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4,5-Bis(2-cyanoethylsulfanyl)-1,2-dithiole-3-thione

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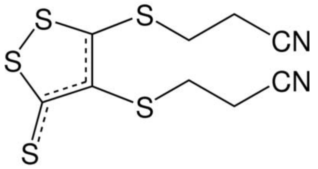
Key indicators: single-crystal X-ray study; T = 120 K; mean σ(C–C) = 0.002 Å; R factor = 0.033; wR factor = 0.086; data-to-parameter ratio = 21.5.

The bonding in the C—C—C—S$_{\rm thione}$ fragment of the title molecule, $C_9H_8N_2S_5$, is highly conjugated. Owing to strong S···S [3.4842 (4) Å] and S···N [3.1223 (13) and 3.1425 (14) Å] intermolecular interactions, a kind of one-dimensional double molecular chain can be found along the a direction of the unit cell.

Related literature

For related literature, see: Mori *et al.* (1995); Rowland & Taylor (1996); Yu *et al.* (2003); Kini *et al.* (1990).



Experimental

Crystal data

$C_9H_8N_2S_5$
M_r = 304.47
Triclinic, $P\bar{1}$
a = 8.0216 (4) Å
b = 8.9771 (3) Å
c = 9.4799 (5) Å
α = 91.251 (3)°
β = 112.426 (2)°
γ = 92.418 (2)°
V = 629.93 (5) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 0.89 mm^{-1}
T = 120 (2) K
0.40 × 0.35 × 0.10 mm

Data collection

Rigaku R-AXIS SPIDER IP diffractometer
Absorption correction: multi-scan (*CrystalClear*; Rigaku, 2007) $T_{\rm min}$ = 0.825, $T_{\rm max}$ = 1.000
12836 measured reflections
3811 independent reflections
3721 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.040

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.033
$wR(F^2)$ = 0.086
S = 1.10
3811 reflections
177 parameters
All H-atom parameters refined
$\Delta\rho_{\rm max}$ = 0.56 e Å^{-3}
$\Delta\rho_{\rm min}$ = −0.30 e Å^{-3}

Table 1
Selected bond lengths (Å).

C1—C2	1.3837 (19)	S2—C3	1.7328 (13)
C2—C3	1.4298 (16)	S3—C3	1.6613 (14)
S1—C1	1.7248 (12)	S4—C1	1.7366 (13)
S1—S2	2.0702 (5)	S5—C2	1.7616 (12)

Data collection: *CrystalClear* (Rigaku, 2007); cell refinement: *CrystalClear*; data reduction: *CrystalClear*; program(s) used to solve structure: *SHELXTL* (Bruker, 2000); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: IM2033).

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supplementary materials

Acta Cryst. (2007). E**63**, o4056 [**doi:10.1107/S1600536807044078**]

4,5-Bis(2-cyanoethylsulfanyl)-1,2-dithiole-3-thione

Q. Fang, A. S. Batsanov and J. A. K. Howard

Comment

The rapid progress of molecular conductors or superconductors in the past three decades has been triggered by the successful syntheses of novel and useful organic donors. The synthesis of TTF ($C_6S_4H_4$, tetrathiafulvalene) in 1970 and BEDT-TTF ($C_{10}S_8H_8$, bis(ethylenedithio)-tetrathiafulvalene) in the late 1970 s have resulted in more than one hundred TTF-based organic superconductors, such as κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br with T_c = 11.6 K at ambient pressure (Kini *et al.*, 1991). One kind of promising donors for new molecular conductors still seem to be multi-sulfur heterocyclic compounds with more sulfur atoms fused into the TTF skeleton, such as BEDT-TTP ($C_{14}S_{12}H_8$, 2,5-bis(4,5-ethylenedithio-1,3-dithiol-2-ylidene) −1,3,4,6-tetrathiapentalene) and similar donors (Mori *et al.*, 1995). In the course of exploring some derivatives of BEDT-TTP, we obtained their precursor 4,5-bis(2'-cyanoethylsulfanyl)-[1,3]-dithiole-2-thione (I) (Figure 1) and determined its structure (Yu *et al.*, 2003). Here we report the structure and synthesis of its isomer: 4,5-bis(2'-cyanoethylsulfanyl)-[1,2]-dithiole-3-thione (II).

