

A planar arrangement has been observed for the N—C(O)—N unit and its nitrogen substituents in other isourea structures, with widely varying degrees of out-of-plane twist of the *O*-substituent (Plastas & Stewart, 1969; Brown & Meyers, 1970; Einstein & Field, 1979; Hegarty, McCormack, Brady, Ferguson & Roberts, 1980). In the simplest structure, that of [(H₂N)₂COCH₃]Cl (White & Mason, 1970; Brown & Meyers, 1970), the methyl substituent on oxygen also lies essentially in the molecular plane, as in the present case, with electronic effects not over-ridden by steric factors.

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Structures of the Conducting Salts of Pyrazinoethylenedithiotetrafulvalene (PEDTTTF) and Dimethylpyrazinoethylenedithiotetrafulvalene (DMPEDTTTF): β -(PEDTTTF)₃I₃ and β -(DMPEDTTTF)₃I₃

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Abstract. (A): 2-(Dithiolo[4,5-*b*]dithiin-2-ylidene)-dithiolo[4,5-*b*]pyrazinium iodide, (C₁₀H₆N₂S₆)I, *M_r* = 473.48, triclinic, *P* $\bar{1}$, *a* = 8.179 (2), *b* = 5.588 (1), *c* = 16.735 (2) Å, α = 104.75 (1), β = 89.02 (2), γ = 104.82 (2)°, *V* = 714.1 Å³, *Z* = 2, *D_m* = 2.16, *D_x* = 2.201 g cm⁻³, Cu *K*α, λ = 1.54178 Å, μ = 256.4 cm⁻¹, *F*(000) = 458, *T* = 296 (2) K. (B): 2-(Dithiolo[4,5-*b*]dithiin-2-ylidene)-5,6-dimethyldithiolo[4,5-*b*]pyrazinium iodide, (C₁₂H₁₀N₂S₆)I, *M_r* = 501.50, monoclinic, *C*2, *a* = 34.943 (3), *b* = 6.610 (1), *c* = 7.335 (1) Å, β = 92.13 (1)°, *V* = 1693.0 Å³, *Z* = 4, *D_m* = 2.00, *D_x* = 1.967 g cm⁻³, Cu *K*α, λ = 1.54178, μ = 216.7 cm⁻¹, *F*(000) = 980, *T* = 296 (2) K. Final *R* values are 0.045 (A) and 0.025 (B) for 2126 and 1615 reflections. Anions in both structures are disordered in the *b* direction. Cations pack side by side, in a planar arrangement, through S··S and S··N contacts, the

shortest of which are S··S = 3.427, S··N = 3.315 (A), S··S = 3.375 Å (B). There is also partial (A) to good (B) stacking and intrastack S··S contacts of 3.724 (A) and 3.638 Å (B).

Introduction. With the discovery (Yagubskii, Shchegolev, Laukhin, Kononovich, Kartsovnik, Zvarykina & Buravov, 1984) of superconductivity at ambient pressure in the first sulfur-based organic metal, β -(ET)₂I₃, attempts are being made to modify the structural and physical properties of this material. One approach is to substitute the triiodide anion systematically by various other trihalide anions of differing sizes and polarizabilities (Leung, Emge, Schultz, Beno, Carlson, Wang, Firestone & Williams, 1986). Another approach is to modify the cation (Terzis, Hountas & Papavassiliou, 1986). In this paper we further modified the donor and report on the structures of the title compounds.

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Experimental. Title compounds were prepared by direct reaction of the donor with Bu₄NI in CH₂Cl₂ and slow evaporation of the solvent. Color golden metallic (*A*) and golden-green metallic (*B*). [Both compounds could also be prepared by electrocrystallization and in the case of (*A*) golden as well as black metallic crystals appeared on the Pt electrode.] The donors were prepared according to Papavassiliou, Yiannopoulos & Zambounis (1986).

