bands of restricted dimensionality (see below).

As noted before, radical cation salts are always associated with an 'inert' counterion. It plays a crucial role in the properties [331]. Indeed, the structural organizations and their instabilities [335] depend on the size and the shape, the electrical charge and, eventually, the magnetism of the counterions present. These salts are usually binary or even ternary compounds when either a neutral organic solvent or water are involved. They are defined by the general formula

$$(\text{D}_x)^{n+}\text{X}^{n-}(\text{solv})_y, \text{ usually with } \rho = \frac{n}{x} < 1 \quad (3.4)$$

In most cases the observed stoichiometries for classical mixed-valency salts are 2:1 or 3:2 [22,336-338]. In some cases these are 1:~1 [326], 2:1.75 [261], 3:1 [337] etc. [339]. The stoichiometries of cation-deficient metal 1,2-dichalcogenolenes $(\text{Z}_x)^{n+}\text{A}^{n-}(\text{solv})_y$ (where A = metal 1,2-dichalcogenolene) could be 0.5:1, 0.4:1, 0.33:1, 0.28:1, 0.25:1 [18b,31]. For the complexes of the type $(\text{D}_x)^{n+}\text{A}^{n-}(\text{solv})_y$ the stoichiometries could be 0.5:1, 1:1, 1.2:1 [18b,31,340].

In the pursuit of more highly conducting materials over last years, the initial concept of a regular stack has been abandoned in favor of more exotic molecular arrangements such as those illustrated in Figure 3.3 for tetrachalcogenafulvalene salts (for details see [22,341-410]):

- (1) zig-zag stacking of centrosymmetric dimers as in the case of $(\text{TMTSF})_2\text{X}$ salts (with $\text{X} = \text{ClO}_4$, PF_6 , etc.), the so-called Bechgaard salts (Figure 3.3,I) and sulfur analogs
- (2) strongly dimerized chains with a deformed stacking axis (Figure 3.3,II) as in the case of some $(\text{DMET})_2\text{X}$ salts
- (3) sheets of stacks as in the α -phases (Figure 3.3,III) and β -phases (Figure 3.3,IV) of salts based on ET, EDTTTF, etc.
- (4) sheets of interacting orthogonal dimers, i.e., κ -phases (Figure 3.3,V) or polymeric-like sheets, i.e. τ -phases (Figure 3.3,VI) or salts based on several symmetrical or unsymmetrical tetrachalcogenafulvalenes.

Similar arrangements were observed in metal 1,2-dichalcogenolene complexes (see for example [411-437]).

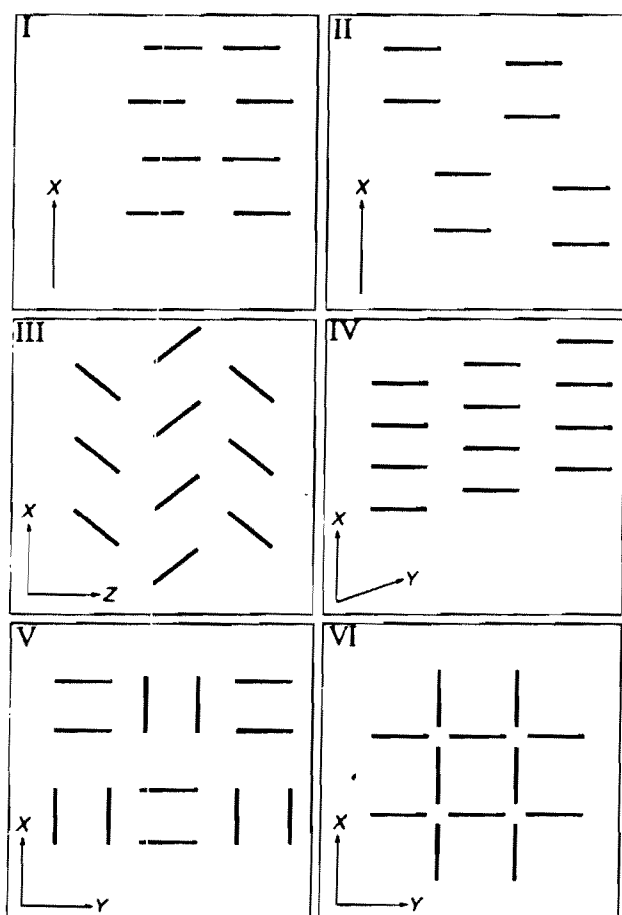


Figure 3.3. Illustration of molecular arrangements in some tetrachalcogenafulvalene salts.

3.4 Crystal structures

As was mentioned before tetrachalcogenafulvalenes and metal 1,2-dichalcogenolenes give a wide variety of CTCs and RISs. These salts are relatively light materials (density less than 2.8 g/cm^3), in most cases stable in moist air, and relatively clean compared with inorganic materials.

The structural properties of these materials depend on the nature of donor or acceptor molecules and the counteranion or the countercation. Sometimes, several different phases are obtained from the same constituents, which generally cannot be recognized from their external appearance. ET iodides, for example, are obtained in at least 12 phases [22]. In a few cases, different phases can be distinguished by their appearance, for example, β' -(12c-7g)₂I₃ is crystallized as golden-bronze needles, γ -(12c-7g)₁I₃ is crystallized as black needles and τ -(12c-7g)₂(I₃)₁(I₃)₋₁ is crystallized as bronze-black plates [351]. The shape of the crystals sometimes indicates the internal structure. For example, needle-like structures usually have a columnar

structure and plate-like crystals, which are easily cleaved, have a lamellar structure. Over the last years, a large number of phases, which are empirically labeled as α -, β -, γ -, δ -, ϵ -, ζ -, η -, θ -, κ -, λ -, ξ -, τ -, α' -, β' -, α -, etc., have been prepared and studied. The crystal structures have mainly been determined by usual X-ray diffraction techniques. The biggest problem in these experiments is the great tendency of some crystals to form twins. In this section the results of X-ray crystal structure analyses of some selected structures (mainly new materials) are described, although there is a large variety of them: Structures based on tetrachalcogenafulvalenes are reported in the literature [43–45, 76, 107, 132, 142, 143, 146, 162, 164, 169, 172–175, 177, 178, 202, 206, 223, 237, 239, 261–263, 280, 287, 290, 326, 329, 339, 341–410]; structures based on metal 1,2-dichalcogenolenes or on both tetrachalcogenafulvalenes and metal 1,2-dichalcogenolenes are reported in [43–45, 294, 301–305, 313–315, 317, 318, 338, 410–437]. In the following sections the structures of salts based on tetrachalcogenafulvalenes first and then the structures based on metal 1,2-dichalcogenolenes or both will be described. They are classified as columnar, lamellar and other structures. The classification is based on the magnitude of interactions in several directions, namely on the values of intermolecular contacts in comparison with van der Waals diameters (which are 2.8, 3.0, 3.7, 4.0 and 4.4 for O, N, S, Se and Te, respectively).

3.4.1 Columnar structures

In the following some columnar structures, of which the room temperature (RT) crystallographic data are summarized in Table 3.7, are described (see refs. [24, 25, 153, 164, 178, 372, 280, 372, 438–441]).

3.4.1.1 Bechgaard salts and sulfur analogs

It was demonstrated 15 years ago (see [24, 25]) that Bechgaard salts (TMTSF)₂X, and sulfur analogs, (TMTTF)₂X, which are q-1D conducting crystals, are crystallized in a triclinic system (space group $P\bar{1}$). The basic architectural feature is the zig-zag columnar stacking of nearly planar TMTSF (2b'-2b') or TMTTF (1b'-1b') molecules (face-to-face stack) parallel to the *a*-axis (i.e., parallel to the needle-axis with the highest electrical conductivity), as illustrated in Figure 3.3(I). The structure is dimerized along the stacking axis, which is more pronounced for sulfur than for the

selenium salts. The unit cell contains one molecular formula (i.e. $Z = 1$). In these columns there are some weak interstack (interchain) $\text{Se} \cdots \text{Se}$ or $\text{S} \cdots \text{S}$ contacts, where the corresponding distances are close to the van der Waals diameters.

3.4.1.2 (EDTTTF)₂AuBr₂

This salt, in which EDTTTF is the unsymmetrical molecule (7c-1a'), is crystallized in the monoclinic system (space group $C2/m$) [439–441]. It has a structure similar to the Bechgaard salts. Similar structures are based on larger donor molecules also described [197].

3.4.1.3 (DMET)₂X- salts

Ten years ago, some salts of the type $(\text{DMET})_2\text{X}$, where DMET is the unsymmetrical molecule (2b'-7c) and $\text{X} = \text{PF}_6, \text{BF}_4, \text{Au}(\text{CN})_2$ etc., have been prepared and studied. Most of these are crystallized in the triclinic system (space group $P\bar{1}$), in which the DMET molecules form columnar stacking with some dimerization (see Figure 3.3.II). There are interstack interactions stronger than those of Bechgaard salts (i.e. shorter $\text{S} \cdots \text{S}$ and $\text{S} \cdots \text{Se}$ contacts) [442].

3.4.1.4 (DMET-TSeT)₂X salts

The salts $(\text{DMET-TSeT})_2\text{X}$, where DMET-TSeT is the unsymmetrical donor molecule (2b'-8c) and $\text{X} = \text{I}_3, \text{AuI}_2, \text{AuBr}_2$ etc., exhibit Bechgaard-salt-like columnar structures. The salts should lie on the border between columnar and planar systems [153,164].

3.4.1.5 (DIMET)₂I₃

This salt, where DIMET is the unsymmetrical molecule (1b'-7c), has a columnar structure, but the intercolumn $\text{S} \cdots \text{S}$ interactions are stronger than those of $(\text{DMET})_2\text{I}_3$ [372].

3.4.1.6 (TMET-STF)₂X

In the crystals of the (TMET-STF) salt, where TMET-STF is the unsymmetrical molecule (2c'-7c), there are two crystallographically independent donor molecules (A, B) each of which constructs independent columns (column A and column B). In the column B network, the stacking arrangement is similar to that of a Bechgaard salt, while in the column A network there are intercolumn contacts [178]. Similar results have been obtained for $(\text{TMET-STF})_2\text{BF}_4$ [280]. $(\text{TMET-STF})_2\text{Au}(\text{CN})_2$ is isostructural with the Bechgaard salts [280].

3.4.2 Lamellar structures

There is a large number of salts with different laminar structures that are q-2D (or 2D) conductors, but only some of them are described here; these are the so-called α -, β -, λ -, θ -, κ -, and τ -phases. Crystals of λ -phase have a needle-like shape, while crystals of other phases have a plate-like shape. Crystals of τ -phase are easily cleaved to thin plates parallel to the ab-plane. The structures of some α -, β -, κ -, and τ -phases are shown in Figures 3.4–3.11. Based upon the observed space group symmetries, unit cell constants, stoichiometries and number of molecules per unit cell, these materials

Table 3.7. Crystallographic data of some columnar structures at RT

	(2b'-2b') ₂ PF ₆ ^a	(2b'-7c) ₂ Au(CN) ₂ ^b	(1b'-7c) ₂ I ₃ ^c	(2b'-8c) ₂ I ₃ ^d	(2c'-7c) ₂ C ₂ O ₄ ^e	(7c-1a') ₂ AuBr ₂ ^f
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$C2/m$
<i>a</i> (Å)	7.297	6.763	6.674	7.826	8.021	7.209
<i>b</i> (Å)	7.711	7.710	7.732	15.908	29.730	29.033
<i>c</i> (Å)	13.522	15.314	15.589	6.737	6.556	6.644
α (deg)	91.29	90.20	97.77	92.72	90	
β (deg)	83.39					
γ (deg)	96.81	98.38	102.42	105.20	111.62	
γ (deg)	75.04	78.88	89.55	93.80	90	
<i>V</i> (Å ³)	71.01					
<i>z</i>	714.3	765.9	780.6	811.4	1501.7	1294.4
	1	1	1	1	2	

^a Ref. [24] and refs. therein; ^b ref. [441]; ^c ref. [372]; ^d ref. [164]; ^e ref. [178]; ^f ref. [440].

are expected to be quite varied. However, it is still possible to make some general comments about the phases under discussion (α , β , λ , θ , κ , τ). The crystals of all phases have layered structures consisting of alternating sheets of donor molecules and sheets of anions or polyanions. The τ -phase is an exception in that its 'donor' sheet is in fact a mixed donor/anion sheet which alternates with an anion sheet. In all phases there are S...S interactions inside the donor sheets. The different phases arise primarily from differences in the packing of the donor molecules and secondarily from differences in the anion characteristics. In phases α , β , θ , λ the donor layer, in general, is made up of nearly planar donor molecules packing face-to-face to form stacks (intrastack packing) and the stacks packing side-by-side (interstack packing) to form a layer. Differences arise in the intrastack direction from relative displacements of the donor molecules along the long molecular axis, along the short in-plane molecular axis and from relative rotations between these axes. There are differences also in the intrastack direction as can be seen in Figure 3.5 for the α -phase which displays the herringbone pattern and Figure 3.7 for the β -phase which has the honeycomb pattern. So it can be said in general, that the structural differences between the phases α , β , θ , λ or even among compounds that belong to the same

phase, arise primarily from different combinations of intra- and interstack packing modes. The donor layer of the κ -phase is made up of almost orthogonal dimers (Figure 3.9). Finally the donor layer of the τ -phase has the characteristic packing mode of Figure 3.11. One more structural parameter that characterizes these phases is that the number of independent donor layers per unit cell can vary from one (Figures 3.4, 3.6, 3.8) to four (Figure 3.10).

In the following sections a more detailed description of each phase, referring each time to a particular compound, is given.

3.4.2.1 α -(BEDT-STrF)₂NH₄Hg(SCN)₄

The structure of this compound, where BEDR-STrF is the donor molecule (7c-11c), which is isostructural with α -(ET)₂NH₄Hg(SCN)₄, is shown in Figures 3.4 and 3.5 [443], and the crystallographic data are given in Table 3.8 [443-445,394,388b]. The difference is about the Se atom disordered over all S positions of the core heteroatoms. The crystal has a layered structure (Figure 3.4) consisting of a donor layer which alternates in the b direction with a polymer [NH₄Hg(SCN)₄]_n⁻ anion layer. It contains one donor layer per unit cell and this layer has the characteristic

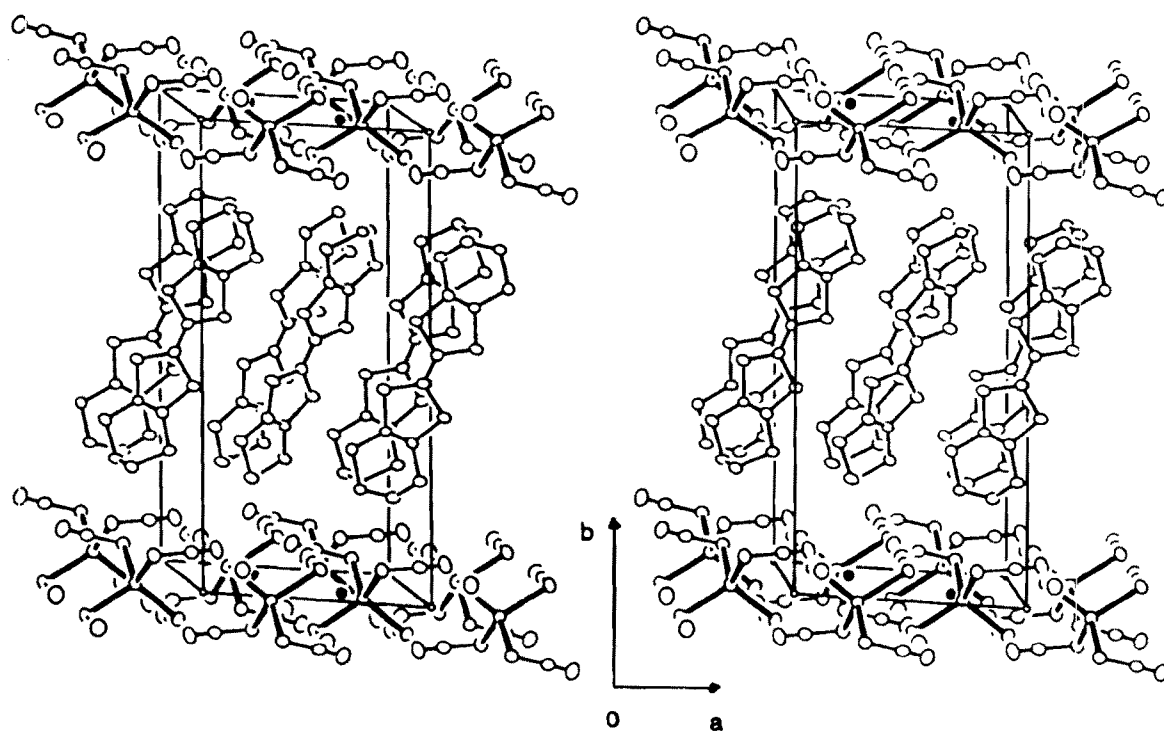


Figure 3.4. Stereoview of crystal structure of α -(BEDT-STrF)₂NH₄Hg(SCN)₄ at room temperature. Solid circles represent N atoms of NH₄.

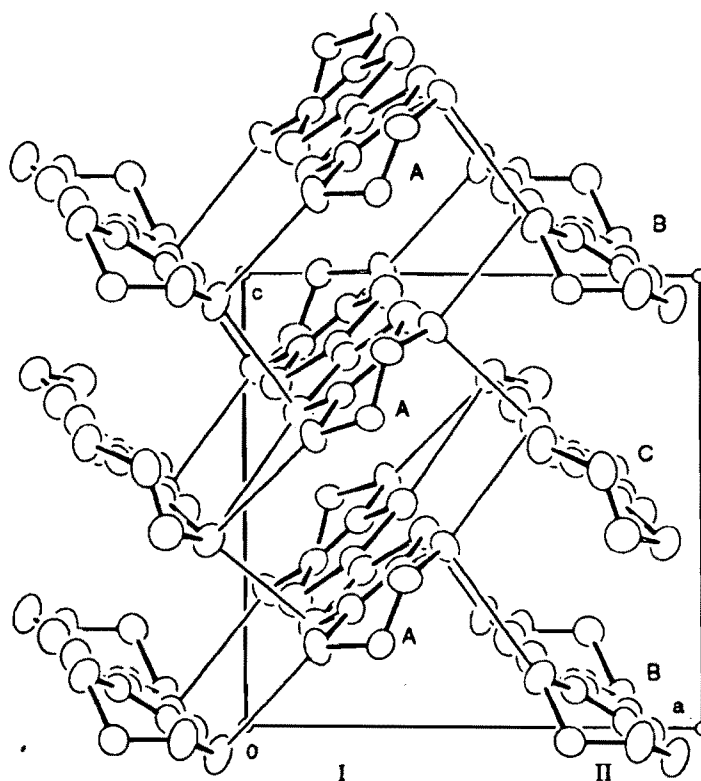


Figure 3.5. Arrangement of donor molecules in α -(BEDT-STrF)₂NH₄Hg(SCN)₄ at room temperature.

herringbone pattern (Figure 3.5) in the interstack directions a .

The donor layer contains three crystallographically different donor molecules (A, B, C, Figure 3.5) which pack in two alternating stacks I and II. Stack I contains parallel donor molecules A-A-A... and stack II the two non-parallel (dihedral angle of 7.7° between mean molecular planes) donor molecules B-C-B-C.... The dihedral angles A-B and A-C are 74.7° and 82.3° respectively. These dihedral angles vary between 60° and 85° in this phase of the various compounds (Table 3.8). All ethylene groups in this structure are ordered. It

should be noted here that while in the α -(ET)₂I₃ structure [22,446] the ethylene groups of the ET molecule in stack I are staggered and those in stack II are eclipsed, in the present structure all ethylene groups are eclipsed.

For some other α -type phases see [78,237,288,382,388b,389f,393,394].

3.4.2.2 β -(BEDT-STrF)₂AuI₂

The crystal structure of this compound is shown in Figures 3.6 and 3.7 and the crystallographic data are

Table 3.8. Crystallographic data of some α -phases at RT

	(7c-7c) ₂ NH ₄ Hg(SCN) ₄ ^a	(7c-11c) ₂ NH ₄ Hg(SCN) ₄ ^b	(7c-7c)KHg(SCN) ₄ ^c	(9c-9c) ₂ I ₃ ^d	(7a-7h-7a) ₂ I ₃ ^e
Space group	P $\bar{1}$	P $\bar{1}$	P $\bar{1}$	P $\bar{1}$	P $\bar{1}$
a (Å)	10.091	10.125	10.082	9.209	13.324
b (Å)	20.595	20.699	20.565	10.816	16.375
c (Å)	9.963	9.9072	9.933	176.607	12.333
α (deg)	103.70	103.60	103.70	96.777	110.59
β (deg)	90.53	90.56	90.91	97.89	99.93
γ (deg)	93.30	93.40	93.06	90.69	86.10
V (Å ³)	2008.1	2027.1	1997	1741.5	2481
z	2	2	2	2	2

^a Ref. [443]; ^b ref. [444]; ^c ref. [445]; ^d ref. [394]; ^e ref. [388b].

Table 3.9. Crystallographic data of some β -phases at RT

	(7c-7c) ₂ I ₃ ^a	(7c-11c) ₂ AuI ₂ ^b	(8c-7b) ₂ I ₃ ^c	(7c-7h-7c) ₂ Au(CN) ₂ ^d	(7c-7c) ₂ CuCl ₂ ^e
Space group	P $\bar{1}$	P $\bar{1}$	P $\bar{1}$	P $\bar{1}$	
a (Å)	10.785	6.605	6.1182	8.916	6.623
b (Å)	9.172	9.024	9.7525	17.916	9.723
c (Å)	17.39	15.385	14.9826	7.944	12.658
α (deg)	82.08	94.931	92.306	101.74	85.98
β (deg)	96.92	98.611	107.586	112.28	79.72
γ (deg)	89.13	110.751	73.209	82.33	79.905
V (Å ³)	1690.3	838.21	814.78	1147.5	789.0
z	1	1	1	1	1

^a Ref. [25], p. 52; ^b ref. [261]; ^c ref. [206]; ^d ref. [388a]; ^e ref. [350].

given in Table 3.9 [261]. It is isostructural with β -(ET)₂AuI₂ and β -(ET)₂I₃ [22,25,262,446]. The difference is that this has the Se atom disordered over all S positions of the core heteroatoms. The layered structure is apparent from the figures; it contains one donor layer and one crystallographically independent donor molecule per unit cell. Therefore the stacks are made of parallel donors (A-A-A...) and subsequent stacks are related by translations. Along the stacks, the molecules are dimerized in their long-axis lateral displacements, but the short S...S contacts are between rather than within the stacks which gives the donor layer its characteristic honeycomb appearance

(Figure 3.7). The ethylene groups are eclipsed in this structure. The crystallographic data of similar β -phases are given in Table 3.9.

For some other β -phases see [206,237,326,350,353,361,384,388b,404,410,439]. A new interesting salt, (DTEDT)[Au(CN)₂]_{0.4}, based on an unsymmetrical donor molecule (1 α' -7h-57 α') is crystallized in β -phase, but the arrangement of donor molecules form uniform stacks (i.e., no dimers). A similar uniform arrangement is also observed in (DTEDT)₃SbF₆ and (BDT-TTF)₂X, where BDT-TTF is (1 α' -7h-1 α') and X = ClO₄, SbF₆ (see [263,290] and refs. therein).

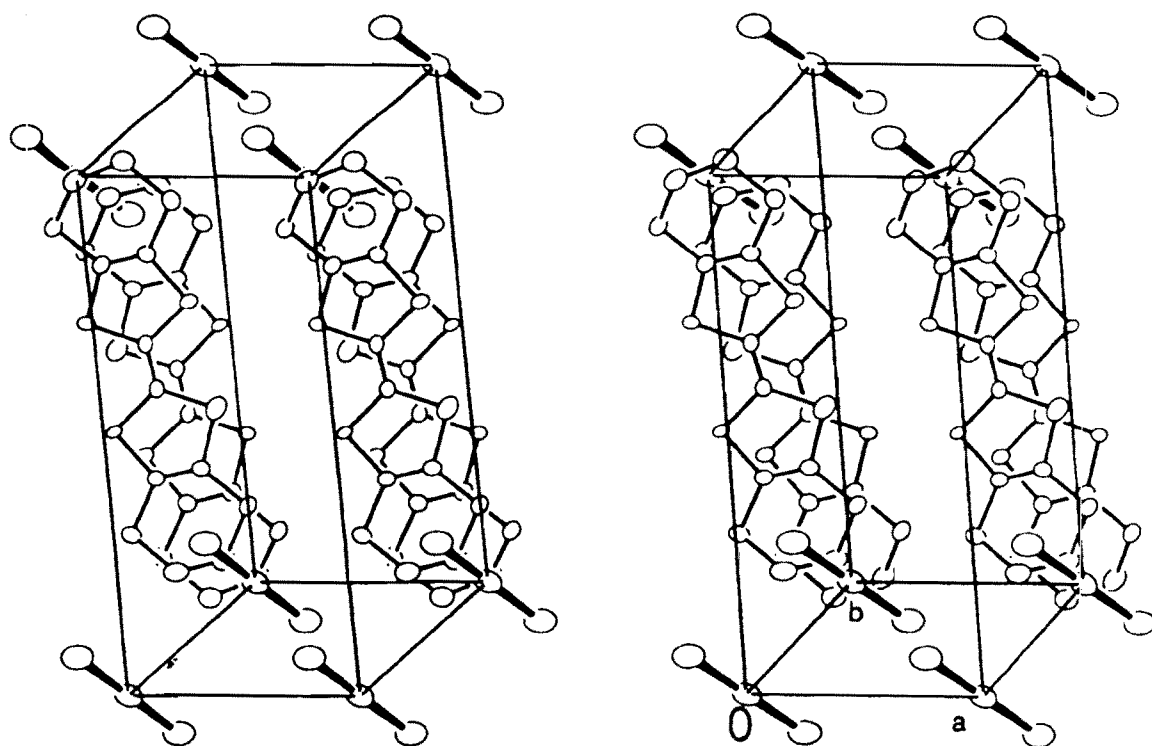


Figure 3.6. Stereoview of crystal structure of β -(BEDT-STrF)₂AuI₂ at room temperature.

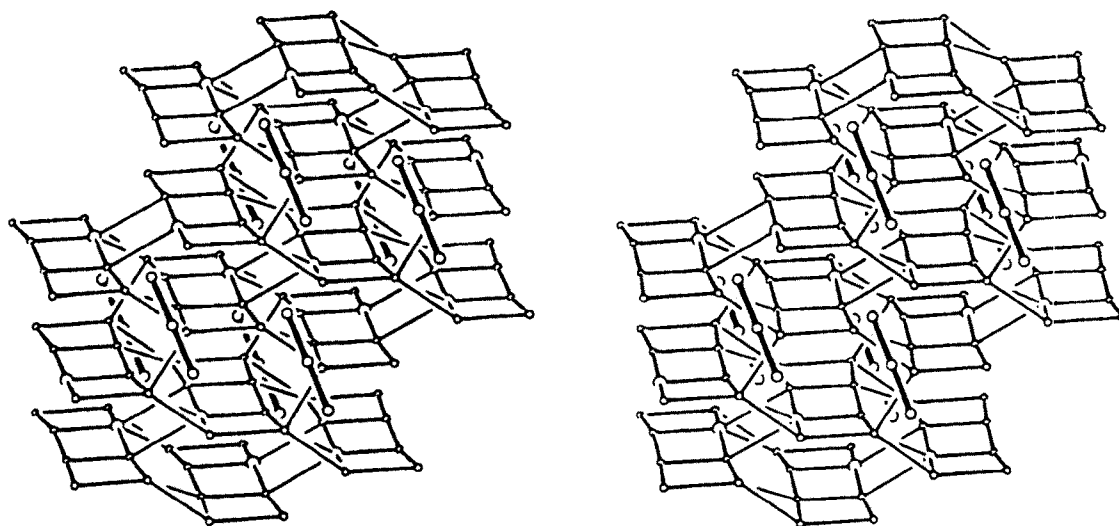


Figure 3.7. Stereoview of donor arrangement in β -(BEDT-STrF) $_2$ AuI $_2$ at room temperature.

3.4.2.3 θ -(ET) $_2$ I $_3$

The crystal structure of the title compound or more correctly of θ -(ET) $_2$ (I $_3$) $_{1-x}$ (AuI $_2$) $_x$ (with $x < 0.02$) [438–447] resembles that of α -(ET) $_2$ I $_3$ and, by extension, of α -[BEDT-STrF] $_2$ NH $_4$ Hg(SCN) $_4$ of Figures 3.4 and 3.5. The donor layer has the characteristic herringbone pattern already described for the α -phase (Figure 3.5). This compound is of higher symmetry than the triclinic of the α -phase; it contains one independent donor molecule inside the donor layer (instead of three in the α -phase), so that all stacks are identical and of the A–A–A... type with the dihedral angle between mean donor planes in adjacent stacks within the range 60–85° observed for the α -phase. another feature that distinguishes this from the α -phase is that the θ -phase contains two, rather than one, donor layer per unit cell. The crystallographic data of this and similar salts of the θ -phase are listed in Table 3.10. For some other θ -phases see [78,172,262,403].

3.4.2.4 λ -(BETS) $_2$ FeCl $_4$

The crystal structure of this salt, where BETS is (9c-9c), has similarities to both the α - and β -phases (see [297,377,395,396]). It contains two independent donor molecules per unit cell which form identical stacks of the alternant A–B–A–B... type. It resembles the α -phase in the intrastack packing since its stacks are similar to I-type in Figure 3.5, but presents analogs with the β -phase for the interstack packing since the donor layer has the honeycomb pattern of Figure 3.7. It contains one donor layer per unit cell as in the case in the α - and β -phases. The crystallographic data of this and similar salts of the λ -phase are listed in Table 3.11.

3.4.2.5 κ -(ET) $_2$ Cu $_2$ (CN) $_3$

The structure of this phase (Figures 3.8 and 3.9) is distinctly different from those of phases α , β , θ , λ ; in this phase the donor layer contains no stacks [373].

Table 3.10. Crystallographic data of some θ -phases at RT

	(7c-7c) $_2$ I $_3$ ^a	(7b-1a') $_2$ Au(CN) $_2$ ^b	(8b-1a') $_2$ Au(CN) $_2$ ^b	(9c-9c) $_3$ HgBr $_4$ ^c	(7c-7c) $_2$ Cu $_2$ (CN) [N(CN) $_2$] $_2$ ^d
Space group	<i>Pnma</i>	<i>Pn2n</i>	<i>Pn2n</i>	$1\bar{4}_1/a$	I222
<i>a</i> (Å)	10.406	10.060	10.198	9.742	11.088
<i>b</i> (Å)	31.454	27.833	28.147	9.742	38.837
<i>c</i> (Å)	4.163	4.061	4.085	75.68	4.201
α (deg)	90	90	90	90	90
β (deg)	90	90	90	90	90
γ (deg)	90	90	90	90	90
<i>V</i> (Å 3)	1362.5	1137.2	1172.6	7182.5	1809.1
<i>z</i>	2	2	2	2	2

^a Ref. [447] and refs. therein; ^b refs. [202,401]; ^c refs. [78,342]; ^d ref. [390].

Table 3.11. Crystallographic data of some λ -phases at RT

	$(9c-9c)_2\text{FeCl}_4^a$	$(9c-9c)_2\text{GaCl}_4^a$	$(9c-9c)_2\text{GaCl}_4^b$
Space group	$\bar{P}1$	$\bar{P}1$	$\bar{P}1$
a (Å)	16.164	16.141	16.165
b (Å)	18.538	18.580	18.612
c (Å)	6.593	6.594	6.608
α (deg)	98.40	98.37	98.41
β (deg)	96.67	96.77	96.69
γ (deg)	112.52	112.55	112.56
V (Å ³)	1773.0	1774.0	1783.5
z	2	2	2

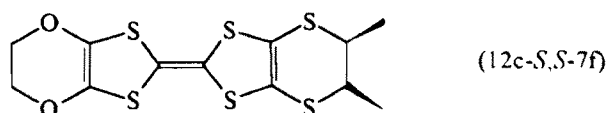
^a Ref. [279,377,395,396]; ^b ref. [386].

