Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

2,3,6,7-Tetrakis(2-cyanoethylthio)tetrathiafulvalene

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Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.008 Å
Disorder in main residue
R factor = 0.065
wR factor = 0.182
Data-to-parameter ratio = 15.6

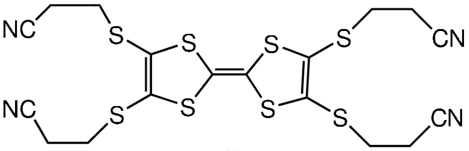
For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Received 5 June 2002
Accepted 9 July 2002
Online 19 July 2002

The centrosymmetric title compound, $C_{18}H_{16}N_4S_8$, has a planar structure, with the exception of the four cyanoethyl groups. The three-dimensional network is stabilized by a variety of S···S and S···C interactions.

Comment

Tetrathiafulvalene (TTF) derivatives and their charge-transfer (CT) salts have received continuous attention since the first high-electrical conductive CT salt TTF–TCNQ (7,7,8,8-tetracyanoquinodimethane) was discovered (Williams *et al.*, 1992). Although the crystal structures of tetrakis(alkylthio)–TTF have been reported, from alkyl = methyl to alkyl = octyl, (Nakano *et al.*, 1992) relatively few crystal structures have been reported for substituted alkyl derivatives. In this regard, it was thought of interest to ascertain the influence of the presence of the electron-withdrawing cyano groups upon the crystal packing of the title compound, (I).



(I)

Molecules of (I) are located about centres of inversion (Fig. 1 and Table 1). Disorder exists in one of the two independent cyano groups, so that the major component had a site occupancy factor of 0.72 (2). Except for the four cyanoethyl groups, the other atoms comprising the molecule are basically coplanar, with the maximum deviation from their least-squares plane being 0.150 (2) Å for the atom S4 (Fig. 2). The ordered cyanoethyl group atoms (H not included) are coplanar, with the maximum deviation from the least-squares plane being 0.036 (5) Å for C7. This plane forms a dihedral angle of 86.9 (4)° with the above-mentioned molecular plane. This result is in accord with that observed (Nakano *et al.*, 1992) in tetrakis(*n*-butylthio)–TTF (TBuT–TTF). Relative to the molecular plane and in accordance with the crystal symmetry, the four cyanoethyl groups adopt an opposite-side arrangement (Fig. 2). However, relative to the five-membered ring plane, the cyanoethyl groups adopt a same-side arrangement (Liu *et al.*, 2002). The latter arrangement is in contrast with the molecular structure of its precursor 4,5-bis(2-cyanoethylthio)-1,3-dithiol-2-one (BCET–DTO), which also adopts the opposite-side arrangement for the two cyanoethyls (Liu *et al.*, 2002). From the molecular packing perspective, the opposite-side arrangement will facilitate the close packing arrangement of the molecules (Nakano *et al.*, 1992; Tanaka *et al.*, 1999).

DOI: 10.1107/S1600536802012199

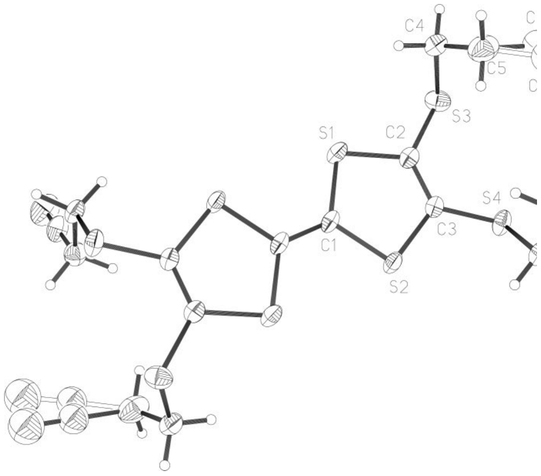


Figure 1
A view of (I), showing the atomic numbering scheme. Displacement ellipsoids are drawn at the 30% probability level (Bruker, 1997).

