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Structures of the Conducting Salts of Ethylenedithiotetrathiafulvalene (EDTTTF) and Methylenedithiotetrathiafulvalene (MDTTTF): (EDTTTF) I_3 and (MDTTTF) I_3

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Abstract. (I): 2-(2-Dithiolylylidene)-5,6-dihydrodithiolo[4,5-*b*]dithiinium triiodide, $C_8H_6S_6^+I_3^-$, $M_r = 675.2$, monoclinic, $P2_1/c$, $a = 15.307(2)$, $b = 9.622(1)$, $c = 12.013(1)$ Å, $\beta = 110.69(1)^\circ$, $V = 1655.0(4)$ Å³, $Z = 4$, $D_m = 2.74$, $D_x = 2.709$ g cm⁻³, Mo $K\alpha$, $\lambda = 0.71069$ Å, $\mu = 62.80$ cm⁻¹, $F(000) = 1228$, $T = 296(2)$ K. (II) 2-(2-Dithiolylylidene)-dithiolo[4,5-*d*]dithiolium triiodide, $C_7H_4S_6^+I_3^-$, $M_r =$

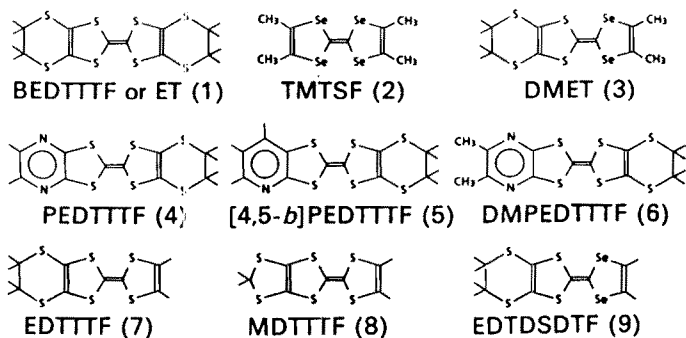
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661.2, monoclinic, $P2_1/c$, $a = 14.583(2)$, $b = 9.350(1)$, $c = 11.995(1)$ Å, $\beta = 107.76(1)^\circ$, $V = 1557.5(4)$ Å³, $Z = 4$, $D_m = 2.86$, $D_x = 2.820$ g cm⁻³, Mo $K\alpha$, $\lambda = 0.71069$ Å, $\mu = 66.73$ cm⁻¹, $F(000) = 1204$, $T = 296(2)$ K. Final R values are 0.0374 (I) and 0.0301 (II) for 1774 and 1920 observed [$F_o \geq 5.0\sigma(F_o)$] reflections. The two salts are isostructural. The packing comprises sheets of donors with strong S...S contacts separated by half of the I_3^- ions. The remaining I_3^- ions are embedded in the sheets, thus preventing the formation of donor stacks. The salts are semiconductors with a tendency towards temperature-independent conductivity above room temperature.

Introduction. Molecular crystals based on multichalcogen π -donor molecules have attracted considerable interest in the field of organic metals and superconductors (Williams & Carneiro, 1986; Ishiguro, 1988). A large number of salts of these donors with a variety of anions such as I_3^- , IBr_2^- and AuI_2^- have been synthesized and structurally characterized. Until recently only salts of the symmetrical BEDTTTF (1) and TMTSF (2) afforded the ambient-pressure superconducting state. But Kikuchi *et al.* (1987) have synthesized superconductors with the unsymmetrical donor DMET (3), which is half (1) and half (2). We have modified (1) to give the unsymmetrical donors PEDTTTF (4), [4,5-*b*]-PEDTTTF (5) and DMPEDTTTF (6) but they did not afford the superconducting state (Psycharis, Hountas, Terzis & Papavassiliou, 1988; Terzis, Psycharis, Hountas & Papavassiliou, 1988). We have recently synthesized new unsymmetrical donors, EDTTTF (7), MDTTTF (8) (Papavassiliou, Zambounis, Mousdis, Gionis & Yiannopoulos, 1988) and EDTDSDTF (9) (Papavassiliou, Mousdis, Yiannopoulos, Kakoussis & Zambounis, 1988), and in this and the following two reports we present the structures of their salts with I_3^- , IBr_2^- , AuI_2^- and $AuBr_2^-$. At least one of these, (8)₂AuI₂ (Hountas *et al.*, 1990; Papavassiliou, Mousdis, Zambounis *et al.*, 1988) and possibly two more, (7)₂IBr₂ and (9)₂IBr₂, are superconductors (Terzis, Hountas, *et al.*, 1988).