Crystals are elongated hexagonal plates and data crystals were 0.03 × 0.14 × 0.46 mm (*A*) and 0.04 × 0.11 × 0.35 mm (*B*). *D_m* by flotation in CHCl₃/C₂H₄Br₂. Intensity data collected on a Syntex P2₁ computer-controlled diffractometer. Lattice parameters from 15 intermediate sinθ reflections. Data in range 2θ < 120° [range of *hkl*: -9→8, 0→6, -18→18 (*A*); -41→41, -7→0, 0→8 (*B*)], ω/2θ scan mode, scan speed 2-15° (2θ) min⁻¹, scan width 1.8° (2θ) plus α₁-α₂ divergence. Three reflections monitored periodically showed < 3.0% intensity fluctuation, Lorentz-polarization and analytical absorption corrections performed [*T_{min}*/*T_{max}* 0.06/0.52 (*A*), 0.12/0.43 (*B*)] with SHELX76 (Sheldrick, 1976). Data collected/unique/*R_{int}*, 2397/2126/0.014 (*A*), 1750/1615/0.018 (*B*). All data used. Structures solved by Patterson search method. Full-matrix refinement based on *F* with SHELX76 minimizing ∑w(|*F_o*| - |*F_c*|)², w = 1/(σ² + 0.001|*F_o*|²) from counting statistics, H (calculated) isotropic riding on carbons at 1.01 Å. Refinement converged (*A*): *R* = 0.045, *wR* = 0.063, *S* = 1.84, |Δ/σ|_{max} = 0.52 (disordered atoms), (Δρ)_{max}/(Δρ)_{min} 0.4/-0.4 e Å⁻³ and (*B*): *R* = 0.025, *wR* =

0.030, *S* = 0.62, |Δ/σ|_{max} = 0.42 (disordered atoms), (Δρ)_{max}/(Δρ)_{min} 0.5/-0.4 e Å⁻³. All 'large' peaks in final difference map around I atoms. Atomic scattering factors from *International Tables for X-ray Crystallography* (1974). The final atomic parameters are given in Table 1,* bond lengths and angles in Fig. 1. Other enantiomorph (*B*) tested and rejected on basis of final *R* = 0.029, *wR* = 0.037 and several very bad bond distances.

Discussion. In both structures rotation photographs, around the *b* axis (*A*) and *c* axis (*B*), showed weak diffuse layer lines in addition to the Bragg layer lines. The diffuse lines are so weak that it is difficult to find with certainty a relation *b'n = bm* (*A*) or *c'n = cm* (*B*) for *n* and *m* integers for a possible superstructure [the approximate values are in (*A*) *n* = 12 and *m* = 7 and in (*B*) *n* = 1, *m* = 3]. In both structures the I₃⁻ is disordered so we cannot be certain that we do not have I⁻ and I₂ instead. The resonance Raman spectra however clearly show the intense fundamental (109 cm⁻¹) and overtone progression of I₃⁻. The presence of molecular I₂ (*ca* 180-205 cm⁻¹) would be easily detectable by resonance Raman spectroscopy as was shown in (phenacetin)₂H⁺I₃⁻I₂ where peaks at 120s and 187vs cm⁻¹ were observed (Herbstein & Kapon,

* 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 44238 (22 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Fractional coordinates (×10⁴) and equivalent isotropic temperature factors (Å² × 10³) with e.s.d.'s in parentheses