There are distinct differences in the bond lengths of the five-membered ring in (I) and those in its precursor BCET–DTO (Liu *et al.*, 2002). In BCET–DTO, the bond lengths of C1—S1 [1.768 (2) Å] and C1—S2 [1.763 (3) Å] appear to be longer than S1—C2 [1.745 (2) Å] and S2—C3 [1.748 (2) Å], whereas in (I), the C—S bond lengths are virtually equal, within experimental error. This observation suggests greater delocalization of π-electron density over the five-membered ring in (I), compared to the situation in BCET–DTO.

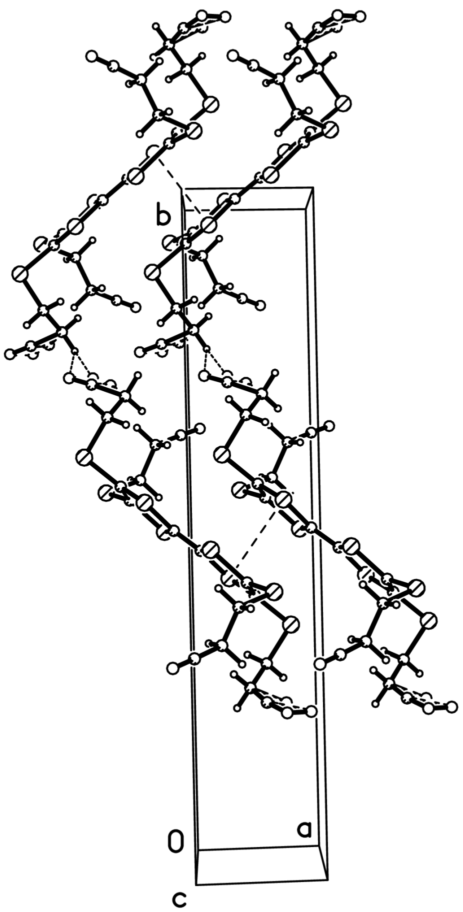


Figure 2
The crystal packing of (I), viewed along the *c* axis (Bruker, 1997).

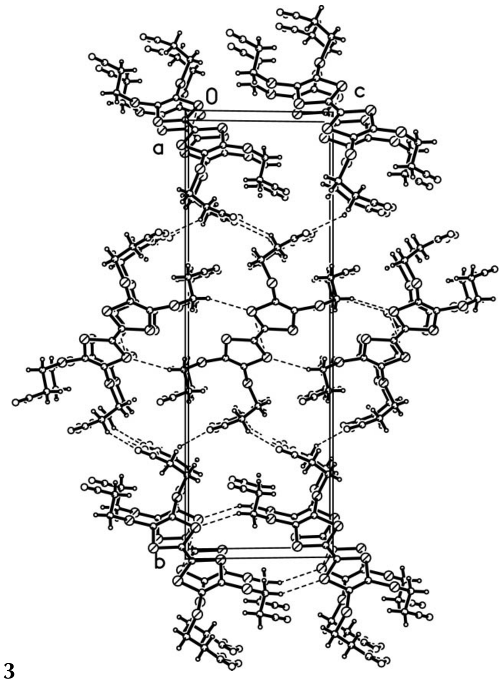


Figure 3
The crystal packing of (I), viewed along the *a* axis (Bruker, 1997).

Representations of the crystal packing of (I) are shown in Figs. 2 and 3. The molecules form stacks along the *a*-axis direction and in this direction the adjacent molecules superimpose on each other completely. Compared with the crystal packing of TBuT–TTF, (I) has more efficient packing, as reflected in the shortest intra-stack S···S contact of 3.610 (2) Å, compared with 3.659 (5) Å in TBuT–TTF. In addition, other short contacts in (I) include S1···S3 [3.664 (2) Å], S3···C1 [3.378 (5) Å], S4···C9 [3.438 (6) Å] and S1···H7B [2.9464 Å].

