DUAX, W. L., WEEKS, C. M. & ROHRER, D. C. (1976). *Topics in Stereochemistry*, Vol. 9, edited by N. L. ALLINGER & E. L. ELIEL, pp. 271–383. New York: John Wiley.
EGGLESTON, D. S. & LAN-HARGEST, H. Y. (1990). *Acta Cryst.* C**46**, 1686–1691.
JOHNSON, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
MARTIN, C. K. A. (1977). *Adv. Appl. Microbiol.* **22**, 29–58.
SHELDRICK, G. M. (1976). *SHELX*76. Program for crystal structure determination. Univ. of Cambridge, England.
SHELDRICK, G. M. (1986). *SHELXS*86. Program for the solution of crystal structures. Univ. of Göttingen, Germany.
WEEKS, C. M., STRONG, P. & OSAWA, Y. (1976). *Cryst. Struct. Commun.* **5**, 915–918.

Acta Cryst. (1992). C**48**, 488–490

Structure of Bis(butylenedithio)tetrathiafulvalene: an Organic π-Donor Molecule

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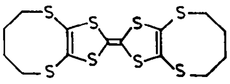
(*Received* 14 *February* 1991; *accepted* 22 *July* 1991)

Abstract. 2,2′-Bi(5,6,7,8-tetrahydro-1,3-dithiolo-[4,5-*b*][1,4]dithiocinylidene) (BBDT-TTF), $C_{14}H_{16}S_8$, $M_r = 440.75$, m.p. = 424 K, monoclinic, $P2_1/c$, $a = 5.233\,(1)$, $b = 14.274\,(4)$, $c = 13.430\,(3)$ Å, $\beta = 109.44\,(2)°$, $V = 944.10$ Å^3, $Z = 2$, $D_x = 1.551$ Mg m^{-3}, λ(Mo $K\alpha$) = 0.7107 Å, μ(Mo $K\alpha$) = 0.857 mm^{-1}, $F(000) = 456$, $T = 288$ K, final $R = 0.0403$, $wR = 0.0400$ for 132 parameters and 2167 observed reflections. The C_6S_8 backbone of the BBDT-TTF molecule is planar and stacked along the *a* axis. Three intermolecular S···S distances [S2···S2$^{\rm i}$ = 3.686 (1), S1···S4$^{\rm ii}$ = 3.668 (1) and S3···S4$^{\rm iii}$ = 3.705 (1) Å; (i) $2 - x$, $1 - y$, $-z$; (ii) $-1 + x$, y, z; (iii) $-1 + x$, $\frac{3}{2} - y$, $-\frac{1}{2} + z$] are close to the sum of the van der Waals radii of sulfur. In the crystal, the molecules are arranged in pairs.

Introduction. Ambient-pressure superconductivity has been observed in several cation-radical salts derived from the neutral organic electron donor bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF) (Parkin, Engler, Schumaker, Lagir, Lee, Scott & Greene, 1983). For the crystal packing, in particular, two-dimensional S···S intermolecular interactions seem to play an important role in allowing the superconducting state at low temperatures (Williams & Kuroda, 1990). Investigations are being undertaken to understand the phenomena and also to increase the transition temperature (T_c) for organic supercoductors. These considerations have prompted the synthesis of the title compound (Kumar, Singh, Das, Sinha & Mishnev, 1991). The present work comprises the crystal structure analysis of BBDT-TTF and a comparative study of its structural parameters with those of related sulfur-containing π-donor molecules.



BBDT-TTF

Experimental. Reaction of 4,5-dimercapto-1,3-dithiole-2-thione disodium salt with 1,4-dibromobutane afforded 4,5-(butylenedithio)-1,3-dithiole-2-thione. The thione was coupled in the presence of triethylphosphite to yield the title compound (Kumar, Singh, Das, Sinha & Mishnev, 1991). The compound was purified by column chromatography (silica gel, CH_2Cl_2) and was recrystallized as dark-orange needles from dichloromethane solution.

