

**Structures and Conductivities of the Synthetic Metal Salts of
Ethylenedithiotetrafulvalene (EDTTTF) and Ethylenedithodiselenadithiafulvalene
(EDTSDTF): 211-(EDTTTF)₂IBr₂, 211-(EDTSDTF)₂IBr₂ and
212-(EDTTTF)₂AuBr₂**

BY A. TERZIS AND A. HOUNTAS

Institute of Materials Science, NRC 'Demokritos', Aghia Paraskevi Attikis, 153 10 Athens, Greece

G. C. PAPAVALASSIOU

*Theoretical and Physical Chemistry Institute, National Hellenic Research Foundation,
8 Vassileos Constantinou Ave., 116 35 Athens, Greece*

AND B. HILTI AND J. PFEIFFER

Central Research Laboratories, Ciba-Geigy AG, CH-4002 Basel, Switzerland

(Received 27 February 1989; accepted 19 May 1989)

Abstract. (I): Bis[2-(2-dithiolylydene)-5,6-dihydrodithiolo[4,5-*b*]dithiin]ium dibromiodate(1-), $2C_8H_6S_6^{1/2+} \cdot IBr_2^-$, $M_r = 875.7$, triclinic, $P\bar{1}$, $a = 6.242$ (1), $b = 8.353$ (1), $c = 13.443$ (2) Å, $\alpha = 91.27$ (1), $\beta = 94.48$ (1), $\gamma = 110.06$ (1)°, $V = 655.6$ (2) Å³, $Z = 1$, $D_m = 2.21$, $D_x = 2.217$ g cm⁻³. Mo $K\alpha$, $\lambda = 0.71069$ Å, $\mu = 50.84$ cm⁻¹, $F(000) = 423$, $T = 296$ (2) K. (II): Bis[2-(2-diselenolylydene)-5,6-dihydrodithiolo[4,5-*b*]dithiin]ium dibromiodate(1-), $2C_8H_6S_4Se_2^{1/2+} \cdot IBr_2^-$, $M_r = 1063.3$, triclinic, $P\bar{1}$, $a = 6.298$ (1), $b = 8.384$ (2), $c = 13.528$ (3) Å, $\alpha = 91.46$ (2), $\beta = 94.48$ (2), $\gamma = 109.60$ (1)°, $V = 669.9$ (3) Å³, $Z = 1$, $D_m = 2.58$, $D_x = 2.635$ g cm⁻³. Mo $K\alpha$, $\lambda = 0.71069$ Å, $\mu = 100.68$ cm⁻¹, $F(000) = 495$, $T = 296$ (2) K. (III): Bis[2-(2-dithiolylydene)-5,6-dihydrodithiolo[4,5-*b*]dithiin]ium dibromaurate(1-), $2C_8H_6S_6^{1/2+} \cdot AuBr_2^-$, $M_r = 945.8$, monoclinic, $C2/m$, $a = 7.209$ (2), $b = 29.023$ (8), $c = 6.655$ (1) Å, $\beta = 111.62$ (2)°, $V = 1294.4$ (5) Å³, $Z = 2$, $D_m = 2.44$, $D_x = 2.426$ g cm⁻³. Mo $K\alpha$, $\lambda = 0.71069$ Å, $\mu = 95.92$ cm⁻¹, $F(000) = 898$, $T = 296$ (2) K. Final R values are 0.0231 (I), 0.053 (II), 0.0262 (III) for 2080, 1837 and 947 observed [$F_o \geq K\sigma(F_o)$, $K = 4.0$ for (I) and (II), $K = 6.0$ for (III)] reflections, respectively. (I) and (II) are isostructural. They retain the metallic state down to 2 K and they are potential superconductors. (III) undergoes a metal-to-semiconductor transition at 125 K under ambient pressure and this is lowered to 25 K under 0.38 GPa pressure.