In this report we present the structures of the salts (7)I₃ and (8)I₃.



Experimental. The title compounds were prepared by electrocrystallization of the donor ($1.55 \times 10^{-3} M$) and Bu_4NI_3 ($5 \times 10^{-3} M$) in CH_2Cl_2 , using platinum electrodes, at $1 \mu A cm^{-2}$ and 295 K. The crystals used for data collection were an elongated flat prism $0.08 \times 0.13 \times 0.32$ mm (I) and a flat prism $0.10 \times 0.23 \times 0.29$ mm (II). D_m by flotation in $CHCl_3/C_2H_2Br_4$. Intensity data collected on a Syntex $P2_1$ computer-controlled diffractometer with Mo $K\alpha$ Nb-filtered radiation. Cell parameters from 15 intermediate 2θ reflections. θ - 2θ scan, $2\theta \leq 48.0^\circ$, scan speed variable 2 - $20^\circ min^{-1}$, scan range 1.6° (I), 1.8° (II) (2θ) plus $\alpha_1 - \alpha_2$ divergence, background counting 0.5 of scan time. Data collected/unique reflections/ R_{int} 2900/2604/0.021 (I) and 2979/2462/0.013 (II). Range of hkl $-17 \rightarrow 0$, $0 \rightarrow 11$, $-12 \rightarrow 13$ (I), $0 \rightarrow 16$, $-10 \rightarrow 0$, $-13 \rightarrow 13$ (II). Three reflections monitored periodically showed $< 3.0\%$ intensity fluctuation and no crystal decay. Lp and analytical absorption corrections applied [T_{min}/T_{max} 0.43/0.63 (I), 0.26/0.56 (II)] with *SHELX76* (Sheldrick, 1976). The structure of (II) was solved by direct methods with *SHELX86* (Sheldrick, 1986). Although a group of three strong peaks in the E map indicated the position of an I_3^- ion with acceptable I—I distances and I—I—I angle close to 180° , the structure would not refine. It was assumed that the origin was misplaced and shifted to space group $P1$. The E map revealed the positions of three I_3^- ions.

After two structure-factor and Fourier-map calculations the positions of all the I_3^- ions were revealed and the positions of the symmetry elements were apparent. At this point we applied an appropriate shift vector to the positions of all the atoms and moved back to space group $P2_1/c$. Refinement then proceeded normally. In the case of (I) the coordinates of (II) were used as the starting model. There is disorder in (I) at the ethylene group C(7)—C(8) and in (II) at the methylene group C(7). The ethylene disorder is evident in many ET-based structures (Terzis, Psycharis *et al.*, 1988). The difference map shows two positions, A and B , for the ethylene and methylene groups. The site occupancies for these two positions were refined keeping the sum of the two constant at 1. They refined to 0.496 (5) (I) and 0.703 (5) (II) for position A . In subsequent refinements they were kept constant at 0.5 and 0.7, respectively. H-atom positions for the disordered groups were calculated at 1.08 Å and were not refined. H(1) and H(2) were located from the difference map and refined isotropically.

Full-matrix refinement based on F with *SHELX76* minimizing $\sum w\Delta^2$, $w = 1/(\sigma^2 + 0.00025|F_o|^2)$ from counting statistics. Number of refined parameters 184 (I) and 166 (II). $wR = 0.0426$ (I) and 0.0383 (II) for observed data. $R/wR = 0.0606/0.0465$ (I) and 0.0421/0.0425 (II) for all data. $\Delta\rho_{max}/\Delta\rho_{min} = 1.061/$

