

Fig. 1. Atomic labelling in the BEDT-TTF molecule.

**Related literature.**  $\beta$ -(BEDT-TTF)<sub>2</sub>AuI<sub>2</sub> is an ambient-pressure superconductor with  $T_c \approx 5$  K (Wang *et al.*, 1985; Carlson *et al.*, 1986; Amberger, Fuchs & Polborn, 1985; Heidmann, Veith, Andres, Fuchs, Polborn & Amberger, 1986; Talham, Kurmoo, Day, Obertelli, Parker & Friend, 1986; Schwenk, Parkin, Lee & Greene, 1986). For a review of superconductivity in organic compounds, see Williams, Beno, Wang, Leung, Emge, Geiser & Carlson (1985). Organic conductors very often exhibit low-temperature phase transitions, *i.e.* the modulated structure of the superconductor  $\beta$ -(BEDT-TTF)<sub>2</sub>I<sub>3</sub> [which at room temperature is isostructural to  $\beta$ -(BEDT-TTF)<sub>2</sub>AuI<sub>2</sub>] below 175 K (Leung, Emge, Beno, Wang, Williams, Petricek & Coppens, 1985). Since the interesting physical properties in these materials appear at low temperatures, it is essential to know their crystal structures at such temperatures. In addition, the detailed analysis of structure-properties relationships (*e.g.* band electronic structures, non-bonded donor-to-anion interactions, electron-phonon coupling) require accurate positional parameters which, because of reduced thermal motion, can only be obtained at low temperatures and for this reason this low-temperature study was carried out. In the title compound we find no evidence of any structural change except for a lattice contraction between 298 K (Wang *et al.*, 1985) and 120 K. The present structure determination is more accurate than the room-temperature study, as evidenced by the better

agreement factors ( $R = 0.043$ ,  $wR = 0.033$  at 298 K) and a reduction in the bond length and angle e.s.d.'s by *ca* 25%. The major difference is found in the intermolecular S...S contacts which are important for electrical conduction. The S...S distances listed in Table 2 are reduced by 0.046–0.087 Å from their room-temperature values.

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## Structure of 3,4;3',4'-Bis(propylenedithio)-2,2',5,5'-tetrathiafulvalene (BPDT-TTF)

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**Abstract.** C<sub>12</sub>H<sub>12</sub>S<sub>8</sub>,  $M_r = 412.7$ , monoclinic,  $P2_1/c$ ,  $a = 10.484$  (1),  $b = 12.308$  (1),  $c = 13.040$  (2) Å,  $\beta = 96.553$  (9)°,  $V = 1671.7$  (3) Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 1.64$  Mg m<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.71073$  Å,  $\mu = 1.013$  mm<sup>-1</sup>,  $F(000) = 848$ ,  $T = 298$  K. The structure of the neutral organic electron donor molecule, BPDT-

TTF, is reported. The overall structure of this product is that of a twisted chair containing fused five- and seven-atom heterocyclic rings. The molecules are arranged in sheets in the lattice and do not display any unusual intermolecular contacts. Convergence to conventional  $R$  values of  $R = 0.060$  and  $wR = 0.036$  was obtained using 2952 averaged reflections with  $F_o > 0.0$  and 354 variable parameters.