The donor molecules (with 3.5 Å between them) form face-to-face orthogonal dimers and these dimers pack with dihedral angles close to 90° with their immediate neighbors to form the donor layer (Figure 3.9). The S...S contacts are not within but between dimers. The donor layer, one per unit cell, Figure 3.8, alternates with a flat $[\text{Cu}_2(\text{CN})_3]_n^-$ anion layer, of edge-sharing 18-atom hexagonal rings (six Cu atoms and six CN groups) (Figure 3.8). One ethylene group of the donor is ordered and the other is disordered. The crystallographic data of this and similar salts of κ -phase are listed in Table 3.12. For similar κ -phases see

[78, 143, 166, 173, 174, 206, 261, 279, 326, 342, 346, 352, 360–362, 368, 376, 389, 395, 402, 405].

3.4.2.6 τ -(EDO-*S,S*-DMEDT-TTF)₂-(AuBr₂)_{0.75}

The structure of this phase (Figure 3.10 and 3.11), where EDO-*S,S*-DMEDT-TTF is the unsymmetrical donor molecule (12c-*S,S*-7f), with a chiral structure,



is distinctly different from all other phases [261,300,407]. The donor layer contains no stacks. Every donor molecule is perpendicular to its closest neighbors (Figure 3.11) and it has S...S closed contacts with them. This pattern of orthogonal monomers is similar to the 'honeycomb' pattern of the β -phase (Figure 3.7), where a 'honeycomb' of hexagons, is present, while in τ -phase a 'honeycomb' of octagons and tetragons is observed. The other distinctive feature of this phase is that some of the anions (those that are crystallographically well behaved and well defined)

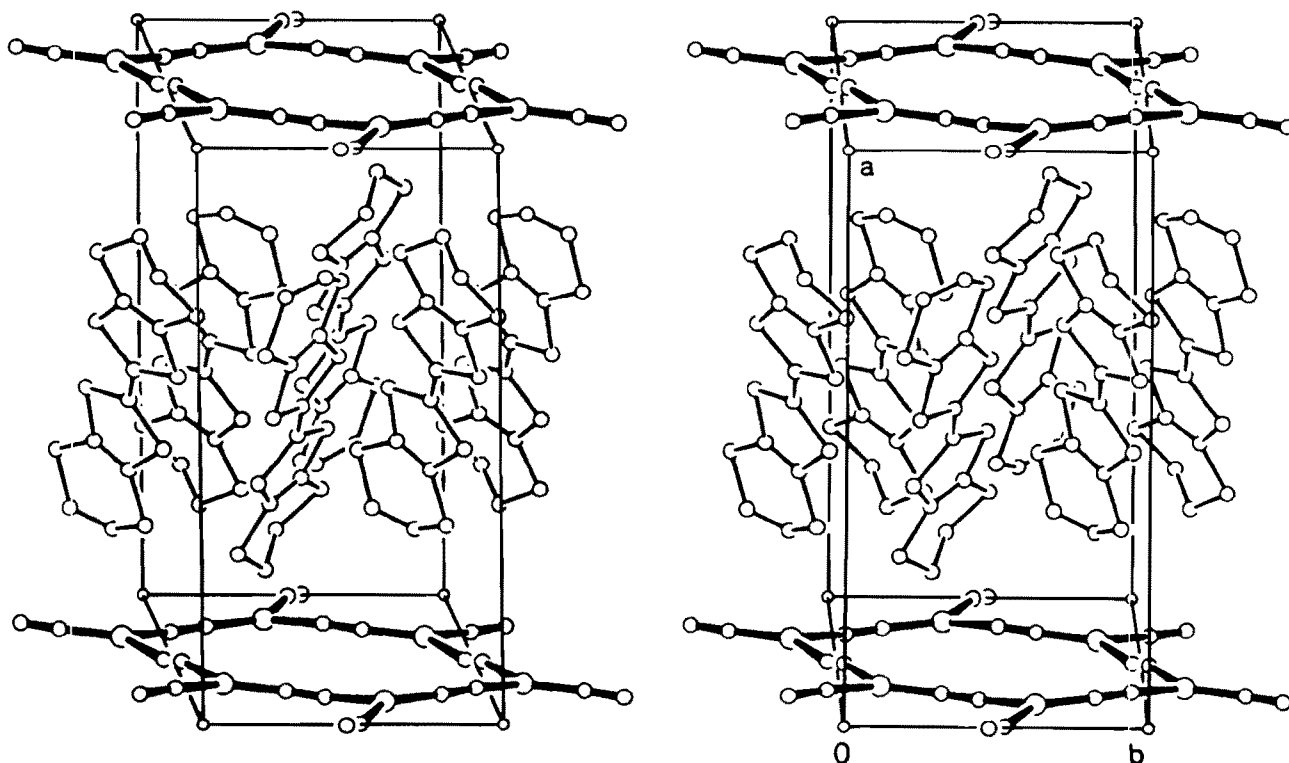


Figure 3.8. Stereoview of crystal structure of κ -(ET)₂Cu₂(CN)₃ at room temperature.

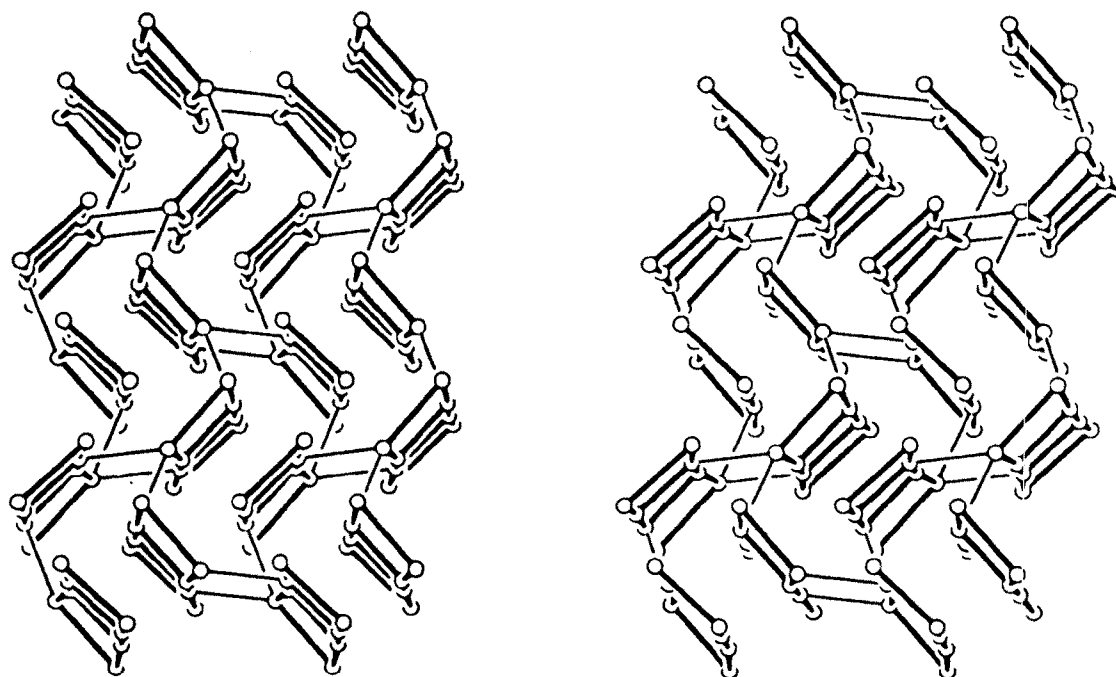
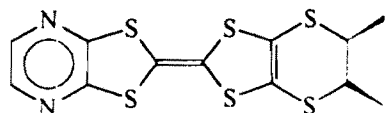


Figure 3.9. Arrangement of donor molecules in κ -(ET) $_2$ Cu $_2$ (CN) $_3$ at room temperature.

occupy positions within the donor layer, in the middle of the octagons (Figure 3.11), while the remaining anions, which are not well defined crystallographically, form the anion layer which alternates with the donor/anion layer. There are four donor/anion layers per unit cell. In this structure, the ethylene-dioxo group is disordered, while the dimethyl-ethylene group is ordered.

In a similar structure, τ -(P-S,S-DMEDT-TTF) $_2$ -(AuBr $_2$) $_1$ (AuBr $_2$) $_{0.75}$, where P-S,S-DMEDT-TTF is (13a'-S,S-7f) (a molecule also with a chiral structure), the dimethyl-ethylene group is disordered [383]. The



(13a'-S,S-7f)

crystallographic data of some salts of the τ -phase are listed in Table 3.13; for other τ -phases see [261,309,341,391,407,443].

3.4.3 Other typical structures

A number of RCSs (or CTCs) have structures that belong to different phases than those described in the previous paragraphs. They are characterized as γ - [359a], δ - [359b], ϵ - [359d], ζ - [359e] etc. [22] phases. Some others have a columnar-like [164,237,239,246,260,262,272,280,287,298,385,387,388b], or a lamellar-like [117,146,162,164,165,169,175,202,249,279,343-345,348,351,353,356,358,359f,367,379,381,387,389,392,400], etc. and [76,79,107,132-142,172-175,177,179,184,197,204,205,223,237,262,263,272,276,279,280,285b,324,339a,343,357,

Table 3.12. Crystallographic data of some κ -phases at RT

	(7c-7c) $_2$ Cu $_2$ (CN) $_3$ ^a	(7c-11c) $_2$ Cu $_2$ (CN) $_3$ ^b	(9c-9c) $_2$ FeCl $_4$ ^c	(7b-1a') $_2$ AuI $_2$ ^d	(7c-7c) $_2$ Cu(SCN) $_2$ Cl ^e	(7c7c) $_2$ I $_3$ ^e
Space group	P2 $_1$ /c	P2 $_1$ /c	Pnma	Pbnm	P2 $_1$	P2 $_1$ /c
<i>a</i> (Å)	16.542	16.4	11.483	10.797	16.256	16.387
<i>b</i> (Å)	8.549	8.6	35.720	7.789	8.456	8.466
<i>c</i> (Å)	13.253	13.5	8.383	28.991	13.143	12.832
α (deg)	90	90	90	90	90	90
β (deg)	64.51	68	90	90	110.28	108.56
γ (deg)	90	90	90	90	90	90
<i>V</i> (Å 3)	1691.9	1765.39	3438	2438.1	1694.8	1687.6
<i>z</i>	2	2	4	4	2	2

^a Ref. [373] and refs. therein; ^b ref. [206]; ^c ref. [395]; ^d ref. [448]; ^e ref. [22].

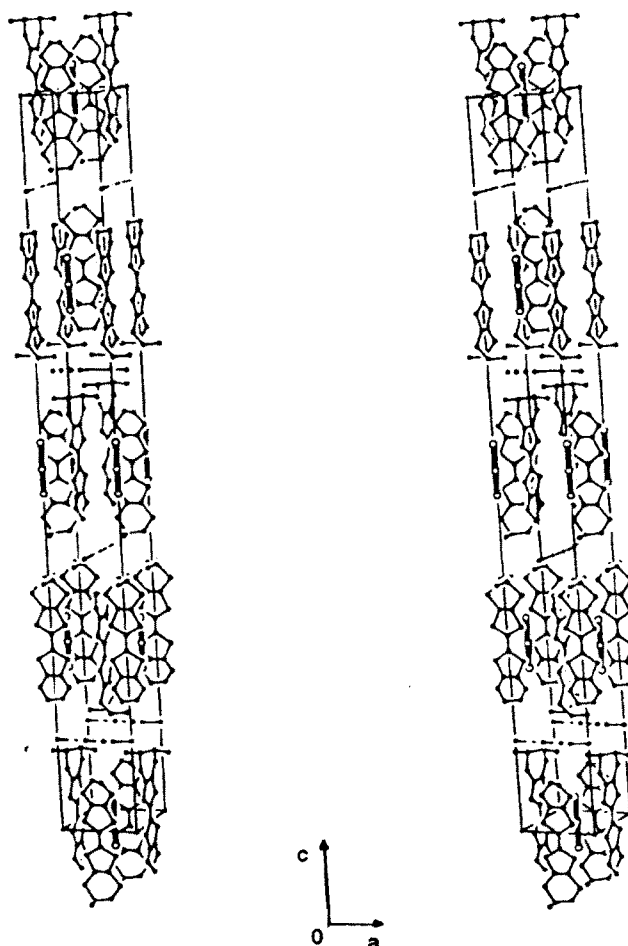


Figure 3.10. Stereoview of crystal structure of τ -(EDO-S,S-DMEDT-TTF) $_2$ (AuBr $_2$)(AuBr $_2$) $_{0.75}$ at room temperature.

359e, 363–366, 372, 374, 378, 380, 384, 385, 389c, 393, 397, 398, 400–404] structure. (ET) $_4$ Cu(C $_2$ O $_4$) $_2$ has been characterized as an q-3D system [349,371]; for similar structures see [336,337,344], where there are intrastacking interactions as well as side-by-side interactions.

3.4.4 Counter anion structures

The counter anion in the RCSs based on tetrachalcogenofulvalenes interact only weakly with the donor-molecule cations [463] and play a secondary role in the physical properties of salts (see below). They are isolated molecules, e.g., I $_3^-$, AuI $_2^-$, Au(CN) $_2^-$ [237,261], CoW $_{12}$ O $_{40}$ [389] and C $_{60}$ [397], infinite chains, e.g., (PbBr $_3$) $_n^{n-}$ [398], [Cu $_2$ I $_2$] $_n^{n-}$ [392] or infinite sheets, e.g., [Cu $_2$ (CN)] $_3$ $_n^{n-}$ [373] and (NH $_4$ Hg(SCN) $_2$) $_n^{n-}$ [460,461]. Sometimes anions (e.g. I $_3^-$, AuBr $_2^-$) form a 3D network [261,300,326].

3.4.5 Structures based on metal 1,2-dichalcogenolenes

They form similar crystal structures, which can be classified following the same pattern. For example, the compound Ni(dddt) $_2$ (HSO $_4$) $_2$ (see Table 3.6) has a columnar-like structure [431,420], while some other salts have lamellar structures, i.e., α -(9d-9d)[Ni(dmit) $_2$] $_2$ [436], α -(Me $_2$ Et $_2$ N)[Ni(dmit) $_2$] $_2$ [433,435], α -(7c-1a')-[Ni(dmit) $_2$] $_2$ [422], α -(7c-1a')[Pd(dmit) $_2$] $_2$ [411], β -(9d-9d)[Ni(dmit) $_2$] $_2$ [436], β -(Me $_4$ N)[Pd(dsit) $_2$] $_2$ [425], (Me $_4$ N)[Pd(dmit) $_2$] $_2$ [414,431], β -Me $_4$ A[Pd(dmise) $_2$] $_2$ (A = N, P, As, Sb) [431], β -[M(dddt) $_2$] $_2$ X [426], β -Me $_4$ N[Au(dmit) $_2$] $_2$ [419] and κ -(Me $_4$ P)[Ni(dsit) $_2$] [411]. Besides, the following salts [Pt(dddt) $_2$]FeCl $_4$ [429], Me $_2$ Et $_2$ N[Pd(dmit) $_2$] $_2$ [418], Cs[Pd(dmit) $_2$] $_2$ [415,416], (EDTTTF) $_x$ [Pd(dmit) $_2$] $_y$ [431b] exhibit a lamellar-like structure. The structure of (Me $_3$ NH)[-

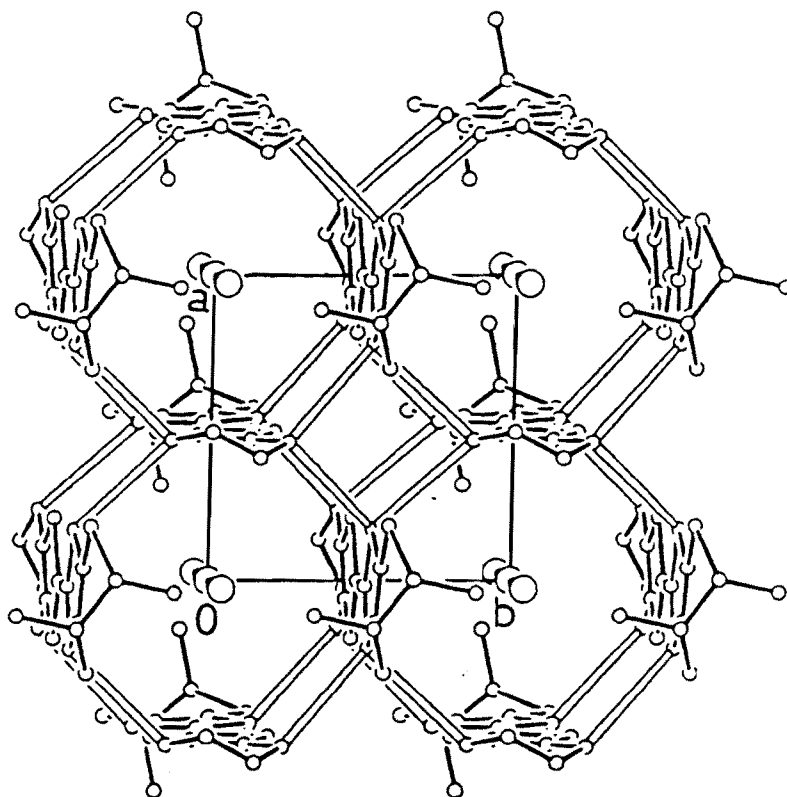


Figure 3.11. Molecular arrangement of donor molecules of τ -(EDO-S,S-DMEDT-TTF)₂(AuBr₂)(AuBr₂)_{0.75} at room temperature.

Ni(dmise)₂ has 3D character [433,335]. For some other structures see [294,313–315,317,410, 413,417,420,421,423,424,432b,437].

3.4.6 Structural disorder

Besides their inherent thermal agitation atoms and molecules exhibit natural or induced disorders which are called intrinsic and extrinsic, respectively. Different cases of intrinsic disorders are known: orientational or even conformational disorders of cations or anions, compositional disorder as in solid state solutions and

positional disorder as in polymer-like chains or sheets. The main origins of extrinsic disorder occur either during the preparation and crystallization process, where impurities and defects are introduced, or under irradiation with for example UV light. The induced disorders are associated with some chemical changes.

3.4.7 Temperature and pressure dependences

In a number of RISs or CTCs, on going from room temperature to lower temperatures some changes in the

Table 3.13. Crystallographic data of some τ -phases at RT

	(12c-S,S-7f) ₂ (AuBr ₂) ₁ (AuBr ₂) _{0.75} ^a	(13a'-S,S'-7f) ₂ (AuBr ₂) ₁ (AuBr ₂) _{0.75} ^{a,b}	(7c-7g) ₂ (I ₃)(I ₃) _y ^{c,d}	(7c-12c) ₂ (AuI ₂) ₁ (AuI ₂) _v ^e
Space group	I4 ₁ 22	I4 ₁ 22	P4 ₂ c	P4 ₂ c
a (Å)	7.4048	7.3546	7.563	7.4854
b (Å)	7.4046	7.3546	7.563	7.4854
c (Å)	67.995	67.978	34.032	34.0318
α (deg)	90	90	90	90
β (deg)	90	90	90	90
γ (deg)	90	90	90	90
V (Å ³)	3728.2	3676.9	1946.6	1906.84
Z	8	8	4	4

^a Refs. [261,300,407]; ^b refs. [383,391]; ^c ref.[326]; ^d ref. [341a]; ^e ref. [341].

crystal structures take place which affect the physical properties of these compounds (see Sections 3 and 5). For some recent work see [435,449–451]. In the case of α -(BETS)₂I₃, where BETS is (9c-9c), for example, changes in the crystallographic data and minor changes in the crystal packing take place on going from room temperature to 13 K [451]. Some changes of the crystal structure have been observed in α' -(ET)₂Au(CN)₂ [450], (ET)₃Cl₂.2H₂O [449], β -(ET)₂I₃ [446], κ -(ET)₂I₃ [451b] and α -(Me₂Et₂N)[Ni(dmit)₂]₂ [435]. Some of them are due to the disorder–order transition of counterions and in edge groups of donor molecule at low temperatures [22,446]. κ -(ET)₂I₃ is monoclinic of space group P2₁/c at room temperature and becomes monoclinic of space group P2₁ below 150 K, because the conformation of the ethylene group is changed at $T < 170$ K [451b]. α -(Me₂Et₂N)[Ni(dmit)₂]₂ is monoclinic with space group C2/c at room temperature and becomes monoclinic with space group P2₁/c at 11 K, because the cation Me₂Et₂N is disordered at room temperature and it becomes ordered at 11 K [435]. Similar results have been observed under high pressure [446,450,452].

4 SOLID STATE PHYSICAL PROPERTIES

4.1 Theoretical background

The physical properties of the molecular CT salts and more specifically of the RISs are mainly determined by two basic sets of criteria. These are the conditions needed to observe a metallic state at around room temperature and the existence of different instabilities giving rise at lower temperatures to various possible ground states.

4.1.1 Conducting character in narrow electronic bands

The theoretical models are based upon two complementary approaches described in the following and resumed quantitatively in Section 4.1.1.1 (see [333a], refs. cited therein, and [453]).

4.1.1.1 Electron correlations and Hubbard models

A quantitative approach is to define the Coulomb interactions, not only the on-site interaction but also several near-neighbor interactions, which cannot be

negligible, compared with the bandwidth. A valuable approximation is to consider the two first terms: The extended Hubbard Hamiltonian is, in second quantization notation (site representation):

$$H = \varepsilon \sum_{p,\sigma} n_{p,\sigma} - t \sum_{p,\sigma} (C_{p+1,\sigma}^+ C_{p,\sigma} + C_{p,\sigma}^+ C_{p+1,\sigma}) + U \sum_p n_{p\uparrow} n_{p\downarrow} + V \sum_p n_{p+1} n_p + (H_{e-p}) \quad (3.5)$$

where $C_{p,\sigma}^+$ and $C_{p,\sigma}$ are the creation and annihilation operators, respectively, of an electron of spin σ on the site p , n_p is the occupation operator, ε and t are the one-electron site energy and transfer integral, respectively, as defined in the tight-binding model and U , V are the on-site and next-neighbor Coulomb interactions.

H_{e-p} is the Hamiltonian term just to remind us that it is necessary to take account of the interactions between electrons and phonons, intramolecular vibrations, and lattice phonons for explaining some physical properties. The two first terms of H are representative of a model for non-interacting electrons and considered as a topological approach. The next two terms are essentially molecular characteristics, which include the charge distributions on a monomer and a dimer. Nevertheless, the basic issue is the order of magnitude and the sign of U and V in these charge-transfer salts. The first estimates give $U > V > 0$ with $U > 1$ eV, which is comparable to, or larger than, the bandwidth Δ .

Starting from this point, two main approaches have been developed:

- (i) The weak-coupling limit, where U , V are considered as perturbations of the one-electron model (U , $V < |t|$). A vast literature has been developed ('g-ology' models) that predicts different electronic instabilities and associated ground states.
- (ii) The strong-coupling limit (U , $V \gg |t|$), where the strong electron–electron interactions lead to a charge localization on molecular sites or between them.

The easiest case to investigate is the zero-bandwidth or atomic limit; here, the standard Hubbard Hamiltonian (with $V \equiv 0$) is equivalent to a Heisenberg spin Hamiltonian:

$$H_{sp} = J \sum_i S_i S_{i+1}$$

where

$$J = [2(t)^2/U]p[1 - \sin(2\pi\rho)/2\pi\rho] \quad (3.6)$$

J is the exchange integral responsible for an AF coupling ($J > 0$ in the present case). For an extended Hubbard model, it is necessary to use an effective U_{eff} (instead of a bare U) which depends upon the band filling.

One drastic consequence of this model is the decoupling of charge and spin excitations, with the appearance of an energy gap along the energy axis. There is a split of the initial electronic band into two ($U_{\text{eff}1}$), or more ($V_{\text{eff}1}$) sub-bands, which are separated by a Hubbard gap. The value of this gap has been calculated for a 1D extended Hubbard model.

(i) Non interacting electrons. The tight-binding method is normally developed in association with the extended Hückel theory for these molecular solids [334] to determine their electronic structure through a calculation method to evaluate the transfer integral (t), which is a measure of interactions. Usually the dispersion energy $E(k)$ (where k is the associated wave vector), the Fermi surface and the density of states $N(E)$ are calculated for comparison with the experimental data. Without going into detail, two specific characteristics are relevant for these molecular solids: firstly, the effect of electronic dimensionality, which is due to the presence of overlapping of π -type orbitals in a privileged direction (1D systems) or in a given plane (2D systems). This electronic dimensionality is fully characterized by the analysis of the corresponding Fermi surfaces. Secondly, rather small overlap be-

tween neighboring orbitals, which results in narrow electronic bandwidths compared with those for the usual atomic metals. Currently the estimated bandwidth is: $W \approx 2zt \leq 1$ eV (where z is the number of nearest neighbors, depending on the structural arrangement).

Some examples of 1D, q-1D and 2D electronic structures and Fermi surfaces are shown in Figure 3.12. This approach takes into account only the topology of electronic interactions. Examples of real systems, such as Bechgaard salts and β -ET phases have structures and Fermi surfaces close to those given in Figures 3.12(b) and 3.12(c), respectively (see [22,24,454]). Starting from this one-electron band description we see that in the presence of a single valency system, i.e. with $\rho = 1$, we should have a conducting state.

(ii) Interacting electrons and correlated models. It turns out that a standard band model for non-interacting electrons in crystalline solids cannot explain several important phenomena such as the metal-insulator transition, and the occurrence at low temperatures of a superconducting state or a magnetic ordering [455].

The introduction of electrons, which interact both with one another and with the lattice vibrations, has been a great advance in the understanding of the physical properties in these materials:

(a) The interactions between electrons, inducing a metal-insulator transition known as Mott-

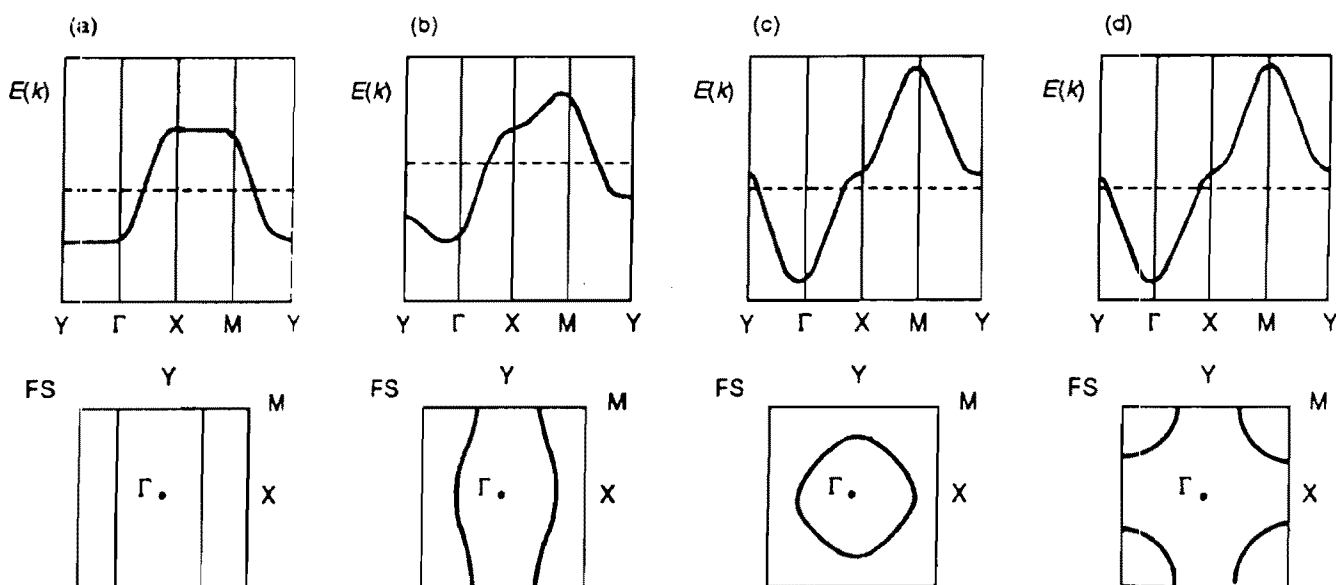


Figure 3.12. Some examples of ideal band structures and corresponding Fermi surfaces (FSs) (a and b are the unit cell parameters; t_a and t_b are the transfer integrals along the a and b axis respectively): (a) half-filled 1D band ($t_a < 0$; $t_b = 0$); (b) half-filled quasi-1D band ($t_a < t_b$); (c) less than half-filled 2D band ($t_a = t_b$); (d) more than half-filled 2D band ($t_a = t_b$). Γ , X, Y and M refer to $(0,0)$, $(a^*/2,0)$, $(0,b^*/2)$ positions and $(a^*/2,b^*/2)$, respectively, in the Brillouin zone.

Hubbard type in the absence of any structural disorder.

- (b) The interactions with both lattice phonons and intramolecular vibrational modes, as revealed by the studies on optical properties (IR and Raman spectroscopy).

Both interactions are significant but usually the electronic correlations are predominant and will mainly be considered. As introduced by [Hubbard] [456] the influence of Coulombic interactions (U) between electrons on the same molecule is crucial. Indeed, it has been shown that the electronic structure is changed by introducing U : the initial band is split into two bands, the lower and upper bands, with the opening of a gap when $U/W \approx 1$. This result has been established within the mean field approximation and does not appear to be strongly dimensionality dependent except for an ideal 1D situation. It appears therefore that for $U > W$ (large U approximation) with a single formal valency state, i.e. with $\rho = 1$, we observe an insulating state.

In order to get a partially filled band, and therefore a conducting state in the absence of any other effect, it is necessary to be in the presence of a mixed valence state with ρ as a non-integer value (of Robin-Day classification [333]). To complete this overall picture the existence of long-range electronic correlations have also to be considered, when the involved energies are larger than the electronic bandwidth. It has been shown that, at least for 1D electronic systems, it is necessary to deal with the Coulombic correlations between first neighbor sites ($V < U$). These are the so-called extended Hubbard models [456].

Resuming this point two main approaches have been developed: so-called small and big U approximation as explained in the earlier.

4.1.2 Instabilities and different ground states in low-dimensional systems

It is noteworthy to indicate, that, as demonstrated by different theoretical approaches, a pure one-dimensional (1D) electron system differs from a 3D one in several fundamental ways. Let us recall the following important points [457]:

- (i) The 1D system is always unstable against the basic interactions: electron-electron and/or electron-phonon interactions may lead to a variety of broken symmetry ground states.

- (ii) There exists no long-range order in an ideal 1D system, with only short-range interactions, at any non-zero temperature.
- (iii) Any arbitrary small amount of disorder leads to a localization of all the electronic states.

Several works have shown the real effect of a reduced electronic dimensionality in these molecular compounds, especially for the q-1D Bechgaard salts [458] but existing also under a weaker form in q-2D systems. In these q-1D systems, an interchain coupling exists which controls the nature of the phase transition [459]. The 'g-ology' model predicts the occurrence of several types of order [460]:

- (i) the charge density wave (CDW) state associated with a periodic lattice distortion which opens a gap at the Fermi level, as initially proposed by Peierls in 1955 (see [461]).
- (ii) the spin density wave (SDW) which corresponds to a spin modulation state and an antiferromagnetic (AF) order.
- (iii) the singlet pairing superconducting state or even the triplet pairing superconducting state [24].

A Peierls distortion may be detected from the corresponding structural distortion in two limiting cases: For a free electron gas ($t \gg U$), a charge excitation (CDW) with a characteristic wave vector at $2k_F$ will condense at the phase transition ('electronic' Peierls distortion). For a highly correlated gas, where the Coulomb interactions are strong ($U \gg t$), a spin charge separation is occurring. A spin excitation (SDW) will be present at $2k_F$, accompanied by a $4k_F$ charge excitation which gives rise to a similar phase transition: the 'magnetic' Peierls distortion. For both cases, an insulating non-magnetic state is observed at temperatures below the phase transition (T_c).

The other instabilities cannot be evidenced by a structural investigation but in fact by a change of the electronic or the magnetic properties as known from different experimental situations of Bechgaard salts [333] (see Figure 3.13 for a significant example).

4.2 Electronic band structure calculation

Over the years, electronic band structure calculations have been made on a number of salts based on tetrachalcogenafulvalenes and metal 1,2-dichalcogenolenes, mainly by applying the extended Hückel tight-

binding theory [334] under the conditions outlined in the previous subsection (see [430,446,462–466]). For band structure and Fermi surface calculations the experimental data of crystal structure solutions have been used. For some examples, see [290,300,326,384,388,391,395,431,435,438,441,446,447,449–452,462–472] and references cited therein. In the case where there is a disorder in the active part of the system (e.g. disorder in the heteroatom) the calculation is difficult or impossible. Very few attempts have been made outside the domain of the extended Hückel method (see [453,454,465,466]). Results concerning ideal systems are shown in Figure 3.12. Electronic band structures and Fermi surfaces can be determined with parameters obtained for example from optical reflectance spectra generally at any temperature (see [300,394,438,447]) and more accurately from the Shubnikov–de Haas or de Haas–van Alphen experiments at very low temperatures (see [24,467]). In the next paragraphs, the calculated electronic band structures and Fermi surfaces of some selected salts are described.