As shown in Figure 2, the five-membered 1,2-dithiole ring is basically planar and the plane (plane 1) can be extended to three peripheral sulfur atoms (S3, S4 and S5) and the C4 atom. Of these nine atoms, S4 shows the biggest deviation from the plane, 0.051 (1) Å. Four atoms (C4, C5, C6 and N1) of one side-chain of the molecule are within the second plane (Plane 2) and the five atoms (S5, C6, C7, C8 and N2) of the other side-chain are arranged in the third plane (Plane 3). The dihedral angels between these planes are 71.6 (1)° (between planes 1 and 2), 84.0 (1)° (1 and 3), and 56.7 (1)° (2 and 3).

The bonding in the C1—C2—C3—S3 fragment of the 1,2-isomer is highly conjugated with the bond lengths being 1.384 (2), 1.430 (2) and 1.661 (1) Å for the C1—C2, C2—C3 and terminal C3—S3 bonds, respectively. The π-conjugation may involve three more atoms (S1, S2 and S4) because of the "conjugated" bond lengths C1—S1 (1.725 (1) Å), C3—S2 (1.733 (1) Å), and C1—S4 (1.737 (1) Å). However, the π-conjugation is not circular because the S1—S2 bond length (2.0702 (5) Å) is indicative for a single bond. By comparison, the conjugation in (I) is not very significant because of the double C═C (1.346 (1) Å) and the terminal double C═S bond (1.644 (1) Å).

As shown in Figure 3, in the crystal of (II) each molecule participates in six strong S···*S* and *S*···N intermolecular interactions with its three neighbours. Three of these six contacts are symmetrically independent, *viz*. S4···S5A ($-x$, $-y$, $1 - z$) of 3.484 (2) Å, S1···N1B ($1 + x$, y, z) of 3.112 (2) and S2···N1B ($1 + x$, y, z) of 3.142 (2) Å. These contacts are significantly shorter than the standard intermolecular (van der Waals) contact distances S···S of 3.60 Å and S···N of 3.45 Å (Rowland & Taylor, 1996). These intermolecular interactions help to form a kind of supramolecular planar moiety involving 20 atoms: nine from the main molecular plane (Plane 1) of the concerned molecule, another nine from the main plane of the adjacent molecule ($-x$, $-y$, $1 - z$) and two N1 atoms from other two molecules. Furthermore, due to these S···*S* and *S*···N interactions, a kind of one-dimensional double chain of molecules can be found along the a-direction. By comparison, there are no short S···S contacts in the crystal of (I), corresponding to the relatively strong intermolecular interactions of (II).

Experimental

The title compound has been synthesized by the route shown in the Scheme. 3-Bromo-propionitrile (12.5 ml, 0.15 mmol) was added to a stirred 200 ml acetone solution containing $(Bu_4N)_2[Zn(dmit)_2]$ (28.5 g, 0.030 mmol). After reacting for 12 h at 320 K, the solvent was removed. The residue was dissolved in 250 ml CH_2Cl_2, and 200 ml water was added. After being stirred overnight and the water layer removed, 100 ml CH_3OH was added into the CH_2Cl_2 solution. Needle-shaped orange crystals of (4,5-bis(2'-cyanoethylsulfanyl)-[1,3]-dithiole-2-thione) (I) formed quickly when most of the CH_2Cl_2 had evaporated. The solvent remaining in the mother-liquor was removed, the residual mixture which contained both (I) and (II), was separated by column chromatography on silica gel (eluent CH_2Cl_2). The yields based on $(Bu_4N)_2[Zn(dmit)_2]$ for (I) and (II) were 81% and 9%, respectively. The orange (I) moved faster in the column ($R_f = 1/2$), followed by 4,5-bis(2'-cyanoethylsulfanyl)-[1,2]-dithiole-3-thion (II) of the same colour ($R_f = 0.3$), indicating higher polarity of (II). When most of the CH_2Cl_2 evaporated, platelet crystals of (II) have been obtained with the m.p. of 438–440 K.

Refinement

All H atoms were located in a difference Fourier map and refined in isotropic approximation without constraints, C—H distances 0.92 (2) to 0.98 (2) Å.

Figures

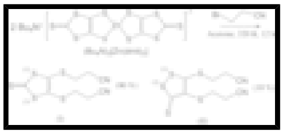

Fig. 1. Reaction scheme for the formation of the title compound.

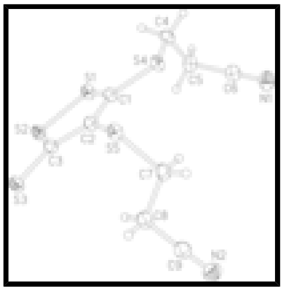

Fig. 2. Molecular structure of the title compound. Displacement ellipsoid are drawn at the 50% probability level.