$$U_{eq} = \frac{1}{3}(U_{11} + U_{22} + U_{33}).$$

	(A)			<i>U_{eq}</i>	(B)			<i>U_{eq}</i>
	<i>x</i>	<i>y</i>	<i>z</i>		<i>x</i>	<i>y</i>	<i>z</i>	
I(1)	267 (2)	1457 (4)	32 (1)	102 (8)	-2506.3 (9)	-251 (6)	7 (5)	59 (1)
I(2)	9849 (3)	3632 (4)	25 (1)	95 (8)	-2477 (1)	-786 (5)	-74 (6)	77 (1)
I(3)	0	0	0	129 (12)	-2424.6 (8)	345.8	85 (5)	77 (1)
I(4), C(11)	0	5000	0	97 (12)	1859 (1)	2296 (7)	-5468 (8)	70 (1)
I(5), C(12)	0	7500	0	107 (11)	2074 (1)	-2073 (7)	-5068 (8)	60 (2)
S(1)	1037 (1)	7341 (2)	4507 (1)	33.8 (4)	473.2 (3)	222 (2)	-6878 (2)	54.1 (6)
S(2)	3352 (1)	12435 (2)	4549 (1)	34.0 (4)	688.6 (3)	-4114 (2)	-6437 (2)	44.6 (5)
S(3)	2323 (1)	7837 (2)	6344 (1)	34.3 (4)	-381.3 (3)	-1076 (2)	-8004 (2)	52.8 (5)
S(4)	4663 (1)	12860 (2)	6407 (1)	36.7 (4)	-176.2 (3)	-5369 (2)	-7639 (2)	48.6 (5)
S(5)	3057 (2)	7873 (2)	8053 (1)	52.5 (5)	-1187.0 (3)	-1820 (2)	-9188 (2)	49.9 (5)
S(6)	6025 (1)	13733 (2)	8107 (1)	46.4 (5)	-927.4 (4)	-6917 (2)	-8815 (3)	83.7 (7)
N(1)	-99 (4)	7150 (5)	3000 (2)	34 (1)	1209 (1)	1179 (5)	-6101 (6)	48 (1)
N(2)	2081 (4)	11979 (5)	3040 (2)	38 (1)	1409.1 (8)	-2895 (6)	-5717 (5)	44 (1)
C(1)	-35 (4)	8255 (6)	2374 (2)	40 (1)	1572 (1)	619 (6)	-5682 (6)	45 (1)
C(2)	1019 (4)	10610 (7)	2391 (2)	42 (1)	1669 (1)	-1422 (6)	-5513 (6)	45 (1)
C(3)	941 (4)	8488 (6)	3635 (2)	30 (1)	955 (1)	-288 (7)	-6286 (5)	43 (1)
C(4)	2037 (4)	10915 (6)	3656 (2)	30 (1)	1052 (1)	-2312 (5)	-6107 (5)	36 (1)
C(5)	2537 (4)	10026 (6)	5055 (2)	28 (1)	336 (1)	-2308 (6)	-6986 (6)	41 (1)
C(6)	3113 (4)	10226 (6)	5841 (2)	29 (1)	-27 (1)	-2849 (6)	-7472 (5)	42 (1)
C(7)	3511 (4)	9448 (6)	7270 (2)	35 (1)	-740 (1)	-2841 (6)	-8556 (5)	43 (1)
C(8)	4611 (4)	11744 (6)	7293 (2)	33 (1)	-644 (1)	-4797 (6)	-8402 (5)	43 (1)
C(9A)	4110 (9)	10100 (9)	8977 (5)	69 (1)	-1488 (2)	-4000 (10)	-8870 (10)	58 (2)
C(10A)	5730 (9)	11800 (9)	8825 (5)	86 (1)	-1355 (2)	-5850 (10)	-9833 (9)	57 (2)
C(9B)	4790 (8)	9834 (9)	8793 (4)	57 (1)	-1457 (3)	-4090 (10)	-9820 (10)	51 (2)
C(10B)	4949 (7)	12686 (9)	8955 (3)	43 (1)	-1389 (3)	-5890 (10)	-8510 (10)	58 (2)

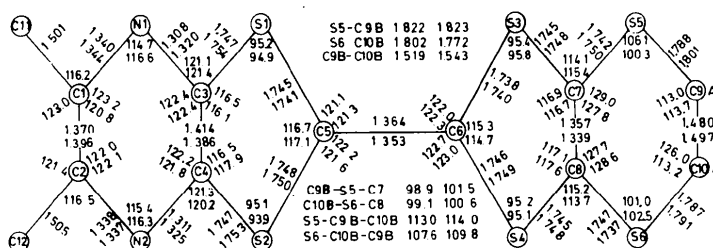
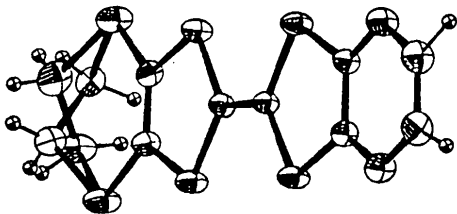


Fig. 1. Atom numbering and bond distances and angles. Top numbers refer to (A), bottom numbers to (B). E.s.d.'s involving S atoms: 0.003–0.004 Å for distances, 0.2° for angles; involving disordered C(9)–C(10): 0.006–0.009 Å, 0.4–0.9°; all others: 0.004–0.005 Å, 0.3–0.4°.

