Table 5. *Central inter-ring C—C bond lengths (Å) and carbocyclic ring angles C(2)—C(1)—C(n) (°) at the central C(1) atom in the solid state of various 1,1′-(R)(R)-1,1′-bicycloalkyl molecules*

Carbocyclic ring *n*	*R* = nitro	*R* = cyano	*R* = phenyl
3	1.476 (3)*	1.501 (4)‡	1.527 (4)¶
4	1.508 (9)*	–	1.569 (3)¶
5	1.486 (4)†	1.537 (5)§	1.575 (5)**
6	1.579 (3)†	1.582 (10)§	1.627 (5)**
7	1.601 (9)†	1.591 (6)§	1.630 (5)**
8	–	–	1.622††
3	59.1 (1)*	58.6 (2)‡	59.6 (1)¶
4	89.0 (2)*	–	87.3 (1)¶
5	105.4 (3)†	101.9 (2)§	98.9 (3)**
6	110.2 (1)†	108.9 (4)§	105.5 (2)**
7	113.2 (6)†	111.4 (3)§	108.0 (4)**
8	–	–	107.6††

* Kai *et al.* (1982); † Lam, Huang & Hambley (1990); ‡ Schrumpf & Jones (1987); § Koh, Huang & Sim (1992); ¶ this work; ** Zhang *et al.* (1993); †† Bernlöhr *et al.* (1984).

The structures of (1) and (2) were solved by direct methods using *XS* (*SHELXTL-Plus*; Siemens, 1989) and refined by full-matrix least-squares analysis using *XLS* (*SHELX*76: Sheldrick, 1976; *SHELXS*86: Sheldrick, 1985). Data were reduced using the above-mentioned programs. C atoms were refined anisotropically whereas H atoms were placed at calculated positions with fixed isotropic displacement parameters.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: AS1191). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Bis(methylthio)ethylenedithiotetrathiafulvalene

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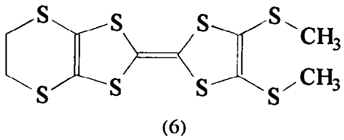
Abstract

The title compound {alternative nomenclature: 2-[4,5-bis(methylthio)-1,3-dithiol-2-ylidene]-5,6-dihydro-1,3-dithiolo[4,5-*b*][1,4]dithiine}, $C_{10}H_{10}S_8$, is a molecular crystal with typical values for bond distances and angles. The molecules form columns along the *c* axis. The intermolecular S···S distances indicate the presence of van der Waals interactions between the columns.

Comment

Many charge-transfer complexes based on donors containing the tetrathiafulvalene (TTF) unit have been reported (Bechgaard *et al.*, 1981; Bender *et al.*, 1984; Karpova, Konovalikhin, Dyachenko, Lyubovskaya & Zhilyaeva, 1992; Mori *et al.*, 1990; Qian *et al.*, 1988; Shibaeva, Kaminskii & Yagubskii, 1985). We have prepared a new organic compound, (6), which is a derivative of TTF.



(6)

The bond distances and angles at S are dependent on the hybridization state of the C atom to which S is bound, so that S—C_{sp^3} is longer than S—C_{sp^2} and the angles are wider in the case of an sp^2-hydridized C

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atom; the values found are similar to those in related molecules such as BEDT-TTF (Kobayashi *et al.*, 1984; Karpova *et al.*, 1992; Shibaeva *et al.*, 1985). With the exception of the methyl and ethylene groups, all the atoms in the molecule lie in one of two planes: plane 1 is defined as containing S3, S4, C1, C2, S1, S2, C3, C4, S5 and S6; plane 2 by S3, S4, C5, C6, S7 and S8. The mean deviations of atoms from these planes are 0.05 and 0.02 Å, respectively. The planes share a common edge defined by S3—S4 and the dihedral angle between them is 24°. In the BEDT-TTF molecule (in its complexes) the situation is somewhat different in that all atoms except those of the ethylene group are coplanar owing to a charge-transfer interaction (Dressel, Eldridge, Wang, Geiser & Williams, 1992; Karpova *et al.*, 1992; Mori *et al.*, 1990; Shibaeva *et al.*, 1985).

