2475 reflections
330 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0324P)^2 + 2.48P]$
where $P = (F_o^2 + 2F_c^2)/3$

Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 3. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²) for (3)*

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_jU_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
C1	0.11402 (14)	0.0429 (5)	0.2715 (4)	0.0511 (14)
C2	0.0749 (2)	0.0127 (6)	0.3187 (6)	0.057 (2)
C3	0.1050 (2)	−0.1946 (7)	0.3330 (7)	0.061 (2)
C4	0.13447 (15)	−0.0986 (5)	0.2833 (4)	0.0514 (14)
C5	0.1663 (2)	−0.0702 (7)	0.3723 (5)	0.055 (2)
C6	0.1367 (2)	0.1418 (7)	0.3513 (7)	0.070 (2)
C7	0.1154 (2)	0.0757 (10)	0.1361 (6)	0.079 (2)
C8	0.1476 (2)	−0.1284 (10)	0.1538 (6)	0.084 (2)
C9	0.0367 (2)	−0.1941 (8)	0.3478 (7)	0.068 (2)
C10	0.0004 (2)	−0.1492 (6)	0.2890 (5)	0.057 (2)
C11	−0.0305 (2)	−0.1103 (7)	0.3562 (6)	0.071 (2)
C12	−0.0638 (2)	−0.0721 (7)	0.3028 (7)	0.074 (2)
C13	−0.0671 (2)	−0.0712 (6)	0.1796 (6)	0.064 (2)
C14	−0.0366 (2)	−0.1086 (7)	0.1107 (6)	0.074 (2)
C15	−0.0031 (2)	−0.1472 (7)	0.1647 (6)	0.069 (2)
C16	0.1840 (2)	0.1173 (7)	0.5102 (6)	0.063 (2)
C17	0.19892 (13)	0.0272 (6)	0.6096 (5)	0.0476 (14)
C18	0.1801 (2)	0.0156 (7)	0.7172 (6)	0.066 (2)
C19	0.1929 (2)	−0.0675 (8)	0.8099 (6)	0.078 (2)
C20	0.2252 (2)	−0.1417 (8)	0.7965 (7)	0.083 (2)
C21	0.2457 (2)	−0.1280 (7)	0.6909 (7)	0.079 (2)
C22	0.2318 (2)	−0.0442 (8)	0.5972 (7)	0.076 (2)
N1	0.06974 (12)	−0.1341 (5)	0.2907 (4)	0.0552 (12)
N2	0.15356 (12)	0.0494 (4)	0.4413 (4)	0.0535 (12)
O1	0.14755 (13)	0.0023 (6)	0.0922 (4)	0.103 (2)

Table 4. *Cremer & Pople ring-puckering parameters (Cremer & Pople, 1975; Cremer, 1979) for the C_4N rings in (1) and (2), and the two C_4N rings and C_4O ring in (3)*

The τ values are the torsion angles about the conjoining bond in the three rings: calculations by *PARST* (Nardelli, 1983).

	Q (Å)	φ (°)	τ (°)	Comments
(1)	0.420 (5)	104.6 (7)	−2.7 (5)	C_3 symmetry
(2)	0.368 (4)	105.8 (6)	−1.5 (4)	N1 ring (tolyl)
	0.402 (4)	107.4 (6)	−0.5 (4)	N2 ring
	0.443 (3)	105.1 (5)	−2.2 (4)	N3 ring
(3)	0.448 (6)	109.6 (7)	1.1 (6)	Aza ring (N1)
	0.406 (6)	110.8 (7)	1.9 (6)	Aza ring (N2)
	0.361 (6)	113 (1)	3.3 (6)	Furan ring

For all compounds, program(s) used to solve structures: *SHELXS*86 (Sheldrick, 1990); program(s) used to refine structures: *SHELXL*93 (Sheldrick, 1993); molecular graphics: *ORTEP* (Johnson, 1965); software used to prepare material for publication: *SHELXL*93.