1972). So we can be quite certain none or very little (less than 8% of the total) I is in the form of I^- and I_2 and in our refinement models we assumed the presence of I_3^- only. In trying to find an I_3^- model for refinement we strove for a satisfactory final difference map, internal consistency in the site occupancies and reasonable anisotropic temperature factors and bond distances and angles. In (B) the final model has bond lengths of 2.952 (6) and 2.921 (5) Å for I(1)–I(2) and I(1)–I(3) respectively and an I(2)–I(1)–I(3) angle of 174°. All three I atoms have site occupation factors of 0.3333. In (A) a difference map, calculated with a model that contained all the mass except the I atoms, showed two large broad peaks ($13 e \text{ \AA}^{-3}$) at $y = 0.17$ and 0.34 ($x \approx z \approx 0.0$) but there was high electron density (never lower than $6 e \text{ \AA}^{-3}$) along the whole y axis. A larger number of I positions had to be used.

The five I atoms (Table 1) I(1) to I(5) have site occupation factors 0.29, 0.29, 0.11, 0.11, 0.20 respectively and satisfied the above criteria. Three different I_3^- models are generated: I(3)–I(4)–I(3) ($x, 1+y, z$) and I(5) ($x, 1-y, z$)–I(5)–I(5) ($x, 2-y, z$) with bond length 2.794 Å and angle 180°, I(1)–I(2) ($1-x, 1-y, z$)–I(1) ($x, 1+y, z$) with bond lengths 2.796 (4) and 2.798 (4) Å and angle 174.8 (4)°. There is a further disorder in both structures at the ethylene group C(9)–C(10) (Fig. 1). This disorder is evident in many ET-based structures (Leung *et al.*, 1986). The difference map shows two positions, A and B, for the ethylene group. The site occupancies for the two positions were refined, keeping the sum of the two constant at 1. They refined to 0.40 (A) and 0.65 (B) for position A. This disorder is illustrated below.



In both structures the cations pack side by side and we observe strong S...S contacts (3.5 Å) in the plane of the molecules (Fig. 2) and weaker S...S intrastack contacts [<3.80 Å (A); <3.72 Å (B)] (Fig. 3). In

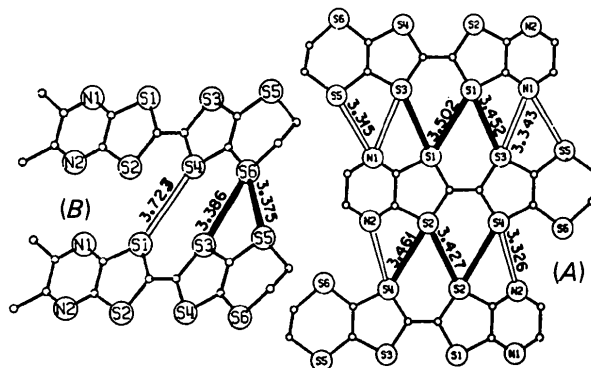


Fig. 2. Planar arrangement of donors and S...S and S...N contacts.

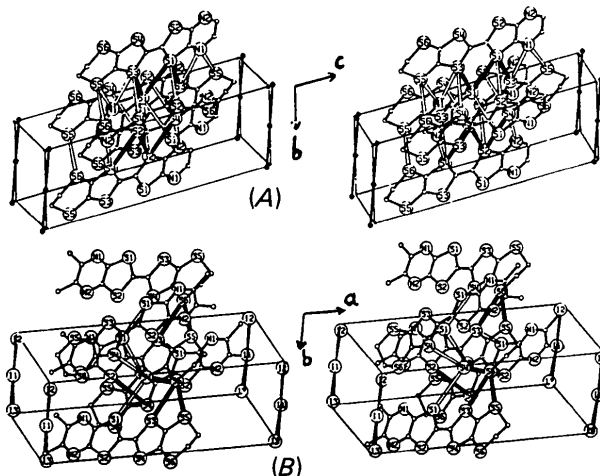


Fig. 3. Stereofigures of (A) and (B). In (B) only half of the a axis is shown.

