Acta Crystallographica Section E
Structure Reports
Online

ISSN 1600-5368

2,3-Bis(2-cyanoethylsulfanyl)-6,7-tetramethylenetetrathiafulvalene

Jean-Pierre Legros,[a]* Jean-Marc Fabre[b] and Lakhemici Kaboub[c]

[a]Laboratoire de Chimie de Coordination, UPR CNRS 8241, 205 route de Narbonne, F-31077 Toulouse Cedex, France, [b]Institut Charles Gerhardt, UMR CNRS 5253, AM2N, ENSCM 8 rue de l'Ecole Normale, F-34296 Montpellier Cedex 5, France, and [c]Laboratoire de Chimie des Matériaux Organiques, Centre Universitaire de Tébessa, Route de Constantine, 12000 Tébessa, Algeria
Correspondence e-mail: jean-pierre.legros@lcc-toulouse.fr

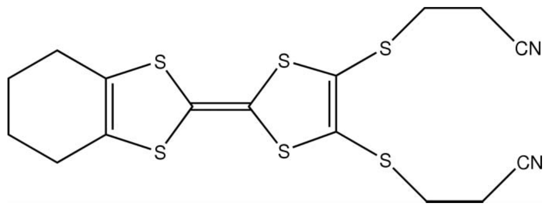
Received 2 July 2007; accepted 17 July 2007

Key indicators: single-crystal X-ray study; T = 180 K; mean σ(C–C) = 0.002 Å; R factor = 0.026; wR factor = 0.051; data-to-parameter ratio = 28.0.

One of the possible strategies for the synthesis of electrically conductive molecular materials based on unsymmetrically substituted tetrathiafulvalenes implies the use of a precursor bearing cyanoethylsulfanyl groups attached to the tetrathiafulvalene (TTF) core. The title compound, $C_{16}H_{16}N_2S_6$, is such a precursor. The two cyanoethylsulfanyl groups are attached to the two adjacent C atoms of one of the two C_3S_2 rings of the TTF core and protrude on both sides of the molecule. In the crystal structure, the TTF core is not planar and adopts a boat conformation; the two C_3S_2 rings are folded around the S$\cdots$S hinges, the dihedral angles being 12.19 (6) and 22.70 (4)°. There are no unusual intermolecular contacts in the solid state. The crystal studied was a partial inversion twin, with contributions of 0.72 (4) and 0.28 (4) for the two twin domains.

Related literature

For general background on molecular metals based on tetrathiafulvalene (TTF) derivatives, see: Fabre (2000); Yamada & Sugimoto (2004); Batail (2004). For the synthesis of the title compound, see: Binet *et al.* (1996). Analogous precursors are used to obtain functionalized TTF derivatives (Legros *et al.*, 2000; Benbellat *et al.*, 2006) and oligo-TTF (Carcel *et al.*, 2006).



Experimental

Crystal data

$C_{16}H_{16}N_2S_6$
M_r = 428.67
Orthorhombic, $Pca2_1$
a = 30.4738 (14) Å
b = 8.8963 (4) Å
c = 6.9150 (3) Å
V = 1874.68 (15) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.73 mm^{-1}
T = 180 (2) K
0.40 × 0.25 × 0.15 mm

Data collection

Oxford Diffraction Xcalibur diffractometer with CCD detector
Absorption correction: numerical [using a multifaceted crystal model based on expressions derived by Clark & Reid (1995)]
$T_{\min}$ = 0.83, $T_{\max}$ = 0.90
19080 measured reflections
6122 independent reflections
5344 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.026

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.026
$wR(F^2)$ = 0.051
S = 0.96
6122 reflections
219 parameters
1 restraint
H-atom parameters constrained
$\Delta\rho_{\max}$ = 0.34 e Å^{-3}
$\Delta\rho_{\min}$ = −0.25 e Å^{-3}
Absolute structure: Flack (1983), with 2592 Friedel pairs
Flack parameter: 0.28 (4)

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2006); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2006); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1993); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPIII* (Burnett & Johnson, 1996), *CAMERON* (Watkin *et al.*, 1993) and *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

The authors are grateful to Dr Carine Duhayon for collecting the data. This work was in part achieved in the framework of a 'Franco–Algerian Cooperation Programme' (PROFAS); we warmly thank the participating organizations.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: CF2117).