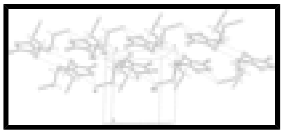

Fig. 3. Packing of (II) in the crystal structure showing one-dimensional double molecular chain structure by short S···*S* and *S*···N intermolecular interactions. [Symmetry code: (A) −*x*, −*y*, 1 − *z*; (B) 1 + *x*, *y*, *z*]

4,5-Bis(2-cyanoethylsulfanyl)-1,2-dithiole-3-thione

Crystal data

$C_9H_8N_2S_5$

$M_r = 304.47$

Triclinic, $P\overline{1}$

$Z = 2$

$F_{000} = 312$

$D_x = 1.605$ Mg m^{-3}

Hall symbol: -P 1

a = 8.0216 (4) Å

b = 8.9771 (3) Å

c = 9.4799 (5) Å

α = 91.251 (3)°

β = 112.426 (2)°

γ = 92.418 (2)°

V = 629.93 (5) Å^3

Melting point: 439(1) K

Mo $K\alpha$ radiation
λ = 0.71073 Å

Cell parameters from 4653 reflections

θ = 2.3–35.5°

μ = 0.89 mm^{-1}

T = 120 (2) K

Platelet, orange

0.40 × 0.35 × 0.10 mm

Data collection

Rigaku R-AXIS SPIDER IP diffractometer

Radiation source: fine-focus sealed tube

Monochromator: graphite

T = 120(2) K

wide ω scans

Absorption correction: multi-scan (CrystalClear; Rigaku, 2007)

$T_{\rm min}$ = 0.825, $T_{\rm max}$ = 1.000

12836 measured reflections

3811 independent reflections

3721 reflections with $I > 2\sigma(I)$

$R_{\rm int}$ = 0.040

$\theta_{\rm max}$ = 30.5°

$\theta_{\rm min}$ = 2.3°

$h = -11 \rightarrow 11$

$k = -12 \rightarrow 12$

$l = -13 \rightarrow 13$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)]$ = 0.033

$wR(F^2)$ = 0.086

S = 1.10

3811 reflections

177 parameters

Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map

Hydrogen site location: difference Fourier map

All H-atom parameters refined

$w = 1/[\sigma^2(F_o^2) + (0.0355P)^2 + 0.1882P]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\rm max}$ = 0.001

$\Delta\rho_{\rm max}$ = 0.57 e Å^{-3}

$\Delta\rho_{\rm min}$ = −0.30 e Å^{-3}

Extinction correction: none

Special details

Experimental. scan: Number of images: 41 Slice: 51.0000 − 175.0000 Image width: 3.0000 Exp time: 300.0000 Rotation axis: Omega Omega: 0.0000 Chi: 0.0000 Phi: 0.0000 XTD: 127.4000 2theta: −0.0164 scan: Number of images: 40 Slice: 20.0000 − 140.0000 Image width: 3.0000 Exp time: 300.0000 Rotation axis: Omega Omega: 0.0000 Chi: 54.0000 Phi: 0.0000 XTD: 127.4000 2theta: −0.0164 scan: Number of images: 40 Slice: 20.0000 − 140.0000 Image width: 3.0000 Exp time: 300.0000 Rotation axis: Omega Omega: 0.0000 Chi: 54.0000 Phi: 180.0000 XTD: 127.4000 2theta: −0.0164;