A crystal, 0.25 × 0.30 × 0.40 mm, was used for intensity data collection on a Syntex $P2_1$ diffractometer with graphite-monochromated Mo $K\alpha$ ($\lambda = 0.7107$ Å) radiation. The lattice parameters were refined from 25 reflections in the range $8 \le \theta \le 12°$. A total of 2759 unique reflections were scanned, $\omega/2\theta$ mode, in the range $2 \le 2\theta \le 60°$; $0 \le h \le 7$, $0 \le k \le 20$ and $-17 \le l \le 17$. Intensity control reflections (219 and $2,\bar{1},\overline{16}$), checked in 3600 s intervals,

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Table 1. *Atomic coordinates* (× 10^5 *for* S *atoms*, × 10^4 *for remaining non*-H *atoms) and equivalent isotropic temperature factors* U_{eq} ($Å^2 \times 10^3$) *with e.s.d.'s in parentheses*

$$U_{eq} = \tfrac{1}{3}\textstyle\sum_i\sum_j U_{ij}a_i^*a_j^*(\mathbf{a}_i.\mathbf{a}_j).$$

	x	y	z	U_{eq}
S(1)	46335 (13)	57612 (4)	85388 (4)	38 (1)
S(2)	86171 (12)	58774 (4)	106918 (4)	36 (1)
S(3)	73017 (15)	72487 (4)	76689 (5)	45 (1)
S(4)	119298 (12)	73519 (4)	100918 (5)	43 (1)
C(1)	5670 (4)	5337 (1)	9843 (2)	31 (2)
C(2)	7291 (5)	6564 (1)	8754 (2)	34 (2)
C(3)	5661 (7)	8315 (2)	7898 (2)	52 (3)
C(4)	7464 (9)	8978 (2)	8751 (3)	66 (4)
C(5)	7843 (7)	8717 (2)	9888 (2)	55 (3)
C(6)	10633 (6)	8387 (2)	10556 (2)	49 (3)
C(7)	9113 (4)	6613 (1)	9729 (2)	33 (2)

Table 2. *Bond distances* (Å) *and bond angles* (°) *with e.s.d.'s in parentheses*

C(1)—S(1)	1.760 (2)	C(6)—S(4)	1.818 (3)
C(2)—S(1)	1.749 (2)	C(7)—C(4)	1.743 (2)
C(1)—S(2)	1.761 (2)	C(7)—C(2)	1.341 (3)
C(7)—S(2)	1.750 (2)	C(4)—C(3)	1.541 (4)
C(2)—S(3)	1.755 (2)	C(5)—C(4)	1.520 (4)
C(3)—S(3)	1.821 (3)	C(6)—C(5)	1.512 (4)
C(1)—C(1)′	1.337 (4)		

C(2)—S(1)—C(1)	95.5 (1)	C(4)—C(3)—S(3)	115.5 (2)
C(7)—S(2)—C(1)	95.6 (1)	C(5)—C(4)—C(3)	116.1 (3)
C(3)—S(3)—C(2)	101.0 (1)	C(6)—C(5)—C(4)	116.7 (3)
C(7)—S(4)—C(6)	102.0 (1)	C(5)—C(6)—S(4)	116.5 (2)
S(2)—C(1)—S(1)	114.0 (1)	S(4)—C(7)—S(2)	118.3 (1)
S(3)—C(2)—S(1)	116.7 (1)	C(2)—C(7)—S(2)	117.3 (2)
C(7)—C(2)—S(1)	117.6 (2)	C(2)—C(7)—S(4)	124.4 (2)
C(7)—C(2)—S(3)	125.7 (2)		

Table 3. *Important structural parameters for* BBDT-TTF *and three related structures*

	BMDT-TTF	BEDT-TTF	BPDT-TTF	BBDT-TTF
C1═C1′ (Å)	1.327	1.319	1.341	1.337 (3)
S_e/S_i*	0.99	1.16	1.17	1.13
Shape of the C_6S_8 core	Planar	Tub shape	Tub shape	Planar
Minimum intermolecular S···S distance (Å)	3.566	3.688	3.615	3.686 (1)

* S_e and S_i are the distances between the S atoms in exterior and interior rings respectively.