References

Altomare, A., Cascarano, G., Giacovazzo, C. & Guagliardi, A. (1993). *J. Appl. Cryst.* **26**, 343–350.
Batail, P. (2004). Editor. *Chem. Rev*. **104**, 4887–5782.
Benbellat, N., Le Gal, Y., Golhen, S., Gouasmia, A., Ouahab, L. & Fabre, J.-M. (2006). *Eur. J. Org. Chem.* pp. 4237–4241.
Binet, L., Fabre, J.-M., Montignoul, C., Simonse, K. B. & Becher, J. (1996). *J. Chem. Soc., Perkin Trans. 1*, pp, 783–788.
Burnett, M. N. & Johnson, C. K. (1996). *ORTEPIII*. Report ORNL-6895. Oak Ridge National Laboratory, Tennessee, USA.
Carcel, C., Kaboub, L. & Fabre, J.-M. (2006). *Synth. Met.* **156**, 1271–1279.
Clark, R. C. & Reid, J. S. (1995). *Acta Cryst.* A**51**, 887–897.
Fabre, J.-M. (2000). *J. Phys. IV*, **10**, 3–19.
Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.
Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.
Legros, J.-P., Dahan, F., Binet, L., Carcel, C. & Fabre, J.-M. (2000). *J. Mater. Chem.* **10**, 2685–2691.
Oxford Diffraction (2006). *CrysAlis CCD* and *CrysAlis RED*. Versions 1.171.31.5. Oxford Diffraction Ltd, Abingdon, Oxfordshire, England.
Sheldrick, G. M. (1997). *SHELXL97*. University of Göttingen, Germany.
Watkin, D. M., Pearce, L. & Prout, C. K. A. (1993). *CAMERON*. University of Oxford, England.
Yamada, Y. & Sugimoto, T. (2004). *TTF Chemistry: Fundamentals and Applications of Tetrathiafulvalene.* Kodansha: Springer.

doi:10.1107/S1600536807034873

supplementary materials

Acta Cryst. (2007). E**63**, o3572 [**doi:10.1107/S1600536807034873**]

2,3-Bis(2-cyanoethylsulfanyl)-6,7-tetramethylenetetrathiafulvalene

J.-P. Legros, J.-M. Fabre and **L. Kaboub**

Comment

The search for molecular systems liable to afford interesting electrical properties – such as metallic or even superconducting behaviour – follows several strategies. One of them is to use unsymmetrically substituted tetrathiafulvalenes as building blocks (Fabre, 2000; Yamada & Sugimoto, 2004; Batail, 2004). When these target molecules are to be functionalized with hydroxyl or amine groups (*e.g.* in order to obtain H-bond networks) one of the possible synthesis strategies implies the use of a precursor bearing cyanoethylthio groups attached to the tetrathiafulvalene (TTF) core (Binet *et al.*, 1996). The title compound was synthesized in this context and its crystal structure was determined to ascertain that the expected precursor was really obtained. The molecular structure is shown in Fig. 1. The main features of the structure are as follows. The two cyanoethylthio groups protrude on both sides of the TTF core, almost perpendicular to the external S3/S4/C5/C6/S7/S8 plane (Fig. 2). The TTF core is not planar and shows a boat conformation: the two C_3S_2 rings are folded around the S···S hinges. The central C1/C2/S1/S2/S3/S4 group is planar; the external S1/S2/C3/C4 and S3/S4/C5/C6 planes make dihedral angles of 12.19 (6)° and 22.70 (4)° respectively with the central plane (Fig. 2). The crystal investigated was an inversion twin, with contributions of 0.72:0.28 (4) for the twin domains. In this crystal structure there are no unusual intermolecular interactions, and no packing effect can be invoked to explain the folding of the TTF core (Fig. 3).

Experimental

The title compound was synthesized as described in the literature for the analogous compound 2,3-bis(2-cyanoethylthio)-6,7-dimethyltetrathiafulvalene (Binet *et al.*, 1996). The red crystals (mp. 424 K) of the studied compound were isolated by slow evaporation of a solution in acetonitrile.