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**Experimental.** BPDT-TTF was prepared by  $(\text{EtO})_3\text{P}$ -induced coupling of 4,5-propylenedithio-1,3-dithiole-2-thione (Mizuno, Garito & Cava, 1978). Crystals suitable for X-ray analysis obtained by crystallization from chlorobenzene. Orange rectangular prism of dimensions  $0.232 \times 0.48 \times 0.058$  mm bounded by the faces (100),  $(\bar{1}00)$ ,  $(01\bar{1})$ ,  $(0\bar{1}1)$ ,  $(011)$  and  $(0\bar{1}\bar{1})$ . Monoclinic symmetry suggested on the basis of interaxial angles and confirmed by axial rotation photographs. Refined cell parameters obtained from the setting angles of 25 reflections with  $30 \leq 2\theta \leq 35^\circ$ . Data collection carried out at ambient temperature using the  $\omega$ -scan technique in bisecting geometry (Nicolet P3F diffractometer, graphite monochromator,  $\text{Mo K}\alpha$  radiation). 6475 reflections measured with  $4 \leq 2\theta \leq 50^\circ$  ( $+h, \pm k, \pm l, h \leq 12, |k| \leq 14, |l| \leq 15$ ) and averaged to give 2952 unique reflections ( $wR_{\text{int}} = 0.023$ ). Scan rate variable,  $2\text{--}30^\circ \text{ min}^{-1}$ ; scan range,  $-0.8$  in  $\omega$  from  $K\alpha_1$  to  $+0.8$  from  $K\alpha_2$ . Backgrounds estimated from a 96-step peak profile. Three standards ( $2\bar{3}\bar{1}$ ,  $2\bar{1}\bar{2}$ ,  $\bar{1}21$ ) measured every 97 data; no significant variations. Data corrected for absorption, Lorentz and polarization effects. Absorption corrections applied using a Gaussian quadrature procedure following accurate measurement of crystal dimensions and assignment of indices to crystal faces. Minimum and maximum transmission 0.464 and 0.890 respectively. Structure solution and refinement carried out using a locally modified version of the *UCLA Crystallographic Program Package* (Strouse, 1978). S positions from *MULTAN78* (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978); C and H from difference Fourier maps. All non-hydrogen atoms refined anisotropically. Refinement based on  $F$  with weights of the form  $w^{-1} = \sigma(F_o)^2$  where  $\sigma(F_o) = [\sigma(F_o^2)^2 + (0.02F_o^2)^2]^{1/2}/2F_o$ . Neutral atomic scattering factors, including terms for anomalous dispersion, taken from *International Tables for X-ray Crystallography* (1974). Convergence to conventional  $R$  values of  $R = 0.060$  and  $wR = 0.036$  with a goodness-of-fit indicator of 1.108 obtained using 2952 reflections with  $F_o > 0.0$  and 354 variable parameters. Max. shift/ $\sigma$  for final cycle 0.13. Difference Fourier map calculated after last cycle of refinement essentially featureless with a maximum residual electron density of  $0.54 \text{ e } \text{\AA}^{-3}$ . A

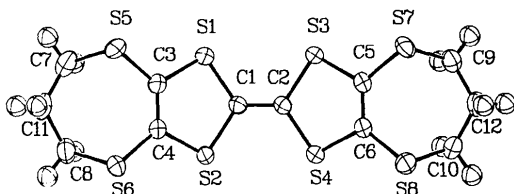


Fig. 1. A view of the BPDT-TTF molecule illustrating the atomic numbering scheme. Thermal ellipsoids have been drawn at the 50% probability level.

perspective view of the BPDT-TTF molecule is shown in Fig. 1. Atomic positional parameters, bond distances and angles are summarized in Tables 1 and 2.\* Fig. 2 is a stereoview showing the packing.

\* Lists of structure factors, H-atom coordinates and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43645 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Fractional coordinates and equivalent isotropic thermal parameters

The complete temperature factor is  $\exp[-8\pi^2 U_{\text{eq}}(\sin^2\theta)/\lambda^2]$ , where  $U_{\text{eq}} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$  in units of  $\text{\AA}^2$ .