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*	$U_{\rm iso}$*/$U_{\rm eq}$
S3	0.78564 (4)	0.08290 (4)	0.87088 (4)	0.02157 (9)
S1	0.46153 (4)	0.27359 (4)	0.42090 (4)	0.01932 (8)
S2	0.71016 (4)	0.23908 (4)	0.59050 (4)	0.01981 (9)
S4	0.11016 (4)	0.14093 (4)	0.42447 (4)	0.01854 (8)
S5	0.32847 (4)	0.01628 (4)	0.74868 (4)	0.01852 (8)
C3	0.63223 (17)	0.13923 (14)	0.70953 (15)	0.0171 (2)
C1	0.34299 (16)	0.17310 (14)	0.50870 (15)	0.0169 (2)
C2	0.43995 (16)	0.11596 (14)	0.64918 (14)	0.0167 (2)
C4	0.04858 (18)	0.23962 (16)	0.24812 (15)	0.0198 (2)
H4'	0.132 (3)	0.221 (2)	0.206 (2)	0.023 (4)*
H4	−0.060 (3)	0.193 (2)	0.187 (3)	0.031 (5)*
C5	0.02689 (19)	0.40643 (16)	0.26544 (18)	0.0234 (3)
H5'	0.137 (3)	0.454 (2)	0.342 (3)	0.030 (5)*
H5	0.002 (3)	0.452 (2)	0.170 (3)	0.029 (5)*
C6	−0.12281 (19)	0.43476 (16)	0.31424 (17)	0.0235 (3)
C7	0.24831 (17)	0.17041 (16)	0.82867 (16)	0.0205 (2)
H7'	0.189 (3)	0.240 (2)	0.749 (2)	0.029 (5)*
H7	0.159 (3)	0.127 (2)	0.863 (3)	0.030 (5)*
C8	0.40294 (19)	0.25499 (18)	0.95806 (19)	0.0251 (3)
H8'	0.488 (3)	0.300 (2)	0.924 (3)	0.032 (5)*
H8	0.460 (3)	0.189 (3)	1.034 (3)	0.051 (7)*
C9	0.33548 (19)	0.37807 (17)	1.02277 (17)	0.0244 (3)
N1	−0.23980 (19)	0.45526 (17)	0.35162 (18)	0.0316 (3)
N2	0.27916 (19)	0.47209 (17)	1.07180 (17)	0.0312 (3)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S3	0.01647 (14)	0.02912 (18)	0.01666 (17)	0.00163 (12)	0.00343 (12)	0.00306 (13)
S1	0.01699 (14)	0.02243 (16)	0.01872 (16)	−0.00061 (11)	0.00692 (12)	0.00612 (12)
S2	0.01538 (14)	0.02338 (17)	0.02032 (17)	−0.00245 (11)	0.00665 (12)	0.00366 (12)
S4	0.01426 (13)	0.02114 (16)	0.01837 (16)	−0.00064 (11)	0.00410 (12)	0.00548 (12)
S5	0.01756 (14)	0.01897 (16)	0.01959 (16)	−0.00034 (11)	0.00763 (12)	0.00545 (12)
C3	0.0164 (5)	0.0181 (5)	0.0166 (5)	−0.0002 (4)	0.0062 (4)	0.0010 (4)
C1	0.0157 (5)	0.0171 (5)	0.0176 (6)	−0.0005 (4)	0.0062 (4)	0.0025 (4)
C2	0.0149 (5)	0.0184 (6)	0.0169 (6)	−0.0004 (4)	0.0063 (4)	0.0033 (4)
C4	0.0185 (5)	0.0234 (6)	0.0157 (6)	0.0003 (5)	0.0045 (5)	0.0032 (5)
C5	0.0220 (6)	0.0237 (6)	0.0278 (7)	0.0039 (5)	0.0127 (5)	0.0091 (5)
C6	0.0241 (6)	0.0220 (6)	0.0246 (7)	0.0036 (5)	0.0090 (5)	0.0078 (5)

C7	0.0172 (5)	0.0247 (6)	0.0209 (6)	0.0018 (5)	0.0085 (5)	0.0045 (5)
C8	0.0211 (6)	0.0266 (7)	0.0260 (7)	0.0028 (5)	0.0071 (5)	0.0006 (5)
C9	0.0241 (6)	0.0281 (7)	0.0212 (6)	0.0015 (5)	0.0086 (5)	0.0058 (5)
N1	0.0296 (6)	0.0359 (7)	0.0335 (7)	0.0053 (5)	0.0161 (6)	0.0080 (6)
N2	0.0331 (7)	0.0340 (7)	0.0291 (7)	0.0037 (5)	0.0147 (6)	0.0017 (6)

Geometric parameters (Å, °)

C1—C2	1.3837 (19)	C4—H4	0.92 (2)
C2—C3	1.4298 (16)	C5—C6	1.4715 (19)
S1—C1	1.7248 (12)	C5—H5'	0.98 (2)
S1—S2	2.0702 (5)	C5—H5	0.96 (2)
S2—C3	1.7328 (13)	C6—N1	1.143 (2)
S3—C3	1.6613 (14)	C7—C8	1.529 (2)
S4—C1	1.7366 (13)	C7—H7'	0.98 (2)
S4—C4	1.8153 (14)	C7—H7	0.96 (2)
S5—C2	1.7616 (12)	C8—C9	1.471 (2)
S5—C7	1.8178 (15)	C8—H8'	0.94 (2)
C4—C5	1.527 (2)	C8—H8	0.93 (3)
C4—H4'	0.920 (19)	C9—N2	1.144 (2)