4.2.1 Band structures of columnar compounds

It has been demonstrated some years ago that the $(\text{TMTSF})_2\text{X}$ salts have a columnar structure. From the band structure calculations, it has been found that the intrastack transfer integrals of these salts are larger than

the interstack ones. They give an open orbit Fermi surface with a q-1D character, similar to that of Figure 3.12(b) (see [464] and refs. therein). However, recently some new materials with columnar structure have been prepared, as described in Section 3.4, and the band structures calculated. Figure 3.14 shows the schematic projections of the structure along the long donor molecular axis, the charge-transfer integrals, the electronic band structure and the Fermi surface of $(\text{EDTTTF})_2\text{AuBr}_2$, where EDTTTF is the donor (7c-1a') [440]. One can see that the (large intrastack and small interstack) transfer integrals and Fermi surface are close to those of $(\text{TMTSF})_2\text{X}$. Calculations on $(\text{DMET-TSeT})_2\text{X}$ compounds showed that they belong to q-1D systems with a pair of open and warped Fermi surfaces [153,164]. Calculations on $(\text{TMET-STF})_2\text{ClO}_4$ showed a q-1D behavior for column A and 2D behavior for column B [178].

4.2.2 Band structures of lamellar compounds

The electronic band structures of α -, β -, κ -, τ - etc. phases have quite different features, but they have more or less closed Fermi surfaces. Some examples of calculated electronic band structures from room-temperature crystallographic data are presented below.

4.2.2.1 α -($\text{ET})_2\text{NH}_4\text{Hg}(\text{SCN})_4$ and other α -phases

Figure 3.15(I) shows the electronic band structure and Fermi surface of α -($\text{ET})_2\text{NH}_4\text{Hg}(\text{SCN})_4$ [468,469]. The Fermi surface consists of two parts: a pair of open orbits (1D) and a single (2D) closed orbit, called α -orbit (see also Figures 3.12b and 3.12d for comparison). At room temperature all compounds of this series, α -($\text{ET})_2\text{MHg}(\text{SCN})_4$ ($\text{M} = \text{K}, \text{Rb}, \text{Tl}, \text{NH}_4$) have the same structure (see [443,468,469]). For the structures of some other α -phases see [393,394,435,446,451a,462].

4.2.2.2 β -($\text{ET})_2\text{I}_3$ and other β -phases

Figure 3.15(II) shows the electronic band structure and Fermi surface of β -($\text{ET})_2\text{I}_3$ [441]. The Fermi surface is characterized by a cylinder with closed orbits. The shape of the cylinder changes on going from one salt to another of the β -phases (see [25,440]) at room temperature. For the structures of some other β -phases see [263,290,353,441,446,384]. The salt (7c-7h-

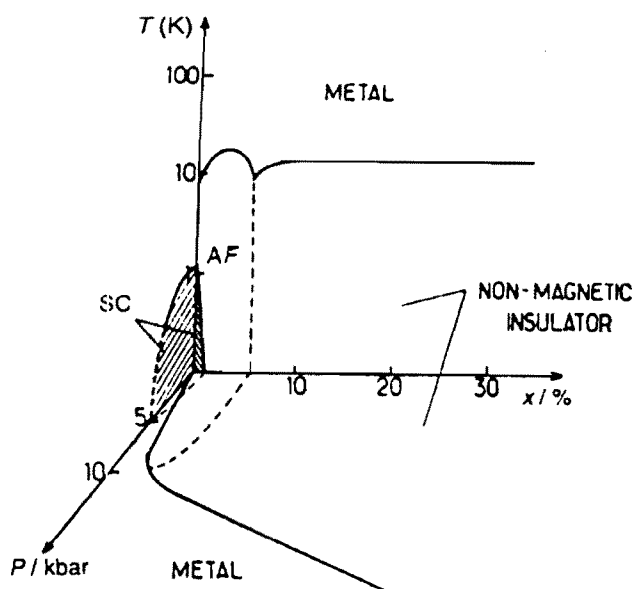


Figure 3.13. Phase diagram (T, P, x) for different ground states found experimentally in $[(\text{TMTTF})_x(\text{TMTSF})_{1-x}]_2(\text{ClO}_4)$ alloys [333].

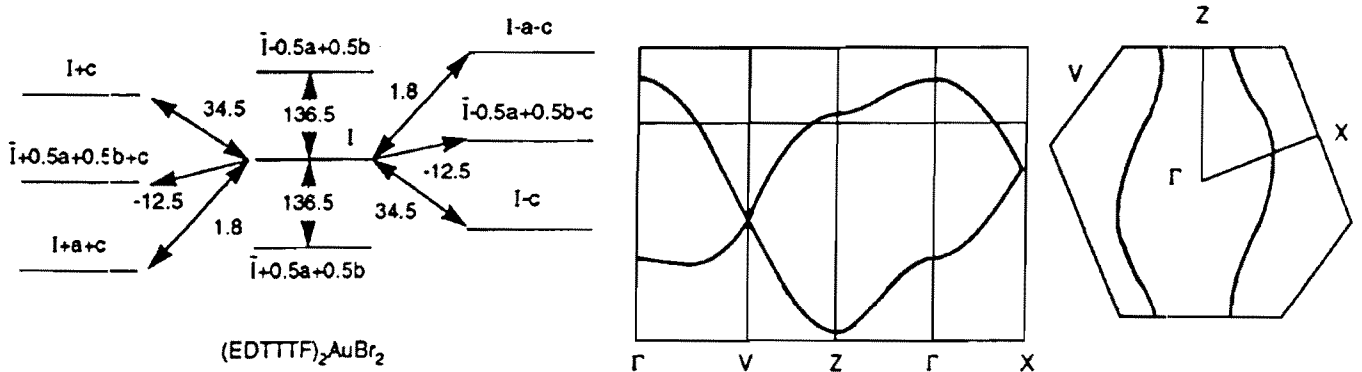


Figure 3.14. Transfer integrals (in meV; shown in schematic projections of the structure along the long molecular axis), electronic band structure and Fermi surface of $(\text{EDTTTF})_2\text{AuBr}_2$ [440] at room temperature.

$7c)_2\text{Au}(\text{CN})_2$ has a β -phase arrangement of donor molecules, but the Fermi surface is basically 1D [388a].

4.2.2.3 θ -(ET) $_2\text{I}_3$ and other θ -phases

The salt θ -(ET) $_2\text{I}_3$ has higher symmetry than the α -phase so as to afford a considerably simpler band structure with a large 2D (free-electron-like) Fermi surface [447,470]. For some other structures of θ -phase see [172,202a,390].

4.2.2.4 λ -(BETS) $_2\text{GaCl}_4$

The calculations for this salt yield a 2D closed Fermi surface and a corrugated extended Fermi surface [386,395].

4.2.2.5 κ -(MDTTTF) $_2\text{AuI}_2$ and other κ -phases

Figure 3.15(III) shows the electronic band structure and Fermi surfaces of κ -(MDTTTF) $_2\text{AuI}_2$ [441,463]. Similar Fermi surfaces have been obtained for some other κ -phases, which differ slightly from compound to compound mainly in the gap of the orbits at the points of the Brillouin zone labeled by G in Figure 3.15(IIIb). κ -(MDTTTF) $_2\text{AuI}_2$ [471], κ -(ET) $_2\text{I}_3$ [451b] and κ -(ET) $_2\text{Cu}(\text{CN})_3$ [373] have no gap, but κ -(ET) $_2\text{Cu}(\text{SCN})_2$ [452,463,470,471] has a finite gap Fermi surface at room temperature. This means that the Fermi surface in κ -(ET) $_2\text{Cu}(\text{SCN})_2$ consists of a closed orbit (α) and a pair of open orbits. for the band structures of other κ -phases see [173,174,395,441,446,463].

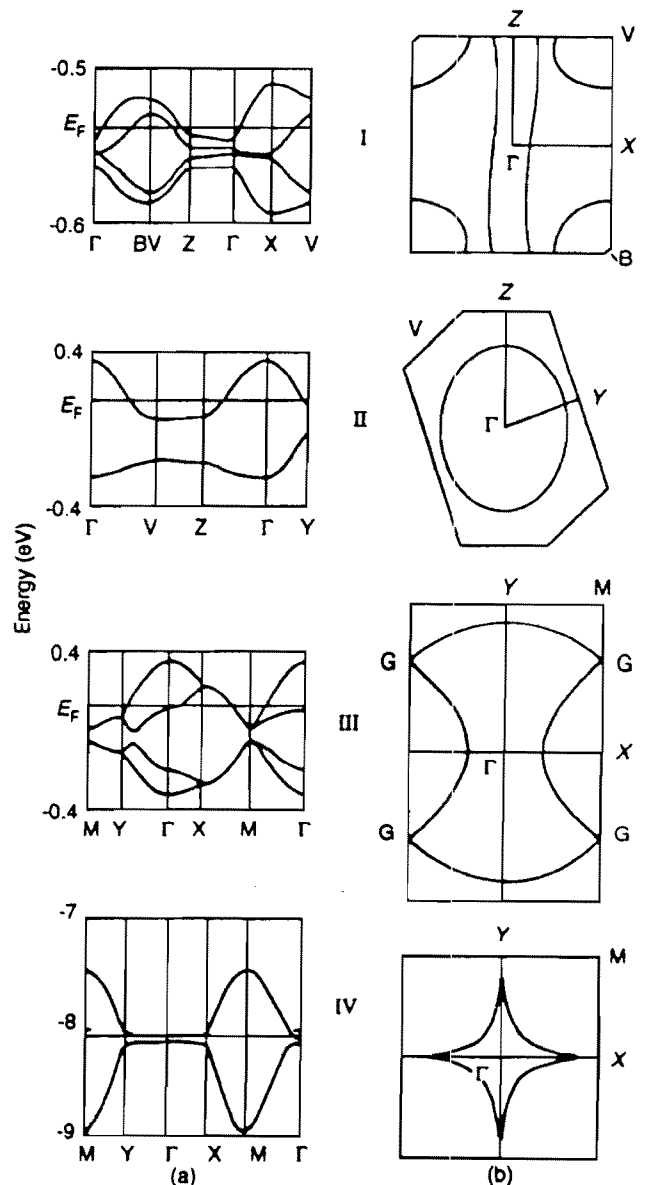


Figure 3.15. Electronic band structures (a) and Fermi surfaces (b) of α -(ET) $_2\text{NH}_4\text{Hg}(\text{SCN})_4$ (I), β -(ET) $_2\text{I}_3$ (II), κ -(MDTTTF) $_2\text{AuI}_2$ (III) and τ -(EDO-S,S-DMEDT-TTF) $_2$ -(AuBr_1) $_1$ (AuBr_2) $_{0.75}$ at room temperature.

4.2.2.6 τ -(EDO-*S,S*-DMEDT-TTF)₂-(AuBr₂)₁(AuBr₂)_{0.75} and other τ -phases

Figure 3.15(IV) shows the electronic band structure and Fermi surface of τ -(EDO-*S,S*-DMEDT-TTF)₂-(AuBr₂)₁(AuBr₂)_{0.75} [407]. The Fermi surface is star-like shaped inside the Brillouin zone. For a hypothetical three-quarters filled band the Fermi surfaces touch the Brillouin zone, i.e. the structure is similar to that of Figure 3.12(d). Similar structures were found for other τ -phases of Table 3.13 [326,391].

4.2.3 Band structures of other phases

Some other phases characterized as 1D [164,237,272,280,353,385,388], 2D [175,202,344,348,358,378,393] etc. [175,202,272,379,385,389] have been described recently. (ET)₄Cu(C₂O₄)₂ has a q-3D Fermi surface [349,371]. For similar structures based on metal 1,2-dichalcogenolenes see [480] and ref. cited in Section 3.4.1.5.

4.2.4 Temperature and pressure dependences

In a number of salts, the electronic band structure depends on the temperature [435,449,451,462] and/or the pressure [450,452]. The knowledge of the band structure and orbits in the Fermi surfaces at low temperature and/or at high pressure are required in some salts, because a lot of phenomena (e.g., magnetic, superconducting phases) are observed under these special conditions (see [435,447,451b,467–471]). A characteristic example is the changes in band structure, the Fermi surface and the corresponding (α -, β -, γ -) orbits of κ -(ET)₂I₃ at low temperature: there are no gaps at room temperature at G-points, but there are finite gaps at temperatures lower than 150 K [471b]. At low temperature the structure of κ -(ET)₂I₃ is similar to that of the room-temperature structure of κ -(ET)₂Cu(SCN)₂ [452,463]. In the case of α -phase salts the Fermi surface is highly sensitive to slight changes of the crystal structure, for example by decreasing the temperature [462]. From the data of the crystal structure of κ -(ET)₂Cu(SCN)₂ under high pressure, the calculated band structure showed that the 2D character of this material should be enhanced by pressure [452].

4.3 Experimental investigations and comparison with the theory

4.3.1 Structural organization and transport properties

The initial requirement for obtaining an organic conductor has been the occurrence of segregated stacks of either donor or acceptor molecules or both in a direction privileged by the overlap of π molecular orbitals. This was realized in the early 1960s (see Figure 3.2). The ground state of a charge-transfer complex can be either neutral or ionic. In the first case mixed DA stacks are observed with a possible neutral-to-ionic phase transition induced by temperature or pressure which gives rise to very spectacular changes of the physical properties [322,332]. In the second case two different situations occur for $\rho = 1$ or $\rho < 1$. The most interesting one is a regular segregated stack with mixed valency as the archetypical organic metal TTF-TCNQ which exhibits the 'herringbone' double stacking of segregated donor and acceptor molecules [335]. In such a situation a privileged direction is always present which gives rise to more or less well-defined anisotropic electronic and magnetic properties.

For summarizing the electrical conduction associated with the different (1D and 2D) crystal structures, the temperature dependences of d.c. resistivity along the privileged axis or sheet is presented in Figure 3.16 for different series of materials using semilogarithmic coordinates. A classification on the basis of both the absolute and the room temperature dependences of the d.c. electrical conductivity has been proposed [23]:

- (A) simple radical-ion salts with low conductivity and semiconducting behavior $\sigma(T) = \sigma_0 \exp(-E_a/kT)$ with the activation energy $0.1 < E_a < 0.4$ eV. A complete charge transfer ($\rho = 1$) is evidenced from X-ray structural data and from infrared spectroscopy results; these compounds are Mott-Hubbard insulators as already defined; a few examples are: KTCNQ and some 1:1 salts based on tetrachalcogenafulvalenes [336].
- (B) Complex radical-ion salts with non-regular stacks (most often mixed-valence dimers or tetramers). The conductivity is higher than for the salts of group A and the activation energy ranges between 0.4 and 0.7 eV; examples: Cs₂(TCNQ)₃, b'-(7c-11c)₂AuBr₂ [341].

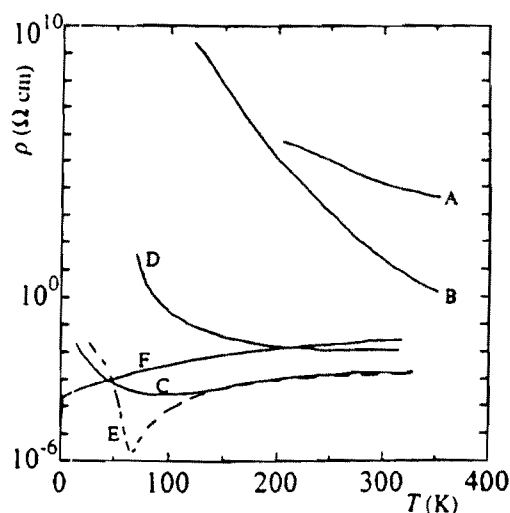


Figure 3.16. Temperature dependence of d.c. electrical resistivity of several selected structures. (A–F) See text.

- (C) Conducting complex radical-ion salts with a broad metal–semiconductor transition at around 150–250 K and an insulating phase at low temperatures; example: TTF-TCNQ.
- (D,E) Highly conducting salts $(\text{TMTSF})_2\text{X}$, where X is a small, symmetric inorganic anion. At room temperature their conductivity has a metallic behavior and a value in the range 10^2 – 10^3 S cm^{-1} with an electrical anisotropy 50–100. As the temperature goes down the d.c. electrical conductivity increases by two or three orders of magnitude with a maximum lower than at 50 K. In the Bechgaard salts with octahedral anions (PF_6 , AsF_6 , ...) the metallic character is preserved down to 20 K until a metal–superconductor transition occurs in competition with a spin density wave (SDW) formation [473].
- (F) $(\text{ET})_2\text{X}$ and related salts, (α -, β -, κ -, τ -phases) which are q-2D or 2D organic conductors exhibiting always a moderate conductivity at room temperature with a small anisotropy ratio and often a superconducting state at around liquid ^4He temperature. Conductivity data of some salts based on tetrachalcogenfulvalenes and belonging to several phases are listed in Table 3.14.

One can see that most of the compounds with columnar structure have a high σ_{RT} value and some of them are superconducting at very low temperatures.

The salts of the type α - $(\text{ET})_2\text{NHg}(\text{SCN})_4$ (where $\text{M} = \text{NH}_4$, K , Rb , and Tl) have remarkably different conductivity properties especially at low temperature [22,443–445]. These are due to small variation in the anion composition. Compound $(7c-11c)_2\text{NH}_4\text{Hg}(\text{SCN})_4$ which is isostructural with $(7c-7c)_2\text{NH}_4\text{Hg}(\text{SCN})_4$ is a semiconductor, perhaps because of the disorder of the Se atoms [443]. Superconductors with $T_c \geq 5$ K (κ -phases, λ -phase) have $\sigma_{\text{RT}} = 10$ – 100 S/cm [20,22,474]. In some cases the temperature dependence of resistivity is different from those of Figures 3.16, 3.17, i.e., the curves show maxima or minima in the sensitivity because of several different effects such as structural changes, order–disorder, and induced localization effects [475–480] (see below). In some cases [261,386,444] the behavior varies from sample to sample.

Superconducting salts have been obtained only from the following molecules: $(1a'-7h-57a')$, $(1b'-1b')$, $(2b'-2b')$, $(12c-12c)$, $(7b-1a')$, $(2b'-7c)$, $(7c-7c)$, $(9c-9c)$, $(7c-S,S-7f)$, $\text{Ni}(\text{dmit})_2$ and $\text{Pd}(\text{dmit})_2$. Also, some alloys of $(7c-7c)$ with $(7b-7b)$, $(7c-9c)$, $(7c-11c)$ give superconducting salts. Superconducting salts based on these molecules show a negative pressure effect. This means that the T_c of the corresponding superconductors decreases and approaches 0 K under high pressure, and the materials remain metallic. However, in contrast to the effects of hydrostatic pressure, uniaxial stress increases T_c [445b].

Recently, in some cases, it has been found that the electrical anisotropy is very large (10^4) [45,300,391]. Figure 3.17 shows the resistivity temperature dependence of τ - $(\text{P-S,S-DMEDT-TTF})_2(\text{AuBr}_2)_1(\text{AuBr}_2)_{0.75}$ [261,383,391] in-crystal-plane and out-of-plane. The compound behaves as a 2D metal. Moreover, compounds with stoichiometry 1: ~ 1 [206,326,341a] or stoichiometry 1:1 [388b] were found to remain metallic down to low temperatures.

To resume the experimental situation it is necessary to point out that these longitudinal or planar electrical conducting temperature dependences have to be classified following the rule of [Ioffe and Riegel] [333]. There is a borderline between real metals where the electronic motion is wave-like and conductors where the electronic motion is rather of hopping type. The critical regime occurs when the mean free path of charge carriers (l), is about the distance between molecular sites (i.e., $k_F l \approx 1$, where k_F is the Fermi wave vector). For molecular metals this d.c. conductivity critical value is estimated to be 300 – 500 cm^{-1} [41].

To observe a superconducting state at lower temperature, the necessary condition is to obtain, in one or

Table 3.14. Conductivity data and the corresponding structural data of selected salts

Salt	Structure/space group	σ_{RT} (S/cm)	Transition (at)	Ref.
(2b'-2b') ₂ PF ₆	columnar P $\bar{1}$	≈ 650	$T_c = 0.9$ K	24,25a
(2b'-7c) ₂ Au(CN) ₂	columnar P $\bar{1}$	≈ 650	$T_c = 0.8$ (5 kbar)	442,25a
(1b'-7c) ₂ I ₃	columnar P $\bar{1}$	≈ 650	$T_{M-1} = 41$ K	372,25a
(2b'-8c) ₂ I ₃	columnar P $\bar{1}$	≈ 650	$T_{M-1} = 4.2$ K	164,25a
(2c'-7c) ₂ CIO ₄	columnar P $\bar{1}$	≈ 650	$T_{M-1} = 22$ K	178
(1a'-7c) ₂ AuBr ₂	columnar C2/m	≈ 300	$T_{M-1} = 15$ K(13 kbar)	438,440
(1b'-1b') ₂ Br	columnar C2/m	800	$T_c = 0.8$ K(26 kbar)	464
(7c-7c) ₂ NH ₄ Hg(SCN) ₄	α -phase P $\bar{1}$	23	$T_c = 1.15$ K	444
(7c-11c) ₂ NH ₄ Hg(SCN) ₄	α -phase P $\bar{1}$	2	$T_{M-1} \leq 300$ K	443
(7c-7c) ₂ KHg(SCN) ₄	α -phase P $\bar{1}$	20-100	$T_c = 0.2$ K	444,445
(9c-9c) ₂ I ₃	α -phase P $\bar{1}$	165	$T_{M-1} = 70$ K	394
(7c-7c) ₂ I ₃	α -phase P $\bar{1}$		$T_{M-1} = 135$ K	45,394
(7a'-7h-7a') ₂ I ₃	α -phase P $\bar{1}$	0.03		388b
(7c-7c) ₂ AuI ₂	β -phase P $\bar{1}$		$T_c = 5$ K	22,25
(7c-11c) ₂ AuI ₂	β -phase P $\bar{1}$		$T_{M-1} \leq 5$ K	261
(8c-7b) ₂ I ₃	β -phase P $\bar{1}$	55-63	$T_{M-1} > 300$ K	206
(7c-7h-7c) ₂ Au(CN) ₂	β -phase P $\bar{1}$	400	$T_{M-1} < 0.7$ K	388a
(7c-7c) ₂ CuCl ₂	β -phase P $\bar{1}$	0.01	$T_{M-1} > 300$ K	350
(7c-7c) ₂ I ₃	θ -phase Ppnma	30	$T_c = 3.6$ K	447
(7b-1a') ₂ Au(CN) ₂	θ -phase Pn2n	160	$T_{M-1} > 300$ K	202,401
(8b-1a') ₂ Au(CN) ₂	θ -phase Pn2n	12-41	$T_{M-1} = 15$ K	202,401
(9c-9c) ₄ HgBr ₄	θ -phase I41a	10	$T_{M-1} < 4$ K	78,342
(7c-7c) ₂ Cu(CN)[N(CN) ₂] ₂ '	θ -phase I222	1.7-16	$T_{M-1} > 300$ K	390
(9c-9c) ₂ FeCl ₄	λ -phase P $\bar{1}$	20	$T_{M-1} = 8.5$ K	395
(9c-9c) ₂ GaCl ₄	λ -phase P $\bar{1}$	45	$T_c = 9.5$ K	377
(7c-7c) ₂ I ₃	κ -phase P2 ₁ /c	50	$T_c = 3.6$ K	22
(7c-7c) ₂ Cu ₂ (CN) ₃	κ -phase P2 ₁ /c	20-40	$T_c = 5$ K	373
(7c-11c) ₂ Cu ₂ (CN) ₃	κ -phase P2 ₁ /c	30	$T_{M-1} < 2$ K	206
(9c-9c) ₂ FeCl ₄	κ -phase Pnma	100	$T_{M-1} < 2$ K	395
(1a'-7b) ₂ AuI ₂	κ -phase Pbnm	20-40	$T_c = 5$ K	439,448
(7c-7c) ₂ Cu[N(CN) ₂]Cl	κ -phase Pnma	2	$T_c = 12.8$ K (0.3 kbar)	22
(12c-S,S-9f) ₂ (AuBr ₂)(AuBr ₂) _{0.75}	τ -phase I4 ₁ 22	160	$T_{M-1} = 6$ K	261,300
(13a'-S,S-9f) ₂ (AuBr ₂)(AuBr ₂) _{0.75}	τ -phase I4 ₁ 22	150	$T_{M-1} = 7$ K	383,391
(7c-7g) ₂ (I ₃)(I ₃) _y	τ -phase P42c	45	$T_{M-1} < 4$ K	326,341a
(7c-12c) ₂ (AuI ₂)(AuI ₂) _y	τ -phase P42c	4.6×10^{-5}	$T_{M-1} > 300$ K	341
(1a'-7c) ₂ [Pd(dmit) ₂] ₃	P $\bar{1}$	120		431b
α -(1a'-7c) ₂ [Pd(dmit) ₂] ₂	P $\bar{1}$	58	$T_{M-1} < 0.5$ K	431b
α -(1a'-7c)[Pd(dmit) ₂]	P $\bar{1}$		$T_c = 1.3$ K	422
β -(Me ₄ N)[Ni(dmise) ₂] ₂	C2/c	100	$T_{M-1} = 150$ K	432
β -(Me ₄ N)[Ni(dmit) ₂] ₂	C2/c		$T_c = 5$ K(7 kbar)	432
β -(Me ₄ N)[Pd(dmit) ₂] ₂	C2/c		$T_c = 6.5$ K(6.2 kbar)	432
[Ni(ddd _t) ₂] ₃ (HSO ₄) ₂	P $\bar{1}$		$T_{M-1} = 25$ K	431a

two space directions, a coherent regime, in the absence of any disorder effect, at low temperature. If such a condition is fulfilled the occurrence of a superconducting (i.e., zero resistivity) state is forecasted. One complementary point necessary to mention is the possible contributions of collective transport mechanisms giving experimental evidence for the onset of density wave states (CDW or SDW state) [457]. These non-linear metallic properties (Frohlich mechanism) and the associated Peierls-type phase transitions are considered out of the scope of this review.

4.3.2 Optical properties and basic interactions

As already pointed out, the band of an intermolecular CT occurs at lower energy than any other. This is clearly the signature of the existence of a CT compound which appears in the visible or the near infrared range [8]. A classical example is the optical absorption spectra of several TCNQ salts [322,331]. Also, a number of salts based on tetrachalcogenafulvalenes show similar behavior. The spectra are illustrated in Figure 3.18. The

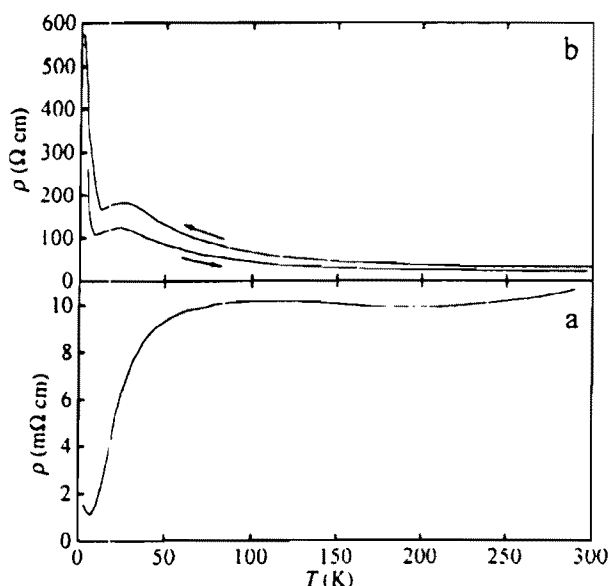
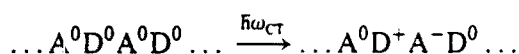
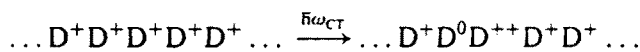


Figure 3.17. Resistivity temperature dependence of a τ -(P,S,S)-DMEDT-TTF_{0.2}(AuBr₂)(AuBr₂)_{0.75} single crystal, in-plane (a) and out-of-plane (b).

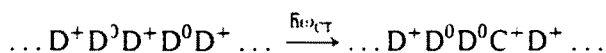
high-frequency bands are due to intramolecular electronic excitations in all compounds but different assignments are given for the low-frequency ones. For either the neutral salt, such as (ET)C₆₀ and (EDTTF)C₆₀ [268d], for which $\rho = 0$:



or an ionic salt, such as (MT)X, (ET)ReO₄ [22] and (EDTTF)I₃ [336] for which $\rho = 1$:



a CT band is observed, labeled a 'B-band' in Torrance's classification [322]. In the case of a mixed-valence compound, such as (TMTTF)₂X (see [333,481]) and (ET)₂X [373,481] for which $\rho = 1/2$:



a new absorption band, called 'A-band' is detected at a still lower frequency than the previous one (at 4000–3500 cm⁻¹). It is easy to show that for a completely ionic system ($\rho = 1$) this elementary excitation is associated with the creation of a doubly occupied site, whereas for a partially ionic one ($\rho = 1/2$) we have to take account of the electrostatic interaction between two closed neighboring molecules. In a zero order approximation, which neglects completely the electron transfer interaction, the energies needed to realize the charge transfer, correspond to the short range Coulomb

correlation value for the on-site (e.g., D⁺⁺) repulsion energy (U) and the energy between two consecutive sites (e.g., D⁺D⁺) (V) [268,322,323]. These parameters (U and V) are those introduced in the extended Hubbard model [456] (see earlier).

In parallel with these electronic correlations electron-phonon interactions are also very important in these compounds. In molecular solids the electrons are coupled both to the intermolecular lattice phonons and to the intramolecular vibrational modes [481]. The conventional electron-lattice phonon interaction arises from modulation of the transfer integral t by the acoustic phonons. In general, for estimating the coupling strength, the value of the transfer integral is expanded in perturbation series. Usually, the first order electron-phonon coupling term is considered as the leading contribution to the electrical resistivity and also as the origin of the Peierls instability through dimensionless electron-phonon coupling constants [473].

Information about these lattice modes and their coupling to electrons are gathered at very low frequencies, below 200 cm⁻¹, by either resonance Raman scattering [482] or from far infrared reflectivity experiments [483]. The second coupling originates from the modulation of the on-site energy which is mainly due to the electronic coupling of the intramolecular vibrational modes. This is a large effect which is experimentally observed as a readjustment of atomic bond lengths to the mean electronic charge (polaronic effect). The linear electron-molecular vibration (EMV) coupling is associated with the internal degree of freedom of the molecule for a non-degenerate electronic state. As it was demonstrated in [484] an intermolecular charge transfer polarized along a stack

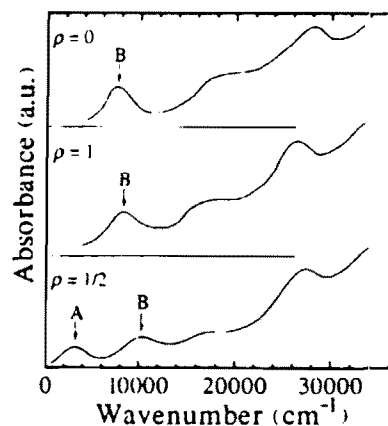


Figure 3.18. Illustration of electronic absorption spectra of neutral ($\rho = 0$), ionic ($\rho = 1$) and mixed valency ($\rho = 1/2$) compounds. (A,B) See text.

of dimers or any multimers induces (via linear EMV coupling) vibrations which are normally infrared inactive because they are intrinsically a_g modes. These vibronic modes are activated only if the translational lattice symmetry is broken initially or following a structural phase transition. EMV coupling manifests itself both in absorption and reflectance spectra. Absorption is usually measured when it is not possible to grow large crystals of good quality. In this case, polycrystalline salt (i.e., randomly oriented crystallites) is dispersed in an appropriate matrix which should be transparent in the frequency range under investigation. KBr pellet or Nujol technique as well as thin deposits on CaF_2 -, quartz-, etc.-plates [300,488] are most frequently used. In Figure 3.19 typical infrared spectra obtained [373] from a polycrystalline κ -(ET) $_2$ Cu $_2$ (CN) $_3$ salt dispersed in a KBr pellet is shown. They exhibit both an intense CT band (of 3400 cm^{-1}) characteristic of a mixed valence state and two vibronic multiplets at around 1340 and 440 cm^{-1} ($\nu_{\text{C}=\text{C}}$ central and $\nu_{\text{C}-\text{C}}$ internal vibrations, respectively).