Introduction. Continuing our search for unsymmetrical organic molecules which yield superconducting charge-transfer salts we have synthesized MDTTTF,

EDTTTF and EDTSDTF [for structural formulas corresponding to these and any following abbreviations refer to Hountas, Terzis, Papavassiliou, Hilti & Pfeiffer (1990)], and reported on the structures and conductivities of the salts of MDTTTF and EDTTTF with I_3^- (Hountas *et al.*, 1990). These salts had 1:1 composition and therefore they were poor candidates for affording the superconducting state. It was possible to overcome this limitation by changing the anion from I_3^- to IBr_2^- or $AuBr_2^-$, and salts with the promising 2:1 composition, 211-(EDTTTF)₂IBr₂ (I), 211-(EDTSDTF)₂IBr₂ (II) and 212-(EDTTTF)₂AuBr₂ (III), were synthesized. [The modifier *MSL*- in front of the compound names is a notation suggested by Williams *et al.* (1987) to convey critical structural features of the donor network.] In this report we present the structures and the conductivity of these salts.

Experimental. All three salts have a great tendency to form twins. In the case of (III), the two individua of the twin are of equal size in most of the crystals and give a pseudo-orthorhombic cell. Once this had been recognized (from the existence of non-sensical systematic absences) the following procedure was used to obtain a 'single' crystal. We started with a very large crystal mounted along the a axis. If the oscillation photograph indicated the existence of mirror symmetry, the crystal was cut and the new pieces mounted again along a . If the mirror symmetry disappeared the $1kl$ level was recorded in order to estimate the intensity ratio of the two individua from the non-overlapping reflections. We continued to cut

the crystals until this intensity ratio was better than 9:1. A similar procedure of cutting the crystals in different directions until the intensity ratio improved to better than 9:1 (I) and 8:2 (II) was followed for (I) and (II). We could not improve the ratio further in (II) because we did not have very large crystals to begin with.

Compounds (I) to (III) were prepared by electrocrystallization (Hountas *et al.*, 1990). Crystals used for data collection were $0.05 \times 0.30 \times 0.31$ mm (I), $0.02 \times 0.29 \times 0.44$ mm (II) and $0.03 \times 0.25 \times 0.45$ mm (III). D_m by flotation in $\text{CHCl}_3/\text{C}_2\text{H}_2\text{Br}_4$. Intensity data collected on a Syntex P_2 computer-controlled diffractometer with Mo $K\alpha$ Nb-filtered radiation. Cell parameters from 15 intermediate 2θ reflections. θ - 2θ scan, $2\theta \leq 50.0^\circ$, scan speed variable 2 - $20^\circ \text{ min}^{-1}$, scan range 1.6° (2θ) plus $\alpha_1 - \alpha_2$ divergence, background counting 0.5 of scan time. Data collected/unique reflections/ R_{int} 2990/2328/0.007 (I), 2544/2336/0.016 (II) and 1277/1178/0.010 (III). Range of hkl $0 \rightarrow 7$, $-15 \rightarrow 15$, $-9 \rightarrow 9$ (I), $-6 \rightarrow 7$, $0 \rightarrow 9$, $-16 \rightarrow 16$ (II), $0 \rightarrow 8$, $-34 \rightarrow 0$, $-7 \rightarrow 7$ (III). Three reflections monitored periodically showed $< 3.0\%$ intensity fluctuations and no crystal decay. Lp and analytical absorption correction applied [$T_{\text{min}}/T_{\text{max}}$ 0.26/0.77 (I), 0.14/0.92 (II), 0.13/0.72 (III)] with *SHELX76* (Sheldrick, 1976). The structures of (I) and (III) were solved by the Patterson method. The final parameters of (I) were used as the starting model for (II). H-atom positions for (I) and (III) were located from a difference Fourier map and refined isotropically; those for (II) were calculated at 1.08 \AA and only the temperature factor was refined. Full-matrix refinement based on F with *SHELX76* minimizing $\sum w\Delta^2$; unit weights gave a satisfactory analysis of variance. An attempt was made to refine (III) and its enantiomorph in space groups $C2$ and Cm . While somewhat lower R values were obtained [$R/wR = 0.0233/0.0238$ ($C2$) and $0.0236/0.0243$ (Cm) for observed data] bond distances were unsatisfactory, equivalent bonds were far from being equal and the standard deviations were three to five times larger. Refinement proceeded in $C2/m$. Number of parameters refined 166 (I), 145 (II), 87 (III). $wR = 0.0252$ (I), 0.0579 (II), 0.0266 (III), for observed data. $R/wR = 0.0275/0.0306$ (I), $0.0727/0.0844$ (II), $0.0390/0.0585$ (III) for all data. In the last cycles of refinement for (II), certain lines of reflections ($\bar{1}2l$, $13l$, $\bar{3}1l$, $21l$, $50l$, $05l$, $00l$) were given zero weight because it was known from Weissenberg photographs that they were coincident for the two individua of the twin. This left a total of 1837 observed reflections. $\Delta\rho_{\text{max}}/\Delta\rho_{\text{min}} = 0.80/-0.41$ (I), $1.01/-1.21$ (II), $0.67/-0.79$ (III) e \AA^{-3} . All 'large' peaks in the final difference map were around I and Au atoms. $|\Delta/\sigma|_{\text{max}} = 0.071$ (I), 0.006 (II), 0.091 (III). $S =$