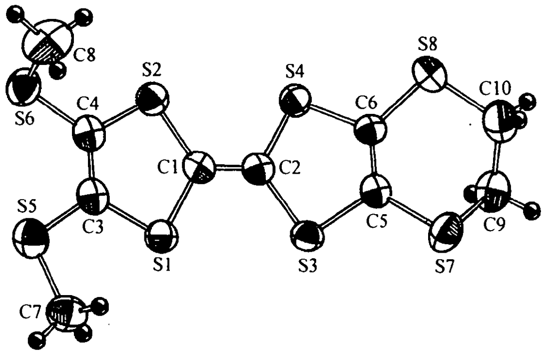


Fig. 1. Molecular structure showing the atom-labelling scheme and 50% probability displacement ellipsoids. Small spheres represent the H atoms.

Molecules are packed face-to-face along the *c* axis and side-by-side along the *a* axis, similar to the packing of BEDT-TTF in β_d-(BEDT-TTF)$_2$I$_3$ (Qian *et al.*, 1988). There are several intermolecular contacts within the relevant van der Waals sum of 3.70 Å [S7···S7^{v} 3.624 (5), S4···S6^{ii} 3.679 (4) and S3···S8^{iii} 3.661 (3) Å; symmetry codes: (ii) $1-x,1-y,-z$; (iii) $x,y,1+z$; (v) $2-x,-y,-z$] which are instrumental in determining the crystal packing.

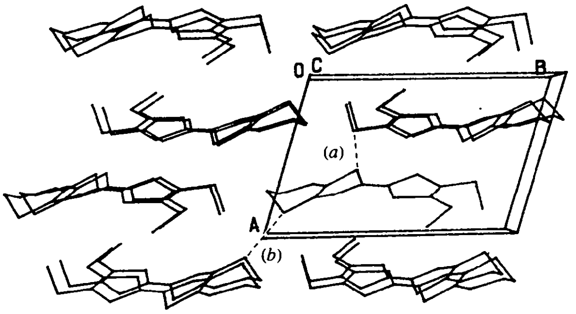
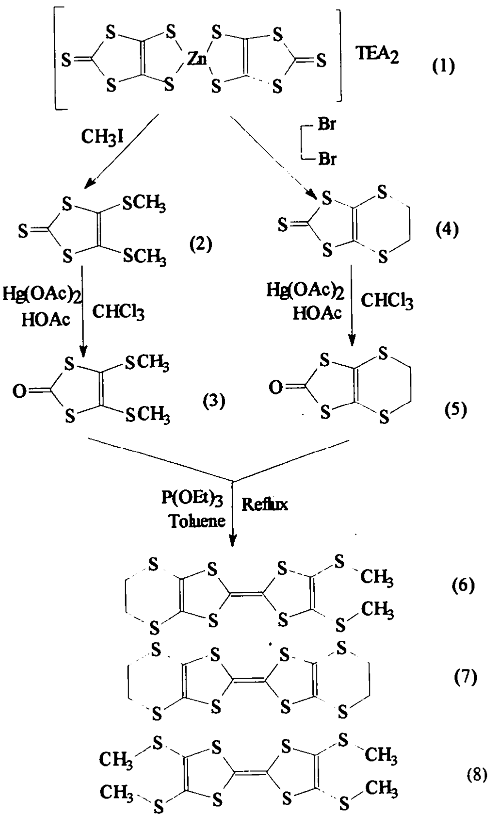


Fig. 2. Packing diagram viewed down the *c* axis. Inter-column contacts are shown as dashed lines: (*a*) S4···S6^{ii} and (*b*) S7···S7^{v}.