In these cases, where high quality and large single crystals or a mosaic of oriented single crystals are obtained, polarized optical reflectance measurements can be performed. The polarized spectra give more information on the several kinds of excitation and associated interactions (see [481–487]), as was also pointed out in the spectra of KTCNQ (see [485]), and the spectra of inorganic metal halide mixed-valence systems (see [488]). Figure 3.20-I shows the polarized reflectance spectra of a single crystal of (BPTTTF) $_2$ BF $_4$, where BPTTF is (13a'-13a'), with

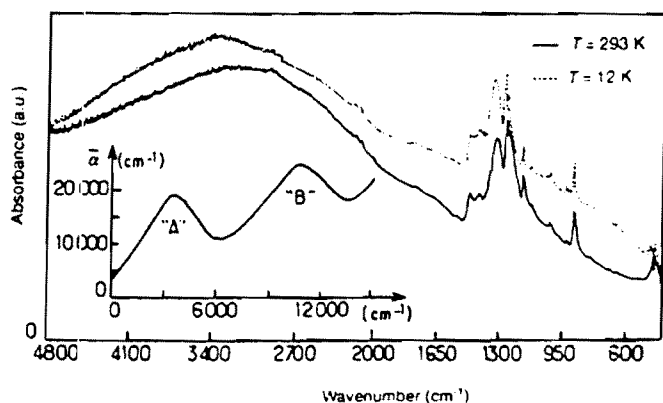


Figure 3.19. Infrared absorption spectra of κ -(ET) $_2$ Cu $_2$ (CN) $_3$ recorded at room temperature (RT) and at $T = 12\text{ K}$ (note the scale change on the abscissa at 2000 cm^{-1}). Inset: electronic absorption spectrum observed at RT with α the mean absorption coefficient.

polarizations parallel and perpendicular to the stacking (chain) axis. Kramers-Kronig analysis of the reflectance spectra show that the compound is a semiconductor, in agreement with the conductivity measurements [337]. The prominent dispersion at *ca* 0.72 eV for the perpendicular polarization is a consequence of the interchain (S...N) interactions [336,337]. When $0 < \rho < 1$, a Drude-like behavior, especially at low temperature, is observed, with an edge (plasma frequency) which usually occurs in the near infrared region (see for example [23,300,438,487]). Figure 3.20-II shows the room temperature polarized reflectance spectrum of τ -(P-S,S-DMEDT-TTF) $_2$ (AuBr $_2$) $_1$ (AuBr $_2$) $_{0.75}$, the Drude fit and the Drude-Lorentz fit for polarization parallel to the *ab*-plane. From the polarized spectra of metallic compounds the transfer integrals (*t*) as well as some other parameters are estimated and then the electronic band structure as well as the Fermi surface can be determined (see for example [300,438]). Also, the polarized Raman spectra on single crystals give information on several different transitions (see [300,486,487]). These examples show that the optical properties of the organic conductors are clearly determined on the one hand by their restricted electronic dimensionality and on the other by the combined effect of electron-electron and electron-phonon interactions.

4.3.3 Magnetic and magnetotransport properties

4.3.3.1 Paramagnetic susceptibility in the conducting state

Strong experimental evidence for the importance of the electron-electron interactions is the enhanced Pauli-type susceptibility.

The magnetic susceptibility measurements allow a determination of the Hubbard U value. From the magnetic data [489] has been estimated $U/4t \approx 1$ in 2-chain compounds such as TTF-TCNQ. This approach has been generalized in [490]. The authors of these papers used an extended Hubbard Hamiltonian and they showed that the magnetic susceptibility varies strongly and systematically as a function of band filling. An important result shows that the extended Hubbard data cannot be mapped systematically onto the results of a Hubbard model with an effective U value.

One valuable example is for a β -phase ET salt where we have plotted also the fit with a Heisenberg model for a 1D regular magnetic chain as initially developed (see equation (3.6)). It appears that a localized

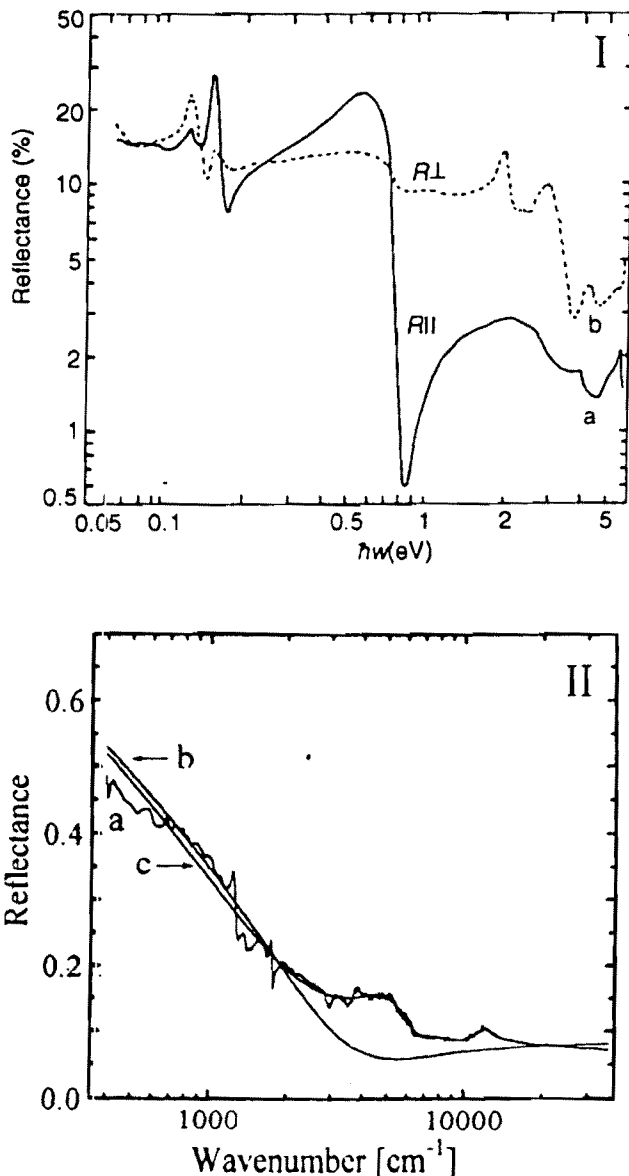


Figure 3.20. I: Room temperature polarized reflectance spectra of $(\text{BPTTTF})_2\text{BF}_4$ (a) with parallel (R_{\parallel}) and (b) with perpendicular (R_{\perp}) polarizations. II: Room temperature polarized reflectance spectrum of $\tau(\text{P-S,S-DMEDT-TTF})_2(\text{AuBr}_2)_1(\text{AuBr}_2)_{0.75}$ (a). Drude fit (b), and Drude-Lorentz fit: (c) for parallel polarization.

description with an effective antiferromagnetic exchange interaction can fit approximately the experimental data. It means that the strength of the intrasite Coulomb interaction is larger than the bandwidth W . This description is in agreement with the presence of an AF ground state at $T_N = 20$ K.

Now, if we examine a rather 2D electronic system as the κ -phase of $(\text{MDTTTF})_2\text{-AuI}_2$ which exhibits a superconducting transition at liquid ^4He temperature ($T_c = 4.3$ K) [439] we can use the same kind of description. Surprisingly, the T dependence of the

paramagnetic susceptibility is better fitted by a 2D quadratic layer Heisenberg AF model (for $S = 1/2$) than by a straightforward Pauli paramagnetic [463].

It turns out that in this class of material we are in the presence of a highly correlated electronic gas, and a simple perturbative approach (weak U regime) does not work. This result is confirmed by the analysis of the density of states at the Fermi level which is, on the one hand, calculated from the tight binding model and on the other hand deduced from the experimental data (magnetism and low temperature electronic specific-heat experiments) (see Table 3.15).

Two facts are extracted from these comparisons:

- (i) The density of states, extracted from specific-heat experiments which depend only on the electron-phonon interaction [491], agrees with the calculated values. Note however that the transfer integrals and associated $N(E_F)$ depend on the calculation technique.
- (ii) The comparison of these values with those extracted from the paramagnetic susceptibility leads to an enhancement factor larger than 2 in these molecular superconductors. This observation confirms the analysis of the paramagnetic susceptibility T dependences.

In conclusion, these different facts evidence the presence of strong electronic correlations in these narrow band compounds which show an intermediate dimensionality (1D-2D). This spin-charge separation is confirmed by the analysis of other physical properties, in particular the IR-visible absorption spectra, which are characteristic of intermolecular charge-transfer bands as well as determination of the plasma frequency by reflectivity experiments on single crystals as demonstrated by authors of ref. [492].

4.3.3.2 Conduction electron spin resonance studies

As a complementary point to the spin susceptibility measurements, the dynamic approach is also sensitive to the electronic correlations but more significantly to the electronic dimensionality. Thanks to selected examples, we will show that the g -factor and the linewidth characteristics are very powerful probes for the phase identifications and the occurrence of phase transitions as long as single crystals are investigated.

As it is described in [493], the spin-phonon mechanism is ineffective for classical metals in an ideal 1D limit. It has been shown that the spin-flip

Table 3.15. Electronic band characteristics in the normal state for archetypical organic superconductors (see [491] and refs. therein)

$N(E_F)$ states/eV (molecule obtained from)	(TMTSF) ₂ ClO ₄ ($T_c = 1.2$ K)	β -(ET) ₂ I ₃ ($T_c = 1.5$ K)	κ -(ET) ₂ Cu(SCN) ₂ ($T_c = 10.5$ K)
(1) Theory			
RT (from crystal structure)	2.0	3.54	3.65
LT ($T < 10$ K)	1.7	3.54	
(2) Specific heat			
LT linear term	2.0	5.0	5.2
(3) Paramagnetism			
RT	4.8	7.0	7.5
LT	3.2	6.3	

LT = low temperature.

scattering matrix element is approximately zero, further reducing the linewidth but not influencing the electrical resistivity and the associated relaxation time τ_{e-p} .

This starting point induces two effects:

- (i) For an effective relaxation process in a pure 1D system, a second mechanism becomes more effective. This is the spin-spin dipolar interaction which is characterized by a specific rotation diagram (presence of a linewidth minimum at the magic angle). The effect of dimensionality on motional narrowing of this dipolar broadening has been extensively investigated in low-dimensional magnetic insulators, but this effect is not observed here for these molecular conductors [494].
- (ii) In order to take into account the spin-phonon relaxation mechanism, it is necessary to introduce a partial 2D character of the electronic states. This point has been introduced by the authors of refs. [495] and [496] who have proposed that the spin flip is associated to the transverse hopping of a charge carrier from one chain to another. It turns out that at moderate temperatures ($T < \theta_D$) in a coherent conductivity regime:

$$\Delta H = \frac{\Delta g^2}{\tau_{e-p}} \left(\frac{t_{\perp}}{t_{\parallel}} \right)^2$$

where t_{\parallel} and t_{\perp} are respectively the effective longitudinal and transverse integrals for a given stack; θ_D is the Debye temperature.

Furthermore, the g -value and linewidth anisotropies are specific to these low-dimensional materials. As demonstrated from experimental results and molecular

orbital calculations [497], it has been shown that the principal values of the g -tensor are molecular characteristics. They are constant for a given series of salts because they are related to the presence of the hetero atom (S or Se).

As pointed out in [493], under anisotropic conductors, $T_1 \neq T_2$ and an anisotropic linewidth is observed so that the motional narrowing effect leads to a reduced anisotropic factor ($\Delta H_{\max}/\Delta H_{\min}$) < 2 , as observed in all these compounds.

For the two major classes of compound, i.e. q-1D systems with almost planar Fermi surface (FS) and anisotropic 2D systems with more or less closed FSs (see Figure 3.20), the ESR characteristics observed at room temperature are given on Table 3.16.

Two main facts are relevant:

- (i) The g -factor values are constant for a given series of sulfur derivatives but they are significantly different between the sulfur and selenium compounds because of different spin-orbit coupling energies.
- (ii) For an homogeneous series of heterocycles, when the spin-orbit coupling is a constant, the average linewidth increases with the electronic dimensionality. Therefore, this quantity probes the electronic effective dimensionality of these conductors: for example the κ -phase compounds are 2D anisotropic systems with a ratio $t_{\perp}/t_{\parallel} = 0.5$ [463].

For a better description, the temperature dependences of these ESR characteristics are noteworthy. In Figure 3.21, two examples are given (a) for a Bechgaard-type

Table 3.16. ESR room temperature characteristics and low T cooperative ground states in selected mixed-valence radical cations salts (see [453,261,407] and refs. therein)

Radical cation salts	EPR characteristics (at RT)		Ground states and transition temperatures	
	g	ΔH (Gauss)	SC	AF
(1) <i>Quasi-1D Bechgaard salts and related compounds:</i>				
(TMTSF) ₂ ClO ₄	2.018	220–270	$T_c = 1.2$ K	
(TMTFF) ₂ Br	2.007	5–8	($T_c = 0.8$ K under P)	$T_N = 14$ K
(ET) ₂ ICl ₂	2.007	10–12		$T_N = 27$ K
(2) <i>Anisotropic 2D α-phase</i>				
(ET) ₂ NH ₄ Hg(SCN) ₄	~ 2.006	55–80	$T_c = 1.15$ K	
(ET) ₂ KHg(SCN) ₄				$T_N \leq 10$ K
<i>κ-phase</i>				
(ET) ₂ CuN(CN) ₂ Br	~ 2.006	60–90	$T_c = 11.6$ K	
(ET) ₂ CuN(CN) ₂ Cl			($T_c = 12.5$ K under P)	$T_N = 45$ K (and 22 K)
<i>τ-phases</i>				
		> 300		

salt and (b) for a κ -phase compound presented on Table 3.16. In both cases, we observe two regimes: a monotonous variation at high temperatures and precursor effects of the phase transitions at low temperatures.

For the (TMTTF)₂Br compound [498], we observe a decrease of the linewidth which can be associated with the metallic behavior at low T in qualitative agreement with the Elliot mechanism. Concerning the (ET)₂Cu(SCN)₂ compound, we observe a linewidth broadening down to 60 K [499]. This behavior is the opposite of the classical behavior (see also [463]) observed for usual metals. This point shows that there is no general rule to explain the relaxation times in these series of radical cation salts as in other molecular conductors [500]. A general theory, including the influence of electron–electron correlations, as already indicated [501], is needed to explain these dynamic effects.

Recently a series of conducting radical cation salts with polyoxometalates has been investigated [389g]. Their general chemical formulae is (BEDT)₈⁽⁸⁻ⁿ⁾(MW₁₂O₄₀)ⁿ⁻⁸, with either paramagnetic $M^{n+} = \text{Co}^{2+}, \text{Cu}^{2+}, \text{Fe}^{3+}$, or diamagnetic $M^{n+} = \text{Bi}^{3+}, \text{Zn}^{2+}, \text{Si}^{4+}, (2\text{H}^+)$; they are crystallized into two allotropic, monoclinic, α -type phases exhibiting a sandwich-type structure. There are two fundamental interests in this series of RISs. The first one is the ability to modulate the electronic charge distributed between the two entities, which can be equal to 4, 5 or 6 electrons. It turns out that with these big Keggin

polyanions, as just before for the metallocyanates, the stability of mixed-valence systems forming organic layers is preserved regardless of their shape, size and charge. It is therefore potentially possible to get 3D electronic systems, with π orbital overlap in all directions, based on these bulky polyoxometalates.

The second interest has to do with the presence of magnetic transition metals and the magnetic coupling between the π mobile electrons and the localized magnetic ions. It has been demonstrated by EPR experiments that only a weak apparent interaction exists for the Co^{2+} compound [389h,i].

4.3.3.3 Hall effect and magnetoresistance

The Hall coefficient at room and lower temperatures has been measured in a number of salts (see [502–507] and refs. therein). In α -(ET)₂KHg(SCN)₄ [502], β -(ET)₂I₃ [503], κ -(ET)₂Cu(SCN)₂ [504] and some other salts [505], the Hall coefficient has positive values, indicating hole carriers. In (DMET)₂Au(CN)₂, where DMET is (2b'-7c), the Hall coefficient changes from positive ($T > 40$ K) to negative ($T \leq 40$ K) [507]. Also, in τ -((P-S,S-DMEDT-TTF)₂(AuBr₂)₁(AuBr₂)_{0.75}) and some similar τ -phases the Hall coefficient has negative values (from around RT to *ca* 4 K) indicating electron carriers (Figure 3.22) [261,383,391]. Some salts of τ -phase also show negative low-field magnetoresistance at low temperatures [261,300]. Similar

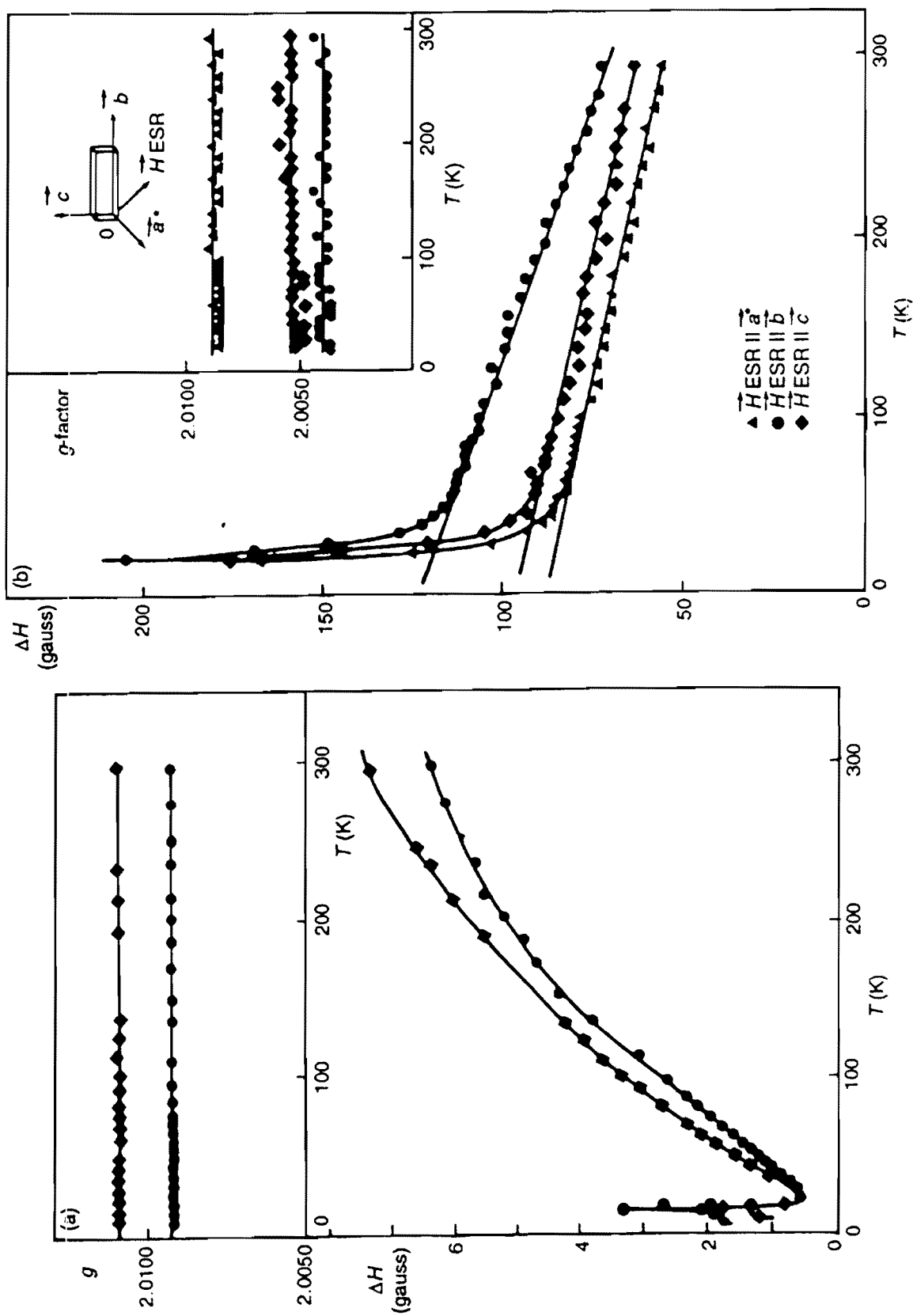


Figure 3.21. Temperature dependences of the ESR characteristics for single crystals of: (a) $(\text{TMTTF})_2\text{Br}$ and (b) $\kappa\text{-(ET)}_2\text{Cu(SCN)}_2$.

results have been obtained from $(DMtTSF)_2X$, where DMtTSF is $(2b'-2c')$ and $X = BF_4, ClO_4, ReO_4$ [480]. Also, the compound $(NHMe_3)[Ni(dmit)_2]_2$ shows negative magnetoresistance at low temperatures [414].

4.3.4 Low temperature behavior and phase transitions

In 1D or 2D anisotropic electron gas the superconducting (SC) ground state competes with charge and spin density wave (CDW, SDW) ground states as theoretically predicted. But these electronic instabilities are also strongly influenced by structural rearrangements and any kind of disorder will be briefly described before reviewing the observed cooperative ground states.

4.3.4.1 Structural phase transitions

Since the first observations by X-ray diffuse scattering techniques of the structural features of the Peierls instability in 1D conductors (Krogmann salt and TTF-TCNQ [25a]) a great number of experimental studies has been devoted to the physics of CDWs. It has been shown that metallic CT complexes with segregated stacks of donors and acceptors (see Figure 3.2) show low temperature CDW instabilities as theoretically predicted for 1D electronic systems. Several experimental studies of this structural instability have been reviewed [475] (for some recent work see ref. [45], pp. 1255–1305).

Concerning the second series of molecular conductors, i.e. RISs that are single chain or layered conductors, a different experimental situation has to

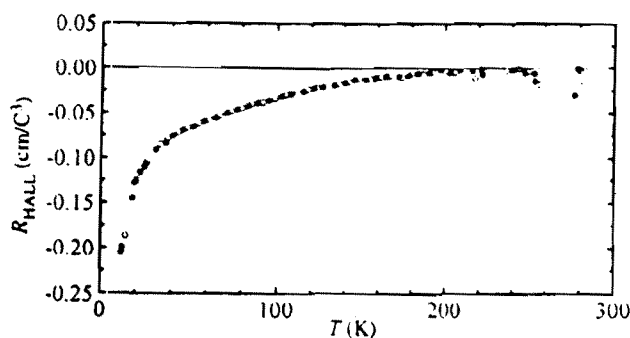


Figure 3.22. Temperature dependence of the Hall coefficient for currents in the ab -plane and magnetic field normal to the plane of τ -(P-S,S-DMEDT-TTF) $_2$ (AuBr) $_1$ (AuBr $_2$) $_{0.75}$.

be examined. Indeed, the CDW instability of the organic part exists but so does the effect of the charge periodicity of the anion sublattice and the effect of additional periodicity due to the ordering of extra degrees of freedom (orientation of non-centrosymmetrical anions for example) [475,480].

Several orientation and conformational degrees of freedom have a key control of these phase transitions and they lead to a subtle interplay between the different possible ground states. To investigate these situations associated with different structural degrees of freedom, detailed structural analyses at low temperature or under hydrostatic pressure are necessary.

4.3.4.2 Influence of disorders

As shown earlier the conductivity properties are strongly related to the structural classification, which has been already presented. It appears nevertheless that we are not always in the presence of ideal tri-periodic molecular systems but with different kinds of disorders. The influence of these disorders is a rather complicated effect. It depends roughly on two parameters, which are the electronic dimensionality and the nature of the local perturbation. As pointed out in Section 4.1, in pure 1D systems any disorder will induce an electronic localization. It appears therefore that this effect will be efficient in disordered 1D conductors but weaker in q -2D ones (see Figure 3.12 for a topological classification).

Concerning the second parameter, the local perturbation can induce a periodic or random potential which schematically modifies drastically or not the site energy (see e - p interaction earlier). The energy of this perturbation compared with the value of the associated transfer integral will give an indication of the localization effect and the associated coherence length of charge carriers.

Various models have been proposed to account for the transport and magnetic properties of these molecular materials [477]. Without going into detail, the influence of disorders on a low-dimensional conductor can be classified in two parts:

- (a) Strong localization effect: the charge transport will be in a diffuse regime ($k_F | < 1$). The basic model is based on interrupted strands of various lengths. The d.c. electrical conductivity will obey Mott's law associated with a variable range hopping (dimensionality arguments lead to $\sigma \propto T^{-1/2}$ for 1D systems). A kind of Mott-

Anderson progressive transition is observed with an insulating low temperature state [477]. For the magnetic properties a random exchange model in linear chain has been considered giving rise to a Curie-type law at low temperatures [477] in agreement with the experimental results. These effects, first observed for TCNQ salts exhibiting a natural disorder, have been studied in detail thanks to controlled irradiation effects [476]. Indeed, the concentration of defects produced by neutron or X-ray irradiation can also easily destroy the superconducting state and induce a pinning of the CDW preventing any electronic instability. The physical consequence is the stabilization of the metallic state at low temperature as in the presence of an intrinsic, small disorder, described in the following part.

- (b) Weak localization effect: The charge transport will be in a coherent regime ($k_F l > 1$) with a metallic state down to very low temperature.

This localization gives rise to non-classical effects which are manifested both in the temperature and the magnetic-field dependences of the electrical resistivity at low temperature. The resistivity value goes through a minimum, then increases logarithmically, while the magnetoresistance is negative [478].

In disordered electronic systems the weak localization effect occurs when the probability for elastic scattering of carriers by static lattice defects is much larger than that for the temperature-dependent classical inelastic-scattering processes. It has been shown that the constructive interferences of these inelastic scattering events in 2D electronic systems leads to an additional contribution to the low temperature resistivity; besides, the magnetic field application tends to destroy this localization effect and then to decrease the zero-field resistivity value [478]. It turns out that in several CT salts such a situation occurs when a weak structural disorder is present in the counterions. A few cases have been reported, for example tetraselenotetracene iodides [479], exhibiting a metallic conductivity down to 0.1 K [479]. Also similar results have been obtained from Bechgaard-type salts [480].

Recently, it has been proposed that τ -salts, which are indeed isotropic 2D metals, exhibit the same quantum effect at low temperature (see Figure 3.17a and refs. [261,300,383,391,407,443]). As also evidenced by controlled mechanism effects, it appears that a weak natural disorder can prevent the occurrence of a superconducting state even when a coherent regime for the free charge carriers is present.

4.3.4.3 Cooperative ground states

(a) Magnetic ground states. The evidence for magnetic ordered states is provided fully by the already described experimental techniques as shown in the following example. Owing to magnetic resonances, the precursor effects are detected by ESR and the analysis of the condensed state is made by antiferromagnetic resonance (AFMR). One example is given on Figure 3.21 for $(\text{TMTTF})_2\text{Br}$, which shows a broadening of the linewidth associated with the presence of a fluctuating internal field for $t \geq T_N$ (a narrowing as well as a broadening of the linewidth can be observed in principle associated with a shift of the g -factor) [499].

Below T_N , the AFMR technique is an excellent probe for characterizing these q-1D salts [508], where the SDW state is condensed. Besides combining different techniques, it is possible to define a magnetic phase diagram as given on Figure 3.23 for a Bechgaard salt: in particular, the classical spin flop field is evidenced by using a torque method to determine the magnetic anisotropy.

Another interesting example concerns the κ -phase series where a magnetic ground state is competing with the SC one. As shown on Figure 3.21 for κ - $(\text{ET})_2\text{Cu}(\text{SCN})_2$, a line broadening is observed at temperatures much larger than T_c , which could indicate the presence of a magnetic fluctuating regime before the appearance of the pairing process [509].

This point is confirmed by the investigations on the parent compound κ - $(\text{ET})_2\text{Cu}[\text{N}(\text{CN})_2]\text{Cl}$ which presents special features [510]. For this salt, a condensed magnetic state occurs at around 45 K where the presence of a weak ferromagnetic [408] (or ferrimagnetic) component is detected by ESR and SQUID measurements (see Figure 3.24). By using a moderate hydrostatic pressure, the SC state can be observed and by applying an external magnetic field a resistive transition is induced, indicative of a re-entrant behavior [511]. These results clearly show the competition between the different ground states in q-2D systems.

Indeed, in the presence of compounds with increased effective dimensionality, the same competition between the different possible ground states together with an increase of the transition temperatures is observed. These facts are summarized in Table 3.16 where T_N and T_c are given for q-1D and q-2D salts. It should be mentioned that a further increase of the dimensionality toward more 3D electronic systems will increase these transition temperatures as indicated by theoretical approaches; however in the following we

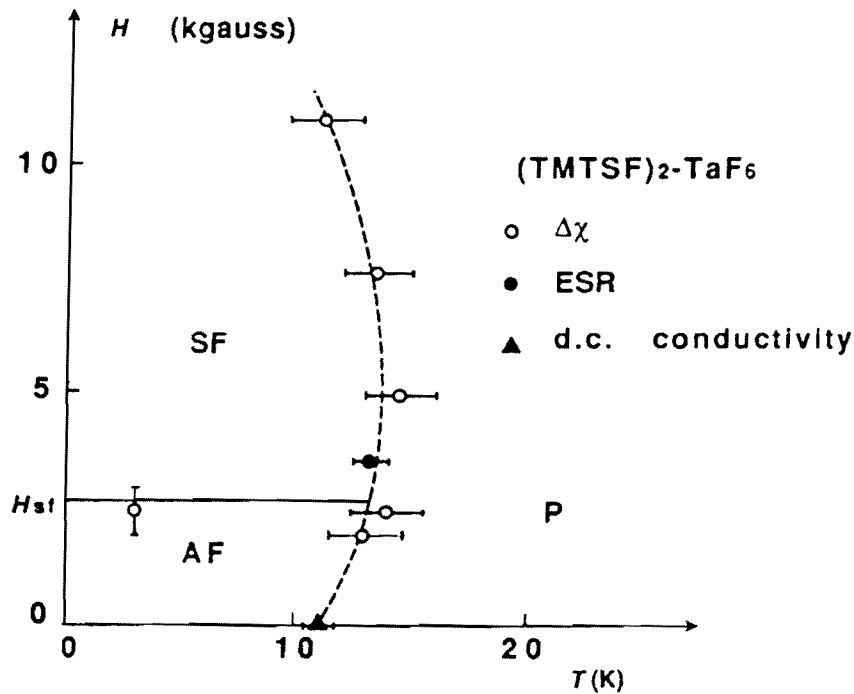


Figure 3.23. Magnetic phase diagram of $(\text{TMTSF})_2\text{TaF}_6$. (H_{sf} indicates the spin-flop magnetic field in the AF state).

will not discuss the mechanisms of these phase transitions.

(b) Superconducting state. We will show the magnetic evidence associated with the onset and the behavior of

the superconducting state [24] in the case of κ -phase salts which exhibit the highest T_c in these series of materials (see Tables 3.14 and 3.16). We will give examples of d.c. and a.c. magnetizations and susceptibilities associated with their anisotropic behavior characteristic of a lamellar structure [512–518]. One

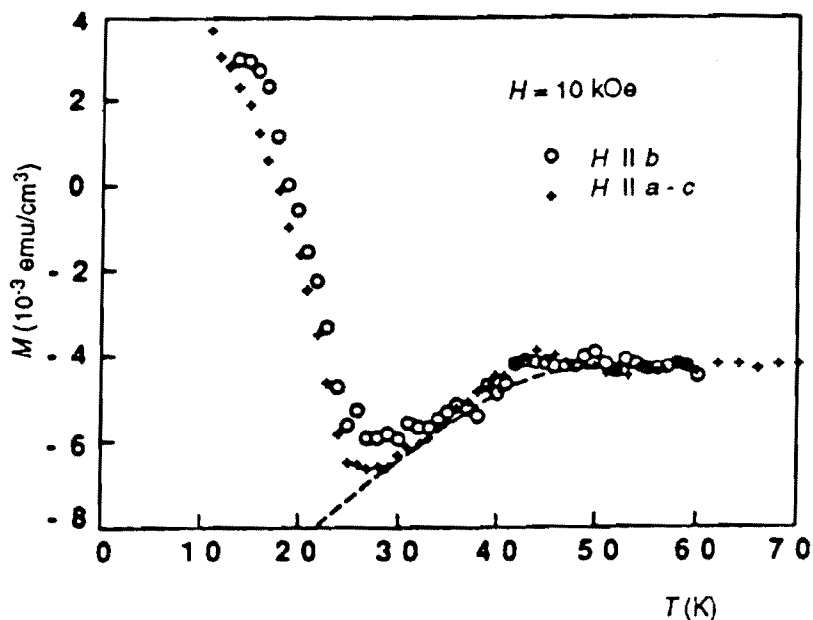


Figure 3.24. Temperature dependence of the magnetization of $\kappa\text{-(ET)}_2\text{Cu}[\text{N}(\text{CN})_2]\text{Cl}$ single crystals revealing a magnetic transition at 45 K (the broken line indicates the spin susceptibility estimated from the intensity of the ESR line) [510].

experimental point has to be mentioned concerning the microwave experiments. Evidently, no ESR signal is found in the SC state but because of the enormous microwave losses when the phase transition is appearing, a shift of the resonance cavity frequency is easily detected at zero applied magnetic field [22]. This is a very convenient contactless technique to check the presence of a SC state. More sophisticated microwave loss techniques are also used to investigate the superconducting characteristics [514].