Refinement

H atoms were located in a difference map then positioned geometrically and refined using a riding model with C—H distances set to 0.97 Å. A common $U_{\rm iso}$(H) was refined and converged to a value of 0.037 (2) $Å^2$.

Figures

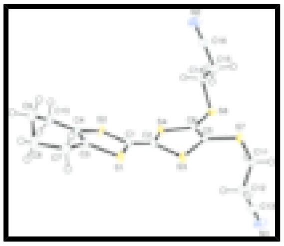


Fig. 1. The molecular structure of the title compound, with atom labels and 50% probability displacement ellipsoids for non-H atoms.

Fig. 2. Side view of the molecule (hydrogen atoms omitted). For overlapping atoms the upper labels refer to the hidden atoms.

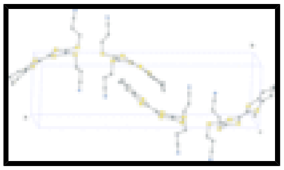


Fig. 3. Unit-cell content (hydrogen atoms omitted).

2,3-Bis(2-cyanoethylsulfanyl)-6,7-tetramethylenetetrathiafulvalene

Crystal data

$C_{16}H_{16}N_2S_6$

$M_r = 428.67$

Orthorhombic, $Pca2_1$

Hall symbol: P 2c -2ac

$a = 30.4738$ (14) Å

$b = 8.8963$ (4) Å

$c = 6.9150$ (3) Å

$V = 1874.68$ (15) Å^3

$Z = 4$

$F_{000} = 888$

$D_x = 1.519$ Mg m^{-3}

Melting point: 424 K

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å

Cell parameters from 6238 reflections

$\theta = 3.0$–32.1°

$\mu = 0.73$ mm^{-1}

$T = 180$ (2) K

Block, orange

0.40 × 0.25 × 0.15 mm

Data collection

Oxford Diffraction Xcalibur diffractometer with CCD detector

Radiation source: fine-focus sealed tube

Monochromator: graphite

$T = 180(2)$ K

φ–ω scans

Absorption correction: numerical [using a multifaceted crystal model based on expressions derived by Clark & Reid (1995)]

$T_{\min} = 0.83$, $T_{\max} = 0.90$

19080 measured reflections

6122 independent reflections

5344 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.026$

$\theta_{\max} = 32.1$°

$\theta_{\min} = 3.0$°

$h = -37 \rightarrow 45$

$k = -13 \rightarrow 12$

$l = -9 \rightarrow 10$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.026$

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0248P)^2]$

	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.051$	$(\Delta/\sigma)_{\max} = 0.003$
$S = 0.96$	$\Delta\rho_{\max} = 0.34$ e Å^{-3}
6122 reflections	$\Delta\rho_{\min} = -0.25$ e Å^{-3}
219 parameters	Extinction correction: none
1 restraint	Absolute structure: Flack (1983), with 2592 Friedel pairs
Primary atom site location: structure-invariant direct methods	Flack parameter: 0.28 (4)
Secondary atom site location: difference Fourier map	

Special details

Experimental. Cooling Device: Oxford Instruments Cryojet. Excalibur (Oxford Diffraction) four-circle Kappa geometry diffractometer equipped with an area CCD detector. Crystal-detector distance (mm): 70.0