Table 1. Positional and equivalent isotropic thermal parameters ($\times 10^4$) 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(1)	0	0	0	515
I(2)	1978.3 (4)	-46.0 (7)	371.3 (7)	686
I(3)	5000	5000	5000	1037
I(4)	4896.7 (5)	3471 (1)	7056.7 (8)	1119
S(1)	1382 (1)	3442 (3)	1670 (2)	551
S(2)	1379 (1)	6460 (3)	1686 (2)	563
S(3)	-834 (1)	3448 (2)	1211 (2)	471
S(4)	-825 (1)	6460 (2)	1233 (2)	459
S(5)	-2854 (1)	3165 (2)	754 (2)	574
S(6)	-2827 (1)	6807 (2)	711 (2)	558
C(1)	2438 (6)	4260 (10)	1926 (7)	551
C(2)	2431 (6)	5640 (10)	1948 (8)	569
C(3)	755 (5)	4949 (8)	1570 (6)	381
C(4)	-202 (5)	4949 (8)	1360 (6)	360
C(5)	-1902 (5)	4258 (9)	987 (6)	356
C(6)	-1897 (5)	5652 (9)	987 (7)	395
C(7A)	-3690 (20)	4290 (20)	930 (20)	694
C(8A)	-3800 (10)	5640 (20)	290 (10)	450
C(7B)	-3540 (10)	4440 (20)	1270 (20)	649
C(8B)	-3780 (20)	5620 (30)	640 (20)	799
(II)				
I(1)	0	0	0	393
I(2)	2020.9 (3)	16.8 (5)	64.8 (4)	499
I(3)	5000	5000	5000	762
I(4)	4885.2 (4)	3056.7 (7)	6878.8 (6)	809
S(1)	1431 (1)	3414 (2)	1527 (1)	408
S(2)	1436 (1)	6515 (2)	1602 (1)	390
S(3)	-845 (1)	3391 (2)	1249 (1)	332
S(4)	-831 (1)	6523 (2)	1340 (1)	340
S(5)	-3003 (1)	3352 (2)	985 (2)	451
S(6)	-2989 (1)	6550 (2)	1076 (2)	451
C(1)	2515 (4)	4262 (8)	1709 (5)	416
C(2)	2511 (4)	5680 (8)	1749 (5)	444
C(3)	788 (4)	4963 (6)	1503 (4)	273
C(4)	-194 (4)	4962 (6)	1390 (4)	268
C(5)	-1910 (4)	4224 (6)	1178 (4)	292
C(6)	-1905 (4)	5676 (6)	1220 (4)	296
C(7A)	-3537 (7)	4920 (10)	1423 (9)	449
C(7B)	-3650 (10)	4970 (20)	710 (20)	362

-0.977 (I) and 0.818/-1.168 (II) e \AA^{-3} . All 'large' peaks in the final difference map are around I atoms. $|\Delta/\sigma|_{\text{max}} = 0.112$ (I) and 0.171 (II). $S = 2.46$ (I) and 3.12 (II). 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-numbering scheme is shown in Fig. 1.

Discussion. There is excellent agreement (usually within one e.s.d.) in the bond distances and angles of the common moieties of the two donor molecules, EDTTTF (I) and MDTTTF (II). The structures have two independent I₃⁻ ions each occupying a center of symmetry (Fig. 2). In most of the conducting salts of donors like ET, PEDTTTF or TMTSF with linear anions like I₃⁻, IBr₂⁻, AuI₂⁻ and AuBr₂⁻ the packing

* Lists of observed and calculated structure factors, anisotropic thermal parameters of the non-H atoms and atomic and thermal parameters of the H atoms have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52258 (24 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. Bond lengths (\AA) and angles ($^\circ$) of the cations with e.s.d.'s in parentheses