We thank (the late) Professor David Ginsburg and Dr Pnina Ashkenazi for encouraging this study and for providing the crystals.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: KA1166). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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1,1-Bis(3′,4,4′-trimethyltetrathiafulvalen-3-yl)ethanol Ethanol Hemisolvate; a New Bifunctional π-Donor Molecule

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(*Received 28 July 1995; accepted 15 January 1996*)

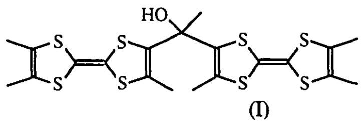
Abstract

The title compound {1,1-bis[2-(4,5-dimethyl-1,3-dithiol-2-ylidene)-5-methyl-1,3-dithiol-4-yl]ethanol ethanol hemisolvate, $C_{20}H_{22}OS_8.0.5C_2H_5OH$} contains bridged tetrathiafulvalene (TTF) molecules. The two TTF moieties of the bifunctional donor are quasi-orthogonal. Donor layers and hydrogen-bonded solvent layers alternate along the c axis.

Acta Crystallographica Section C
ISSN 0108-2701 © 1996

Comment

The flexibility of multifunctional π-donor molecules favours intermolecular contacts and thus structures of higher dimensionality (Fourmigué & Batail, 1992; Fourmigué & Huang, 1993). Various stoichiometries and band-filling control are expected from multiple redox functionalities (Dolbecq *et al.*, 1995). In addition, the title TTF derivative, $(Me_3TTF)_2C(OH)Me$, of the title compound, (I), is capable of engaging in hydrogen-bonded networks. Details of its synthesis have been published elsewhere (Dolbecq, Fourmigué, Batail & Coulon, 1994).



0.5 CH_3CH_2OH

(I)

Bond lengths and angles of the two TTF moieties are essentially equivalent (Table 2). None of them is planar, each dithiole ring being slightly bent along the S···S axis, with dihedral angles of 4.7 (2) and 8.8 (2)° for the one TTF moiety, and 6.5 (2) and 8.4 (2)° for the other. The coordination geometry around the C10 atom is essentially tetrahedral, angles around C10 being close to 109° (Table 2).

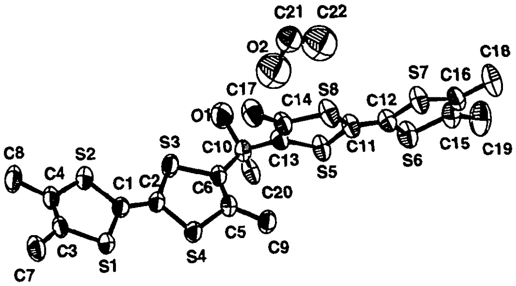


Fig. 1. Molecular structure of the title compound showing 50% probability displacement ellipsoids. H atoms are omitted for clarity.

The dihedral angle between the two TTF units is 101.11 (5)°. This feature, a likely consequence of the intermoiety S···S repulsions, is common among $(TTF)_2A$ dimers, where *A* is S (Bryce, Cooke, Dhindsa, Ando & Hursthouse, 1992), Te (Becker, Bernstein, Bittner, Sarma & Shahal, 1988) or Me_2Si (Fourmigué & Huang, 1993). The structure incorporate solvent molecules: an ethanol molecule is disordered near an inversion centre. This molecule is hydrogen-bonded to the hydroxy group of the donor with an O1···O2 distance of 3.47 (2) Å and an O1—H1···O2 angle of 174.7 (5)°.

We may thus describe the structure as the stacking of double donor layers, made of donor pairs linked by a short S···S contact [S1···S7 = 3.773 (3) Å], and ethanol layers hydrogen-bonded to the donor layers (Fig. 2). Attempts to grow crystals of cation radical salts are currently under investigation.

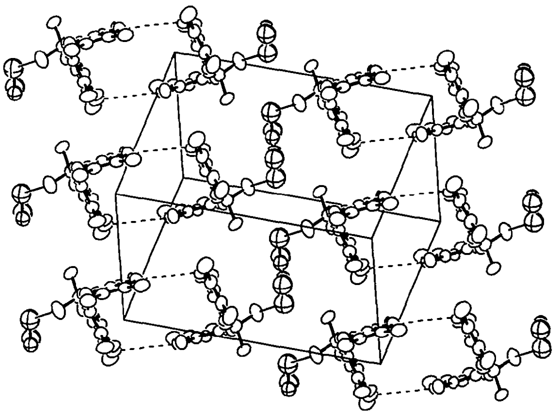


Fig. 2. Packing diagram showing the S···S contacts (dashed) and the hydrogen bonding to the ethanol molecules. Displacement ellipsoids are plotted at the 40% probability level. Note the quasi-orthogonality of the TTF moieties.