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor *wR* and goodness of fit S are based on F^2, conventional *R*-factors *R* are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2\text{sigma}(F^2)$ is used only for calculating *R*-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on F, and R– factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
S1	0.480152 (12)	0.18707 (4)	0.71619 (6)	0.02209 (8)
S2	0.504941 (12)	0.20238 (5)	1.12758 (6)	0.02285 (9)
S3	0.392867 (12)	−0.00712 (4)	0.83085 (6)	0.02141 (8)
S4	0.416522 (12)	0.01365 (4)	1.24278 (6)	0.02122 (8)
S7	0.296701 (12)	−0.05864 (4)	0.90997 (6)	0.02033 (8)
S8	0.325115 (12)	−0.04576 (4)	1.38378 (6)	0.01986 (8)
C1	0.46686 (5)	0.13945 (17)	0.9560 (2)	0.0192 (3)
C2	0.43072 (5)	0.06014 (17)	1.0032 (2)	0.0187 (3)
C3	0.52257 (4)	0.31129 (16)	0.7803 (2)	0.0199 (3)
C4	0.53333 (5)	0.31976 (17)	0.9663 (2)	0.0202 (3)
C5	0.35007 (4)	−0.02832 (16)	0.9997 (2)	0.0166 (3)
C6	0.36087 (4)	−0.01888 (16)	1.1878 (2)	0.0169 (3)
C7	0.54676 (5)	0.38981 (19)	0.6199 (3)	0.0270 (3)
H71	0.5285	0.4690	0.5670	0.0369 (14)*
H72	0.5530	0.3187	0.5172	0.0369 (14)*
C8	0.58959 (6)	0.4571 (2)	0.6940 (3)	0.0354 (4)
H81	0.6115	0.3785	0.7037	0.0369 (14)*
H82	0.6001	0.5313	0.6023	0.0369 (14)*
C9	0.58370 (6)	0.53047 (19)	0.8900 (3)	0.0345 (4)
H91	0.5616	0.6086	0.8805	0.0369 (14)*

H92	0.6111	0.5772	0.9288	0.0369 (14)*
C10	0.56982 (5)	0.41627 (19)	1.0434 (3)	0.0289 (4)
H101	0.5947	0.3537	1.0780	0.0369 (14)*
H102	0.5600	0.4685	1.1587	0.0369 (14)*
C11	0.29071 (5)	−0.25865 (18)	0.9490 (2)	0.0237 (3)
H111	0.2962	−0.2813	1.0841	0.0369 (14)*
H112	0.2608	−0.2882	0.9196	0.0369 (14)*
C12	0.32253 (5)	−0.34943 (19)	0.8223 (3)	0.0280 (4)
H121	0.3174	−0.3249	0.6875	0.0369 (14)*
H122	0.3524	−0.3209	0.8536	0.0369 (14)*
C13	0.31747 (5)	−0.5116 (2)	0.8493 (2)	0.0278 (4)
C14	0.31976 (5)	0.14875 (18)	1.4600 (2)	0.0235 (3)
H141	0.3046	0.1527	1.5833	0.0369 (14)*
H142	0.3487	0.1920	1.4774	0.0369 (14)*
C15	0.29443 (5)	0.24071 (19)	1.3115 (3)	0.0292 (4)
H151	0.3064	0.2212	1.1839	0.0369 (14)*
H152	0.2640	0.2087	1.3116	0.0369 (14)*
C16	0.29636 (5)	0.40254 (19)	1.3501 (2)	0.0258 (3)
N1	0.31410 (5)	−0.63897 (17)	0.8655 (2)	0.0380 (4)
N2	0.29893 (5)	0.52864 (16)	1.3764 (2)	0.0336 (3)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.02102 (17)	0.02499 (19)	0.02027 (18)	−0.00603 (15)	−0.00037 (16)	0.00098 (16)
S2	0.02127 (18)	0.0250 (2)	0.02230 (18)	−0.00701 (15)	−0.00391 (16)	0.00209 (16)
S3	0.01632 (16)	0.0290 (2)	0.01892 (16)	−0.00528 (15)	0.00099 (14)	−0.00146 (16)
S4	0.01668 (16)	0.0275 (2)	0.01951 (17)	−0.00304 (14)	−0.00214 (15)	0.00305 (17)
S7	0.01445 (16)	0.02107 (18)	0.02546 (18)	−0.00232 (14)	−0.00238 (15)	0.00118 (16)
S8	0.02178 (17)	0.01618 (16)	0.02161 (18)	−0.00153 (13)	0.00558 (15)	0.00128 (15)
C1	0.0177 (7)	0.0195 (7)	0.0205 (7)	0.0006 (6)	−0.0012 (6)	−0.0006 (6)
C2	0.0149 (7)	0.0214 (7)	0.0196 (7)	0.0001 (6)	−0.0011 (6)	0.0002 (6)
C3	0.0159 (7)	0.0173 (7)	0.0264 (8)	−0.0001 (5)	0.0023 (6)	0.0004 (6)
C4	0.0145 (7)	0.0177 (7)	0.0285 (8)	−0.0012 (5)	−0.0003 (6)	0.0003 (6)
C5	0.0126 (7)	0.0164 (7)	0.0209 (7)	−0.0015 (5)	0.0017 (6)	0.0003 (6)
C6	0.0150 (6)	0.0157 (7)	0.0200 (7)	0.0003 (5)	0.0028 (5)	−0.0001 (6)
C7	0.0267 (8)	0.0246 (9)	0.0298 (8)	−0.0023 (6)	0.0070 (7)	0.0045 (7)
C8	0.0269 (9)	0.0337 (10)	0.0455 (12)	−0.0107 (7)	0.0107 (8)	0.0008 (8)
C9	0.0285 (9)	0.0288 (9)	0.0460 (11)	−0.0112 (7)	0.0063 (9)	−0.0028 (8)
C10	0.0228 (8)	0.0262 (9)	0.0378 (10)	−0.0061 (7)	−0.0060 (7)	−0.0009 (8)
C11	0.0218 (8)	0.0209 (8)	0.0283 (9)	−0.0052 (6)	0.0017 (6)	−0.0011 (6)
C12	0.0336 (9)	0.0242 (9)	0.0262 (8)	−0.0020 (7)	0.0038 (7)	−0.0020 (7)
C13	0.0315 (9)	0.0299 (9)	0.0221 (9)	0.0002 (7)	−0.0011 (7)	−0.0039 (7)
C14	0.0308 (8)	0.0188 (8)	0.0209 (7)	0.0022 (6)	0.0035 (7)	−0.0003 (6)
C15	0.0348 (9)	0.0202 (8)	0.0326 (9)	0.0032 (7)	−0.0057 (8)	−0.0008 (7)
C16	0.0262 (8)	0.0271 (9)	0.0242 (8)	0.0071 (6)	−0.0007 (7)	0.0004 (7)
N1	0.0528 (10)	0.0283 (8)	0.0329 (9)	0.0008 (7)	−0.0007 (8)	−0.0026 (7)
N2	0.0392 (8)	0.0253 (8)	0.0364 (9)	0.0075 (6)	−0.0032 (7)	0.0001 (7)