	(I)	(II)
I(1)—I(2)	2.901 (1)	2.924 (1)
I(3)—I(4)	2.927 (1)	2.939 (1)
C(1)—C(2)	1.34 (1)	1.33 (1)
C(1)—S(1)	1.724 (9)	1.721 (6)
C(2)—S(2)	1.718 (9)	1.712 (6)
S(1)—C(3)	1.719 (8)	1.721 (6)
S(2)—C(3)	1.717 (8)	1.716 (6)
C(3)—C(4)	1.40 (1)	1.397 (8)
C(4)—S(3)	1.712 (8)	1.728 (5)
C(4)—S(4)	1.715 (8)	1.721 (6)
S(3)—C(5)	1.743 (7)	1.716 (5)
S(4)—C(6)	1.744 (7)	1.721 (6)
C(5)—C(6)	1.34 (1)	1.359 (8)
C(5)—S(5)	1.739 (8)	1.743 (6)
C(6)—S(6)	1.744 (8)	1.740 (6)
S(5)—C(7A)	1.74 (3)	1.807 (9)
S(6)—C(7A)		1.83 (1)
S(6)—C(8A)	1.79 (2)	
C(7A)—C(8A)	1.49 (3)	
S(5)—C(7B)	1.86 (2)	1.76 (2)
S(6)—C(7B)		1.75 (2)
S(6)—C(8B)	1.83 (3)	
C(7B)—C(8B)	1.34 (3)	
C(2)—C(1)—S(1)	116.3 (7)	116.9 (5)
C(1)—C(2)—S(2)	117.9 (7)	117.7 (5)
C(1)—S(1)—C(3)	95.4 (4)	95.1 (3)
C(2)—S(2)—C(3)	94.9 (4)	95.1 (3)
S(1)—C(3)—S(2)	115.4 (4)	115.1 (3)
S(1)—C(3)—C(4)	122.5 (6)	122.6 (4)
S(2)—C(3)—C(4)	122.1 (6)	122.3 (4)
C(3)—C(4)—S(3)	122.5 (6)	121.8 (4)
C(3)—C(4)—S(4)	122.1 (6)	121.9 (4)
S(3)—C(4)—S(4)	115.5 (4)	116.3 (3)
C(4)—S(3)—C(5)	95.9 (4)	94.6 (3)
C(4)—S(4)—C(6)	95.6 (4)	94.6 (3)
S(3)—C(5)—C(6)	116.3 (6)	117.2 (4)
S(3)—C(5)—S(5)	116.2 (5)	124.9 (4)
S(4)—C(6)—C(5)	116.8 (6)	117.2 (4)
S(4)—C(6)—S(6)	113.8 (5)	124.6 (4)
C(6)—C(5)—S(5)	127.5 (6)	117.8 (4)
C(5)—C(6)—S(6)	129.3 (6)	118.1 (4)
C(5)—S(5)—C(7A)	102.4 (8)	92.3 (3)
C(6)—S(6)—C(8A)	101.3 (7)	
S(5)—C(7A)—C(8A)	116 (2)	
S(6)—C(8A)—C(7A)	118 (1)	
C(6)—S(6)—C(7A)		91.8 (3)
S(5)—C(7A)—S(6)		110.7 (5)
C(5)—S(5)—C(7B)	95.1 (7)	92.1 (6)
C(6)—S(6)—C(8B)	101.2 (9)	
S(5)—C(7B)—C(8B)	117 (2)	
S(6)—C(8B)—C(7B)	117 (2)	
C(6)—S(6)—C(7B)		92.2 (6)
S(5)—C(7B)—S(6)		117 (1)

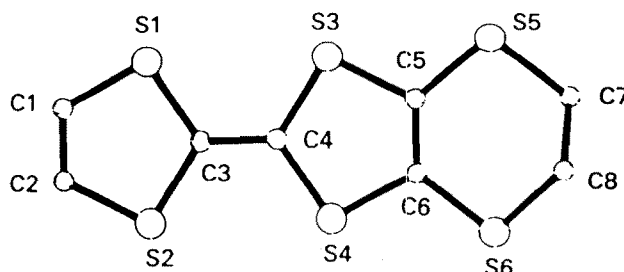


Fig. 1. Atom numbering for (I). For (II) substitute the ethylene C(7)—C(8) group by a methylene C(7).

comprises 'sheets' of donors separated by the anions. The novelty in the present structures is that one of the independent I₃⁻ ions plays the 'normal' role of separating the 'sheets' of donors while the second I₃⁻ is embedded in these 'sheets', with its axis parallel to the long axis of the donor (Fig. 3). The terminal I

atom of the embedded anion, I(2)I(1)I(2)', has only one I...H contact less than 3.4 Å while the terminal I atom of the other anion I(4)I(3)I(4)' has four such contacts. This is perhaps the reason for I(3)—I(4) [2.927 (1) (I), 2.939 (1) (II) Å] being longer than I(1)—I(2) [2.901 (1) (I), 2.924 (1) (II) Å].