indicated no significant intensity variation. The data were corrected for Lorentz and polarization factors neglecting the effects due to absorption and extinction. The multisolution direct-methods package *SHELXS*86 (Sheldrick, 1985) was used for structure determination. Out of 20 trials with 4265 triplets and 94 quartets, four phase permutations lead to identical solutions with CFOM = 0.021 (the next best phase set had CFOM = 0.14). Positions for all the non-H atoms were found from the first 15 peaks in the *E* map. The H atoms were located from difference Fourier maps. In the final refinement, 132 parameters were refined by least-squares methods using 2167 unique $|F_o|$ values with $|F_o| \geq 3\sigma|F_o|$. All H atoms were refined isotropically whereas the non-H atoms were refined with anisotropic thermal parameters. Final $R = 0.0403$ and $wR = 0.0400$, where $w = 1.000/[\sigma^2(|F_o|) + 0.000344(F_o)^2]$, GOF = 1.3828, $(\Delta/\sigma)_{max} = 0.103$. In the final difference map, the maximum and the minimum electron densities ($\Delta\rho$) were 0.533 and $-0.346\,e\,Å^{-3}$ respectively. *SHELX*76 (Sheldrick, 1976) was used for structure refinement and a CYBER-180/840 computer for all computations. Atomic scattering factors were those imbedded in *SHELX*76.

Discussion. The asymmetric unit contains a half-molecule which is attached to the remaining half (at $1 - x$, $1 - y$, $2 - z$) by a center if inversion. Table 1 contains the list of the positional parameters for all non-H atoms in the asymmetric unit; bond distances

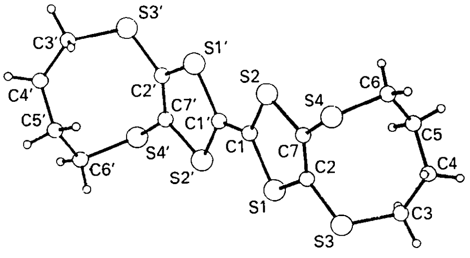

Fig. 1. General view of the molecule.

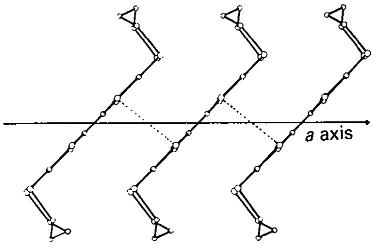

Fig. 2. Stacking of the molecules along the *a* axis.

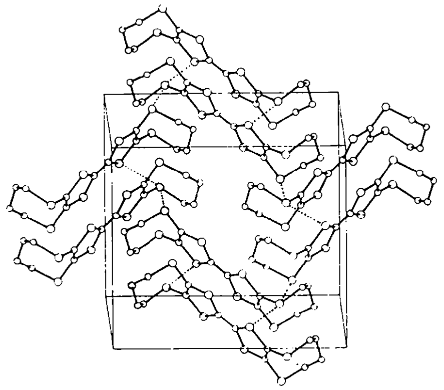

Fig. 3. Unit-cell packing diagram.

with bond angles are in Table 2.* Fig. 1 (Motherwell & Clegg, 1978) shows the stereochemical arrangement of the BBDT-TTF molecule. In the molecule, the C_6S_8 core is highly planar; the maximum deviation being for S(4) [0.039 (5) Å out of the least-squares plane]. An analogous tetrathiafulvalene compound (TTC_8-TTF) reported recently (Nakano, Imaeda, Mori, Maruyama, Inokuchi, Iwasawa & Saito, 1991) also has a planar C_6S_8 core. In the eight-membered exterior ring, atoms S(3), S(4), C(3) and C(6) form a plane (plane 1) within deviations of ±0.039 (5) Å whereas C(4) and C(5) are out of this plane by 0.612 (4) and −0.335 (3) Å respectively. The dihedral angle between the core plane and plane 1 is 78.9 (3)°. The molecules are stacked uniformly as parallel 'Z'-shaped arrays along the *a* axis (Fig. 2). The core planes are inclined to the axis by approximately 45° (66° in the case of BMDT-TTF; Kato, Kobayashi, Kobayashi & Sasaki, 1985). Average $C(sp^3)—S$ and $C(sp^2)—S$ distances are 1.819 (3) and 1.753 (2) Å respectively. Important structural parameters for BBDT-TTF are listed in Table 3 along with those for the analogous sulfur-containing π donors BMDT-TTF, BEDT-TTF (Kobayashi, Kobayashi, Sasaki, Saito & Inokuchi, 1986) and BPDT-TTF (Porter, Kini & Williams, 1987). Similar to BEDT-TTF, BBDT-TTF molecules are arranged in pairs in the crystal (Fig. 3). Three intermolecular S···S distances are close to twice the van der Waals radius of sulfur, 3.70 Å. These distances are $S2\cdots S2^{i} = 3.686\,(1)$, $S1\cdots S4^{ii} = 3.668\,(1)$ and $S3\cdots S4^{iii} = 3.705\,(1)$ Å [(i) $2-x,\ 1-y,\ -z$; (ii) $-1+x,\ y,\ z$; (iii) $-1+x,\ \frac{3}{2}-y,\ -\frac{1}{2}+z$] shown in Figs. 2 and 3 respectively. Electrochemical preparations of the cation-radical salts of BBDT-TTF are in progress.