Starting from these experimental facts, we will describe the characteristics of this type II SC. In these materials the superconducting electrical properties are present up to a field denoted H_{c2} called the upper critical field. However, a type II SC is characterized by a stable mixed state before destruction at H_{c2} , existing in a certain range of magnetic field strength: $H_{c1} \leq H(T) \leq H_{c2}$. Therefore the field is completely excluded only at very weak magnetic field lower than H_{c1} : this is the ideal Meissner state.

In the mixed state, the external field will penetrate partially into the surrounding SC material. This flux penetration or fluxoids is quantified, in agreement with the defined coherence length: it constitutes the vortex lines as described by Abrikosov a long time ago. A new fact which has recently appeared with the high T_c inorganic SC is the existence of an irreversibility line in the mixed state. This line $H_{irr}(T)$ is detected by comparing the magnetization curves when the sample is cooling down under and in the absence of magnetic field, a regime change is observed when the T dependence of the magnetization becomes irreversible for a characteristic field at a given temperature. Different theoretical models have been proposed, in particular by analogy with a phase transition where the lattice of magnetic vortex filaments melt for $H = H_{irr}$ to give a liquid or glassy vortex.

An example of magnetization measurements carried out with a d.c. SQUID magnetometer is given in Figure 3.25 where the Meissner effect is shown for a low field cooled sample ($H_{ext} < H_{c1}$) (approximately up to 60% of the perfect diamagnetic value $\chi_M = -1/4 \pi$ u.e.m. C.G.S. for a d.c. magnetic field applied perpendicular to the conducting layers).

For a wide range of field intensities and temperatures, an entirely reversible magnetization curve has been found indicating the formation of a pinning free homogeneous vortex lattice [514].

Complex susceptibility measurements allow further information to be obtained as shown in Figure 3.26. A sharp transition is observed on the dispersive term whereas the imaginary part forms a sharp peak around

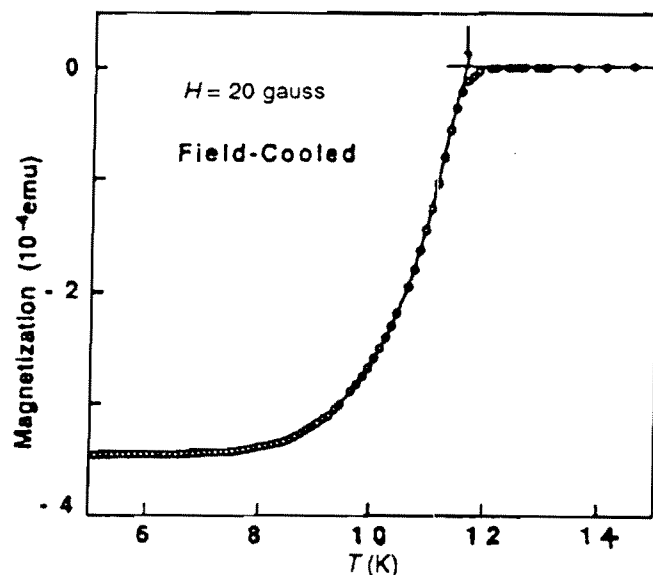


Figure 3.25. Magnetization of κ -(ET) $_2$ Cu[N(CN) $_2$]Br measured upon cooling in a field of $H = 20$ gauss applied perpendicular to the conducting plane [513].

the transition region. This peak diminishes with decreasing a.c. field because the χ component appears due to hysteresis loss caused by the vortex motion; it can be used as a monitor of vortex entrance in the pure SC state at $H > H_{c1}$.

More detailed approaches can be carried out on these non-linear systems with in particular the a.c. susceptibility harmonic analysis. The onset of the third harmonic modulus can be used to detect the irreversibility line [515]; however a delicate analysis with several parameters such as frequency and intensity of the a.c. field is necessary.

One complementary point concerns the anisotropic behavior. As shown in the previous Figures 3.24 and 3.25, the d.c. magnetic field H was applied perpendicular to the conducting planes as shown on Figure 3.27. If H is rotated to be in these planes, a strong difference in the magnetic response is detected [517]. This fact shows that these compounds are very anisotropic; they are lamellar SC compounds on which the basic effect is the Josephson-type coupling between layers and the associated formation of a vortex as recently emphasized [518]. It has been demonstrated that, in the compounds with 1D and 2D bands in the Fermi surface (see Figure 3.15), the 2D band works for SC and the 1D band works for SDW [518]; in other words, there is an interplay of superconductivity with magnetism.

It turns out that currently the physics behind these unconventional SC compounds, on which only an

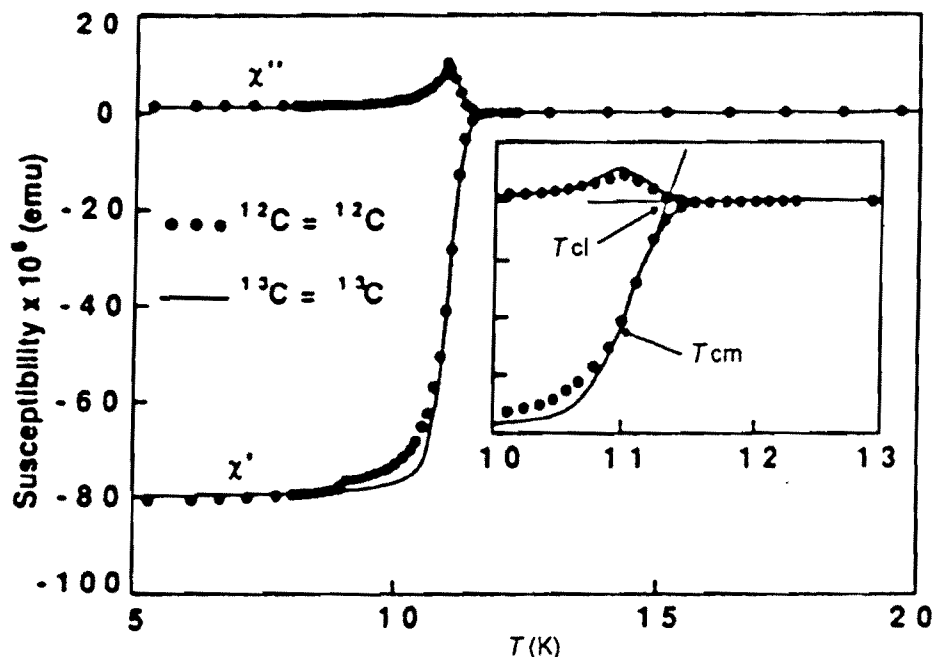


Figure 3.26. Complex susceptibility measurements of κ -(ET) $_2$ Cu[N(CN) $_2$]Br in the vicinity of the superconducting transition (insert: details near T_{cl} and T_{cm}). Crystals containing BEDT molecules with natural abundance isotopic carbon composition are compared with those having their central C=C bond atoms replaced with ^{13}C . Reprinted with permission from ref. 515.

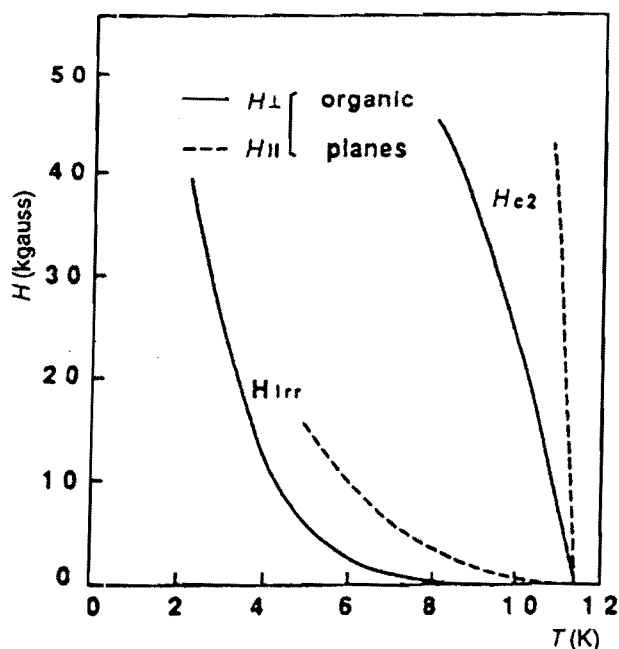


Figure 3.27. Temperature dependence of the upper critical fields (H_{c2} and H_{irr}) for magnetic fields applied perpendicular and parallel to the conducting planes of κ -(ET) $_2$ Cu[N(CN) $_2$]Br. Reprinted with permission from ref. 517.

outline has been given here, is not completely understood. In particular the pairing mechanism is not fully elucidated in spite of many investigations relating to the isotopic effect [515]. Classifying the new series of superconductors, the authors of ref. [519] have proposed to gather together different compounds such as high- T_c cuprates, fullerenes and heavy Fermi compounds which are characterized by a large ratio T_c/T_F (T_F is the Fermi temperature). These materials are correlated systems, as demonstrated by the presence of competitive magnetic ordered states and the electronic interactions should play a role in the pairing mechanism [520].

4.3.5 Quantum magnetooscillation effects

When a high magnetic field (H) is applied to low-dimensional conductors at low temperatures, several magnetooscillation phenomena, caused by Landau sublevels passing through the Fermi level, are observed (see [521–531] and references cited therein). In 2D conductors (with closed orbits) the magnetization oscillation is known as the de Haas–van Alphen (dHvA) effect and the magnetoresistance oscillation as the Shubnikov–de Haas (SdH) effect. These effects have been observed firstly in thin metal films [521,522] and more recently in a number of low-dimensional

synthetic metals [523–531]. Moreover, some new phenomena [524,525] such as the ‘angular-dependent magnetoresistance resonance’ and ‘paramagnetic quantum oscillation’ have been observed, even for materials with open orbits (e.g. q-1D). Also, an effect similar to quantum Hall-effect has been observed in some salts based on TMTSF [505]. Oscillations can be observed in metallic compounds or compounds which are semiconductors or superconductors, becoming metallic under high pressure (or under a magnetic field in the case of superconductors). The form of the corresponding spectra is sensitive to the structure of the material, even for materials of the same phase. However, there are some similarities in the spectra of materials of the same phase. In high magnetic fields, the spectra show lines which are due to the ‘normal’ orbits as well as lines which are due to magnetic breakdown orbits. Magnetic breakdown arises from electrons tunneling through the energy gaps formed in the Brillouin zone (BZ) boundaries (see for example Figure 3.15I,III) by periodic lattice potential.

The experimental results are powerful tools to probe the Fermi surface geometry, the conduction electron relaxation time (τ) and the effective mass (m^*). These parameters are obtained from analysis of the oscillation period or frequency (F) and amplitude (A) via the so-called Lifshitz–Kosevich formula (see for example [521–523]). The temperature (T) and field (H) dependence of SdH oscillation amplitude for the fundamental frequency is expressed by

$$A = A_0 \frac{T \exp(-L\mu T_D/H)}{H^{1/2} \sin h(L\mu T/H)} \sin(2\pi F/H + \Psi) \quad (3.7)$$

where A_0 is a constant, $L = 2\pi^2 m_0 k_B / e\hbar$, $\mu = m^*/m_0$, $T_D = \hbar 2\pi k_B \tau$ (the Dingle temperature) and Ψ is an arbitrary phase; F is directly proportional to the external area of the Fermi surface, namely

$$F = \hbar S / 2\pi e \quad (3.8)$$

The results are sometimes close to those obtained from band structure calculations and/or the optical absorption measurements (reflectance spectra) [438,447,523,526]. Some examples are given below.

Figure 3.28 shows the magnetoresistance of α -(ET)₂KHg(SCN)₄ at 0.1 K for $H \parallel b^*$ axis (whereby the b^* -axis is the normal to the ac -plane) [527]. One can see that magnetoresistance oscillations are observed for $H > ca 7$ T. Figure 3.29 shows the corresponding SdH signal at 0.05 K for $H \parallel b^*$ -axis, obtained by a standard low-frequency field modulation technique [527]. The Fourier transform spectrum is presented in the inset of Figure 3.29. This spectrum

clearly demonstrates an oscillation (α) with frequency $F_\alpha = 673$ T and its harmonics (2α , 3α , 4α), as well as an oscillation (β) with frequency $F_\beta = 4260$ T. These values give the ratio of the corresponding Fermi surfaces as $S_\beta : S_\alpha = 6.33$. The corresponding masses of β - and α -oscillation have been estimated to be $3.7 \pm 0.2 m_0$ and $1.5 \pm 0.1 m_0$, respectively [527].

According to band structure calculations (see Section 4.2) in α -(ET)₂KHg(SCN)₄ and similar salts the Fermi surface consists of (2D) hole closed orbits (α) at the corners of the BZ and (1D) electron open orbits running along the k_c direction. A magnetic breakdown orbit (β) can be formed at high magnetic fields from the α -orbit and the 1D orbit, as it is shown in Figure 3.30. The cross sectional area of the Fermi surface is calculated to be ca 100.6% of the BZ for the β -orbit and 15.9% of the BZ for the α -orbit; the corresponding ratio (100.6/15.9 = 6.33) is the same as that found from SdH oscillations.

SdH Fourier transform spectra of α -(ET)₂MHg(SCN)₄ show the oscillations of α - and β -orbits ($M = \text{Tl, Rb}$) and their harmonics (2α , 3α , etc.)

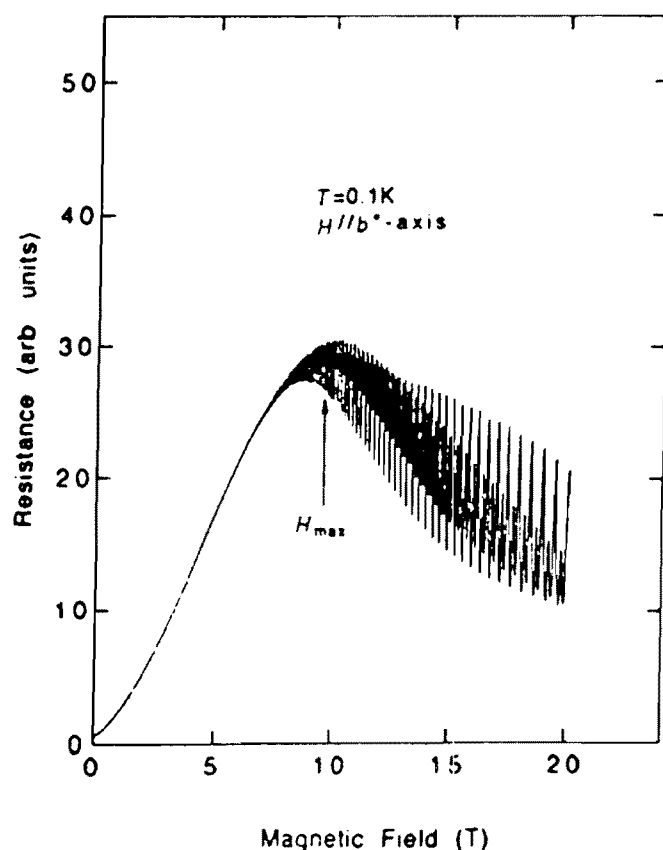


Figure 3.28. Magnetoresistance of α -(ET)₂KHg(SCN)₄ at 0.1 K for $H \parallel b^*$ -axis with electric current in the ac -plane. (Reproduced by permission of Pergamon Press from ref. 527.)

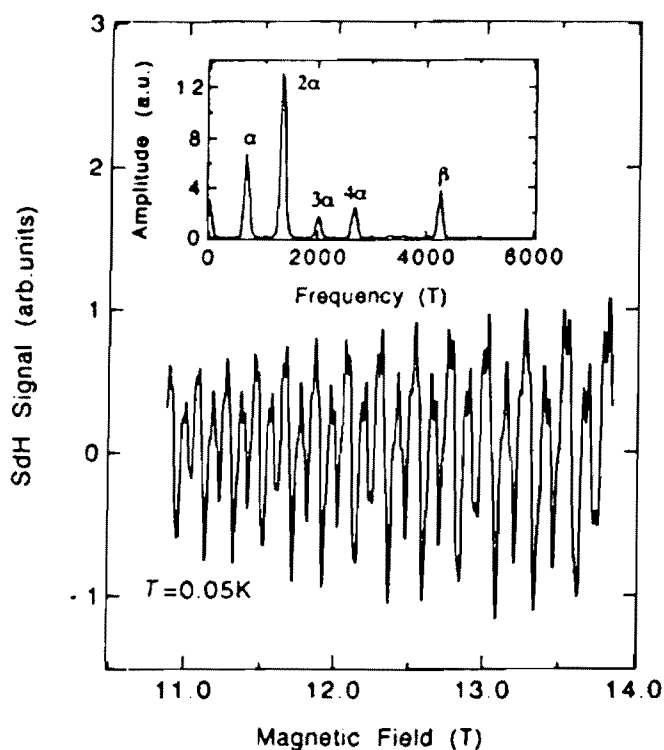


Figure 3.29. SdH signal of α -(ET)₂KHg(SCN)₄ measured at 0.05 K by the field modulation technique. (Reproduced by permission of Pergamon Press from ref. 527.)

or combinations ($\alpha + \beta$, $\beta - \alpha$, etc.) ($M = \text{Ti}$) [524], but in the compound with $M = \text{NH}_4$ the SdH spectrum does not show the breakdown oscillation (β) [527]. The compound with $M = \text{K}$ shows a transition, the so-called 'kink' transition at *ca* 22 T, which is associated with the SDW [445b,525,527,528].

For θ -(ET)₂I₃ the following have been found: a closed orbit oscillation (α) with $F_\alpha = 779$ T ($S_\alpha = 19\%$ BZ) and a breakdown orbit (β) with

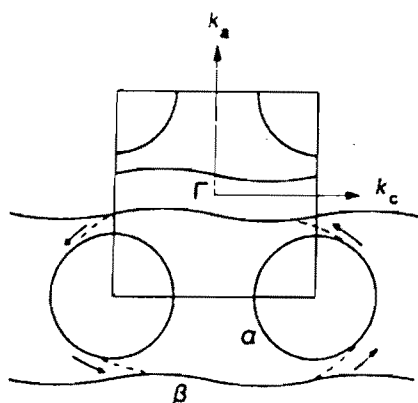


Figure 3.30. Calculated Fermi surface of α -(ET)₂KHg(SCN)₄. (Reproduced by permission of Pergamon Press from ref. 528.)

$F_\beta = 4234$ T ($S_\beta = 102\%$ BZ), the harmonics (2α , 3α , etc. 2β) and some new oscillations of small area [447,470,523,524].

The spectra of β -(ET)₂IBr₂ show the main oscillator at $F = 3842$ T with area 53% BZ and some weaker oscillations [523,524].

The spectra of κ -phases are described in a number of papers (see for example [523,524,526,529]). The SdH spectrum of κ -(ET)₂Cu(SCN)₂ shows an oscillation of α -orbit at *ca* 600 T and oscillation of breakdown orbit (β) at *ca* 3920 T and some others (2α , 2β , $\beta + \alpha$, $\beta - \alpha$, etc.). In the case of κ -(ET)₂I₃ the corresponding oscillations are observed at relatively low fields, i.e. without magnetic breakdown effect, because of the zero gap of the Fermi surfaces at G-points (see Figure 3.15III). Oscillations are also observed in κ -(DMET)₂-AuBr₂, material which is based on unsymmetrical donor molecules (2b'-7c) (see [523] and refs. therein).

Oscillations from λ -(BETS)₂FeCl₄ are described in [530], but there are not yet results for oscillations in τ -phases. Measurements under high pressure and/or magnetic field [300] are necessary to suppress the metal to insulator transition of these compounds, observed at *ca* $6 \geq K$. Magnetooscillations have also been observed in Ni(dmit)₂ complexes [531].

Because of the increasing number and the variety of structures of organic conductors based on tetrachalcogenafulvalenes and metal 1,2-dichalcogenolenes, new results and new quantum magnetotransport effects are expected for these kinds of materials, which have simple Fermi surfaces, in comparison with those of elemental metals (e.g. Mg, Zn).

5 CONCLUSIONS

In this review we have tried to show that the synthetic challenge with these molecular solids is to go from a molecular characteristic to a bulk property, following a more or less rationalized method. The chemical preparation of these new molecular materials is based upon a two-step process:

- (i) the chemical synthesis of π -donor and π -acceptor molecules
- (ii) the control of electronic transfer between molecular blocks by preparing charge-transfer salts (i.e. CTCs or RISs).

The intrinsic molecular characteristics such as size, symmetry and density of π -electrons are necessary basic requirements in these heterocycles but not

sufficient. The second step, which is to prepare single crystals through a supramolecular organization between donors and acceptors, or one of them associated with a counterion, is the key point. Great progress has been realized with the electrocrystallization technique developed for the series of RISs. If these two problems are overcome, the structural and physical properties of these molecular solids can be investigated. It appears, nevertheless, that to reach this goal a lot of chemistry work has to be accomplished in a first step; several new molecules that have been synthesized give new conducting materials (e.g. α -, κ -, λ -, τ -phases). However, following the general guidelines which have been presented in this review, it has been shown that during the last 30 years new series of conducting materials with predicted characteristics such as the onset of magnetic ordering or of a superconducting state at low temperature have been discovered. To summarize this point we can describe these new compounds as strongly correlated electronic or magnetic systems of reduced dimensionality. Playing with the large polymorphism present in these radical cation salts, q-1D or q-2D electronic structures exist; they are associated with the presence of electrons with strong Coulombic interactions. This characteristic is described thanks to Hubbard-type models in physics language, which is equivalent to a mixed-valence state in chemistry language.

Now to finish this review we want to give the actual trends found from this research on new molecular materials and more specifically discuss the development of the series of radical cation salts derived from the TTF backbone.

For the synthetic challenge of finding new materials with interesting cooperative properties, two ways are proposed. On the one hand, there is the development of extended or functionalized π -systems, and on the other hand, manipulation of the role played by the counterion which can offer several facets:

- (i) New developments in the synthesis of donor molecules. Recently new molecules, based on large sulfur heterocycles, and from them, novel series of conducting 1:1 radical cation salts have been synthesized. In particular a single valence salt derived from a bis-fused TTF [388b] presents a metallic behavior at around room temperature. Following the description of a Mott-Hubbard (metal-insulator) transition, it appears that a decrease of the on-site Coulomb repulsion with an increase in the molecular size is responsible for this behavior. A gradual shift

from the 'large U ' to the 'small U ' approximation in these correlated systems has appeared. The rule of homogeneous mixed-valence state to obtain a partially full electronic band is not necessary any more. In the future it will be necessary to stabilize the metallic state at low temperature on examining the possibility of obtaining new compounds with either a magnetic or a superconducting ground state. This situation would be analogous to the case of monovalent C_{60} alkali-metal salts, which are 3D electronic systems. This comparison leads also to the prospect of real 3D systems with π orbital overlapping and delocalization in different spatial directions.

A complementary point, following this analysis, is the hierarchy of the electronic correlations and the electron-phonon interactions. In the presence of extended π -systems, U and V Hubbard parameters decrease and they become about the same order of magnitude as the interactions with the phonon lattice and molecular vibrations. In such a situation a polaronic process occurs; even the case of bipolarons associated with a two electron transfer has been predicted with the possible occurrence of a Bose condensation [333a].

- (ii) Role of counterions. The following counterion characteristics have to be considered; (a) the size, shape and symmetry, with the possibility of an orientational order, but also the formation of a linear or a planar polymeric sublattice; (b) the valence state going from monoanions to polyanions which induce multiple electrostatic interactions and several electron exchanges between partners; (c) the magnetic state, diamagnetic or paramagnetic, in the presence of transition metals with unpaired spins.

They play the role of spacers between organic columns and layers with the presence of Madelung energy which have to be minimized but also acting as an external potential on the electronic gas. In particular, the compound stoichiometry can induce incommensurate-commensurate effects between the two sublattices. Two effects are recognized: the polyanion charge, going up to -6 and acting as an electron reservoir, and the role of localized magnetic moments inducing indirect exchange interactions. In this research for new conducting molecular materials by assembling together inor-

ganic and organic blocks, we have been interested in series of polyanions associated mainly with TTF and ET molecules: tetracyanometallate planar complexes of Pt^{2+} , Ni^{2+} [380b,409b] and polyoxometalates with quasi-spherical shapes, Lindquist and Keggin structures [362].

A magnetic coupling between local moments and conduction electrons is known in ordinary metals (s-d models). This kind of indirect exchange interaction can give rise to a ferromagnetic coupling through the so-called RKKY oscillations [455]. This kind of magnetic interaction has been developed in these hybrid organic-inorganic materials. It appears that to fully succeed with this mechanism, it will be necessary to increase the effective exchange mechanism. The final purpose will be to create a long range magnetic order associated with a conducting character or even to stabilize a superconducting state in a magnetically ordered molecular lattice (see [389g] and refs. therein).

Recently an interesting result has been observed: a magnetic field-induced ferromagnetic ordering of Fe^{3+} ions in λ -(BETS) $_2\text{FeCl}_4$ salt [386b]. This result opens up new ways for future work where the interplay between superconductivity and magnetism, as in heavy fermions, is a fundamental problem. Also, it has been observed that the anion disorder leads to weak localization, which prevents other magnetotransport effects [300,443].

Comparing with conventional systems, such as elemental metals and polyatomic superconductors, the compounds based on tetrachalcogenafulvalenes and metal 1,2-chalcogenolones present some advantages; in particular they can be easily prepared in a pure single crystal form, stable in air. They constitute therefore a completely different family of compounds with reduced dimensionality, on which the physical theories associated with the cooperative magnetism of the onset or a superconductivity state, can be tested to generalize the concepts involved.

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7 REFERENCES

1. F. Wudl, G.M. Smith and E.J. Hufnagel, *J. Chem. Soc., Chem. Commun.* 1453 (1970); D.L. Coffen, *Tetrahedron Lett.* 30, 2633 (1970).
2. W.R.H. Hurstley and S. Smiles, *J. Chem. Soc.* 2263 (1926).
3. E.M. Engler and V.V. Patel, *J. Am. Chem. Soc.* 96, 7376 (1974).
4. R.D. McCullough, G.B. Koc, K.A. Lerstrup and D.O. Cowan, *J. Am. Chem. Soc.* 109, 4115 (1987).
5. G.N. Schrauzer and V.P. Mayereg, *J. Am. Chem. Soc.* 87, 3585 (1965).
6. G.N. Schrauzer and V.P. Mayereg, *J. Am. Chem. Soc.* 84, 3221 (1962).
7. G. Bähr and H. Schletzer, *Chem. Ber.* 90, 438 (1957).
8. G. Briegleb, *Electronen-Donator-Acceptor-Komplexe* Springer-Verlag, Berlin, 1961; R.S. Mulliken and W.B. Person, *Molecular Complexes*, Wiley, New York, 1969; A.R. Katritzky and A.J. Boulton, *Advances in Heterocyclic Chemistry*, Vol. 27, Academic Press, New York, 1980; W.H. Powell, *Pure-Appl. Chem.* 65, 1357 (1993).
9. H. Akamatu, H. Inokuchi and Y. Matsunaga, *Nature* 173, 168 (1954).
10. H. Akamatu and H. Inokuchi, in *Symp. Proc. on Electrical Conductivity in Organic Solids*, H. Kallmann and M. Silver (Eds.), Interscience, New York, 1960, p. 277; For similar compounds prepared recently see H. Tani *et al.*, *Chem. Lett.* 779 (1994).
11. F. Wudl, *J. Am. Chem. Soc.* 97, 1962 (1975).
12. J. Ferraris, D.O. Cowan, V.J. Walatka and J.H. Perlstein, *J. Am. Chem. Soc.*, 95, 948 (1973).
13. F. Wudl, C.H. Ito and A. Nagel, *J. Chem. Soc., Chem. Commun.* 923 (1973).
14. D. Jerome, A. Mazaud, M. Ribault and K. Bechgaard, *J. Phys. Lett.* 41, L95 (1980); K. Bechgaard, C.S. Jacobsen, K. Mortensen, M.J. Pedersen and N. Thoup, *Solid State Commun.* 33, 1119 (1980).
15. S.S. Parkin, E. Engler, R.R. Schumaker, R. Lagier, V.Y. Lee, J.C. Scott and R.L. Greene, *Phys. Rev. Lett.* 50, 270 (1983).
16. K. Kikuchi, M. Kikuchi, T. Namiki, K. Saito, I. Ikemoto, K. Murata, T. Ishiguro and K. Kobayashi, *Chem. Lett.* 931 (1987).
17. G.C. Papavassiliou, G.A. Mousdis, J.S. Zambounis, A. Terzis, A. Hountas, B. Hilti, C.W. Mayer and J. Pfeiffer, *Synth. Met.* 27, B379 (1988).
18. (a) G.C. Papavassiliou, *Z. Naturforsch., Teil B* 36, 1200 (1981); (b) 37, 825 (1982).
19. L. Brossard, M. Ribault, L. Valanide and P. Cassoux, *Physica B/C* 143, 378 (1986).
20. J.M. Williams, A.M. Kini, H.H. Wang, K.D. Carlson, V. Geiser, L.K. Montgomery, G.J. Pyrka, C.M. Watking, J.M. Kommers, S.J. Boryshik, A.V. Strieby Crouch, W.K. Knok, J.E. Schirber, D.L. Overmyer, D. Jung and M.H. Whangbo, *Inorg. Chem.* 20, 3272 (1990).
21. (a) S. Roth, *One-Dimensional Metals, Physics and Materials Science*, VCH, Weinheim, 1994. (b) J.P. Farges (Ed.), *Organic Conductors*, Marcel Dekker, New York, 1994.