Experimental

The procedure for the synthesis of the title compound (6) is as follows:



Compound (3) (2.1 g, 10 mmol) and compound (5) (2.08 g, 10 mmol) were dissolved in anhydrous toluene (200 ml). Triethyl phosphite (60 ml) was added and the resulting mixture refluxed for 3 h before being allowed to stand at room temperature overnight. The solution was filtered and a crop of red crystals of (7) were obtained. The remaining solution was concentrated under reduced pressure and chromatography on silica gel (ethyl acetate:petroleum ether 1:10) gave a small amount of (8) (yellow solid, R_f = 0.5) and 0.3 g of (6) (orange crystals, R_f = 0.28, m.p. = 395–396 K) in 8% yield. Elemental analysis: found C 30.64, H 2.45, S 66.36%; calculated for $C_{10}H_{10}S_8$ C 31.06, H 2.61, S 66.33%. MS (*m*/*z*) 386 (M^+). IR (KBr, cm^{-1}): 2980 (CH$_2$), 2910 (S—C), 1495, 1420, 1405, 1280, 1015, 970, 900, 800, 770, 665. ^{1}H NMR (CDCl$_3$/TMS): δ = 3.39 (*s*, 4H), 2.5 p.p.m. (*s*, 6H). The results of elemental analyses and of the IR, NMR and mass spectra of compounds (3) and (5) correspond to the literature (Stimecke, 1979; Saito, 1986).

Crystal data

$C_{10}H_{10}S_8$
M_r = 386.67
Mo $K\alpha$ radiation
λ = 0.71069 Å

Triclinic
$P\overline{1}$
$a = 8.433\,(2)$ Å
$b = 12.987\,(6)$ Å
$c = 7.743\,(3)$ Å
$\alpha = 98.92\,(4)°$
$\beta = 98.90\,(3)°$
$\gamma = 105.53\,(3)°$
$V = 789.9\,(6)$ Å^3
$Z = 2$
$D_x = 1.63$ Mg m^{-3}
$D_m = 1.60$ Mg m^{-3}
D_m measured by flotation

Cell parameters from 20 reflections
$\theta = 5.85–12.82°$
$\mu = 1.066$ mm^{-1}
$T = 296$ K
Column
$1.0 \times 0.3 \times 0.1$ mm
Orange

Data collection

Rigaku MSC/AFC-5*S* four-circle diffractometer
$\omega/2\theta$ scans
Absorption correction: refined from ΔF (*DIFABS*; Walker & Stuart, 1983)
$T_{\min} = 0.306$, $T_{\max} = 0.665$
2240 measured reflections
2068 independent reflections

1427 observed reflections $[I > 2\sigma(I)]$
$R_{\rm int} = 0.041$
$\theta_{\max} = 22.5°$
$h = 0 \rightarrow 9$
$k = -13 \rightarrow 13$
$l = -8 \rightarrow 8$
3 standard reflections monitored every 151 reflections intensity decay: <2%

Refinement

Refinement on F
$R = 0.060$
$wR = 0.081$
$S = 2.06$
1427 reflections
164 parameters
H-atom parameters not refined
$w = 1/\sigma^2(F)$
$(\Delta/\sigma)_{\max} = 0.002$
$\Delta\rho_{\max} = 0.52$ e Å^{-3}
$\Delta\rho_{\min} = -0.51$ e Å^{-3}

Extinction correction: *TEXSAN* (Molecular Structure Corporation, 1985)
Extinction coefficient: 3.40×10^{-6}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$$B_{\rm eq} = (4/3)\Sigma_i\Sigma_j\beta_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$B_{\rm eq}$
S1	0.7585 (3)	0.4517 (2)	0.5646 (3)	4.03 (9)
S2	0.6169 (3)	0.5230 (2)	0.2466 (3)	3.97 (9)
S3	0.7365 (3)	0.2202 (2)	0.3109 (3)	3.78 (8)
S4	0.5840 (3)	0.2908 (2)	−0.0003 (3)	3.84 (8)
S5	0.8182 (3)	0.6726 (2)	0.8057 (3)	4.9 (1)
S6	0.6669 (3)	0.7489 (2)	0.4519 (3)	4.8 (1)
S7	0.8444 (3)	0.0517 (2)	0.0910 (3)	5.2 (1)
S8	0.6688 (4)	0.1378 (2)	−0.2686 (3)	5.4 (1)
C1	0.682 (1)	0.4205 (6)	0.331 (1)	3.1 (3)
C2	0.671 (1)	0.3247 (6)	0.231 (1)	3.2 (3)
C3	0.756 (1)	0.5875 (6)	0.592 (1)	3.6 (3)
C4	0.693 (1)	0.6208 (6)	0.446 (1)	3.5 (3)
C5	0.754 (1)	0.1578 (6)	0.098 (1)	3.3 (3)
C6	0.681 (1)	0.1885 (6)	−0.044 (1)	3.1 (3)
C7	0.926 (1)	0.5967 (8)	0.934 (1)	5.3 (4)
C8	0.839 (1)	0.8137 (9)	0.352 (2)	7.1 (5)
C9	0.706 (1)	−0.0394 (7)	−0.112 (1)	4.7 (4)
C10	0.729 (1)	0.0139 (8)	−0.273 (1)	6.0 (4)