Table 1. Positional and equivalent isotropic thermal parameters [$\times 10^4$ (I) and (III), $\times 10^3$ (II)] of the non-H atoms with e.s.d.'s in parentheses

$$U_{\text{eq}} = (U_{11} + U_{22} + U_{33})/3.$$

	x	y	z	$U_{\text{eq}} (\text{\AA}^2)$
(I)				
I	0	0	0	356
Br	-1822.1 (9)	2506.9 (6)	44.7 (4)	542
S(1)	2257 (2)	7953 (1)	6403.7 (8)	408
S(2)	7248 (2)	9612 (1)	6616.0 (8)	387
S(3)	2556 (2)	6133 (1)	4298.3 (7)	341
S(4)	7538 (2)	7800 (1)	4506.2 (7)	363
S(5)	2275 (2)	4621 (1)	2271.9 (8)	380
S(6)	8269 (2)	6662 (2)	2524.0 (8)	438
C(1)	3475 (7)	9306 (5)	7443 (3)	463
C(2)	5727 (7)	10069 (5)	7534 (3)	437
C(3)	4842 (6)	8244 (5)	5904 (3)	320
C(4)	4962 (6)	7479 (5)	5013 (3)	310
C(5)	4021 (6)	5855 (5)	3287 (3)	308
C(6)	6314 (6)	6643 (5)	3382 (3)	331
C(7)	4392 (7)	4250 (5)	1554 (3)	432
C(8)	6386 (7)	5833 (6)	1409 (3)	428
(II)				
I	0	0	0	34
Br	-172.7 (3)	253.4 (2)	5.0 (1)	54
Se(1)	212.5 (2)	789.5 (2)	641.1 (1)	50
Se(2)	740.8 (2)	964.3 (2)	663.3 (1)	43
S(3)	257.7 (4)	612.7 (4)	427.0 (2)	31
S(4)	749.5 (4)	773.8 (4)	447.9 (2)	33
S(5)	229.8 (5)	466.9 (4)	223.5 (2)	34
S(6)	821.1 (5)	664.8 (4)	249.6 (2)	40
C(1)	346 (2)	930 (2)	750.2 (9)	44
C(2)	573 (2)	1009 (2)	760.0 (9)	44
C(3)	486 (2)	819 (1)	587.1 (8)	26
C(4)	496 (2)	746 (1)	498.7 (8)	30
C(5)	402 (2)	585 (1)	325.2 (7)	30
C(6)	627 (2)	663 (1)	335.0 (8)	32
C(7)	437 (2)	427 (2)	153 (1)	44
C(8)	634 (2)	583 (2)	138.2 (8)	35
(III)				
Au	0	0	10000	487
Br	2185 (2)	0	8085 (2)	859
S(1)	850 (2)	1753.0 (4)	7370 (2)	372
S(3)	-856 (2)	2865.5 (4)	2632 (2)	362
S(5)	-1030 (2)	3871.4 (5)	2151 (2)	451
C(1)	400 (8)	1230 (2)	6079 (9)	442
C(3)	0	2078 (2)	5000	290
C(4)	0	2542 (2)	5000	299
C(5)	-410 (8)	3402 (2)	3914 (7)	351
C(7)	-900 (10)	4335 (2)	3990 (10)	513

0.84 (I), 2.25 (II), 2.07 (III). Atomic scattering factors from *International Tables for X-ray Crystallography* (1974). The final atomic parameters of the non-H atoms are given in Table 1,* bond lengths and angles in Table 2. The atom-labeling scheme is shown in Fig 1.