	x	y	z	$U_{\text{eq}} (\times 10^4)$
C1	0.9047 (3)	0.5917 (2)	0.0517 (2)	296 (9)
C2	0.8261 (3)	0.6116 (2)	-0.0348 (2)	308 (9)
C3	0.9838 (3)	0.5395 (2)	0.2392 (2)	320 (9)
C4	1.0574 (3)	0.6236 (2)	0.2182 (2)	325 (9)
C5	0.6844 (3)	0.7270 (2)	-0.1661 (2)	356 (10)
C6	0.6101 (3)	0.6437 (2)	-0.1448 (2)	314 (9)
C7	1.1398 (3)	0.4286 (3)	0.3930 (3)	473 (12)
C8	1.2820 (3)	0.5880 (3)	0.3507 (3)	434 (12)
C9	0.5680 (4)	0.7968 (3)	-0.3582 (3)	558 (14)
C10	0.4228 (4)	0.6375 (3)	-0.3173 (3)	509 (13)
C11	1.2407 (4)	0.5124 (3)	0.4319 (3)	476 (12)
C12	0.4347 (4)	0.7496 (3)	-0.3650 (3)	528 (13)
S1	0.88212 (7)	0.48409 (6)	0.13595 (6)	334 (2)
S2	1.04437 (7)	0.66786 (6)	0.08895 (6)	353 (2)
S3	0.84926 (7)	0.71802 (6)	-0.12106 (6)	376 (3)
S4	0.68692 (7)	0.53500 (6)	-0.07377 (6)	331 (2)
S5	0.97733 (8)	0.47840 (8)	0.35940 (6)	458 (3)
S6	1.16797 (8)	0.69369 (7)	0.30517 (6)	422 (3)
S7	0.63670 (8)	0.84621 (7)	-0.23295 (7)	496 (3)
S8	0.44443 (7)	0.62897 (7)	-0.17704 (6)	423 (3)

Table 2. Interatomic distances ( $\text{\AA}$ ) and angles ( $^\circ$ ) with e.s.d.'s in parentheses

C1-C2	1.341 (4)	C5-S7	1.750 (3)
C3-C4	1.338 (4)	C6-S8	1.750 (3)
C5-C6	1.335 (4)	C8-C11	1.510 (5)
C7-C11	1.522 (5)	C10-S8	1.820 (4)
C8-S6	1.820 (3)	C1-S2	1.760 (3)
C10-C12	1.524 (5)	C2-S4	1.763 (3)
C7-S5	1.817 (4)	C3-S1	1.757 (3)
C9-S7	1.814 (4)	C4-S2	1.762 (3)
C1-S1	1.754 (3)	C5-S3	1.764 (3)
C2-S3	1.761 (3)	C6-S4	1.768 (3)
C3-S5	1.746 (3)	C9-C12	1.507 (5)
C4-S6	1.753 (3)		
C2-C1-S1	123.4 (2)	C2-C1-S2	123.1 (2)
S1-C1-S2	113.4 (2)	C1-C2-S3	123.8 (2)
C1-C2-S4	123.6 (2)	S3-C2-S4	112.6 (2)
C4-C3-S5	126.8 (2)	C4-C3-S1	117.2 (2)
S5-C3-S1	116.0 (2)	C3-C4-S6	127.0 (2)
C3-C4-S2	116.9 (2)	S6-C4-S2	116.1 (2)
C6-C5-S7	127.4 (2)	C6-C5-S3	117.1 (2)
S7-C5-S3	115.6 (2)	C5-C6-S8	128.0 (2)
C5-C6-S4	116.7 (2)	S8-C6-S4	115.3 (2)
C11-C7-S5	116.6 (3)	C11-C8-S6	116.0 (2)
C12-C9-S7	116.9 (3)	C12-C10-S8	117.1 (3)
C8-C11-C7	115.3 (3)	C9-C12-C10	116.3 (3)
C1-S1-C3	94.21 (13)	C1-S2-C4	94.03 (13)
C2-S3-C5	93.33 (13)	C2-S4-C6	93.37 (13)
C3-S5-C7	103.3 (2)	C4-S6-C8	102.7 (2)
C5-S7-C9	103.2 (2)	C6-S8-C10	104.0 (2)