We cannot properly speak of stacks of donors in this structure because of the embedded I₃⁻ ions. We can, however, speak of dimers of donors with very good (<3.6 Å) S...S intradimer and interdimer con-

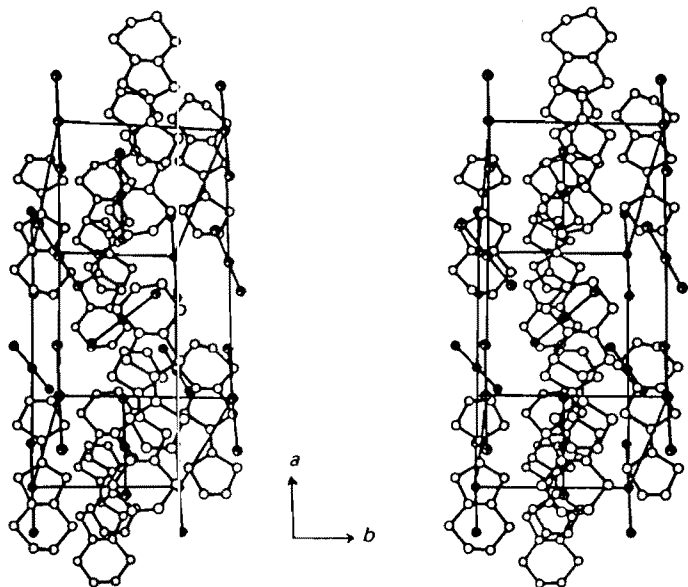


Fig. 2. Stereoview of the packing in (I).

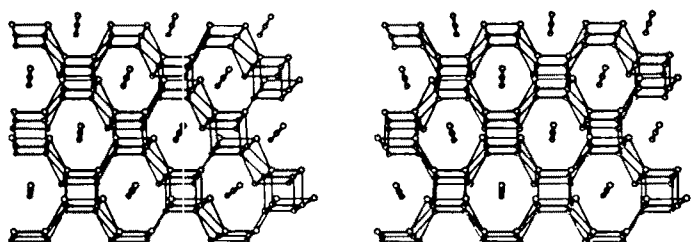


Fig. 3. Stereoview of the 'corrugated sheet' network of short (<3.6 Å) interstack S...S contacts with the embedded I₃⁻ ions. For clarity, only the S atoms of EDTTTF are shown. The coordinates of (I) have been used.

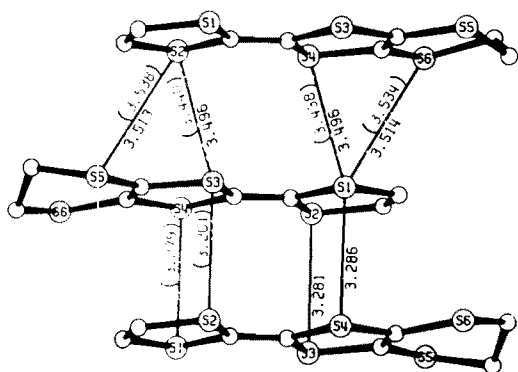


Fig. 4. S...S contacts (<3.6 Å) for (I); those for (II) are in parentheses.

tacts (Figs. 3 and 4), which form a sheet network of donors (Fig. 3) reminiscent of the 'corrugated sheet' network observed in β -(ET)₂I₃-type superconductors (Williams & Carneiro, 1986). The intradimer packing is of the α mode (donor molecules stack directly onto each other with a displacement along the long molecular axis) and 'interstack' packing of the L mode (Fig. 3) (Wang *et al.*, 1986), which is also reminiscent of β -(ET)₂I₃-type superconductors. Salts like the present ones with 1:1 compositions are, however, generally expected to be insulators. The variation of conductivity (σ) of these salts with respect to T was measured (Terzis, Hountas *et al.*, 1988). They behave as semiconductors below room temperature (RT), they have low σ_{RT} ($\approx 2 \times 10^{-3} \Omega^{-1} \text{ cm}^{-1}$), but they show a clear tendency towards a temperature-independent conductivity above RT. It is possible that the composition is not exactly 1:1 but rather (DONOR)_{1-x}I_{3-x} (x being close to zero). One is tempted to suggest that, taking into account the αL mode of packing the donor-sheet networks and the strong S...S contacts, if we could increase x by some means the conductivity would increase markedly.

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