Table 2. *Selected geometric parameters (Å, °)*

S1—C3	1.750 (8)	S6—C4	1.730 (8)
S1—C1	1.770 (8)	S6—C8	1.82 (1)
S2—C1	1.746 (8)	S7—C5	1.739 (8)
S2—C4	1.750 (8)	S7—C9	1.828 (9)
S3—C2	1.756 (8)	S8—C6	1.737 (8)
S3—C5	1.766 (7)	S8—C10	1.81 (1)
S4—C6	1.756 (8)	C1—C2	1.33 (1)
S4—C2	1.766 (8)	C3—C4	1.35 (1)
S5—C3	1.755 (8)	C5—C6	1.35 (1)
S5—C7	1.82 (1)	C9—C10	1.53 (1)
C3—S1—C1	94.8 (4)	C4—C3—S1	117.5 (6)
C1—S2—C4	95.5 (4)	C4—C3—S5	122.1 (6)
C2—S3—C5	93.6 (4)	S1—C3—S5	120.3 (5)
C6—S4—C2	94.1 (4)	C3—C4—S6	123.8 (6)
C3—S5—C7	102.2 (4)	C3—C4—S2	117.0 (6)
C4—S6—C8	101.2 (5)	S6—C4—S2	119.0 (5)
C5—S7—C9	98.6 (4)	C6—C5—S7	125.9 (6)
C6—S8—C10	104.9 (4)	C6—C5—S3	117.1 (6)
C2—C1—S2	123.9 (6)	S7—C5—S3	116.7 (4)
C2—C1—S1	121.6 (6)	C5—C6—S8	127.8 (6)
S2—C1—S1	114.5 (4)	C5—C6—S4	116.8 (6)
C1—C2—S3	125.1 (6)	S8—C6—S4	115.4 (4)
C1—C2—S4	121.5 (6)	C10—C9—S7	110.0 (6)
S3—C2—S4	113.4 (4)	C9—C10—S8	115.7 (6)

Table 3. *Contact distances (Å)*

S1···S2$^{\rm i}$	3.755 (3)	S5···S7$^{\rm iv}$	3.809 (4)
S1···S6$^{\rm i}$	3.798 (4)	S6···S8$^{\rm ii}$	3.719 (4)
S2···S5$^{\rm i}$	3.782 (4)	S7···S7$^{\rm v}$	3.624 (5)
S2···S4$^{\rm ii}$	3.869 (3)	C2···C7$^{\rm iv}$	3.76 (1)
S2···S2$^{\rm ii}$	3.894 (5)	C5···C7$^{\rm iv}$	3.65 (1)
S3···S8$^{\rm iii}$	3.661 (3)	C6···C7$^{\rm iv}$	3.59 (1)
S3···S5$^{\rm iv}$	3.937 (4)	C7···C7$^{\rm vi}$	3.31 (2)
S4···S6$^{\rm ii}$	3.679 (4)		