Geometric parameters (Å, °)

S1—C3	1.7573 (15)	C8—H81	0.970
S1—C1	1.7590 (15)	C8—H82	0.970
S2—C1	1.7514 (15)	C9—C10	1.529 (3)
S2—C4	1.7558 (16)	C9—H91	0.970
S3—C5	1.7605 (14)	C9—H92	0.970
S3—C2	1.7631 (15)	C10—H101	0.970
S4—C2	1.7617 (16)	C10—H102	0.970
S4—C6	1.7620 (14)	C11—C12	1.536 (2)
S7—C5	1.7616 (15)	C11—H111	0.970
S7—C11	1.8089 (16)	C11—H112	0.970
S8—C6	1.7552 (15)	C12—C13	1.463 (2)
S8—C14	1.8162 (16)	C12—H121	0.970
C1—C2	1.3479 (19)	C12—H122	0.970
C3—C4	1.330 (2)	C13—N1	1.143 (2)
C3—C7	1.504 (2)	C14—C15	1.523 (2)
C4—C10	1.503 (2)	C14—H141	0.970
C5—C6	1.344 (2)	C14—H142	0.970
C7—C8	1.524 (2)	C15—C16	1.465 (2)
C7—H71	0.970	C15—H151	0.970
C7—H72	0.970	C15—H152	0.970
C8—C9	1.515 (3)	C16—N2	1.139 (2)