Discussion. (I) and (II) are isostructural. In all three of these structures the donors display the (α, L) interstack-intrastack packing mode (Williams *et al.*, 1987) with (a) the 'corrugated sheet' network of short interstack S...S, S...Se and Se...Se interactions (Fig. 2), and (b) the anions occupying positions between these 'sheets' (Fig. 3). Both of these features

* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52261 (28 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. Bond lengths (Å) and angles (°) of the cations with *e.s.d.*'s in parentheses

For (II) substitute Se(1) and Se(2) for S(1) and S(2), respectively, and for (III) substitute Au for I.

	(I)	(II)	(III)
I—Br	2.706 (1)	2.693 (1)	2.363 (1)
C(1)—C(2)	1.324 (6)	1.35 (2)	1.34 (1)
C(1)—S(1)	1.727 (4)	1.83 (1)	1.716 (5)
C(2)—C(2)	1.727 (4)	1.85 (1)	
S(1)—C(3)	1.738 (2)	1.87 (1)	1.744 (4)
S(2)—C(3)	1.740 (4)	1.87 (1)	
C(3)—C(4)	1.365 (5)	1.34 (1)	1.346 (9)
C(4)—S(3)	1.735 (3)	1.74 (1)	1.740 (4)
C(4)—S(4)	1.733 (4)	1.74 (1)	
S(3)—C(5)	1.750 (4)	1.76 (1)	1.749 (5)
S(4)—C(6)	1.746 (4)	1.75 (1)	
C(5)—C(6)	1.349 (5)	1.34 (1)	1.345 (9)
C(5)—S(5)	1.746 (4)	1.74 (1)	1.744 (5)
C(6)—S(6)	1.740 (4)	1.74 (1)	
S(5)—C(7)	1.800 (4)	1.79 (1)	1.797 (6)
S(6)—C(8)	1.797 (4)	1.80 (1)	
C(7)—C(8)	1.502 (5)	1.50 (2)	1.48 (1)
C(2)—C(1)—S(1)	117.8 (3)	119.7 (9)	117.7 (4)
C(1)—C(2)—S(2)	117.7 (3)	118.5 (9)	
C(1)—S(1)—C(3)	94.8 (2)	93.8 (5)	95.0 (3)
C(2)—S(2)—C(3)	94.8 (2)	93.5 (5)	
S(1)—C(3)—S(2)	114.9 (2)	114.4 (5)	114.5 (4)
S(1)—C(3)—C(4)	122.3 (3)	122.2 (7)	122.8 (2)
S(2)—C(3)—C(4)	122.8 (3)	123.3 (7)	
C(3)—C(4)—S(3)	122.7 (3)	123.2 (8)	122.6 (2)
C(3)—C(4)—S(4)	122.2 (3)	122.4 (8)	
S(3)—C(4)—S(4)	115.1 (2)	114.4 (6)	114.7 (2)
C(4)—S(3)—C(5)	95.6 (2)	96.1 (5)	95.7 (2)
C(4)—S(4)—C(6)	95.4 (2)	95.6 (5)	
S(3)—C(5)—C(6)	116.5 (3)	115.9 (8)	117.0 (2)
S(4)—C(6)—C(5)	117.1 (3)	117.6 (8)	
S(3)—C(5)—S(5)	114.7 (2)	115.2 (6)	114.3 (3)
S(4)—C(6)—S(6)	114.4 (2)	113.9 (6)	
C(6)—C(5)—S(5)	128.7 (3)	128.9 (8)	128.7 (2)
C(5)—C(6)—S(6)	128.5 (3)	128.4 (8)	
C(5)—S(5)—C(7)	100.6 (2)	100.4 (5)	100.9 (3)
C(6)—S(6)—C(8)	101.1 (2)	100.9 (5)	
S(5)—C(7)—C(8)	113.9 (3)	113.8 (8)	115.3 (2)
S(6)—C(8)—C(7)	113.8 (3)	113.3 (8)	

are characteristics of the β form of ET superconductors. A third characteristic of these superconductors is that these 'sheets' are related by translation. This is the case in the present (I) and (II), but in (III) the anions occupy positions on the mirror plane and the 'corrugated sheets' are related by mirror symmetry (Fig. 3). This new feature changes the pattern of H \cdots anion interactions (Fig. 4). In (I) and (II) the H \cdots anion contacts are almost identical to those of the β form of ET superconductors. While the characteristic *A*- and *B*-site terminal groups (Whangbo, Williams, Schultz, Emge & Beno, 1987; Terzis, Hountas & Papavassiliou, 1988) are preserved in (III) the number and pattern of H \cdots anion interactions is different (Fig. 4). The H-atom positions used for the calculation of H \cdots anion interactions were calculated at 1.08 Å and *sp*³ geometry for the ethylene and *sp*² geometry for the vinylene C atoms (even though most H-atom positions were located from difference Fourier maps and subsequently refined) so that comparisons with the β form of ET salts (Williams *et al.*, 1987; Whangbo *et al.*, 1987) would be more meaningful.