Experimental

Crystals were prepared by the reaction of Me_3TTF–Li with $CH_3C(O)Cl$, as described by Dolbecq, Fourmigué, Batail & Coulon (1994). The orange single crystals were obtained by slow evaporation of a solution of the neutral donor in ethanol.

Crystal data

$C_{20}H_{22}OS_8.0.5C_2H_6O$
$M_r = 557.91$
Triclinic
$P\bar{1}$
$a = 7.802 (3)$ Å
$b = 12.138 (2)$ Å
$c = 14.748 (2)$ Å
$\alpha = 95.77 (1)^\circ$
$\beta = 99.33 (2)^\circ$
$\gamma = 104.28 (2)^\circ$
$V = 1321 (1)$ Å^3
$Z = 2$
$D_x = 1.40$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 8.2$–13.6°
$\mu = 0.69$ mm^{-1}
$T = 293$ K
Plate
0.50 × 0.33 × 0.06 mm
Orange

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: none
5021 measured reflections
4648 independent reflections
2803 observed reflections [$I > 3\sigma(I)$]

$R_{int} = 0.025$
$\theta_{max} = 24.97^\circ$
$h = 0 \rightarrow 9$
$k = -14 \rightarrow 13$
$l = -17 \rightarrow 17$
3 standard reflections frequency: 60 min intensity decay: <1.5%

Refinement

Refinement on *F*
$R = 0.053$
$wR = 0.057$

$\Delta\rho_{max} = 1.096$ e Å^{-3} (at 0.64 Å from C21)
$\Delta\rho_{min} = -0.457$ e Å^{-3}

$S = 1.373$
2889 reflections
274 parameters
H atom parameters not refined
Unit weights applied
$(\Delta/\sigma)_{\max} = 2.0$ [for x(O2)]

Extinction correction: none
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, Table 3.2.1)

Table 1. *Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)*

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}/U_{\rm iso}$
S1	−0.1622 (2)	0.1474 (1)	−0.0207 (1)	0.0564 (8)
S2	−0.0705 (2)	0.0689 (1)	0.1583 (1)	0.0593 (8)
S3	0.2295 (2)	0.3084 (1)	0.2339 (1)	0.0580 (8)
S4	0.1399 (2)	0.3922 (1)	0.0564 (1)	0.0557 (8)
S5	0.7656 (2)	0.7153 (1)	0.3269 (1)	0.0617 (9)
S6	1.0818 (3)	0.9469 (2)	0.3863 (1)	0.0685 (9)
S7	1.3101 (2)	0.8545 (2)	0.2773 (1)	0.070 (1)
S8	0.9810 (2)	0.6116 (2)	0.2160 (1)	0.0695 (9)
C1	−0.0277 (8)	0.1791 (5)	0.0901 (5)	0.048 (3)
C2	0.0984 (8)	0.2794 (5)	0.1225 (4)	0.047 (3)
C3	−0.2587 (8)	0.0017 (5)	−0.0135 (5)	0.053 (3)
C4	−0.2167 (8)	−0.0326 (5)	0.0670 (5)	0.056 (3)
C5	0.3205 (8)	0.4810 (5)	0.1398 (4)	0.047 (3)
C6	0.3630 (8)	0.4437 (5)	0.2193 (4)	0.045 (3)
C7	−0.3828 (9)	−0.0675 (6)	−0.0980 (6)	0.070 (4)
C8	−0.285 (1)	−0.1496 (6)	0.0926 (6)	0.076 (4)
C9	0.4032 (9)	0.5938 (5)	0.1107 (5)	0.061 (3)
C10	0.4997 (8)	0.5075 (5)	0.3060 (4)	0.051 (3)
C11	0.9707 (8)	0.7316 (5)	0.2889 (5)	0.054 (3)
C12	1.1027 (8)	0.8300 (5)	0.3137 (4)	0.054 (3)
C13	0.6792 (8)	0.5681 (5)	0.2816 (4)	0.048 (3)
C14	0.7772 (8)	0.5212 (5)	0.2324 (5)	0.056 (3)
C15	1.304 (1)	1.0298 (6)	0.3952 (5)	0.064 (3)
C16	1.4070 (9)	0.9878 (6)	0.3475 (5)	0.061 (3)
C17	0.736 (1)	0.3990 (6)	0.1867 (6)	0.077 (4)
C18	1.600 (1)	1.0440 (7)	0.3440 (6)	0.091 (5)
C19	1.356 (1)	1.1439 (7)	0.4567 (6)	0.094 (5)
C20	0.4222 (8)	0.5917 (6)	0.3543 (5)	0.059 (3)
O1	0.5345 (7)	0.4222 (5)	0.3649 (4)	0.086 (3)
O2†	0.807 (2)	0.556 (1)	0.515 (1)	0.153 (6)
C21†	0.982 (3)	0.539 (1)	0.514 (1)	0.087 (5)
C22†	1.059 (4)	0.637 (2)	0.538 (2)	0.16 (1)