HBS is grateful to DST for financial support and SKK to CSIR for a fellowship.

References

Kato, R., Kobayashi, H., Kobayashi, A. & Sasaki, Y. (1985). *Chem. Lett.* pp. 1231–1234.

Kobayashi, H., Kobayashi, A., Sasaki, Y., Saito, G. & Inokuchi, H. (1986). *Bull. Chem. Soc. Jpn*, **59**, 301–302.

Kumar, S. K., Singh, H. B., Das, K., Sinha, U. C. & Mishnev, A. (1991). *J. Chem. Soc. Chem. Commun.* **14**, 952–954.

Motherwell, W. D. S. & Clegg, W. (1978). *PLUTO78*. Program for plotting molecular and crystal structures. Univ. of Cambridge, England.

Nakano, C., Imaeda, K., Mori, T., Maruyama, Y., Inokuchi, H., Iwasawa, N. & Saito, G. (1991). *J. Mater. Chem.* **1**(1), 37–41.

Parkin, S. S. P., Engler, E. M., Schumaker, R. R., Lagir, R., Lee, V. Y., Scott, J. C. & Greene, R. L. (1983). *Phy. Rev. Lett.* **50**, 270–273.

Porter, L. C., Kini, A. M. & Williams, J. M. (1987). *Acta Cryst.* C**43**, 998–1000.

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

Sheldrick, G. M. (1985). *SHELXS86*. *Crystallographic Computing* 3, edited by G. M. Sheldrick, C. Kruger & R. Goddard, pp. 175–189. Oxford Univ. Press.

Williams, J. M. & Kuroda, H. (1990). *Mol. Cryst. Liq. Cryst.* **181**, 1–367.

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[*] Lists of structure factors, anisotropic thermal parameters, H-atom parameters and least-squares planes have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54518 (13 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Acta Cryst. (1992). C**48**, 490–492

Front Strain in the Structure of 2-Benzylidene-1,1,3,3-tetramethylindan, a Sterically Congested Styrene*

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(*Received* 6 *June* 1991; *accepted* 9 *July* 1991)

Abstract. $C_{20}H_{22}$, $M_r = 262.4$, monoclinic, $P2_1/c$, $a = 8.331\,(3)$, $b = 21.731\,(6)$, $c = 8.804\,(3)$ Å, $\beta = 95.61\,(2)°$, $V = 1586$ Å^3, $Z = 4$, $D_x = 1.099$ Mg m^{-3}, λ(Mo $K\alpha$) = 0.71069 Å, $\mu = 0.057$ mm^{-1}, $F(000) = 568$, $T = 294\,(1)$ K, $R = 0.047$, $wR = 0.046$ for 2274 observed reflections. The title compound carries a planar phenyl substituent in an orthogonal relationship to the C═C double bond. Front strain along this double bond is relieved mainly by expansion of two olefinic angles.

Introduction. The β,β-di-*tert*-alkyl-substituted 2-benzylidene-1,1,3,3-tetramethylindan (1) was pre-

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[*] Sterically Congested Molecules, 3. Part 2: Knorr & Polborn (1991).

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