C3—S1—C1	94.77 (7)	C8—C9—H91	109.3
C1—S2—C4	94.95 (7)	C10—C9—H91	109.3
C5—S3—C2	94.18 (7)	C8—C9—H92	109.3
C2—S4—C6	94.13 (7)	C10—C9—H92	109.3
C5—S7—C11	101.03 (7)	H91—C9—H92	108.0
C6—S8—C14	98.62 (7)	C4—C10—C9	109.78 (15)
C2—C1—S2	123.02 (12)	C4—C10—H101	109.7
C2—C1—S1	122.83 (11)	C9—C10—H101	109.7
S2—C1—S1	114.15 (8)	C4—C10—H102	109.7
C1—C2—S4	123.44 (11)	C9—C10—H102	109.7
C1—C2—S3	123.28 (12)	H101—C10—H102	108.2
S4—C2—S3	113.28 (8)	C12—C11—S7	111.60 (11)
C4—C3—C7	124.49 (14)	C12—C11—H111	109.3
C4—C3—S1	117.44 (11)	S7—C11—H111	109.3
C7—C3—S1	117.83 (11)	C12—C11—H112	109.3
C3—C4—C10	123.92 (15)	S7—C11—H112	109.3
C3—C4—S2	117.35 (11)	H111—C11—H112	108.0
C10—C4—S2	118.63 (12)	C13—C12—C11	112.28 (14)
C6—C5—S3	116.98 (11)	C13—C12—H121	109.1
C6—C5—S7	125.19 (11)	C11—C12—H121	109.1
S3—C5—S7	117.83 (9)	C13—C12—H122	109.1
C5—C6—S8	125.92 (11)	C11—C12—H122	109.1
C5—C6—S4	117.04 (10)	H121—C12—H122	107.9
S8—C6—S4	116.95 (9)	N1—C13—C12	178.0 (2)
C3—C7—C8	110.74 (14)	C15—C14—S8	111.22 (11)

C3—C7—H71	109.5	C15—C14—H141	109.4
C8—C7—H71	109.5	S8—C14—H141	109.4
C3—C7—H72	109.5	C15—C14—H142	109.4
C8—C7—H72	109.5	S8—C14—H142	109.4
H71—C7—H72	108.1	H141—C14—H142	108.0
C9—C8—C7	111.63 (14)	C16—C15—C14	112.62 (14)
C9—C8—H81	109.3	C16—C15—H151	109.1
C7—C8—H81	109.3	C14—C15—H151	109.1
C9—C8—H82	109.3	C16—C15—H152	109.1
C7—C8—H82	109.3	C14—C15—H152	109.1
H81—C8—H82	108.0	H151—C15—H152	107.8
C8—C9—C10	111.53 (15)	N2—C16—C15	177.89 (18)