neither structure do we observe strong S...N contacts (<3.25 Å) although there are weak S...N contacts in (A) (<3.33 Å). Stacking is marginal in (A) and quite good in (B) (Fig. 4). Although the donor molecules are sulfur-based (TTF) similar to ET, their packing is more reminiscent of the selenium-based (TMTSF) $_2X$ salts. In the β -(ET) $_2I_3$, β -(ET) $_2IBr_2$ and (ET) $_2X$ ($X = BrO_4^-$ and ReO_4^-) salts there is 'dimerization' in the stacks and the stacks pack out of phase, which generates the two-dimensional 'corrugated-sheet network' of S...S con-

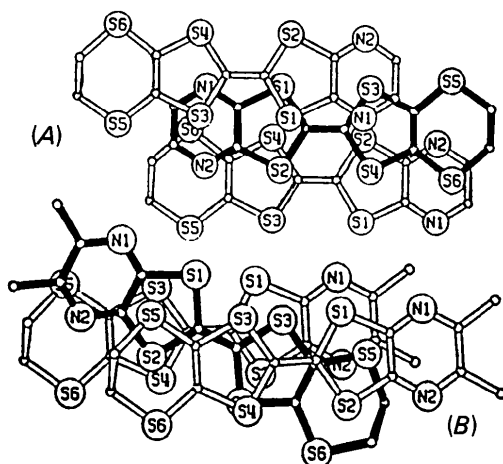


Fig. 4. Projections showing overlap of donors.

tacts (Williams & Carneiro, 1986). In the present structures as with the $(TMTSF)_2X$ salts, while there is no dimerization, the stacks are in phase, which leads to the two-dimensional 'sheet network' of $S \cdots S$ contacts here and $Se \cdots Se$ contacts in $(TMTSF)_2X$ salts (Williams & Carneiro, 1986).

Substitution of the methyl groups (*B*) for the pyrazino hydrogen atoms (*A*) has had the following effects on the packing of the donor molecules: (*a*) the relationship of the neighbors in the plane of the molecule is centrosymmetric in (*A*) and translational in (*B*) (Fig. 2); (*b*) there is better stacking in (*B*) (Fig. 4); and (*c*) there are better intra- and interstack $S \cdots S$ contacts in (*B*) (Figs. 2 and 3). These are dramatic changes since it is known (Williams & Carneiro, 1986)

that minute differences in crystallographic structure are translated into differences in physical behavior.

The I_3^- ions are probably involved in weak van der Waals interactions with the hydrogen atoms but because of the anion disorder we will not discuss them here. The major reason for this anion disorder is probably their mode of packing. They pack in a head-to-tail arrangement almost on a straight line along the *b* axis which probably is not conducive to pinning them down. Preliminary conductivity measurements give $\sigma_{RT} \approx 1-50 \Omega^{-1} \text{ cm}^{-1}$.

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Structures of the Conducting Salts of Pyrazinoethylenedithiotetrafulvalene (PEDTTTF) and [4,5-*b*]Pyridinoethylenedithiotetrafulvalene ([4,5-*b*]PEDTTTF): α -(PEDTTTF) $_2$ IBr $_2$ and α -([4,5-*b*]PEDTTTF) $_2$ IBr $_2$

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Abstract. (I): Bis{2-(dithiolo[4,5-*b*]dithiin-2-ylidene)-dithiolo[4,5-*b*]pyrazinium} dibromiodide, $(C_{10}H_6N_2S_6)_2IBr_2$, $M_r = 979.86$, triclinic, $P\bar{1}$, $a = 8.847$ (1),

$b = 5.671$ (1), $c = 15.818$ (2) Å, $\alpha = 98.44$ (1), $\beta = 89.66$ (1), $\gamma = 107.13$ (1)°, $V = 749.6$ Å³, $Z = 1$, $D_m = 2.20$, $D_x = 2.170$ g cm⁻³, $Cu K\alpha$, $\lambda = 1.54178$ Å, $\mu = 192.03$ cm⁻¹, $F(000) = 475$, $T = 296$ (2) K. (II): Bis{2-(dithiolo[4,5-*b*]dithiin-2-ylidene)dithiolo[4,5-*b*]-

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