† Occupancy = 0.5 (see text); $U_{\rm iso}$.

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

S1—C1	1.744 (6)	S6—C15	1.750 (7)
S1—C3	1.764 (6)	S7—C12	1.752 (7)
S2—C1	1.752 (7)	S7—C16	1.751 (7)
S2—C4	1.762 (6)	S8—C11	1.748 (7)
S3—C2	1.741 (6)	S8—C14	1.763 (6)
S3—C6	1.769 (6)	C1—C2	1.349 (7)
S4—C2	1.755 (7)	C3—C4	1.32 (1)
S4—C5	1.756 (5)	C5—C6	1.320 (9)
S5—C11	1.752 (7)	C11—C12	1.343 (8)
S5—C13	1.764 (6)	C13—C14	1.32 (1)
S6—C12	1.747 (7)		
C1—S1—C3	95.6 (3)	S3—C6—C5	117.0 (4)
C1—S2—C4	94.7 (3)	C6—C10—C13	111.3 (5)
C2—S3—C6	95.2 (3)	C6—C10—C20	108.5 (5)
C2—S4—C5	94.9 (3)	C6—C10—O1	107.7 (5)
C11—S5—C13	95.5 (3)	C13—C10—C20	110.7 (5)
C12—S6—C15	95.6 (3)	C13—C10—O1	107.4 (5)
C12—S7—C16	95.6 (3)	C20—C10—O1	111.2 (6)
C11—S8—C14	95.5 (3)	S5—C11—S8	113.9 (3)
S1—C1—S2	114.2 (3)	S5—C11—C12	121.1 (6)
S1—C1—C2	123.9 (5)	S8—C11—C12	125.0 (6)
S2—C1—C2	121.8 (5)	S6—C12—S7	113.5 (3)
S3—C2—S4	114.7 (3)	S6—C12—C11	122.4 (6)
S3—C2—C1	122.6 (5)	S7—C12—C11	124.1 (6)
S4—C2—C1	122.6 (5)	S5—C13—C14	117.2 (5)
S1—C3—C4	116.5 (4)	S8—C14—C13	117.2 (5)
S2—C4—C3	118.2 (5)	S6—C15—C16	117.6 (5)
S4—C5—C6	117.9 (4)	S7—C16—C15	117.2 (5)

The H atom of the hydroxy group of the $(\mathrm{Me_3TTF})_2\mathrm{C(OH)Me}$ molecule was found in a difference Fourier map. H atoms of the methyl groups were introduced at ideal positions and simply included in the structure-factor calculations with a common overall displacement parameter ($U_{\rm iso}$ = 0.057 Å²). The $\mathrm{CH_3CH_2OH}$ solvent molecule has a site occupation factor of 0.5. The short C21—C22 bond length [1.18 (3) Å] is probably due to the high thermal motion of the molecule. Maximum residual density is found in the vicinity of this solvent molecule and $(\Delta/\sigma)_{\max}$ is for the x coordinate of the O2 atom of the same ethanol solvent molecule. Attempts to find a better model of the disorder were unsuccessful; the solvent molecule was refined isotropically and H atoms were not considered.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *Xtal DIFDAT SORTRF ADDREF* (Hall, Flack & Stewart, 1994). Program(s) used to solve structure: *Xtal GENEV GENSIN GENTAN*. Program(s) used to refine structure: *Xtal CRYLSQ*. Molecular graphics: *Xtal ORTEP*. Software used to prepare material for publication: *Xtal BONDLA CIFIO*.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: AB1303). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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