22. J.M. Williams, J.R. Ferraro, R.J. Thorn, K. Douglas Carlson, Urs. Geiser, H.H. Wang, A.M. Kin and M.H. Whangbo, *Organic Superconductors*, Prentice Hall, Englewood Cliffs, NJ, 1992.
23. A. Graja, *Low-Dimensional Organic Conductors*, World Scientific, Singapore, 1992.
24. T. Ishiguro and K. Yamaji, *Organic Superconductors*, Springer Series in *Solid State Science* Vol. B88, Springer Verlag, Berlin, 1989.
25. (a) J.R. Ferraro and J.M. Williams, *Introduction to Synthetic Electrical Conductors*, Academic Press, New York, 1987; (b) also J.M. Williams *et al.*, *Prog. Inorg. Chem.* **35**, 51 (1987).
26. M. Adam and K. Müllen, *Adv. Mater.* **6**, 439 (1994).
27. H. Mori, Overview of organic superconductors, *Int. J. Mod. Phys. B* **8**, 1 (1994).
28. G. Schukat and E. Fanghänel, Synthesis, reactions and selected physico-chemical properties of 1,3 and 1,2-tetrachalcogenafulvalenes, *Sulfur Rep.* **14**, 245 (1993); see also G. Schukat, A.M. Richter and E. Fanghänel, *Sulfur Rep.* **7**, 155 (1987).
29. R.-M. Olk, B. Olk, W. Dietzsch, R. Kirmse and E. Hoyer, The chemistry of 1,3-dithiole-2-thione-4,5-dithiole (dmit), *Coord. Chem. Rev.* **117**, 99 (1992).
30. (a) J.M. Williams, H.H. Wang, T.J. Emge, U. Geiser, M.A. Beni, P.C.W. Leung, I.D. Carlson, R.J. Thorn and A.J. Schultz, Rotational Design of Synthetic Metal Superconductors, *Prog. Inorg. Chem.* **55**, 51 (1987). (b) M.R. Bryce, Recent progress in conducting organic charge-transfer salts, *Chem. Soc. Rev.* **20**, 355 (1991).
31. P. Cassoux, L. Valade, H. Kobayashi, A. Kobayashi, R.A. Clark and A.E. Underhill, Molecular metals and superconductors derived from metal complexes of 1,3-dithiol-2-thione-4,5-dithiolate (dmit), *Coord. Chem. Rev.* **110**, 115 (1991).
32. P.I. Clemenson, The chemistry and solid state properties of nickel, palladium and platinum bis(maleonitridithiolate) compounds, *Coord. Chem. Rev.* **106**, 171 (1990).
33. M.D. Ward, Electrochemical aspects of low-dimensional molecular solids, *Electroanal. Chem.* **16**, 181 (1984).
34. U.T. Mueller-Westerhoff and B. Vance, Dithiolenes and related species, in *Comprehensive Coordination Chemistry*, Vol. 2, Pergamon, Oxford, 1987, p. 595.
35. A. Krief, Synthesis of tetraheterofulvalenes... *Tetrahedron* **42**, 1209 (1986).
36. L. Alcacer and H. Norais, Linear chain 1,2-dithiolene complexes, in *Extended Linear-Chain Compounds*, J.S. Miller (Ed.), Vol. 3, Plenum, New York, 1983, p. 319.
37. M. Narita and C.U. Pittman, Jr., Preparation of tetrathiafulvalenes (TTF) and their selenium analogs—tetraselenafulvalenes (TSF), *Synthesis* 489 (1976).
38. J.A. McCleverty, Metal 1,2-dithiolene and related complexes, *Prog. Inorg. Chem.* **10**, 49 (1968).
39. G. Saito and S. Kagoshima (Eds.), Physics and chemistry of organic superconductors, *Springer Proc. Phys.* Vol. **51** Berlin (1990).
40. V.Z. Kresin and W.A. Little, *Organic Superconductivity*, Plenum Press, New York, 1990.
41. R.M. Metzger, P. Day and G.C. Papavassiliou (Eds.), Low-dimensional systems and molecular electronics *NATO ASI Ser. B* Vol. **248** Plenum Press, New York (1990).
42. J.M. Williams and Kuroda (Eds.), Proc. of the symp. on new developments in the chemistry and properties of low-dimensional and conducting solids, *Mol. Cryst. Liq. Cryst.* **181** (1990).
43. M. Hanack, S. Roth and H. Schier (Eds.), Proc. ICSM'90, *Synth. Met.* **41/43** (1991).
44. S. Stafström, W.R. Salaneck, O. Inganäs and T. Hjertberg (Eds.), Proc. ICSM'92, *Synth. Met.* **55/57** (1993).
45. Y.W. Park and H. Lee (Eds.), Proc. ICSM'94, *Synth. Met.* **70** (1995).
46. J. Becher and K. Schemembur (Eds.), Molecular Engineering for Advanced Materials *NATO ASI Ser., Ser. C*, **456** (1995).
47. (a) A. Kobayashi and H. Kobayashi, *Molecular Metals and Superconductors Based on Transition Metal Complexes*, this volume, Chapter 5. (b) T. Nakamura, *Electrically Conductive Langmuir-Blodgett Films*, this volume, Chapter 14. (c) M. Almeida and Henriques, Perylene Based Conductors, this volume, Chapter 2.
48. E.M. Engler, V.V. Patel and R.R. Schumaker, *J. Chem. Soc., Chem. Commun.* 516 (1979); R.R. Schumaker and E.M. Engler, *J. Am. Chem. Soc.* **99**, 5519 (1977); **99**, 5521 (1977); **102**, 665 (1980).
49. K. Kobayashi, *Chem. Lett.*, 1423 (1985).
50. G.C. Papavassiliou, S.Y. Yiannopoulos and J.S. Zambounis, *Mol. Cryst. Liq. Cryst.* **120**, 333 (1985).
51. G.C. Papavassiliou, S.Y. Yiannopoulos and J.S. Zambounis, *J. Chem. Soc., Chem. Commun.* 820 (1986); *Physica B* **143**, 310 (1986).
52. G.C. Papavassiliou, S.Y. Yiannopoulos and J.S. Zambounis, *Chim. Scr.* **27**, 265 (1987); G.C. Papavassiliou (1995) unpublished results.
53. (a) G.C. Papavassiliou, J.S. Zambounis, and S.Y. Yiannopoulos, *Chim. Scr.* **27**, 261 (1987); (b) *Physica B (Amsterdam)* **143**, 307 (1986).
54. G.C. Papavassiliou, S.Y. Yiannopoulos, J.S. Zambounis, K. Kobayashi and K. Umemoto, *Chem. Lett.* 1279 (1987).
55. G.C. Papavassiliou, G.A. Mousdis, V. Gionis, J.S. Zambounis and S.Y. Yiannopoulos, *Z. Naturforsch., Teil B* **42**, 1050 (1987).
56. W. Dölling, M. Augustin and R. Ihrke, *Synthesis* 655 (1987).
57. G.C. Papavassiliou, G.A. Mousdis, V. Gionis, J.S. Zambounis and S.Y. Yiannopoulos, Organic and inorganic low-dimensional crystalline materials, *NATO ASI Ser., Ser. B* **168**, 301 (1987).

58. G.C. Papavassiliou, S.Y. Yiannopoulos and J.S. Zambounis, ref. [57] p. 305; G.C. Papavassiliou, *Chem. Chron., New Ser.* **15**, 161 (1986).
59. G.C. Papavassiliou, V. Gionis, S.Y. Yiannopoulos, J.S. Zambounis, G.A. Mousdis, K. Kobayashi and K. Umemoto, *Mol. Cryst. Liq. Cryst.* **156**, 277 (1988).
60. G.C. Papavassiliou, J.S. Zambounis, G.A. Mousdis, V. Gionis and S.Y. Yiannopoulos, *Mol. Cryst. Liq. Cryst.* **156**, 269 (1988).
61. G.C. Papavassiliou, G.A. Mousdis, S.Y. Yiannopoulos, V.C. Kakoussis and J.S. Zambounis, *Synth. Met.* **27**, B373 (1988).
62. G.C. Papavassiliou, G.A. Mousdis, S.Y. Yiannopoulos and J.S. Zambounis, *Chem. Scr.* **28**, 365 (1988).
63. G.C. Papavassiliou, V.C. Kakoussis, G.A. Mousdis, J.S. Zambounis and C.W. Mayer, *Chem. Scr.* **29**, 71 (1989).
64. G.C. Papavassiliou, V.C. Kakoussis, J.S. Zambounis and G.A. Mousdis, *Chem. Scr.* **29**, 123 (1989).
65. G.A. Mousdis, V.C. Kakoussis and G.C. Papavassiliou, in ref. [41], p. 181.
66. G.C. Papavassiliou, in ref. [41], p. 143.
67. G.C. Papavassiliou, *Pure Appl. Chem.* **62**, 483 (1990).
68. G.C. Papavassiliou, V.C. Kakoussis, D.J. Lagouvardos and G.A. Mousdis, *Mol. Cryst. Liq. Cryst.* **181**, 171 (1990); G.C. Papavassiliou and V.C. Kakoussis, unpublished work (1995).
69. G.C. Papavassiliou, D.J. Lagouvardos, V.C. Kakoussis and G.A. Mousdis, *Z. Naturforsch., Teil B* **45**, 1216 (1990); see also refs. [67,68].
70. G.C. Papavassiliou, *Synth. Met.* **41/43**, 2535 (1991).
71. G.C. Papavassiliou, V.C. Kakoussis and D.J. Lagouvardos, *Z. Naturforsch., Teil B* **46**, 1269 (1991).
72. G.C. Papavassiliou, D.J. Lagouvardos and V.C. Kakoussis, *Z. Naturforsch., Teil B* **46**, 1730 (1991).
73. J.-M. Fabre, J. Garin and S. Uriel, *Tetrahedron Lett.* **32**, 6407 (1991).
74. M. Joergensen, K.A. Lestrup and K. Bechgaard, *J. Org. Chem.* **56**, 5685 (1991).
75. H. Müller, A. Lert and H.P. Fritz, *Leibigs Ann. Chem.* 395 (1991); O. Ya. Neiland, K.A. Balodis, V.Yu. Khodorkovskii and Zh.V. Tilika, *Khim. Geterotsikl. Soedin.* 1278 (1991).
76. R.P. Shibaeva, V.E. Korotkov, L.P. Rosengerg, N.D. Kushch, E.E. Laukhing, G.G. Abashev, E.B. Vagubskii, L.I. Buravov, A.V. Zuarykina and A.G. Khomenenko, *Synth. Met.* **41/43**, 1963 (1991).
77. J.M. Fabre, J. Amouroux, L. Giral and D. Chasseau, *Synth. Met.* **41/43**, 2049 (1991).
78. R. Kato, H. Kobayashi and A. Kobayashi, *Synth. Met.* **41/43**, 2093 (1991).
79. C. Berning, F. Deilacher, M. Hoch, H.J. Keller, W. Perji, P. Armbruster, R. Geiger, S. Kahlich and D. Schweitzer, *Synth. Met.* **41/43**, 2101 (1991). See also ref. [53].
80. N. Santalo, J. Veciana, C. Roviva, E. Molins, C. Miravittles and J. Claret, *Synth. Met.* **41/43**, 2205 (1991).
81. T. Suzuki, H. Yamochi, H. Isotalo, C. Fite, H. Kasmai, K. Lion, G. Srdanov and F. Wudl, *Synth. Met.* **41/43**, 2225 (1991); K. Hartke and T. Lindenblatt, *Synthesis* 281 (1990). See also ref. [68].
82. C.W. Mayer, J.S. Zambounis, B. Hilti, E. Minder, I. Pfeiffer and G. Ribs, *Synth. Met.* **41/43**, 2251 (1991).
83. A. Belyasmine, A. Gorgues, M. Jubault and G. Duguay, *Synth. Met.* **41/43**, 2323 (1991).
84. A. Khanous, A. Gorgues and M. Jubault, *Synth. Met.* **41/43**, 2327 (1991).
85. H. Gruber, J. Patzsh, M. Schrödner, H.-K. Roth and E. Fanghänel, *Synth. Met.* **41/43**, 2331 (1991).
86. H. Müller, A. Lert, H.P. Fritz and K. Andres, *Synth. Met.* **41/43**, 2381 (1991).
87. H. Nakano, S. Ikegawa, K. Miyawaki, K. Yamado, T. Nogami and Y. Shirota, *Synth. Met.* **41/43**, 2409 (1991).
88. M. Jorgensen, K. Lertrup and K. Bechgaard, *Synth. Met.* **41/43**, 2561 (1991).
89. M. Salle, A. Gorgues, M. Jubault and Y. Gouriou, *Synth. Met.* **41/43**, 2575 (1991).
90. M. Salle, A. Belyasmine, A. Gorgues, M. Inrault and N. Soyer, *Synth. Met.* **41/43**, 2579 (1991).
91. W. Dölling, A. Vogt and M. Augustin, *Z. Naturforsch., Teil B* **46**, 133 (1991).
92. J.S. Zambounis and C.W. Mayer, *Tetrahedron Lett.* **32**, 2741 (1991).
93. J.S. Zambounis and C.W. Mayer, *Tetrahedron Lett.* **32**, 2737 (1991). See also refs. [62,63,70].
94. F. Bertho-Thorarl, A. Robert, A. Sonizi, K. Boubekeur and P. Patail, *J. Chem. Soc., Chem. Commun.* 843 (1991).
95. A. Moore and M.R. Bryce, *J. Chem. Soc., Chem. Commun.* 1638 (1991).
96. K. Kumar, H.B. Singh, K. Das, V.C. Shinha and A. Mishnev, *J. Chem. Soc., Chem. Commun.* 952 (1991).
97. Y. Gimbert and A. Morandpour, *Tetrahedron Lett.* **32**, 4897 (1991).
98. N. Beye, R. Wegner, A.M. Richter and E. Fanghänel, *Tetrahedron Lett.* **32**, 479 (1991).
99. M. Bryce, M.A. Coffin, M.B. Hursthouse, A.I. Karaulov, K. Müllen and H. Scheich, *Tetrahedron Lett.* **32**, 6029 (1991).
100. M. Bryce and G.J. Marshallsay, *Tetrahedron Lett.* **32**, 6033 (1991).
101. S.K. Kumar, H.B. Singh, J.P. Jasinski, E.S. Paight and R.J. Butcher, *J. Chem. Soc., Perkin Trans. 1* 3341 (1991).
102. T.K. Hansen, M.V. Lakshmikantham, M.P. Cara and J. Becher, *J. Chem. Soc., Perkin Trans. 1* 2873 (1991).
103. T.K. Hansen, I. Hawkin, K.S. Varma, S. Edge, S. Larsen, J. Becher and A.E. Underhill, *J. Chem. Soc., Perkin Trans. 2* 1963 (1991).
104. A.J. Moore, M.R. Bryce, D.J. Ando and M.B. Hursthouse, *J. Chem. Soc., Chem. Commun.* 320 (1991).
105. T.K. Hansen, M.V. Kakshnikantham, M.P. Cara, R.M. Metzger and J. Becher, *J. Org. Chem.* **56**, 2720 (1991).

106. T. Jorgensen, J. Becher, T.K. Hansen, K. Christinsen, P. Roepstorff, S. Larsen and A. Nygaard, *Adv. Mater.* **3**, 486 (1991).
107. M. Adam, A. Bohnen, V. Enkelmann and K. Müllen, *Adv. Mater.* **3**, 600 (1991).
108. A.J. Moore and M.R. Bryce, *Synthesis* **26** (1991).
109. E.S. Kozlor, A.A. Yurchenko and A.A. Tolmacher, *Ukr. Khim. Zh.* (Ed.) **57**, 107 (1991).
110. M. Vanderyver, M. Roulliy, J.P. Bourgoïn, A. Bareaud, V. Gionis, V.C. Kakoussis, G.A. Mousdis, J.D. Morand and O. Noel, *J. Phys. Chem.* **95**, 246 (1991).
111. H. Müller, H.P. Fritz, R. Nemetschek, R. Hackl, W. Biberacher, C.-P. Heidmenn, *Z. Naturforsch., Teil B* **47**, 718 (1992).
112. D.J. Lagouvardos and G.C. Papavassiliou, *Z. Naturforsch., Teil B* **47** 898 (1992).
113. G.C. Papavassiliou, *Mater. Res. Soc. Symp. Proc.* **247**, 523 (1992).
114. J. Röhrich and K. Müllen, *J. Org. Chem.* **57**, 2374 (1992).
115. M. Mizutani, K. Tanaka, K. Ideda and K. Kawabata, *Mater. Res. Soc. Symp. Proc.* **247**, 541 (1992); *Synth. Met.* **46**, 201 (1992).
116. T.K. Hansen, M.V. Lakshmikantham, M.P. Cara, R.E. Niziurski-Mann, F. Jensen and J. Becher, *J. Am. Chem. Soc.* **114**, 5035 (1992).
117. S. Aonuma, Y. Okano, H. Sawa, R. Kato and H. Kobayashi, *J. Chem. Soc., Chem. Commun.* 1193 (1992).
118. T.K. Hansen, T. Jorgensen and J. Becher, *J. Chem. Soc., Chem. Commun.* 1550 (1992).
119. M. Adam, P. Wolf, H.J. Räder and K. Müllen, *J. Chem. Soc., Chem. Commun.* 1624 (1992).
120. J.Y. Becker, J. Burnstein, M. Dayan and L. Shahal, *J. Chem. Soc., Chem. Commun.* 1135 (1992).
121. M. Kozaki, S. Tanaka and Y. Yamashita, *J. Chem. Soc., Chem. Commun.* 1137 (1992).
122. M.R. Bryce, M.A. Coffin and W. Clegg, *J. Org. Chem.* **57**, 1696 (1992).
123. Y. Misaki, H. Nishikawa, H. Fujiwara, K. Kawakami, T. Yamabe, H. Yamochi and G. Saito, *J. Chem. Soc., Chem. Commun.* 1408 (1992).
124. Y. Misaki, H. Nishikawa, K. Nomura, T. Yamabe, H. Yamochi, G. Saito, T. Sato and M. Shiro, *J. Chem. Soc., Chem. Commun.* 1410 (1992).
125. K. Christiansen, J. Becker and T.K. Hansen, *Tetrahedron Lett.* 3035 (1992).
126. V.Yu. Khodorkovsky, G.V. Tormos, O.Ya. Neilands, N.Y. Kolotilo and A.Ya. Il'chenko, *Tetrahedron Lett.* **33**, 973 (1992); G.V. Tormos, O.J. Neilands and M.P. Cava, *J. Org. Chem.* **57**, 1008 (1992).
127. A.J. Moore and M.R. Bryce, *Tetrahedron Lett.* **33**, 1373 (1992).
128. Ph. Blanchard, M. Sallé, G. Duguay, M. Jubault and A. Gorgues, *Tetrahedron Lett.* **33**, 2685 (1992).
129. Y. Misaki, H. Nishikawa, K. Kawakami, T. Uehara and T. Yamabe, *Tetrahedron Lett.* **33**, 4321 (1992).
130. M. Salle, A. Gorgues, M. Jubault, K. Boubekeur and P. Batail, *Tetrahedron* **48**, 3081 (1992).
131. C. Gemell, J.D. Kolburn, H. Ueck and A.E. Underhill, *Tetrahedron Lett.* **33**, 3923 (1992).
132. A. Iznoka, R. Kumai and T. Sugawara, *Chem. Lett.* 285 (1992).
133. Y. Yamasha, S. Tanaka, K. Imueda, H. Inokuchi and M. Sano, *Chem. Lett.* 419 (1992).
134. Y. Misaki, H. Nishikawa, K. Kawakami, S. Koyonagi, T. Yamabe and M. Shiro, *Chem. Lett.* 2321 (1992).
135. V.Y. Khodorkovski, J.Y. Becker and J. Bernstein, *Synthesis* 1071 (1992).
136. T. Joergensen, B. Girmay, T.K. Hansen, J. Becher, A.E. Underhill, M.B. Hursthouse, M.E. Harman and J.D. Kilburn, *J. Chem. Soc., Perkin Trans. I* **21**, 2907 (1992).
137. T.K. Hansen, S.K. Varma, S. Edge, A. Charlton, A.E. Underhill and J. Becker, *J. Chem. Soc., Perkin Trans. I*, 1807 (1992).
138. J.D. Singh and H.B. Singh, *J. Chem. Soc., Perkin Trans. I* 2913 (1938).
139. M.R. Bryce, G. Marshallsay and A.J. Moore, *J. Org. Chem.* **57**, 4859 (1992).
140. T. Hansen, T. Joergensen, P.C. Stein and J. Becher, *J. Org. Chem.* **57**, 6403 (1992).
141. J. Röhrich and K. Müllen, *J. Org. Chem.* **57**, 2374 (1992).
142. A. Izuoka, R. Kumai, T. Tachikawa and T. Sugawawa, *Mol. Cryst. Liq. Cryst.* **218**, 213 (1992).
143. L.K. Montgomery, T. Burgin, C. Husting, L. Tilley, J.C. Huffman, K.D. Larson, J.D. Duedek, G.A. Yagoni, U. Geiser and J.M. Williams, *Mol. Cryst. Liq. Cryst.* **211**, 283 (1992).
144. A. Otsaka, G. Saito, K. Ohfughi and M. Konno, *Phosphorus Sulfur Silicon Relat. Elem.* **67**, 333 (1992).
145. K. Day, U.C. Sinha, S. Kalyankumar, H.B. Singh and A. Mishnev, *Acta Crystallogr., Sect. C* **48**, 488 (1992).
146. T. Tachikawa, A. Izuoka, R. Kumai, T. Sugawara and Y. Sugawara, *Solid State Commun.* **82**, 19 (1992).
147. M. Adam, V. Enkelmann, H.-J. Räder, I. Röhrich and K. Müllen, *Angew. Chem.* **104**, 331 (1992).
148. U. Schöberl, J. Salbeck and J. Daub, *Adv. Mater.* **4**, 41 (1992).
149. H. Mora, J.M. Fabre, L. Giral and C. Montginoul, *Bull. Soc. Chim. Belg.* **101**, 741 (1992).
150. D. Lorsy, M.-P. le Paillard and A. Robert, *Tetrahedron Lett.* **34**, 5289 (1993).
151. I.V. Sudmole, B.Yu. Khodorkovsky, A.S. Edginya and O.Ya. Neilands, *Khim. Geterotsikl. Soedin* **6**, 761 (1993).
152. J.M. Fabre, D. Serhani, K. Saoud and A.K. Gousmia, *Bull. Soc. Chim. Belg.* **102**, 615 (1993).
153. K. Oshima, K. Kato, Y. Maryuama, R. Kato, A. Kobayashi and H. Kobayashi, *Synth. Met.* **55/57**, 2780 (1993).

154. A.S. Benhamed-Gasmi, P. Frere, M. Jubault, A. Gorgues, J. Cousseau and B. Garrgues, *Synth. Met.* **55/57**, 1751 (1993).
155. P. Frere, A. Gorgues, M. Jubault, F. Texier, J. Cousseau and G. Duguay, *Synth. Met.* **55/57**, 1803 (1993).
156. A.E. Underhill, I. Hawkins, S. Edge, S.B. Wilkes, K.S. Varma, A. Kobayashi and H. Kobayashi, *Synth. Met.* **55/57**, 1914 (1993).
157. A.E. Underhill, B. Girmay and J.D. Kilburn, *Synth. Met.* **55/57**, 1920 (1993).
158. V.Y. Khodorkovsky, J.Y. Becker and J. Bernstein, *Synth. Met.* **55/57**, 1931 (1993).
159. T.K. Hansen and P.C. Stein, *Synth. Met.* **55/57**, 1972 (1993).
160. J.M. Fabre, S. Chakroune, A. Gorgues and L. Duahab, *Synth. Met.* **55/57**, 1979 (1993).
161. H. Nishikawa, K. Kawakami, H. Fujiwara, T. Vehara, Y. Misaki, T. Yamabe, T. Mori and M. Shiro, *Synth. Met.* **55/57**, 1983 (1993).
162. T. Nogami, T. Ishida, H. Yoshikawa, M. Tanaka, T. Naito, H. Kobayashi and A. Kobayashi, *Synth. Met.* **55/57**, 2039 (1993).
163. J.M. Fabre, S. Chakroune, L. Giral, A. Gorgues and M. Salle, *Synth. Met.* **55/57**, 2073 (1993).
164. R. Kato, S. Aonuma, Y. Okano, H. Sawa, A. Kobayashi and H. Kobayashi, *Synth. Met.* **55/57**, 2084 (1993).
165. M. Adam, V. Scherer, Y.-J. Shen and K. Müllen, *Synth. Met.* **55/57**, 2108 (1993).
166. P. Blanchard, G. Duguoy, J. Cousseau, M. Salle, M. Jubault, A. Gorgues, K. Boubekeur and P. Batail, *Synth. Met.* **55/57**, 2113 (1993).
167. A. Graja, M. Salle and A. Gorgues, *Synth. Met.* **55/57**, 2118 (1993).
168. J. Hellberg and M. Moge, *Synth. Met.* **55/57**, 2124 (1993).
169. M. Salle, M. Jubault, A. Gorgues, J. Cousseau, K. Boubekeur, M. Fourmigue, P. Batail and E. Canadel, *Synth. Met.* **55/57**, 2132 (1993).
170. U. Geiser, J.M. Williams, K.D. Carlson, A.M. Kini, H.H. Wang, R.A. Klemm, J.R. Ferraro, S.K. Kumar, K.A. Lykke, P. Wurz, D.H. Parker, S. Fleshler, J.D. Dudek, N.L. Eastman, P.B. Mobley, J.M. Seaman, J.D.B. Sutin, G.A. Yaconi and P. Stout, *Synth. Met.* **55/57**, 2314 (1993).
171. Y. Misaki, K. Kawakami, H. Nishikawa, H. Fujiwara, T. Yamabe and M. Shiro, *Chem. Lett.* 455 (1993).
172. T. Mori, H. Inokuchi, Y. Misaki, H. Nishikawa, T. Yamabe, H. Mori and S. Tanaka, *Chem. Lett.* 733 (1993).
173. Y. Misaki, H. Nishikawa, T. Yamabe, T. Mori, H. Inokuchi, H. Mori and S. Tanaka, *Chem. Lett.* 1341 (1993).
174. Y. Misaki, H. Nishikawa, K. Kawakami, T. Yamabe, T. Mori, H. Inokuchi, H. Mori and S. Tanaka, *Chem. Lett.* 2073 (1993).
175. T. Mori, H. Inokuchi, Y. Misaki, H. Nishikawa, T. Yamabe, H. Mori and S. Tanaka, *Chem. Lett.* 2085 (1993).
176. Y. Misaki, T. Matsui, K. Kawakami, H. Nishikawa, T. Yamabe and M. Shiro, *Chem. Lett.* 1337 (1993).
177. Y. Misaki, H. Nishikawa, T. Yamabe, T. Mori, H. Inokuchi, H. Mori and S. Tanaka, *Chem. Lett.* 729 (1993).
178. Y. Okano, H. Sawa, S. Aonuma and R. Kato, *Chem. Lett.* 1851 (1993).
179. S. Ikegawa, K. Miyawaki, T. Nogami and Y. Shirota, *Bull. Chem. Soc. Jpn.* **66**, 2770 (1993).
180. H. Müller and V. Veiba, *Synthesis* 853 (1993); see also ref. [68].
181. M. Fourmigué, F.C. Krebs and J. Larsen, *Synthesis* 509 (1993).
182. A.J. Moore, M.R. Bryce, G. Cooke, G.J. Marshallsay, P.J. Shabara, A.S. Batsanov, J.A.K. Howard and S.T.A.K. Daley, *J. Chem. Soc., Perkin Trans. 1* 1403 (1993).
183. M.A. Coffin, M.R. Bryce, A.S. Batsanov and J.A.K. Howard, *J. Chem. Soc., Chem. Commun.* 552 (1993).
184. Y. Misaki, H. Fujiwara and T. Yamabe, *J. Chem. Soc., Chem. Commun.* 949 (1993).
185. A.S. Batsanov, M.R. Bryce, J.N. Heaton and J.A.K. Howard, *J. Chem. Soc., Chem. Commun.* 1701 (1993).
186. K. Takahashi, T. Nihira and K. Tomitani, *J. Chem. Soc., Chem. Commun.* 1617 (1993).
187. J. Ronkali, M. Giffard, P. Frère, M. Jubault and A. Gorgues, *J. Chem. Soc., Chem. Commun.* 689 (1993).
188. Y. Yamashita, K. Ono, S. Tanaka, K. Imaeda, H. Inokuchi and M. Sano, *J. Chem. Soc., Chem. Commun.* 1803 (1993).
189. H. Müller and Y. Ueba, *Bull. Chem. Soc. Jpn.* **66** 1773 (1993).
190. H. Meier and Y. Dai, *Tetrahedron Lett.* **34**, 5277 (1993).
191. A. Belyasmine, P. Frere, A. Gorgues, M. Jubault, G. Duguay and P. Hydhomme, *Tetrahedron Lett.* **34**, 4005 (1993).
192. (a) P. Frère, A. Belyasmine, A. Gorgues, G. Duguay, K. Boubekeur and P. Batail, *Tetrahedron Lett.* **34**, 4519 (1993); (b) A.S. Benahmed-Gasmi, P. Frere, A. Belyasmine, K.M.A. Malik, M.B. Hursthouse, A.J. Moore, M.R. Bryce, M. Jubault and A. Gorgues, *Tetrahedron Lett.* **34**, 2131 (1993); (c) K. Ikeda, K. Kawabata, K. Tanaka and M. Mizutani, *Synth. Met.* **55/57**, 2007 (1993).
193. M.A. Sipyagin, S.V. Pal'tsun, A.V. Piyuk, N.N. Sveshnikov, V.I. Kozlovskii and Z.G. Alier, *Zh. Org. Khim.* **29**, 1872 (1993).
194. G.J. Marshallsay, M.R. Bryce, G. Cooke, T. Joergensen, J. Becher, C.D. Reynolds and S. Wood, *Tetrahedron* **49**, 6849 (1993).
195. W.H. Weston, E.E. Eduok, R.P. Kashyap and M. Krawiec, *Tetrahedron* **49**, 3035 (1993).