In going from (I) to (II) the anion remains the same and S(1) and S(2) of the donor are substituted

by larger Se atoms. This, as it turns out, leaves the hydrogen pocket formed by 12 donor molecules (Fig. 4) essentially unchanged and the H \cdots anion interactions in (I) and (II) are almost identical. On the other hand, the larger Se atoms increase in number and shorten significantly the chalcogen-chalcogen contacts (Fig. 2, Table 3). Three new interstack contacts, Se(1) \cdots Se(2) \cdots , Se(1) \cdots S(3) and Se(1) \cdots S(4), now

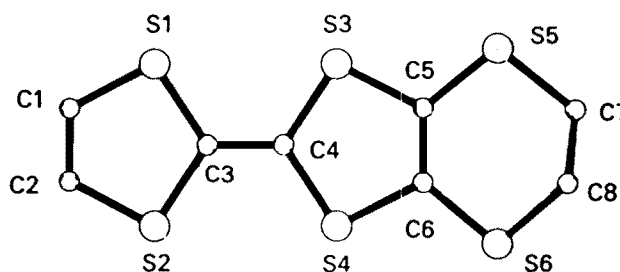


Fig. 1. Atom numbering for (I). For (II) substitute S(1) and S(2) by Se(1) and Se(2). For (III) substitute the ethylene C(7)—C(8) group by a methylene C(7) group.

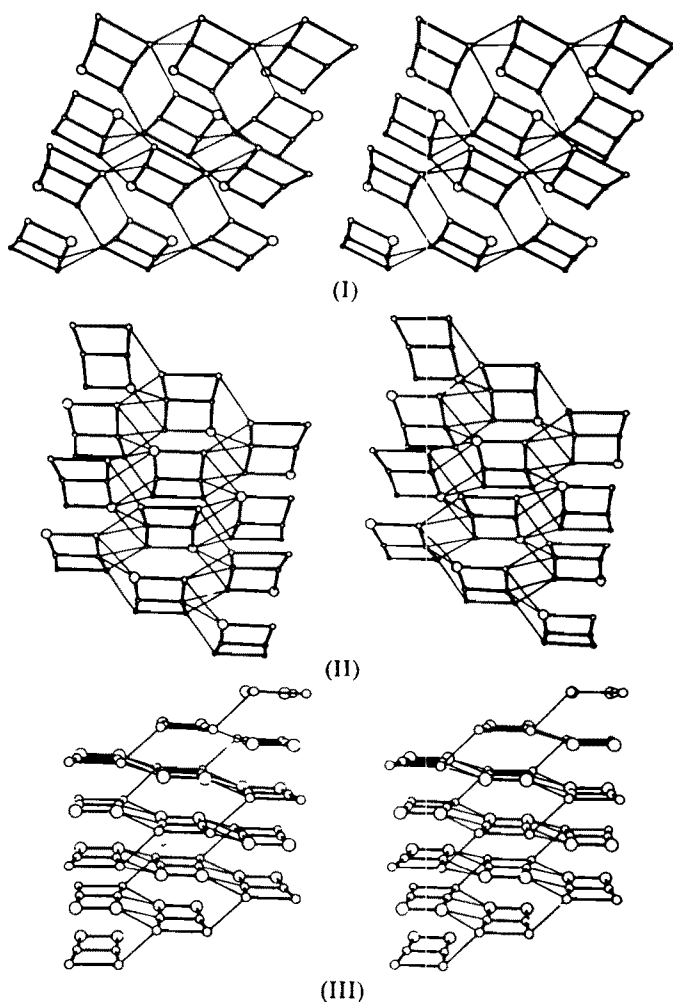


Fig. 2. Stereoviews of the 'corrugated sheet' of chalcogen-chalcogen contacts. To improve clarity only S and Se atoms are drawn, and S(1) and Se(1) are given a larger radius. 'Contacts' for (III) are between 3.60 and 3.68 Å (see Table 3).