Symmetry codes: (i) $1-x, 1-y, 1-z$; (ii) $1-x, 1-y, -z$; (iii) $x, y, 1+z$; (iv) $2-x, 1-y, 1-z$; (v) $2-x, -y, -z$; (vi) $2-x, 1-y, 2-z$.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1985). Program(s) used to solve structure: *TEXSAN*. Program(s) used to refine structure: *TEXSAN*. Molecular graphics: *TEXSAN*. Software used to prepare material for publication: *TEXSAN*.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: BM1022). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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A Key Intermediate in the Synthesis of Pentamidine: 4,4′-[1,5-Pentanediylbis(oxy)]-bisbenzonitrile

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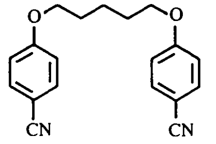
(*Received 24 April 1995; accepted 29 August 1995*)

Abstract

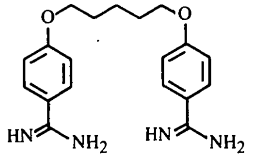
The title compound, $C_{19}H_{18}N_2O_2$, has an extended conformation at the central pentanediyl chain. The molecule has approximate twofold symmetry through atom C(9). The dihedral angle between the end-to-end phenyl rings is 1.3 (1)°, indicating the overall planarity of the molecule. This facilitates stacking of the phenyl rings in the crystal.

Comment

4,4′-[1,5-Pentanediylbis(oxy)]bisbenzonitrile, (I), is the key intermediate in the synthesis of pentamidine, (II) {4,4′-[1,5-pentanediylbis(oxy)]bisbenzenecarboximidamine}, the drug of choice for the treatment and prevention of TB rhodesiense and TB gambiense infections (Katzung, 1984).



(I)



(II)

A perspective view of the title molecule showing the atom-numbering scheme is shown in Fig. 1. The molecular dimensions are as expected (Table 2), with aromatic C—C bond lengths ranging from 1.372 (4) to 1.398 (4) Å and non-aromatic C—C bond lengths ranging from 1.497 (3) to 1.518 (3) Å. The two oxybenzonitrile fragments of (I) have approximate C_2 symmetry through atom C(9) of the linking pentanediyl chain, but the structural differences between the two

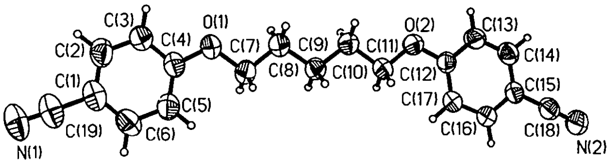


Fig. 1. The molecular structure and atomic numbering scheme of the title compound. The displacement ellipsoids of the C, N and O atoms are drawn at the 50% probability level and H atoms are represented as spheres of arbitrary radii.

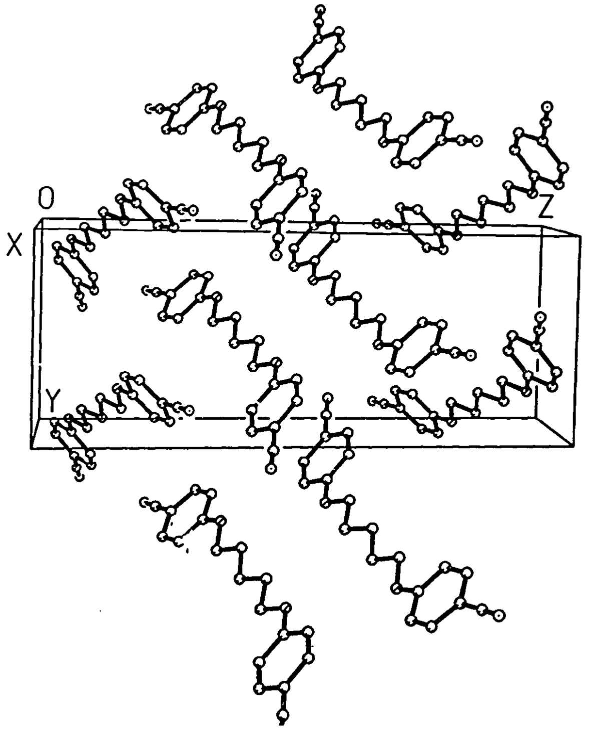


Fig. 2. A view of the crystal packing showing the stacking of the ring systems between inversion-related molecules.

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