196. C.S. Velazquez, J.E. Hutchison and R.W. Murray, *J. Am. Chem. Soc.* **115**, 7897 (1993).
197. F.C. Krebs, J. Larsen, K. Boubekeur and M. Fourmigué, *Acta Chem. Scand.* **47**, 910 (1993).
198. T.K. Hansen, T. Joergensen, F. Jense, P.H. Teygesen, K. Christiansen, M.B. Hursthouse, M.E. Harman, M.A. Malik, B. Girmay, A.E. Underhill, M. Begtrup, D.J. Kilburn, K. Belmore, P. Roeptorff and J. Becher, *J. Org. Chem.* **58**, 1359 (1993).
199. I.V. Sudmale, G.V. Tormos, V.Yu. Khodorkorsky, A. Edzina, O.J. Neilands and M.P. Cava, *J. Org. Chem.* **58**, 1355 (1993); M. Formigue, I. Johannsen, K. Boubekeur, C. Nelson and P. Batail, *J. Am. Chem. Soc.* **115**, 3752 (1993).
200. R.D. McCullough, J.A. Belot and J. Seth, *J. Org. Chem.* **58**, 6480 (1993).
201. J. Becher, O. Simonsen, H. Saether, T.K. Hansen, T. Joergensen and S. Boewadt, *Heterocycles* **35**, 445 (1993).
202. (a) H. Mori, I. Hirabayashi, S. Tanaka, T. Mori, Y. Moruyama and H. Inokuchi, *Solid State Commun.* **88**, 411 (1993); (b) see also ref. [64] and G.C. Papavassiliou *et al.* in ref. [39], p. 247.
203. J. Roncali, M. Giffard, M. Jubault and A. Gorgues, *Synth. Met.* **60**, 163 (1993).
204. J.M. Fabre, D. Serhani, K. Saoud, S. Chakroune and M. Hoch, *Synth. Met.* **60**, 295 (1993); see also refs. [67,68].
205. (a) R. Wegner, N. Beye, E. Fanghänel, U. Scherer, R. Wirschem and K. Müllen, *Synth. Met.* **53**, 353 (1993); (b) U. Scherer, Y.-J. Shen, M. Adam, W. Bietsch, V. Shütz and K. Müllen, *Adv. Mater.* **5**, 109 (1993).
206. G.C. Papavassiliou, D.J. Lagouvardos, A. Terzis, A. Hountas, B. Hilti, J.S. Zambounis, C.W. Mayer, J. Pfeiffer, W. Hofherr, P. Delhaes and J. Amiell, *Synth. Met.* **55/57**, 2174 (1993).
207. M. Salle, M. Jubault, A. Gorgues, K. Boubekeur, M. Fourmigué, P. Batail and E. Canadell, *Chem. Mater.* **5**, 1196 (1993).
208. V.N. Baumer, V.A. Starodub, V.P. Batulin, E.E. Lakin, V.P. Kuznetsov and O.A. Dyanchenko, *Acta Crystallogr., Sect. C*, **49**, 2051 (1993).
209. M. Fourmigué and Y.-Sh. Uang, *Organometallics* **12**, 797 (1993).
210. D.D. Doxsee, C.P. Galloway, T.B. Rauchfuss, S.R. Wilson and X. Yang, *Inorg. Chem.* **32**, 5467 (1993).
211. E. Fanghänel, L. van Hinh and G. Schukat, *J. Prakt. Chem.* **335**, 599 (1993).
212. T. Otsubo, Y. Kochi, A. Bitoh and F. Ogura, *Chem. Lett.* 2047 (1994).
213. M. Iyoda, M. Fukuda, M. Yoshida and S. Sasaki, *Chem. Lett.* 2369 (1994).
214. U. Kux and M. Iyoda, *Chem. Lett.* 2327 (1994).
215. R.P. Parg, J.D. Kilburn and T.G. Ryan, *Synthesis* 195 (1994).
216. B.W. Knight, S.T. Purrington, R.D. Bereman and P. Singh, *Synthesis* 460 (1994).
217. J. Garin, J. Orduna, S. Uriel, A.J. Moore and M.R. Bryce, *Synthesis* 489 (1994).
218. N. Svenstrup, K.M. Rasmussen, T.K. Hansen and J. Becher, *Synthesis* 809 (1994).
219. R.P. Parg, J.D. Kilburn, M.C. Petty, C. Pearson and T.G. Ryan, *Synthesis* 613 (1994).
220. G.J. Marshall, T.K. Hansen, A.J. Moore, M.R. Bryce and J. Becher, *Synthesis* 926 (1994); H. Meier, Y. Dai, H. Schuhmacher and H. Kolshorn, *Chem. Ber.* **127**, 203 (1994).
221. M. Adam, E. Fanghänel, K. Müllen, Y.-J. Shen and R. Wegner, *Synth. Met.* **66**, 275 (1994).
222. H. Meier, Y. Dai, H. Schuhmacher and H. Kolshorn, *Chem. Ber.* **127**, 2035 (1994).
223. K. Boubekeur, C. Lenoir, P. Batail, R. Carlier, A. Kallec, M.-P. LePailard, D. Lorg and A. Robert, *Angew. Chem., Int. Ed. Engl.* **33**, 1379 (1994).
224. K. Lahlil, A. Moradpour, C. Merienne and C. Bowlas, *J. Org. Chem.* **59**, 8030 (1994).
225. T.K. Hansen, M.R. Bryce, J.A.K. Howard and D.S. Yüfit, *J. Org. Chem.* **59**, 5324 (1994).
226. M.A. Fox and H.-I. Pan, *J. Org. Chem.* **59**, 6519 (1994).
227. J. Joergensen, K. Bechgaard, T. Bjoernholm, P. Sommer-Larsen, L.G. Hansen and K. Schaumburg, *J. Org. Chem.* **59**, 5877 (1994).
228. G.J. Marshall and M.R. Bryce, *J. Org. Chem.* **59**, 6847 (1994).
229. A.I. Kotor, C. Faulmann, P. Cassoux and E.B. Yagubskii, *J. Org. Chem.* **59**, 2626 (1994).
230. K. Ono, S. Tanaka, K. Imaeda and Y. Yamashita, *J. Chem. Soc., Chem. Commun.* 899 (1994).
231. J. Becher, J. Lau, P. Leriche, P. Moerk and N. Svenstrup, *J. Chem. Soc., Chem. Commun.* 2715 (1994).
232. C. Wang, A. Ellem, V. Khodorkovsky, J.Y. Becker and J. Bernstein, *J. Chem. Soc., Chem. Commun.* 2115 (1994); C. Wang, A. Ellem, J.Y. Becker and J. Bernstein, *Tetrahedron Lett.* **35**, 8489 (1994); V.Y. Khodorkovsky *et al.* *Adv. Mater.* **6**, 656 (1994).
233. H. Brisset, C. Thobie-Gautier, M. Jubault, A. Gorgues and J. Roncali, *J. Chem. Soc., Chem. Commun.* 1765 (1994).
234. S. Nakatsuji, Y. Amano, H. Kawamura and H. Anzai, *J. Chem. Soc., Chem. Commun.* 841 (1994); J. Hellberg *et al.* *J. Mater. Chem.* **5**, 1549 (1995).
235. J. Hellberg, M. Moge, D. Bauer and J.-U. VonSchütz, *J. Chem. Soc., Chem. Commun.* 817 (1994); also in ref. [45], p. 1135.
236. Y. Misaki, K. Kawakami, T. Matsui, T. Yamabe and M. Shiro, *J. Chem. Soc., Chem. Commun.* 459 (1994).
237. T. Naito, A. Taneko, T. Udagawa, H. Kobayashi, R. Kato, A. Kobayashi and T. Nogami, *J. Chem. Soc., Faraday Trans.* **90**, 763 (1994).
238. P. Frere, A. Gorgues, M. Jubault, A. Riou, Y. Gouriou and J. Roncali, *Tetrahedron Lett.* **35**, 1991 (1994).
239. E. Aqad, J.Y. Becker, J. Bernstein, A. Ellem, V. Khodorkovski and L. Shapiro, *J. Chem. Soc., Chem.*

- Commun.* 2775 (1994); T. Nogami and T. Ishida unpublished (1995).
240. R.M. Renner and G.R. Burns, *Tetrahedron Lett.* **35**, 269 (1994).
241. M.V. Lakshmikanthan and M.R. Cava, *Curr. Sci.* **66**, 28 (1994).
242. F. Qi, J. Min-Hua, Q. Zheng, C. Jin-Hua, L. Hong, Y. Wen-Tao and Z. Zhuang, *J. Mater. Chem.* **4**, 1041 (1994).
243. M. Wagner, R.-M. Olk and E. Hoyer, *J. Prakt. Chem./Chem.-Ztg.* **336**, 177 (1994); G.G. Abashev, V.S. Russkikh and E.V. Shklyayeva, *J. Org. Chem. USSR* **30**, 621 (1994).
244. F. Qi, Y. Wen-Tao, X. Jian-Hua, L. Hong and J. Min-Hua, *Acta Crystallogr., Sect. C*, **50**, 1519 (1994).
245. C.P. Galloway, D.D. Doxsee, D. Fenske, T.B. Rauchfuss, S.R. Wilson and X. Yang, *Inorg. Chem.* **33**, 4537 (1994).
246. Y. Yamashita, K. Ono, S. Tanaka, K. Imaeda and H. Inokuchi, *Adv. Mater.* **6**, 295 (1994).
247. K. Hartke and C. Timpe, *Pharmazie* **49**, 117 (1994).
248. D.S. Marynick, S. Seong, R.L. Meline, M. Pomerantz, *Mater. Res. Soc. Symp. Proc.* **328**, 221 (1994).
249. K. Swaminathan, R.J. Carroll, J.D. Singh and H.B. Singh, *Acta Crystallogr., Sect. C* **50**, 1958 (1994).
250. A.M. Richter, J. Bauroth, E. Fanghänel, L. Kutschabsky and R. Radeaglia, *J. Prakt. Chem./Chem.-Ztg.* **336**, 355 (1994).
251. C. Rovira, J. Veciana, N. Santalo, J. Tarres, J. Cirujeda, E. Molins, J. Lorca and E. Espinosa, *J. Org. Chem.* **59**, 3307 (1994); J.A. Belot and D. McCullough, unpublished (1995).
252. F. Guyon, C. Lenoir, M. Formigué, J. Larsen and J. Amoudrunt, *Bull. Soc. Chim. Fr.* **131**, 217 (1994).
253. M.R. Bryce, W. Devonport and A.J. Moore, *Angew. Chem., Int. Ed. Engl.* **33**, 1761 (1994).
254. M.R. Bryce, A.S. Batsanov, W. Devonport, J.N. Heaton, J.A.K. Howard, G.J. Marshallsay, A.J. Moore, P.J. Skabara and S. Wegener, in ref. [46], p. 235.
255. A. Robert and D. Lorcy, in ref. [46], p. 251; S. Zeltner, R.M. Olk, M. Wagner and B. Olk, *Synthesis* 1445 (1994).
256. J.Y. Becker, E. Agad, J. Bernstein, A. Ellern, V. Khodorkovsky, T. Peger, L. Shahal, L. Shapiro and C.-S. Wang, in ref. [46], p. 277.
257. E. Fanghänel, N. Beye, R. Wegner, J. Bierwisch, R. Hermann, L. van Hinh, B. Gäbler and K. Strucnk, in ref. [46], p. 295.
258. A. Gorgues, M. Jubault, A. Belyamsine, M. Salle, P. Frerre, V. Morisson and Y. Goriou, in ref. [46], p. 311.
259. M. Formigue, A. Dolbecq, F.C. Krebs and J. Larsen, in ref. [46], p. 325.
260. J.M. Fabre, S. Chakroune, A. Jaridan and L. Zanik, *Synth. Met.* **70**, 1127 (1995); T. Imakubo *et al.*, *J. Chem. Soc., Chem. Commun.* 2493 (1995) and unpublished work; see also refs. [64,65].
261. G.C. Papavassiliou, D.J. Lagouvardos, A. Terzis, C.P. Raptopoulou, B. Hilti, W. Hofherr, J.S. Zambounis, G. Rihs, J. Pfeiffer, P. Delhaes, K. Murata, N.A. Fortune and N. Shirakawa, *Synth. Met.* **70**, 787 (1995); unpublished results.
262. Y. Misaki, H. Fujiwara, T. Maruyama and T. Yamabe, *Synth. Met.* **70**, 1147 (1995).
263. Y. Misaki, T. Matsui, K. Kawakami, H. Fujiwara, T. Yamabe, T. Mori, H. Mori, S. Tanaka and M. Shiro, *Synth. Met.* **70**, 1149 (1995); Y. Misaki *et al.*, *Chem. Lett.* 1125 (1995).
264. R.P. Parg, J.D. Kilburn and T.G. Ryan, *Synth. Met.* **70**, 1163 (1995); A.J. Moore *et al.*, *Synthesis* 675 (1995); T. Le Hoerff *et al.*, *J. Mater. Chem.* **5**, 1589 (1995).
265. J. Hellberg and M. Moge, *Synthesis*, submitted (1995); G.C. Papavassiliou, unpublished (1995).
266. T. Inoue, H. Yamochi, G. Saito and K. Matsumoto, *Synth. Met.* **70**, 1139 (1995).
267. C. Faulmann, P. Cassoux, A.I. Kotov and E.B. Yagoubskii, *Acta Crystallogr., Sect. C* **51**, 149 (1995).
268. (a) K. Takahashi and T. Ise, *Chem. Lett.*, 77 (1995); (b) unpublished results (1995); (c) T. Akutagawa and G. Saito, *Bull. Chem. Soc. Jpn.* **68**, 1753 (1995); (d) G. Saito *et al.* *Synth. Met.* **64**, 359 (1994).
269. U. Kux, H. Suzuki, S. Sasaki and M. Iyoda, *Chem. Lett.* 183 (1995); C. Wang *et al.*, *J. Mater. Chem.*, **5**, 1559 (1995); T. Imakubo, H. Sawa and R. Kato, *J. Chem. Soc., Chem. Commun.* 1667 (1995); *Synth. Met.* **73**, 117 (1995); M. Iyoda *et al.*, *J. Mater. Chem.*, in press.
270. O. Neilands, S. Belyakov, V. Tilika and A. Edzina, *J. Chem. Soc., Chem. Commun.* 325 (1995).
271. P. Lariche, A. Gorgues, M. Jubault, J. Becher, J. Orduna and J. Gavin, *Tetrahedron Lett.* **36**, 1275 (1995).
272. T. Nogami and T. Ishida, *Synth. Met.*, submitted.
273. K. Takahashi and K. Tomitani, *J. Chem. Soc., Chem. Commun.* 821 (1995); unpublished results (1995).
274. K. Takahashi, K. Tomitani, T. Ise and T. Shirahata, *Chem. Lett.* 619 (1995).
275. J. Yamada *et al.*, *J. Org. Chem.* in press; see also ref. [291].
276. Y. Yamashita, unpublished; Y. Yamashita, S. Tanaka and K. Imueda, *Synth. Met.* **71**, 1965 (1995).
277. B. Garreau, D. de Montaizon, P. Cassoux, J.P. Legros, J.M. Fabre, K. Saoud and S. Chakroune, *New J. Chem.* **19**, 161 (1995).
278. L.M. Goldenberg, J.Y. Becker, O.P.T. Levi, K. Pramanik and A. Chakravorty, *J. Chem. Soc., Chem. Commun.* 90 (1995).
279. T. Naito, H. Tomita, A. Tateno, T. Udagawa, H. Kobayashi and A. Kobayashi, *Synth. Met.* **70**, 1157 (1995); M. Tomura, S. Tanaka and Y. Yamashita, unpublished (1995).
280. Y. Okano, H. Sawa, S. Aonuma and R. Kato, *Synth. Met.* **70**, 1161 (1995).
281. P. Leriche, A. Gorgues, M. Jubault, J. Becher, S. Uriel, J. Orduna and J. Cavin, *Synth. Met.* **70**, 1143 (1995).

282. V. Morisson, M. Salleé, P. Freère, A. Belyasmine, A. Gorgues, M. Jubault, S. Uriel, P. Batail, K. Boubeker, J. Ordura and J. Garin, *Synth. Met.* **70**, 1155 (1995); T. Nozdryn, J. Cousseau, R. Andrea, M. Sallé, A. Guy, J. Corcali, A. Gorgués, M. Jubault, S. Uriel, J. Orduna and J. Garin, *Synth. Met.* **70**, 1159 (1995).
283. J. Garin, *Adv. Heterocycl. Chem.* **62**, 249 (1995); N. Svenstrup and J. Becher, *Synthesis* 215 (1995).
284. M. Iyoda, M. Fukuda, S. Sasaki and M. Yoshida, *Synth. Met.* **70**, 1171 (1995); J.Y. Becker, J. Bernstein, A. Ellern, H. Gersthtenman and V. Khodorkovsky, *J. Mater. Chem.* **5**, 1557 (1995); H. Mizouchi *et al.*, *J. Am. Chem. Soc.* **117**, 3260 (1995).
285. (a) U. Kux and M. Iyoda, *Synth. Met.* **70**, 1173 (1995); (b) C. Wang, A. Ellern, J.Y. Becker and J. Bernstein, *Adv. Mater.*, **7**, 644 (1995); also ref. [213].
286. H. Müller and Y. Ueda, *Synth. Met.* **70**, 1181 (1995).
287. J.-S. Lee, K. Chang, W.-J. Wang and G.H. Lee, *Synth. Met.* **70**, 1121 (1995).
288. G.C. Papavassiliou, D.J. Lagouvardos and J.S. Zambounis, unpublished results; see also ref. [229].
289. G.C. Papavassiliou and Y. Misaki, unpublished (1995).
290. Y. Misaki, N. Higuchi, H. Fujimara, T. Yamabe, T. Mori, H. Mori and S. Tanaka, *Angew. Chem., Int. Ed. Engl.* **34**, 1222 (1995); Y. Misaki *et al.*, *J. Mater. Chem.* **5**, 1571 (1993); unpublished results.
291. J. Yamada, Y. Amano, S. Takasaki, R. Nakanishi, K. Matsumoto, S. Satoki and H. Anzai, *J. Am. Chem. Soc.* **117**, 1149 (1995); J. Yamada *et al.*, *Chem. Lett.* 1069 (1995).
292. N. Sato and I. Kawamoto, submitted.
293. J.J. Novoa, M.C. Rovira, C. Rovira, J. Veciana and J. Tarres, *Adv. Mater.* **7**, 233 (1995).
294. A.E. Underhill, A. Charlton, S.B. Wilkes, I.R. Butler, A. Kobayashi and H. Kobayashi, *Synth. Met.* **70**, 1101 (1995); A.E. Underhill, N. Robertson and D.L. Parkin, *Synth. Met.* **71**, 1955 (1995); N. Robenson *et al.*, *Tetrahedron Lett.* **36**, 7297 (1995).
295. R. Andreu, J. Garin, J. Orduna, M. Suviron, S. Uriel, J. Cousseau, V. Morisson and A. Gorgues, *Synth. Met.* **70**, 1111 (1995).
296. R. Andreu, J. Garin, J. Orduna, M. Suviron and S. Uriel, *Synth. Met.* **70**, 1113 (1995).
297. A. Bitoh, Y. Kohchi, T. Otsubo, F. Ogura and K. Ikeda, *Synth. Met.* **70**, 1123 (1995); K. Matsuo *et al.*, *Chem. Lett.* 523 (1995); J. Tanabe *et al.*, *Chem. Lett.* 579 (1995); T. Otsubo, Y. Aso, and K. Takimiya, *Adv. Mater.* in press.
298. K. Kawabata, K. Tanaka, M. Mizutani and N. Mori, *Synth. Met.* **70**, 1141 (1995); K. Sako, M. Kusakabe, T. Watanabe and H. Tatemitsu, *Synth. Met.* **71**, 1949 (1995).
299. J. Lau, O. Simonsen and J. Becher, *Synthesis* 521 (1995); M.R. Bryce *et al.*, *J. Mater. Chem.* **5**, 1481 (1995).
300. G.C. Papavassiliou D.J. Lagouvardos, I. Koutselas, K. Murata, A. Graja, I. Olejniczak, J.S. Zambounis, L. Ducasse and J.P. Ulmet, *Synth. Met.*, in press; I. Olejniczak, W. Pukachi and G.C. Papavassiliou, *Adv. Mater. Opt. Electr.*, in press.
301. H. Kobayashi, R. Kato and A. Kobayashi, *Synth. Met.* **41/43**, 2495 (1991).
302. B. Olk, R.-M. Olk, J. Sieler and E. Hoyer, *Synth. Met.* **41/43**, 2585 (1991).
303. R.-M. Olk, B. Olk, J. Rohloff, J. Reinhold, J. Sieler, K. Trübenbach, R. Kirense and E. Hoyer, *Z. Anorg. Allg. Chem.* **609**, 103 (1992); H. Poleschner, R. Radeglia and J. Fuchs, *J. Organomet. Chem.* **427**, 213 (1992).
304. G. Matsubayashi, S. Tanaka and A. Yokozawa, *J. Chem. Soc., Dalton Trans.* 1827 (1992).
305. E. Fanghänel, J. Biewish, A.M. Richter and N. Bey, *Synth. Met.* **47**, 87 (1992).
306. D.-Y. Noh, M. Mizuno and J.-O. Choy, *Synth. Met.* **55/57**, 1705 (1993); M. Mizuno, *Synth. Met.* **55/57**, 2154 (1993).
307. C.J. Bowlas, A.E. Underhill and D. Thetford, *Synth. Met.* **55/57**, 2158 (1993).
308. R.D. McCulloch, J. Seth, J.A. Belot, S.A. Majetich and A.C. Carter, *Synth. Met.* **55/57**, 1989 (1993).
309. N.C. Schiödt, T. Björnholm, C.S. Jacobsen and K. Bechgaard, *Synth. Met.* **55/57**, 2164 (1993).
310. Ch. Wang, J.-H. Liao, J.-H. Chou and M.G. Kanatzidis, unpublished (1995).
311. S. Dahm, W. Strunz, H.J. Keller and D. Schweitzer, unpublished (1995).
312. (a) O.A. Dyachenko, S.V. Konovalikhin, A.I. Kotor, G.V. Shilov, E.B. Yagubskii, Ch. Faulmann and P. Cassoux, *J. Chem. Soc., Chem. Commun.* 508 (1993); (b) C. Faulmann, P. Cassoux, E. Yagoubskii and L.V. Vetoshkina, *New J. Chem.* **17**, 385 (1993); see also ref. [294].
313. T.-M. Yao, X.-Z. You, C. Li and L.-F. Li, *Acta Crystallogr., Sect. C* **50**, 67 (1994).
314. R.-M. Olk, R. Kirmse, E. Hoyer, C. Faulman and P. Cassoux, *Z. Anorg. Allg. Chem.* **620**, 90 (1994); see also refs. [18,66,68].
315. G. Chung, R. Bereman and P. Singh, *J. Coord. Chem.* **33**, 331 (1994); see also U. Geiser, S.F. Tykto, T.J. Allen, H.H. Wang, A.M. Kini and J.M. Williams, *Acta Crystallogr., Sect. C* **47**, 1164 (1991).
316. C.A.S. Hill, A. Charlton, A.E. Underhill, S.N. Oliver, S. Kershaw, R.J. Manning and B.J. Ainslie, *J. Mater. Chem.* **4**, 1233 (1994).
317. X. Yang, D.D. Doxsee, T.B. Rauchfuss and S.R. Wilson, *J. Chem. Soc., Chem. Commun.* 821 (1994); M. Tomura and Y. Yamashita, *J. Mater. Chem.* **5**, 1753 (1995).
318. F. Bigoli, P. Deplano, F.A. Devillanova, V. Lippolis, P.J. Lukes, M.L. Mercuri, M.A. Pellinghelli and E.F. Trogu, *J. Chem. Soc., Chem. Commun.* 371 (1995).
319. Y.S.J. Veldhuizen, J.G. Haasnoot, J. Reedijk and P. Cassoux, unpublished (1995); Y.S.J. Veldhuizen, N. Veldman, A.L. Spek, J.G. Haasnoot and J. Reedijk,

- Recl. Trav. Chim. Pays-Bas* **114**, 337 (1995); K. Lahlil *et al.*, *J. Am. Chem. Soc.* in press (1995).
320. (a) G.C. Papavassiliou, unpublished results (1995); see also S. Ikegawa, T. Nogami and Y. Shirota, *Bull. Chem. Soc. Jpn.* **63**, 262 (1990); (b) G.C. Papavassiliou and D.J. Lagouvardos, unpublished results (1995); see also F. Wudl, E.T. Zellers and S.D. Cox, *Inorg. Chem.* **24**, 2866 (1985).
321. Z.G. Soos, *Annu. Rev. Phys. Chem.* **25**, 121 (1974).
322. J.B. Torrance, *Acc. Chem. Res.* **12**, 79 (1979).
323. A.F. Garito and A.J. Heeger, *Acc. Chem. Res.* **7**, 232 (1974).
324. (a) H. Mueller and Y. Uepa, *Bull. Chem. Soc. Jpn.* **66**, 32 (1993); (b) H. Mueller, *Synth. Met.* submitted; (c) P. Frere *et al.*, *J. Chem. Soc., Chem. Commun.* 2071 (1994).
325. A.V. Skripov, A.P. Stepanov, V.A. Merzhanov, R.N. Lyubovskaya and R.B. Lyubovskii, *JETP Lett.* **49** 265 (1989); H.H. Wang *et al.*, *Mater. Chem.* **2**, 482 (1990).
326. G.C. Papavassiliou, D.J. Lagouvardos, V.C. Kakoussis, A. Terzis, A. Hountas, B. Hilti, C. Mayer, J.S. Zambounis, J. Pfeiffer, M.-H. Whangbo, J. Ren and D.B. Kang, *Mater. Res. Soc. Symp. Proc.* **247**, 535 (1992).
327. K. Kawabata, K. Shimotani and M. Mizutani, *Synth. Met.* **39**, 191 (1990); K. Kawabata, K. Shimotani and T. Sambongi, unpublished (1995); T. Sumimoto *et al.*, *Mol. Cryst. Liq. Cryst.* **267**, 163 (1995).
328. J. Moldenhauer, U. Niebling, D. Schweitzer, B. Gompf, W. Eisenmergev, P. Bele, H. Brunner and H.J. Keller, unpublished (1995).
329. N. Fortune, Y. Kobayashi and C. Bostock, submitted.
330. M. Vandevyver, in ref. [41], p. 503; G.V. Tormos, M.P. Cava, X.L. Wu, A.J. McKinley and R.M. Metzger, *Synth. Met.* **52**, 131 (1992); H. Isolato *et al.*, *J. Chem. Soc., Chem. Commun.* **573** (1994); L.M. Goldenberg *et al.*, *J. Chem. Soc., Chem. Commun.* **475** (1995); *J. Mater. Chem.* **5**, 191 (1995); I. Nakamura *et al.*, *J. Phys. Chem.* **98**, 1882 (1994); M.R. Bryce and M.C. Petty, *Nature* **374**, 771 (1995); L.M. Goldenberg *et al.*, *J. Chem. Soc., Chem. Commun.* **475** (1995); *J. Mater. Chem.* **5**, 1593 (1995); C. Person *et al.*, *ibid.* **5**, 1601 (1995); R.P. Parts *et al.*, *ibid.* **5**, 1609 (1995).
331. P. Delhaes, *Mol. Cryst. Liq. Cryst.* **96**, 229 (1983).
332. J.B. Torrance, B.A. Scott, F.B. Kaufman and P.E. Seiden, *Solid State Commun.* **88**, 971 (1993).
333. (a) P. Delhaes, in ref. [41], p. 43; (b) P. Delhaes and V.M. Yartsev, *Spectroscopy of New Materials*, XXII, R.J.H. Clark and R.E. Hester (Eds.), Wiley, 1993, pp. 199-289; (c) P. Delhaes, in ref. [46], p. 333.
334. R. Hoffman, *Rev. Mod. Phys.* **60**, 601 (1988).
335. J.P. Pouget, in *Organic and Inorganic Low Dimensional Crystalline Materials*, P. Delhaes and M. Drillon (Eds.), Plenum Press, New York, 1987, p. 187.
336. A. Terzis, A. Hountas and G.C. Papavassiliou, *Acta Crystallogr., Sect. C* **42**, 1584 (1986); A. Terzis, V. Psycharis, A. Hountas and G.C. Papavassiliou, *Acta Crystallogr., Sect. C* **44**, 128 (1988); A. Terzis *et al.*, *Synth. Met.* **27**, B97 (1988); A. Hountas *et al.*, *Acta Crystallogr.* **46**, 220 (1990); A.E. Underhill, B. Kaye, G.C. Papavassiliou and S. Yiannopoulos, *Mol. Cryst. Liq. Cryst.* **134**, 59 (1986).
337. G.C. Papavassiliou, A. Terzis, A.E. Underhill, H.P. Geserich, B. Kaye, A. Hountas and S.Y. Yiannopoulos, *Synth. Met.* **19**, 703 (1987); V. Psycharis, A. Hountas, A. Terzis and G.C. Papavassiliou, *Acta Crystallogr., Sect. C* **44**, 125 (1988); G.C. Papavassiliou *et al.*, *J. Mol. Struct.* **143**, 215 (1986).
338. R. Swietlik, N.D. Kushch, L.A. Kushch and E.B. Yagubskii, *Phys. Status Solidi B* **181**, 499 (1994).
339. (a) L. Quahab, M. Fettouhi, I.F. Halet, V.M. Yartsev, G. Garrigou-Lagrange, P. Delhaes and C. Sourisseau, *New J. Chem.* **17**, 399 (1993); (b) R.N. Lyubovskaya, S.A. Konovalikhin, U.A. Dyachenko and R.B. Lyubovskii, *Synth. Met.* **70**, 1145 (1995).
340. G.C. Papavassiliou, *Mol. Cryst. Liq. Cryst.* **86**, 159 (1982).
341. (a) G.C. Papavassiliou, D. Lagouvardos, V. Kakoussis, G. Mousdis, A. Terzis, A. Hountas, B. Hilti, C. Mayer, J. Zambounis, J. Pfeiffer and P. Delhaes, in ref. [40], p. 367; (b) A. Terzis, A. Hountas, B. Hilti, G. Mayer, J.S. Zambounis, D. Lagouvardos, V. Kakoussis, G. Mousdis and G.C. Papavassiliou, *Synth. Met.* **41/43**, 1715 (1991).
342. T. Naito, A. Miyamoto, H. Kobayashi, R. Kato and A. Kobayashi, *Chem. Lett.* 1945 (1991); R. Kato *et al.*, *Chem. Lett.* 1045 (1991).
343. J. Kahlisch, D. Schweitzer, I. Heinen, S.E. Lan, B. Nuber, H.J. Keller, K. Winzer and H.W. Helberg, *Solid State Commun.* **80**, 191 (1991).
344. H. Mori, I. Hirabayashi, S. Tanaka, T. Mori, Y. Marugama and H. Inokuchi, *Solid State Commun.* **80**, 411 (1991).
345. N.P. Karpova, S.V. Konovalikhin, O.A. Dyachenko, R.N. Lyubovskaya and E.I. Shibaeva, *Acta Crystallogr., Sect. C* **48**, 62 (1992).
346. S. Triki, L. Ouahab, D. Grandjean and J.M. Fabre, *Acta Crystallogr., Sect. C* **47**, 645 (1991).
347. M. Quian, P. Luger, J. Buschmann and Y. Gau, *Acta Crystallogr., Sect. C* **47**, 339 (1991).
348. C. Lenoir, K. Boubekeur, P. Patail, E. Canadell, P. Auban, O. Traetteberg and D. Jerome, *Synth. Met.* **41/43**, 1939 (1991).
349. M. Quian, R. Ruderf, Q. Luger, C. Ge and X. Wang, *Acta Crystallogr., Sect. C* **47**, 2082 (1991).
350. X. Bu, P. Coppens, B. Lederde and M.J. Naughton, *Acta Crystallogr., Sect. C* **47**, 2082 (1991); X. Bu, Z. Su and P. Coppens, *Acta Crystallogr., Sect. C* **47**, 279 (1991).
351. A. Kawamoto, M. Tanaka and J. Tanaka, *Bull. Chem. Soc. Jpn.* **64**, 3160 (1991).
352. U. Geiser, H.H. Wang, K. Douglas Carlson, J.M. Williams, H.A. Charlier, Jr., J.E. Heindl, G.A. Yaconi, B.J. Love, M.W. Lathrop, J.E. Schirber, D.L. Over-

- ymyer, J. Ren and M.-A. Whangbo, *Inorg. Chem.* **30**, 2586 (1991).
353. H. Mori, S. Tanaka, T. Mori, Y. Maruyama, H. Inokuchi and G. Saito, *Solid State Commun.* **78**, 49 (1991).
354. V.V. Gritsenko, O.A. D'Yachenko, G.V. Shilov, L.O. Atormyan, R.N. Lyubovskaya and M.Z. Aldoshina, *Izv. Akad. Nauk SSSR, Ser. Khim.* 2055 (1991).
355. S.V. Konovalikhin, O.A. Dyachenko, A.B. Zolotov, V.V. Gritsenko, L.O. Atormyan and E.E. Laukhina, *Izv. Akad. Nauk SSSR, Ser. Khim.* 811 (1991).
356. R.P. Shibaeva and L.P. Rozenberg, *Sov. Phys.-Crystallogr.* **35**, 676 (1991); R.P. Shibaeva, V.E. Korotkov and L.P. Rozenberg, *Sov. Phys.-Crystallogr.* **36**, 820 (1991); V.E. Korotkov and R.P. Shibaeva, *Sov. Phys.-Crystallogr.* **36**, 825 (1991); R.P. Shibaeva and L.P. Rozenberg, *Sov. Phys.-Crystallogr.* **36**, 655 (1991); V.E. Korotkov and R.P. Shibaeva, *Sov. Phys.-Crystallogr.* **36**, 644 (1991).
357. E. Günther, S. Hünnig, J.-U. van Schütz, U. Langohr, H. Rieder, S. Söderholm, H.-P. Werner, K. Peters, H.G. von Schnering and H.J. Lindner, *Chem. Ber.* **125**, 1919 (1992).
358. T. Mori, K. Kato, Y. Maruyama, H. Inokuchi, H. Mori, I. Hirabayashi and S. Tanaka, *Solid State Commun.* **82**, 177 (1992).
359. (a) X. Bu, I. Cisarova, P. Coppens, B. Lederle and M.J. Naughton, *Acta Crystallogr., Sect. C* **48**, 516 (1992); (b) X. Bu, I. Cisarova and P. Coppens, *Acta Crystallogr., Sect. C* **48**, 1558 (1992); (c) X. Bu, P. Coppens, B. Lederle and M.J. Naughton, *Acta Crystallogr., Sect. C* **48**, 1560 (1992); (d) X. Bu, I. Cisarova and P. Coppens, *Acta Crystallogr., Sect. C* **48**, 1562 (1992); (e) *Acta Crystallogr., Sect. C* **48**, 1563 (1992); (f) X. Bu and P. Coppens, *Acta Crystallogr., Sect. C* **48**, 1565 (1992).
360. X. Bu and P. Coppens, *Acta Crystallogr., Sect. C* **48**, 1565 (1992); O.A. Dyachenko *et al.*, *Synth. Met.* **62**, 193 (1994).
361. M. Fettouhi, L. Ouahab, D. Grandjean, G. Mousdis and P. Delhaes, *Acta Crystallogr., Sect. C* **48**, 2141 (1992); M. Fettouhi, L. Ouahab, D. Grandjean, G. Mousdis and P. Delhaes, *Acta Crystallogr., Sect. C* **48**, 1920 (1992).
362. L. Ouahab, M. Bencharif, A. Mhani, D. Pelloquin, J.F. Halet, O. Pena, J. Padiou, D. Grandjean, C. Garrigou-Lagrange, J. Amiel, and P. Delhaès, *Chem. Mater.* **4**, 666 (1992); C.J. Gomez-Garcia, E. Coronado, S. Triki, L. Ouahab and P. Delhaès, *Adv. Mater.* **5**, 283 (1993).
363. H.H. Wang *et al.*, *Chem. Mater.* **4**, 247 (1992).
364. A. Izuoka, T. Tachikawa, T. Sugawara, Y. Saito and A. Shinohara, *Chem. Lett.* 1049 (1992).
365. A. Izuoka, T. Tachikawa, T. Sugawara, Y. Suzuki, M. Konno, Y. Saito and A. Shinohara, *J. Chem. Soc., Chem. Commun.* 1473 (1992).
366. M.B. Inone, M. Inoue, M.A. Bruck and Q. Fernando, *J. Chem. Soc., Chem. Commun.* **515** (1992).
367. L.I. Buranov, A.G. Khomenko, N.D. Kushch, V.N. Laukhin, A.I. Schegolev, E.B. Yagubskii, L.P. Rosenberg and R.P. Shibaeva, *J. Phys. I* **2**, 529 (1992).
368. J.S. Zambounis, C.W. Mayer, K. Hanenstein, B. Hilti, W. Hother, J. Pfeiffer, M. Bürkle and G. Rihs, *Adv. Mater.* **4**, 33 (1992); *Mater. Res. Soc. Symp. Proc.* **247**, 509 (1992).
369. P. Blanchard, K. Boubekeur, M. Salle, G. Duguay, M. Jubault, A. Gorges, J.D. Martin, E. Canadell, P. Aubansenzier, D. Jerome and P. Batail, *Adv. Mater.* **4**, 579 (1992).
370. G.A. Mousdis *et al.*, *Synth. Met.* **48**, 219 (1992).
371. P. Wang *et al.*, *Synth. Met.* **49/50**, 253 (1992).
372. K. Saito *et al.*, *Synth. Met.* **52**, 87 (1992).
373. G.C. Papavassiliou, D.J. Lagouvardos, A. Terzis, J. Amiel, C. Garrigou-Lagrange, P. Delhaes, B. Hilti and J. Pfeiffer, *Synth. Met.* **61**, 267 (1993).
374. S. Matsumiya, A. Izuoka, T. Sugawara, T. Taruishi, Y. Kawada and M. Tokumoto, *Bull. Chem. Soc. Jpn.* **68**, 1949 (1993).
375. T. Tachikawa, A. Izuoka and T. Sugawara, *Solid State Commun.* **88**, 207 (1993).
376. H. Yamochi, T. Komatsu, N. Matsukawa, G. Saito, T. Mori, M. Dusunoki and K.-I. Sakaguchi, *J. Am. Chem. Soc.* **115**, 11319 (1993); H. Yamochi, T. Komatsu, G. Saito, M. Kusunoki and K.-I. Sakaguchi, *Mol. Cryst. Liq. Cryst.* **234**, 137 (1993); T. Komatsu *et al.*, unpublished (1995).
377. H. Kobayashi, T. Udagawa, H. Tomita, K. Bun, T. Naito and A. Kobayashi, *Chem. Lett.* 1559 (1993).
378. A. Pénicaud, K. Boubekeur, P. Batail, E. Canadell, P. Auban-Senzier and D. Jerome, *J. Am. Chem. Soc.* **115**, 4101 (1993).
379. J.C. Fitzmaurice, A.M.Z. Slawin, D.J. Williams and J.D. Woollins, *J. Chem. Soc., Chem. Commun.* 1479 (1993); H. Mori, I. Hirabayashi, S. Tanaka and Y. Maruyama, *Bull. Chem. Soc. Jpn.* **66**, 2156 (1993); L.F. Veiros and E. Canadell, *J. Phys. I* **4**, 939 (1994).
380. (a) S. Jarchow, M. Fourmigué and P. Batail, *Acta Crystallogr., Sect. C* **49**, 1936 (1993); (b) M. Fettouhi, L. Ouahab, D. Grandjean, J. Amiel, R. Canet and P. Delhaès, *Synth. Met.* **55/57**, 1893 (1993).
381. R.P. Shibaeva and V.E. Zanolnik, *Crystallogr. Rep.* **38**, 195 (1993).
382. L.I. Buranov *et al.*, *J. Phys. I* **4**, 441 (1994).
383. N.A. Fortune, K. Murata, G.C. Papavassiliou, D.J. Lagouvardos and J.S. Zambounis, *Mater. Res. Soc. Symp. Proc.* **328** 307 (1994).
384. Y. Misaki, H. Fujiwara, T. Yamabe, T. Mori, H. Mori and S. Tanaka, *Chem. Lett.* 1653 (1994).
385. T. Mori, Y. Misaki, H. Fujiwara and T. Yamabe, *Bull. Chem. Soc. Jpn.* **67**, 2685 (1994).
386. (a) L.K. Montgomery, T. Burgin, J.C. Huffman, J. Ren and M.H. Whangbo, *Physica C (Amsterdam)* **219**, 490 (1994); (b) F. Goze, V.N. Laukhin, L. Brossard, A. Avdouard, J. Pulmet, S. Askenazy, T. Naito, H.