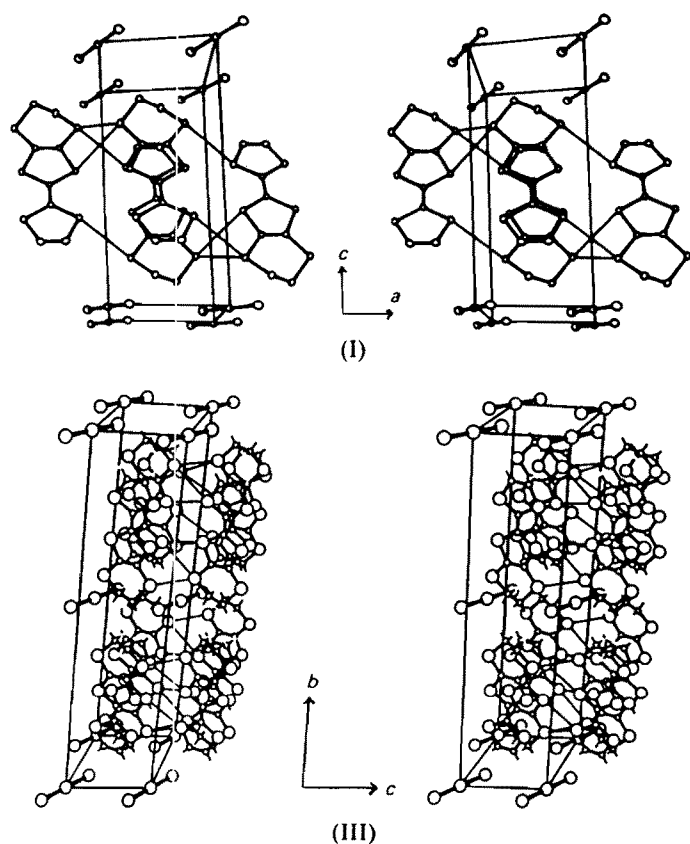


Fig. 3. Stereoviews of the molecular packing. (II) is similar to (I).

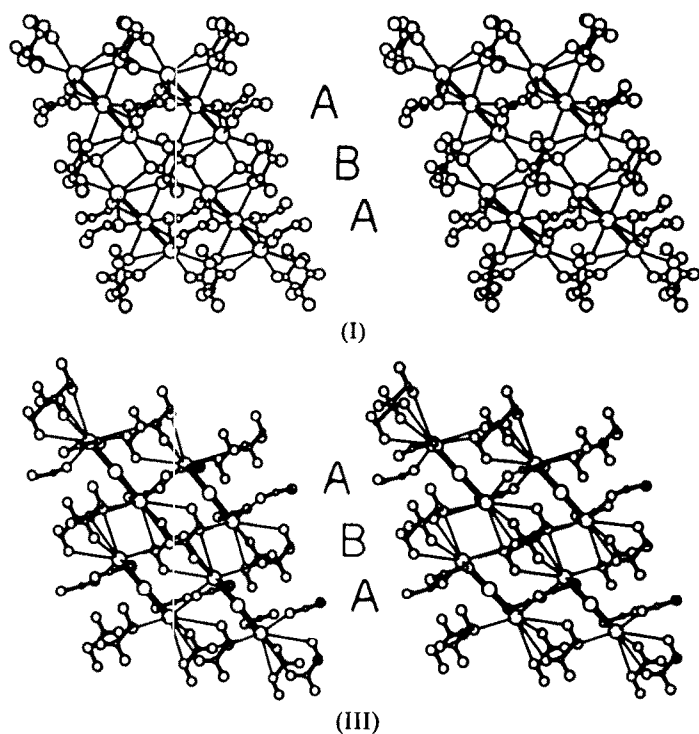


Fig. 4. Stereoviews of H...anion interactions. (II) is similar to (I). Only the terminal ethylene and vinylene groups and the anions are shown. Light lines indicate H...I (< 3.43 Å) and H...Br (< 3.20 Å (I), < 3.30 Å (II)) interactions.