Experimental

To a 50 ml three-necked flask were added 2.88 g of 4,5-bis (2-cyanoethylthio)-1,3-dithiol-2-one (Svenstrup *et al.*, 1994) and trimethyl phosphite (15 ml). The resulting mixture was stirred at 383 K under nitrogen for about 1.5 h and then cooled to room temperature to give an intense orange–red solid after filtering and washing with methanol. A portion of the solid was dissolved in dichloromethane (40 ml) in a 50 ml conical beaker. The beaker was then covered with a filter paper and allowed to stand in air for several weeks, yielding a precipitate of large and long crystals.

Crystal data

$C_{18}H_{16}N_4S_8$
$M_r = 544.82$
Monoclinic, $P2_1/n$
$a = 5.1016$ (13) Å
$b = 26.753$ (5) Å
$c = 8.8805$ (15) Å
$\beta = 96.031$ (16)°
$V = 1205.3$ (4) Å^3
$Z = 2$
$D_x = 1.501$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 41 reflections
$\theta = 5.1$–$12.4°$
$\mu = 0.76$ mm^{-1}
$T = 293$ (2) K
Plate, orange
0.56 × 0.38 × 0.08 mm

Data collection

Bruker *P*4 diffractometer
$\theta/2\theta$ scans
Absorption correction: ψ scan
(*XSCANS*; Bruker, 1996)
$T_{\min} = 0.75$, $T_{\max} = 0.951$
2991 measured reflections
2104 independent reflections
1761 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.051$
$\theta_{\max} = 25.0°$
$h = -1 \rightarrow 6$
$k = -31 \rightarrow 1$
$l = -10 \rightarrow 10$
3 standard reflections
every 97 reflections
intensity decay: 1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.065$
$wR(F^2) = 0.182$
$S = 1.10$
2103 reflections
135 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0792P)^2 + 2.9598P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.60$ e Å^{-3}
$\Delta\rho_{\min} = -0.47$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

S1—C1	1.742 (5)	C1—C1^{i}	1.350 (10)
S1—C2	1.755 (5)	C2—C3	1.339 (7)
S2—C1	1.758 (4)	C4—C5	1.494 (9)
S2—C3	1.761 (5)	C7—C8	1.508 (8)
S3—C2	1.750 (5)	C8—C9	1.469 (8)
S3—C4	1.808 (6)	C5—C6′	1.4709 (10)
S4—C3	1.749 (5)	C5—C6	1.4709 (10)
S4—C7	1.815 (5)	C6—N1	1.1507 (9)
N2—C9	1.133 (8)	C6′—N1′	1.1510 (10)
C1—S1—C2	95.5 (2)	C2—C3—S2	117.3 (4)
C1—S2—C3	95.0 (2)	S4—C3—S2	118.1 (3)
C2—S3—C4	101.7 (3)	C5—C4—S3	113.4 (4)
C3—S4—C7	102.8 (2)	C8—C7—S4	112.9 (4)
C1^{i}—C1—S1	123.2 (5)	C9—C8—C7	111.1 (5)
C1^{i}—C1—S2	121.9 (5)	N2—C9—C8	178.7 (8)
S1—C1—S2	114.9 (3)	C6′—C5—C6	26.1 (9)
C3—C2—S3	126.8 (4)	C6′—C5—C4	130.4 (10)
C3—C2—S1	117.2 (4)	C6—C5—C4	106.2 (7)
S3—C2—S1	115.7 (3)	N1—C6—C5	175.2 (12)
C2—C3—S4	124.2 (4)	N1′—C6′—C5	174.4 (15)

Symmetry code: (i) $1 - x, -y, -z$.

After location in a difference map, all H atoms were fixed geometrically and allowed to ride on their attached atoms, with $U_{\rm iso}({\rm H}) = 1.2U_{\rm eq}({\rm C})$.

Data collection: *XSCANS* (Bruker, 1996); cell refinement: *XSCANS*; data reduction: *XSCANS*; program(s) used to solve structure: *SHELXTL* (Bruker, 1997); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

This work was supported by the National Natural Science Foundation of China (grant No. 20172034) and by a grant from the State Key Program of China.

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