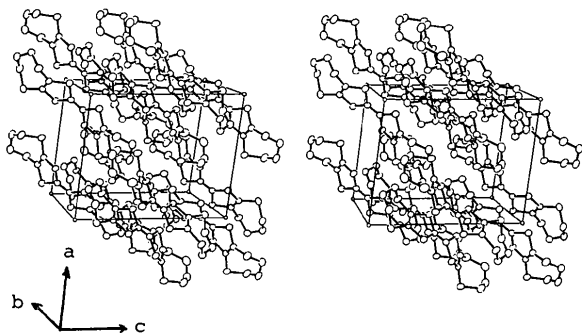


Fig. 2. A stereoview packing diagram of the unit cell of BPDT-TTF. Hydrogen atoms have been omitted for clarity.

**Related literature.** The X-ray crystal structures and conductivity properties of (BPDT-TTF)<sub>2</sub>I<sub>3</sub> (Kobayashi, Takahashi, Kato, Kobayashi & Sasaki, 1984) and (BPDT-TTF)<sub>3</sub>(PF<sub>6</sub>)<sub>2</sub> (Kato, Mori, Kobayashi, Sasaki & Kobayashi, 1984) have been reported. The subject of tetrathiafulvalene-based organic synthetic metals has been reviewed (Williams, Beno, Wang, Leung, Emge, Geiser & Carlson, 1985).

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## Structural Chirality of (–)-N-(3,4,4-Trimethyl-5-hexenoyl)camphorsultam\*

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**Abstract.** The title compound (I) was obtained by BF<sub>3</sub>OEt<sub>2</sub>-mediated asymmetric 1,4-addition of PBU<sub>3</sub>-stabilized methylcopper to the camphorsultam derivative (*E*)-10,10-dimethyl-4-(4,4-dimethyl-2,5-hexadienoyl)-3-thia-4-azatricyclo[5.2.1.0<sup>1,5</sup>]decane 3,3-dioxide (II). (I): C<sub>19</sub>H<sub>31</sub>NO<sub>3</sub>S, *M<sub>r</sub>* = 353.5, orthorhombic, *P*2<sub>1</sub>2<sub>1</sub>2, *a* = 11.628 (2), *b* = 21.310 (7), *c* = 8.0574 (12) Å, *V* = 1996.6 (8) Å<sup>3</sup>, *Z* = 4, *D<sub>x</sub>* = 1.176 g cm<sup>-3</sup>, λ(Mo *Kα*) = 0.71069 Å, μ = 1.692 cm<sup>-1</sup>, *F*(000) = 768, m.p. 405–406 K, [α]<sub>D</sub><sup>20°C</sup> = –47.0° (*c* = 1.14% in CHCl<sub>3</sub>), room temperature, *R* = 0.049 for 1334 observed reflections [*|F<sub>o</sub>*| ≥ 3σ(*F<sub>o</sub>*)

and *|F<sub>o</sub>*| ≥ 8.0]. The structural chirality of enantiomerically pure (I) was confirmed from the known absolute configuration of the camphorsultam moiety as well as by least-squares refinement of the absolute-structure parameter *x* = –0.02 (16) [Bernardinelli & Flack (1985). *Acta Cryst.* **A41**, 500–511].

**Experimental.** Single crystals of (I) were grown from an ethanol solution at room temperature. Colourless crystal of average dimensions 0.24 × 0.28 × 0.30 mm; Philips PW 1100 diffractometer, graphite-monochromated Mo *Kα*; cell dimensions from 21 reflections (2θ = 24–36°); data collection: sinθ/λ ≤ 0.505 Å<sup>-1</sup>, *h* 0–10, *k* 0–20, *l* 0–8 and all antireflections of these; ω/2θ scans, ω-scan angle 1.2°; two standard

\* (1*S*,5*R*)-10,10-Dimethyl-4-[(3*R*)-3,4,4-trimethyl-5-hexenoyl]-3-thia-4-azatricyclo[5.2.1.0<sup>1,5</sup>]decane 3,3-dioxide.