Table 3. S...S (< 3.7 Å), S...Se (< 3.9 Å) and Se...Se (< 4.0 Å) interstack distances

Those distances marked with an asterisk are considered contacts, taking the van der Waals radii of S and Se to be 1.80 and 1.93 Å, respectively. For (II) substitute Se(1) and Se(2) for S(1) and S(2). See Fig. 2.

	(I)	(II)	(III)
S(1)···S(2)	> 3.7	3.755 (2)*	
S(1)···S(3)	> 3.7	3.702 (2)*	3.605 (2)
S(1)···S(4)	> 3.7	3.726 (3)*	
S(1)···S(5)	3.546 (1)*	3.566 (2)*	3.632 (2)
S(2)···S(3)†	> 3.7	3.778 (3)	
S(2)···S(4)	3.692 (1)	3.686 (3)*	
S(2)···S(6)	3.496 (1)*	3.496 (3)*	
S(3)···S(4)†	3.672 (1)	3.682 (4)	
S(3)···S(6)	3.593 (2)*	3.652 (4)	
S(5)···S(6)	3.508 (2)*	3.532 (5)*	
S(5)···S(5)	—	—	3.678 (2)

† Intra-stack distance.

appear and the intrastack distance Se(2)···S(3) of 3.778 (3) Å is not much longer than 3.73 Å, the sum of the van der Waals radii (Table 3). It is seen therefore that the substitution of the two S atom by Se is structurally advantageous, since it greatly improves the chalcogen-chalcogen contacts without affecting adversely the H...anion interactions, and both of these are significant criteria for possible superconductivity (Williams *et al.*, 1987).

In going from (I) to (III) the donor remains the same and the anion, IBr_2^- (which has a length of 9.3 Å as estimated from the sum of the two bond lengths and the van der Waals radii of the terminal atoms), is substituted with the shorter AuBr_2^- (8.6 Å). This changes both the H...anion interactions (Fig. 3) and the pattern of S...S contacts of which there is now not one below 3.6 Å. Furthermore, there is now an energetically unfavorable H...H interaction (Whangbo *et al.*, 1987) [$\text{H}(7A)\cdots\text{H}(7A)(x, 1-y, z) = 2.00$ (4) Å] while there is no H...H distance less than 2.40 Å in (I) and (II). This is clearly an unfavorable substitution and it is reflected in the conductivity of this salt. While (I) and (II) retain the metallic state down to 2 K and their conductivity behavior makes them candidates for superconductivity (Papavassiliou *et al.*, 1988), since the room-temperature conductivity σ_{RT} is $10^3 \Omega^{-1} \text{cm}^{-1}$ and the normalized resistance $R(2 \text{ K})/R(295 \text{ K})$ is about 0.01, (III) undergoes a metal-to-semiconductor transition at 125 K under ambient pressure and this transition takes place at 25 K under 0.33 GPa pressure (Hilti, Mayer, Pfeiffer, Terzis & Papavassiliou, 1989).

References

- HILTI, B., MAYER, C., PFEIFFER, J., TERZIS, A. & PAPAVALIIOU, G. C. (1989). In preparation.
 HOUNTAS, A., TERZIS, A., PAPAVALIIOU, G. C., HILTI, B. & PFEIFFER, J. (1990). *Acta Cryst.* C46, 220–223.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)

PAPAVASSILIOU, G. C., MOUSDIS, G. A., ZAMBOUNIS, J. S., TERZIS, A., HOUNTAS, A., HILTI, B., MAYER, C. W. & PFEIFFER, J. (1988). *Synth. Met.* **27**, 379-383.

SHELDRIK, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.

TERZIS, A., HOUNTAS, A. & PAPAVASSILIOU, G. C. (1988). *Solid State Commun.* **66**, 1161-1162.

WHANGBO, M. H., WILLIAMS, J. M., SCHULTZ, A. J., EMGE, T. J. & BENO, M. A. (1987). *J. Am. Chem. Soc.* **109**, 90-94.

WILLIAMS, J. M., WANG, H. H., EMGE, T. J., GEISER, U., BENO, M. A., LEUNG, P. C. W., CARLSON, K. D., THORN, R. J., SCHULTZ, A. J. & WHANGBO, M. H. (1987). *Prog. Inorg. Chem.* **35**, 51-218.