Fig. 1

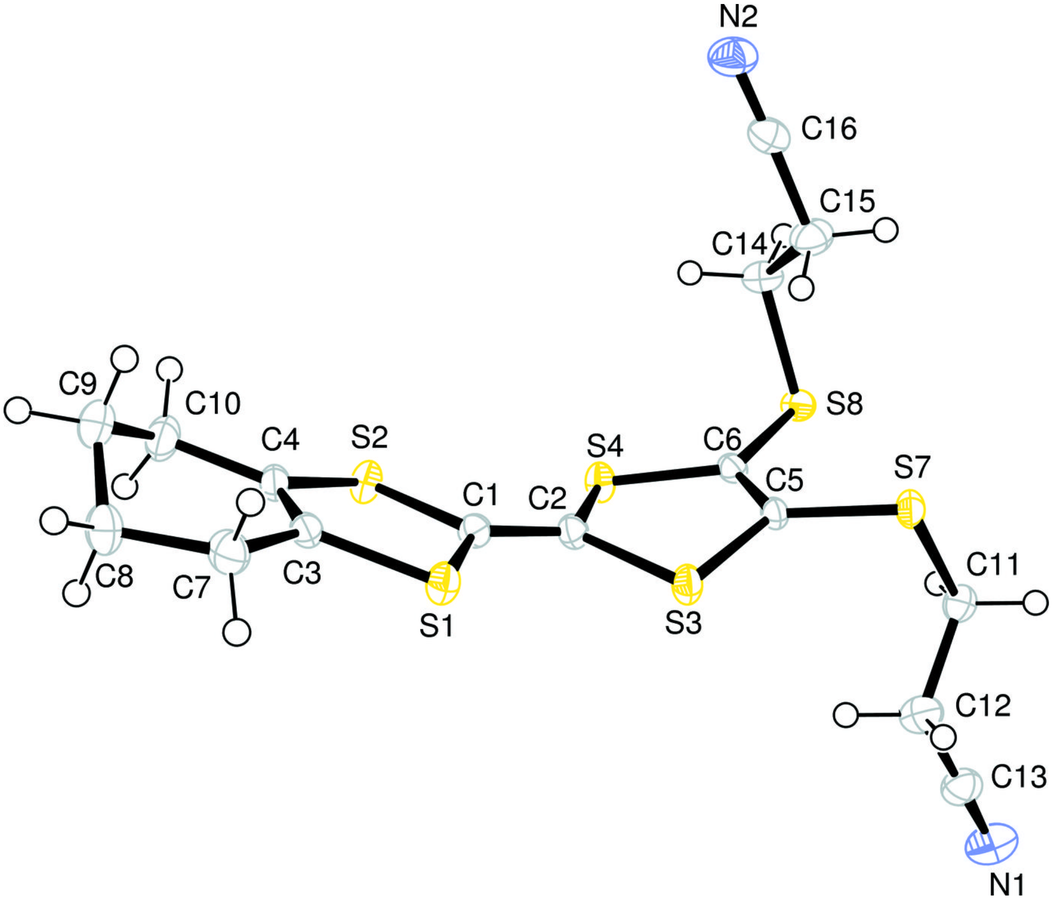

N2
C16
C15
C14
C9
C10
C4
S2
C1
C2
S4
C6
C5
S8
S7
C8
C7
C3
S1
S3
C11
C12
C13
N1

Fig. 2

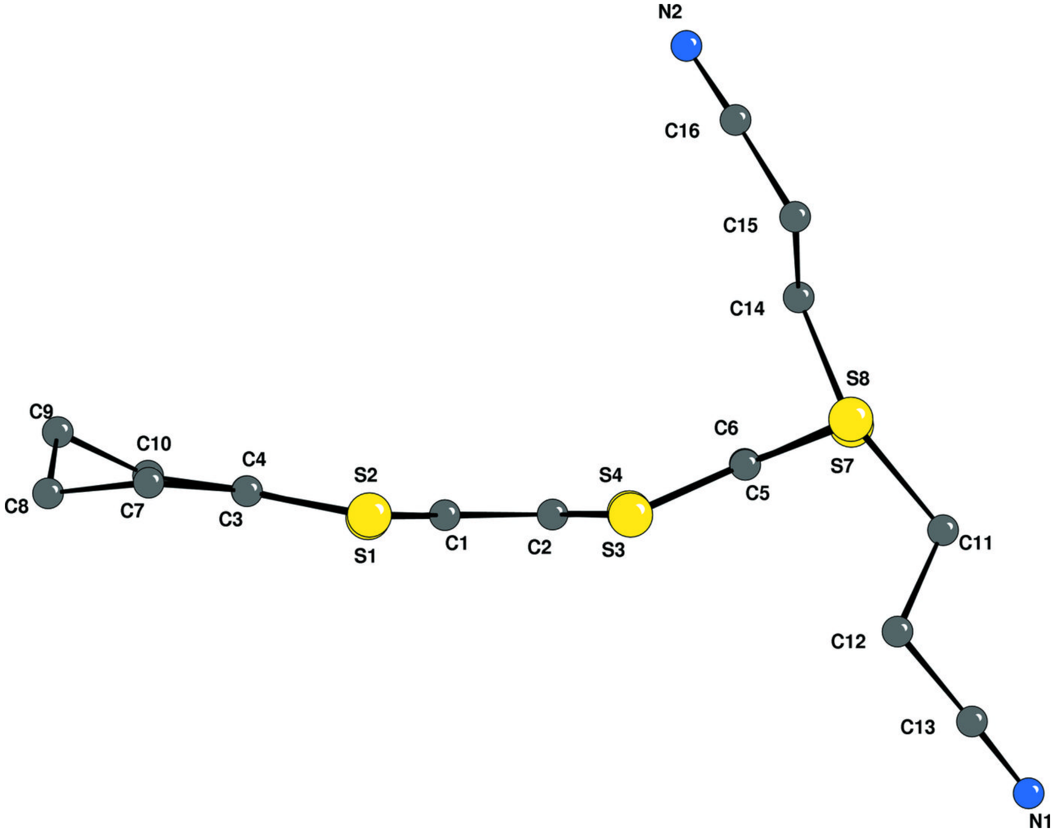

N2
C16
C15
C14
S8
C9
C10
C4
S2
S4
C6
C8
C7
C3
S1
C1
C2
S3
C5
S7
C11
C12
C13
N1

Fig. 3