- Kobayashi, A. Kobayashi, M. Tokumoto and P. Cassoux, *Europhys. Lett.* **28** (6), 427 (1994).
387. Y. Misaki, H. Nishikawa, T. Yamabe, T. Mori and H. Inokuchi, *Bull. Chem. Soc. Jpn.* **67**, 2368 (1994).
388. (a) T. Mori, Y. Misaki and T. Yamabe, *Bull. Chem. Soc. Jpn.* **67**, 3187 (1994); (b) T. Mori, H. Inokuchi, Y. Misaki, T. Yamabe, H. Mori and S. Tanaka, *Bull. Chem. Soc. Jpn.* **67**, 661 (1994).
389. (a) J.A. Schlueter, U. Geiser, J.M. Williams, H.H. Wang, W.-K. Knok, J. Fendrich, K. Douglas Carlson, C. Achenbach, J. Dudek, D. Neumann, T. Roy, J. Schirber and W. Bayless, *J. Chem. Soc., Chem. Commun.* 1599 (1994); (b) M.-L. Doublet, E. Canadell and R.P. Shibaeva, *J. Phys. I* **4**, 1479 (1994); (c) J. Thiel, X. Bu and P. Coppens, *Acta Crystallogr., Sect. C* **50**, 23 (1994); (d) U. Geiser *et al.*, *Inorg. Chem.* **23**, 5101 (1994); (e) S. Hebrard *et al.*, *Acta Crystallogr., Sect. C* **50**, 1892 (1994); (f) P. Guionneau *et al.*, *Acta Crystallogr., Sect. C* **50**, 1894 (1994); (g) C.J. Gomez-Garcia *et al.*, *Angew. Chem., Int. Ed. Engl.* **33**, 224 (1994).
390. T. Komatsu, H. Sato, N. Matsukawa, T. Nakamura, H. Yamocho, G. Saito, M. Kusunoki, K. Sakagura and S. Kagoshima, *Synth. Met.* **70**, 779 (1995); T. Komatsu *et al.*, *Bull. Chem. Soc. Jpn.*, submitted (1995).
391. J.S. Zambounis, J. Pfeiffer, G.C. Papavassiliou, D.J. Lagouvardos, A. Terzis, C.J. Raptopoulou, P. Delhaes, L. Ducasse, N. A. Fortune and K. Murata, *Solid State Commun.* **95**, 211 (1995).
392. M. Munakata, T. Kuroda-Sowa, M. Maekawa, A. Hirota and S. Kitagawa, *Inorg. Chem.* **34**, 2705 (1995).
393. H. Mori, S. Tanaka, T. Mori and Y. Maruyama, *Bull. Chem. Soc. Jpn.* **68**, 1136 (1995); H. Mori, H. Hirabayashi, S. Tanaka, T. Mori and Y. Maruyama, *Synth. Met.* **70**, 789 (1995).
394. M. Inokuchi, H. Tajima, A. Kobayashi, T. Ohta, H. Kuroda, R. Kato, T. Naito and H. Kobayashi, *Bull. Chem. Soc. Jpn.* **68**, 547 (1995).
395. H. Kobayashi, H. Tomita, T. Naito, A. Kobayashi, F. Sakai, T. Watanabe and P. Cassoux, *J. Am. Chem. Soc.* in press (1995); H. Kobayashi *et al.*, *J. Chem. Soc., Chem. Commun.* 1225 (1995); L. Brossard *et al.*, unpublished (1995).
396. H. Kobayashi, H. Tomita, T. Udagawa, T. Naito and A. Kobayashi, *Synth. Met.* **70**, 867 (1995).
397. B. Zhang, Y. Li and D. Zhu, *Synth. Met.* **70**, 1483 (1995); D. Wang, W.J. Lee, I. Shickerbakova, M.P. Cava and R.M. Metzger, *Synth. Met.* **70**, 1457 (1995); also S. Glenis *et al.*, unpublished (1995).
398. E.I. Zhilyaeva, R.N. Lyubovskaya, V.V. Gritsenko, O.A. Dyachenko, E.I. Yudanov and R.B. Lyubovskii, *Synth. Met.* **70**, 1183 (1985).
399. C. Rovira, J. Veciana, J. Torr s, E. Molins, M. Mas, D.O. Co wan, S. Yang and H. Lee, *Synth. Met.* **70**, 883 (1995).
400. C.J. Kepert, M.R. Truter, M. Kurmoo and P. Day, *Synth. Met.* **70**, 781 (1995); P. Day *et al.*, *Synth. Met.* **70**, 767 (1995); M. Kurmoo *et al.*, *J. Am. Chem. Soc.* **117**, 12209 (1995); C.J. Kepert *et al.*, unpublished (1995).
401. H. Mori, I. Hirabayashi, S. Tanaka, T. Mori and Y. Maruyama, *Synth. Met.* **70**, 877 (1995).
402. Y. Misaki, H. Nishikawa, H. Fujiwara, T. Yamabe, T. Mori, H. Mori and S. Tanaka, *Synth. Met.* **70**, 1151 (1995).
403. T. Mori, Y. Misaki, H. Nishikawa, Y. Yamabe, H. Mori and S. Tanaka, *Synth. Met.* **70**, 873 (1995).
404. Y. Misaki, H. Nishikawa, T. Yamabe, T. Mori, H. Mori and S. Tanaka, *Synth. Met.* **70**, 1153 (1995); T. Mori, Y. Misaki, T. Yamabe, H. Mori and S. Tanaka, *Chem. Lett.* 549 (1995).
405. J.M. Williams, J.A. Schlueter, Urs. Geiser, H.-H. Wang, J.D. Dudek, M.E. Kelly, S.A. Sirchio and K. Douglas Carlson, unpublished (1995); J.A. Schlueter *et al.* *J. Chem. Soc., Chem. Commun.* 1311 (1995).
406. T. Mori, T. Kawamoto, Y. Misaki, N. Higuchi, K. Kawakami, H. Fujiwara, T. Yamabe, H. Mori, S. Tanaka and H. Tajima, submitted (1995).
407. G.C. Papavassiliou, K. Murata, A. Terzis, J.S. Zambounis and P. Delhaes, *Mol. Cryst. Liq. Cryst.* (in press).
408. Phase transitions in soft ferromagnetism are described by: A.W. Graham, M. Kurmoo and P. Day, *J. Chem. Soc., Chem. Commun.* (1995); A.A. House *et al.*, submitted; S. Glenis *et al.*, unpublished (1995).
409. (a) L. Ouahab, P. LeMagueres, C.J. Gomez-Garcia, P. Delhaes, J. Even and M. Bertault, *Solid State Commun.* in press (1995); (b) M. Fettouhi, L. Ouahab, L. Ducasse, J. Amiel, R. Canet and P. Delhaes, *Chem. Mater.* (1995), in press.
410. H. Mori, I. Hirabayashi, S. Tanaka, T. Mori and Y. Maruyama, *Synth. Met.* **70**, 1177 (1995); N.C. Schiod *et al.*, *Inorg. Chem.* **34**, 3688 (1995).
411. B. Garreau, B. Pomarede, C. Fauhmann, J.-M. Fabre, P. Cassoux and J.-P. Legros, *C.R. Acad. Sci. Paris* **313**(II), 509 (1991); A.M. Kini *et al.*, *Mat. Res. Soc. Symp. Proc.* **173**, 177 (1990).
412. J.P. Cornelissen, E.J. Creyghton, R.A.G. de Graaft, J.G. Haasnoot and J. Reedijk, *Inorg. Chim. Acta* **185**, 97 (1991).
413. H. Strezelecka, J. Ribas, J.-P. Legros, P. Cassoux, P. Petit and J.-J. Andre, *Polyhedron* **10**, 687 (1991).
414. A. Kobayashi, H. Kobayashi, A. Miyamoto, R. Kato, R.A. Clark and A.E. Underhill, *Chem. Lett.* 2163 (1991); J.P. Ulmet *et al.*, *Synth. Met.* **41/43** 2507 (1991).
415. H. Tajima, T. Naito, M. Tamura, A. Kobayashi, H. Kuroda, R. Kato, H. Kobayashi, R.A. Clark and A.E. Underhill, *Solid State Commun.* **79**, 337 (1991).
416. A.E. Underhill, R.A. Clark, I. Mars en, M. Allan, H. Tajima, T. Naito, M. Tamura, H. Kuroda, A. Kobayashi, H. Kobayashi, E. Canadell, S. Ravy and J.P. Pouget, *J. Phys.: Condens. Matter* **3**, 933 (1991).

417. E.B. Yagubskii, A.I. Kotor, A.G. Khomenko, L.I. Buravov, A.I. Schegolev and R.P. Shibaeva, *Synth. Met.* **46**, 255 (1992).
418. H. Kobayashi, K. Bun, T. Naito, R. Kato and A. Kobayashi, *Chem. Lett.* 1909 (1992).
419. R.P. Shibaeva, L.P. Rozenberg, L.A. Kushch, A.I. Kotov, A.G. Khomenko, E.B. Yagubskii and V.E. Zavodnik, *Synth. Met.* **46**, 261 (1992).
420. N.G. Connelly, J.G. Crossley, A.G. Orpen and H. Salter, *J. Chem. Soc., Chem. Commun.* 564 (1992).
421. N.G. Connelly, J. Crossley and A.G. Orpen, *J. Chem. Soc., Chem. Commun.* 568 (1992).
422. H. Tajima, M. Inokuchi, A. Kobayashi, T. Ohta, R. Karo, H. Kobayashi and H. Kuroda, *Chem. Lett.* 1235 (1993).
423. H. Oshio, *Inorg. Chem.* **32**, 4123 (1993).
424. R.P. Shibaeva and V.E. Zavodnik, *Crystallogr. Rep.* **38**, 43 (1993).
425. C. Faulmann, J.-P. Legros, P. Cassoux, J.C. Cornelissen, J.G. Itaasnoot and J. Reedijk, *Synth. Met.* **56**, 2063 (1993).
426. M.-L. Doublet, E. Canadell, J.P. Pouget, E.B. Yagubskii, J. Ren and M.-H. Whangbo, *Solid State Commun.* **88**, 699 (1993).
427. A. Miyazaki, A. Izuoka and T. Sugawara, *Bull. Chem. Soc. Jpn.* **66**, 2832 (1993).
428. M. Lemke, F. Knoch and H. Kish, *Acta Crystallogr., Sect. C* **49**, 1630 (1993).
429. O.A. Dyachenko, V.V. Gritsenko, G.V. Shilov, E.E. Laukhina and E.B. Yagubskii, *Synth. Met.* **58**, 537 (1993).
430. B. Pomarède, B. Garreau, I. Malfant, L. Valade, P. Cassoux, J.-P. Legros, A. Audouard, L. Brossard, J.-P. Ulmet, M.-L. Doublet and E. Canadell, *Inorg. Chem.* **33**, 3401 (1994).
431. (a) M.-L. Doublet, E. Canadell, J.-P. Pouget and R.P. Shibaeva, *J. Phys.* **14**, 1439 (1994); see also [338]; (b) M.L. Doublet, E. Canadell, B. Garreau, J.-P. Legros, L. Brossard, P. Cassoux and J.-P. Pouget, *J. Phys.: Condens. Matter* **7**, 4673 (1995).
432. R. Kato, Y.-L. Liu, H. Sawa, S. Aonuma, A. Ichikawa, H. Takahashi and N. Mori, *Solid State Commun.* **94**, 973 (1995); T. Imakubo *et al.*, *J. Chem. Soc., Chem. Commun.* 1097 (1995).
433. T. Naito, A. Sato, K. Kawano, A. Tateno, H. Kobayashi and A. Kobayashi, *J. Chem. Soc., Chem. Commun.* 351 (1995).
434. E.B. Yagubskii, L.A. Kushch, V.V. Gritsenko, O.A. Dyachenko, L.I. Buranov and A.G. Khomenko, *Synth. Met.* **70**, 1039 (1995).
435. A. Kobayashi, T. Naito and H. Kobayashi, *Synth. Met.* **70**, 1047 (1995).
436. H. Sawa, Y. Okano, S. Aonuma and R. Kato, *Synth. Met.* **70**, 1055 (1995).
437. T. Nakamura, A.E. Underhill, A.T. Coomber, R.H. Friend, H. Tajima, A. Kobayashi and H. Kobayashi, *Synth. Met.* **70**, 1061 (1991); *Inorg. Chem.* **34**, 870 (1995).
438. M. Tamura, K. Yakushi, H. Kuroda, A. Kobayashi, R. Kato and H. Kobayashi, *J. Phys. Soc. Jpn.* **57**, 3239 (1988); M. Tamura *et al.*, *Synth. Met.*, **41/43**, 2499 (1991).
439. G.C. Papavassiliou, G. Mousdis, V. Kakoussis, A. Terzis, A. Hountas, B. Hilti, C.W. Mayer and J.S. Zambounis, in ref. [39], p. 247.
440. A. Terzis, A. Hountas, G.C. Papavassiliou, B. Hilti and J. Pfeiffer, *Acta Crystallogr., Sect. C* **46**, 224 (1990).
441. L. Ducasse, J. Amiell, P. Delhaes, G. Mousdis, G.C. Papavassiliou and A. Terzis, *Synth. Met.* **41/43**, 2483 (1991).
442. Ref. [16]; ref. [41], p. 223.
443. K. Murata, N. Shirakawa, Y. Yoshino, Y. Tsubaki, G. C. Papavassiliou, A. Terzis and J.S. Zambounis, *Synth. Met.* in press.
444. M. Oshima, H. Mori, G. Saito and K. Oshima, in ref. [39], p. 257; H. Mori *et al.*, *Solid State Commun.* **74**, 1261 (1990); H. Mori *et al.*, *Bull. Chem. Soc. Jpn.* **63**, 2188 (1990).
445. (a) M. Yoshimura *et al.*, *Surf. Sci.* **242**, 18 (1991); (b) C.E. Campos *et al.*, *Phys. Rev. B, Condens. Matter* **52**, 7014 (1995).
446. M.-H. Whangbo *et al.*, in ref. [40], p. 243; T. Ozito *et al.*, *Physica B (Amsterdam)* **184**, 494 (1993).
447. M. Tamura, H. Kuroda, S. Uji, H. Aoki, M. Tokumoto, A.G. Swanson, J.S. Brooks, C.C. Agosta and S.T. Hannahs, *J. Phys. Soc. Jpn.* **63**, 615 (1994).
448. A. Hountas *et al.*, *Acta Crystallogr., Sect. C* **46**, 228 (1990).
449. D. Chasseau, S. Hébrard, V. Hays, G. Bravic, J. Gaultier, L. Ducasse, M. Karmoo and P. Day, *Synth. Met.* **70**, 947 (1995).
450. D. Chasseau, P. Guinonneau, M. Rahal, G. Bravic, J. Gaultier, L. Ducasse, M. Kurmoo and P. Day, *Synth. Met.* **70**, 945 (1995).
451. (a) A. Kobayashi, T. Naito and H. Kobayashi, *Synth. Met.* **70**, 1087 (1995); (b) A. Kobayashi, K. Kawano, T. Naito and A. Kobayashi, *J. Mater. Chem.* **5**, 1681 (1995).
452. D. Chasseau, J. Gaultier, M. Rabal, L. Ducasse, M. Kurmoo and P. Day, *Synth. Met.* **41/43**, 2039 (1991).
453. P. Delhaes and L. Ducasse, in NATO ASI Series, *Localized and Itinerant Molecular Magnetism*, Kluwer, Dordrecht, 1996.
454. M.-H. Whangbo, in *Electron Transfer in Biology and the Solid State*, M.K. Johnson *et al.* (Eds.) American Chemical Society, Washington, DC, 1990, p. 269.
455. N.F. Mott, *Metal-Insulator Transitions*, 2nd edition, Taylor and Francis, London, 1990.
456. J. Hubbard, *Phys. Rev. B, Condens. Matter* **17**, 494 (1978).
457. G. Grüner, *Density Waves in Solids*, Addison Wesley, Reading, MA, 1994.

458. D. Jerome, *Science* **252**, 1509 (1991); D. Jerome, *Organic Conductors, Fundamentals and Applications*, J.P. Farges (Ed.), Marcel Dekker, New York, 1994, p. 405.
459. J.P. Pouget, *Semicond. Semimet.* **27**, 88 (1988).
460. V.J. Emery, R. Bruinsma and S. Barisic, *Phys. Rev. Lett.* **48**, 1039 (1982); G.L. Caron and C. Bourbonnais, *Physica B (Amsterdam)* **143** 453 (1986); C. Bourbonnais, D. Jerome and A. Moradpour, *Phys. Rev. B, Condens. Matter* **33**, 7608 (1986).
461. R.E. Peierls, *Quantum Theory of Solids*, Clarendon, Oxford, 1964.
462. L. Ducasse and A. Fritsch, *Solid State Commun.* **91**, 201 (1994).
463. P. Delhaes, J. Amiel, S. Flandrois, L. Ducasse, A. Fritsch, B. Hilti, C.W. Mayer, J. Zambounis and G.C. Papavassiliou, *J. Phys. France* **51**, 1179 (1990).
464. D. Jerome *et al.*, *Synth. Met.* **70**, 719 (1995).
465. J. Kübler, M. Weyer and C.B. Sommers, *Solid State Commun.* **62**, 801 (1987); R.K. Kosowski and M.-H. Whangbo, *Inorg. Chem.* **29**, 360 (1990).
466. E. Demiralp and W.A. Goddard, *J. Phys. Chem.* **98** 9781 (1994).
467. M.V. Kartsovnik, V.N. Laukuin, S.I. Pesotskii, I.F. Schegolev and Y.M. Yakonenko, *J. Phys. I*, **2**, 89 (1991); Y.N. Xu *et al.*, *Phys. Res. B* **52**, 12946 (1995).
468. T. Mori, H. Inokuchi, H. Mori, S. Tanaka, M. Oshima and G. Saito, *J. Phys. Soc. Jpn.* **59**, 2624 (1990).
469. J.S. Brooks *et al.*, *Physica B (Amsterdam)* **201**, 449 (1994).
470. T. Terachina, S. Uji, H. Aoki, M. Tamura, M. Kinoshita and M. Tokumoto, *Solid State Commun.* **91**, 595 (1994).
471. T. Sasaki, H. Sato and N. Toyota, *Physica C (Amsterdam)* **185**, 2687 (1991).
472. E. Canadell, *Synth. Met.* **70**, 1009 (1995).
473. D. Jerome and H. Schultz, *Adv. Phys.* **31**, 299 (1982).
474. T. Mori, *Int. J. Mod. Phys. B* **8**, 1 (1994); J.M. Williams, A.J. Schultz, V. Geiser, D.D. Carlson, A.M. Kini, H.H. Wang, W.K. Knox, M.-H. Whangbo and J.E. Schirber, *Science* **252**, 1501 (1991).
475. D. Jerome and L.D. Caron (Eds.), in *Low-Dimensional conductors and superconductors*, NATO ASI Series, Vol. 155b, Plenum, New York, 1987.
476. L. Zuppiroli, in ref. [475], p. 307.
477. L. Pal, G. Gruner, A. Janossy and J. Solyon (Eds.), *Organic Conductors and Semiconductors*, Vol. 65, Springer-Verlag, Berlin, 1977; H.R. Zeller, *Festk. Prob.* **19**, 31 (1979).
478. D. Belitz and T.R. Kirkpatrick, *Rev. Mod. Phys.* **66**, 261 (1994).
479. P. Delhaes, C. Coulon, S. Flandrois, B. Hilti, C.W. Mayer, G. Rihs and J. Rivory, *J. Chem. Phys.* **73**, 1452 (1980).
480. J.P. Ulmet, L. Beachère, S.A. Askenazy and J.C. Ousset, *Phys. Rev. B, Condens. Matter* **38**, 7782 (1988); W. Biberacher *et al.*, *Synth. Met.* **41/43**, 2337 (1991).
481. R. Bozio and C. Pecile, *Adv. Spectrosc.* **19**, 1 (1991); E. Demirap *et al.*, *J. Am. Chem. Soc.* **117**, 8154 (1995).
482. M. Krauzman, H. Poulet and R.M. Pick, *Phys. Rev. B, Condens. Matter* **33**, 99 (1986); G. Visentini, D. Pedron, R. Bozio, J.M. Williams and J.A. Schlyeter, unpublished (1995).
483. C.C. Holmes and J.F. Eldridge, *Phys. Rev. B, Condens. Matter* **40**, 6138 (1989); M. Dressel *et al.*, *Phys. Rev. B, Condens. Matter* **50**, 13603 (1994).
484. M.J. Rice, V.M. Yarter and C.S. Jacobsen, *Phys. Rev. B, Condens. Matter* **21**, 3437 (1980).
485. D.B. Tanner, C.S. Jacobsen, A.A. Bright and A.J. Heeger, *Phys. Rev. B, Condens. Matter* **16**, 3283 (1977).
486. J.S. Zambounis, A.P. Patsis, E. Kamitsos, C.W. Mayer and G.C. Papavassiliou, *J. Raman Spectrosc.* **26**, 9 (1995).
487. Several papers in ref. [45], pp. 975–987; also in [43,44].
488. G.C. Papavassiliou and C.S. Jacobsen, *J. Chem. Soc., Faraday Trans. (2)* **77**, 191 (1981).
489. J.B. Torrance, Y. Tomkiewicz and B.D. Silverman, *Phys. Rev. B, Condens. Matter*, **15**, 4738–4749 (1977).
490. S. Mazumdar and S.N. Dixit, *Phys. Rev. B, Condens. Matter* **34**, 3683–3699 (1986).
491. P. Delhaès, *Synth. Met.* **41/43**, 1977–1982 (1991).
492. C.S. Jacobsen, K. Mortensen, M. Weger and K. Bechgaard, *Solid State Commun.* **38**, 423–428 (1981).
493. Y. Yafet, *Solid State Phys.* **14**, 1–98 (1963).
494. Y. Tomkiewicz and A. Taranko, *Phys. Rev. B, Condens. Matter* **18**, 733–741 (1978).
495. A.N. Bloch, T.F. Carruthers, T. Poehler and D.D. Cowan, *NATO ASI Ser., Ser. B* **25**, 1–20 (1977).
496. M. Weger, *J. Phys. France Colloq.* **39-C6**, 1456 (1978).
497. M. Tokumoto, H. Anzai, T. Ishiguro, G. Saito, T. Yanabe and H. Teramae, *J. Phys. Soc. Jpn.* **53**, 1504–1512 (1984).
498. P. Delhaès, C. Coulon, J. Amiel and S. Flandrois, *Mol. Cryst. Liq. Cryst.* **50**, 43–58 (1979); C. Coulon, *Ph.D. Thesis*, Bordeaux University, 1987.
499. P. Delhaès, J. Amiel, L. Ducasse, D. Hilti, C.W. Mayer and J. Zambounis, *Physica B (Amsterdam)* **182**, 99–104 (1992).
500. L. Forro, G. Sekretarczyk, Drupsky, D. Schweitzer and H. Keller, *Phys. Rev. B, Condens. Matter* **35**, 2501–2504 (1987).
501. D. Shaltiel, P. Monod and I. Felner, *J. Phys. Lett.* **41**, 567–570 (1980).
502. T. Sasaki, S. Endo and N. Toyota, *Phys. Rev. B, Condens. Matter* **48**, 1928 (1993).
503. K. Murata, M. Ishibashi, Y. Honda, M. Tokumoto, N. Kinoshita and H. Anzai, *J. Phys. Soc. Jpn.* **58**, 3469 (1989).
504. F.L. Platt, M. Doport, W. Hayes, J. Singleton, T. Jannen, M. Kurmoo and P. Day, *Synth. Met.* **41/43**, 2195 (1991); K. Murata, M. Ishibashi, Y. Honda, N.A.

- Fortune, M. Tokumoto, N. Kinoshita and H. Anzai, *Solid State Commun.* **76**, 377 (1990).
505. Several papers in refs. [42–45].
506. N. Fortune, D.J. Fons and K. Murata, *Synth. Met.* **70**, 1001 (1995).
507. K. Murata, K. Kikuchi, Y. Honda, T. Komazaki, K. Saito, K. Kobayashi and I. Ikemoto, in ref. [39], p. 234.
508. C. Cöulon, *NATO ASI Ser., Ser. B*, **168**, 201 (1987).
509. A. Kawamoto *et al.*, *Phys. Rev. Lett.* **74**, 3455 (1995).
510. U. Welp *et al.*, *Phys. Rev. Lett.* **69**, 840 (1992).
511. Y.V. Sushko *et al.*, *J. Phys. Soc. Jpn.* **62**, 3302 (1993).
512. T. Kanoda, K. Akiba, K. Suzuki, T. Takahashi and G. Saito, *Phys. Rev. Lett.* **65**, 127 (1990).
513. M. Lang, N. Toyota, T. Sasaki and S. Hato, *Phys. Rev. B, Condens. Matter* **46**, 5822 (1992).
514. R.C. Haddon, S.H. Clarum, S.V. Shichester, A.P. Ramirez and N.M. Zimmerman, *Phys. Rev. B, Condens. Matter* **43**, 2642 (1991).
515. U. Geiser *et al.*, *Synth. Met.* **55/57**, 2314 (1993).
516. L.A. Angurel *et al.*, in *High Tc SC Films*, L. Corraera (Ed.), Elsevier, Amsterdam, 1992, p. 141.
517. M. Lang, F. Steglich, N. Toyota and T. Sasaki, *Phys. Rev. B, Condens. Matter* **49**, 15227 (1994).
518. P.A. Mansky, P.M. Chaikin and R.C. Haddon, *Phys. Rev. B, Condens. Matter*, **50**, 15929 (1994).
519. Y.J. Uemura *et al.*, *Nature* **351**, 605 (1991); T. Ishiguro, Yu.V. Sushko, H. Ito and G. Saito, *J. Supercond.* **7**, 657 (1994).
520. A.S. Kirelson and V.J. Emery, *Synth. Met.* **65**, 249 (1994).
521. D. Shoenber, *Magnetic Oscillations in Metals*, Cambridge University Press, Cambridge, UK, 1984, chapter 7; Yu. N. Proshin and N. Khuseinov, *Phys. Uspekhi* **38**, 32 (1995).
522. T. Ando, A.B. Fowler and F. Stern, *Rev. Mod. Phys.* **54**, 437 (1982).
523. For a review concerning magnetooscillations in organic crystals, see J. Wosnitza, *Int. J. Mod. Phys. B*, **7**, 2707 (1993).
524. Several papers in: (a) *Physica B (Amsterdam)* **184**, 437–508 (1993); **194–196**, 1993–2007 (1994); **201**, 442–490 (1994); (b) ref. [43], pp. 2163–2241; ref. [44], pp. 2129–2572; ref. [45], pp. 739–763 and 803–857.
525. P.M. Tchaikin *et al.*, *Synth. Met.*, in press; S. Uji *et al.*, *et al.*, *Synth. Met.*, in press; S.J. Blundell and J. Singleton, *et al.*, *Synth. Met.*, in press.
526. J. Gaulfield, W. Lubezynki, F.L. Pratt, J. Singleton, D.Y.K. Ko, W. Hayes, M. Kurmoo and P. Day, *J. Phys., Condens. Matter* **6**, 2911 (1994).
527. S. Uji, H. Aoki, J.S. Brooks, A.S. Perel, G.J. Athas, S.J. Klepper, C.C. Agosta, D.A. Howe, M. Tokumoto, N. Kinoshita, Y. Tanaka and H. Anzai, *Solid State Commun.* **88**, 683 (1993).
528. N. Harrison, A. House, L. Deckers, J. Singleton, F. Herlach, W. Hayes, M. Kurmoo and P. Day, *Phys. Rev. B* **52**, 5584 (1995).
529. M.V. Kartsovnik, G.Y. Logrenov, H. Ito, T. Ishiguro and G. Saito, *Phys. Rev. B* **52**, 15715 (1995).
530. L. Brossard, unpublished (1995) (see [395]).
531. H. Tajima *et al.*, *Synth. Met.* **70**, 1051 (1995).