C1—S1—S2	93.66 (5)	C6—C5—H5'	107.4 (12)
C3—S2—S1	97.63 (5)	C4—C5—H5'	110.3 (13)
C1—S4—C4	103.36 (6)	C6—C5—H5	107.9 (13)
C2—S5—C7	100.01 (6)	C4—C5—H5	109.9 (13)
C2—C3—S3	129.80 (10)	H5'—C5—H5	109.5 (17)
C2—C3—S2	112.88 (10)	N1—C6—C5	179.28 (17)
S3—C3—S2	117.31 (7)	C8—C7—S5	111.61 (9)
C2—C1—S1	117.78 (9)	C8—C7—H7'	109.0 (12)
C2—C1—S4	120.33 (9)	S5—C7—H7'	109.6 (12)
S1—C1—S4	121.88 (8)	C8—C7—H7	112.2 (13)
C1—C2—C3	117.97 (11)	S5—C7—H7	105.9 (13)
C1—C2—S5	120.60 (9)	H7—C7—H7	108.5 (17)
C3—C2—S5	121.43 (10)	C9—C8—C7	110.91 (12)
C5—C4—S4	114.45 (10)	C9—C8—H8'	105.7 (13)
C5—C4—H4'	112.1 (12)	C7—C8—H8'	111.8 (14)
S4—C4—H4'	108.1 (13)	C9—C8—H8	109.7 (16)
C5—C4—H4	109.8 (14)	C7—C8—H8	109.0 (16)
S4—C4—H4	103.3 (14)	H8'—C8—H8	110 (2)
H4'—C4—H4	108.5 (18)	N2—C9—C8	178.41 (15)
C6—C5—C4	111.76 (11)		

C1—S1—S2—C3	−2.15 (6)	S3—C3—C2—C1	−178.61 (11)
S1—S2—C3—C2	1.46 (10)	S2—C3—C2—C1	0.17 (17)
S1—S2—C3—S3	−179.59 (7)	S3—C3—C2—S5	0.80 (19)
S2—S1—C1—C2	2.73 (11)	S2—C3—C2—S5	179.58 (7)
S2—S1—C1—S4	−176.32 (8)	C7—S5—C2—C1	−78.86 (12)
C4—S4—C1—C2	179.01 (11)	C7—S5—C2—C3	101.74 (12)
C4—S4—C1—S1	−1.97 (10)	C1—S4—C4—C5	−83.02 (10)
S1—C1—C2—C3	−2.27 (18)	S4—C4—C5—C6	−63.92 (14)
S4—C1—C2—C3	176.80 (10)	C2—S5—C7—C8	−72.34 (11)

S1—C1—C2—S5	178.32 (7)	S5—C7—C8—C9	−179.28 (10)
S4—C1—C2—S5	−2.62 (17)		

Fig. 1

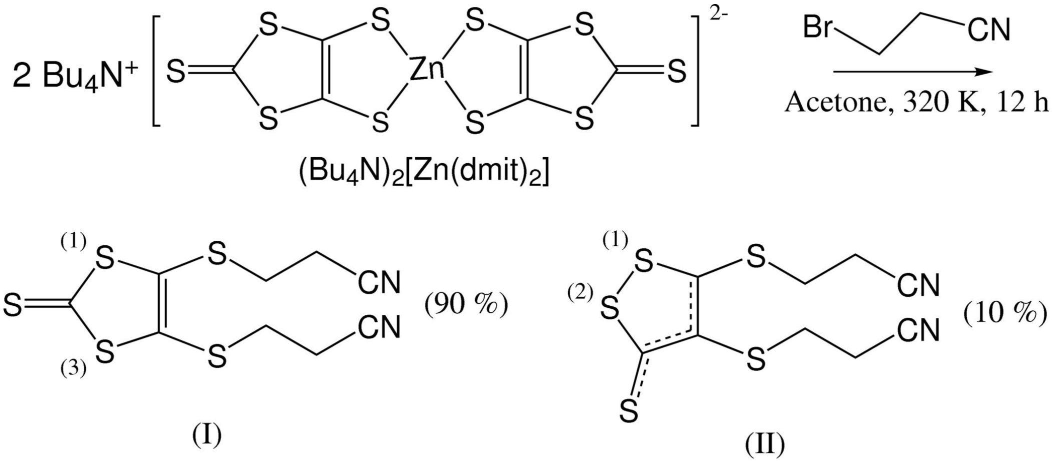

Fig. 2

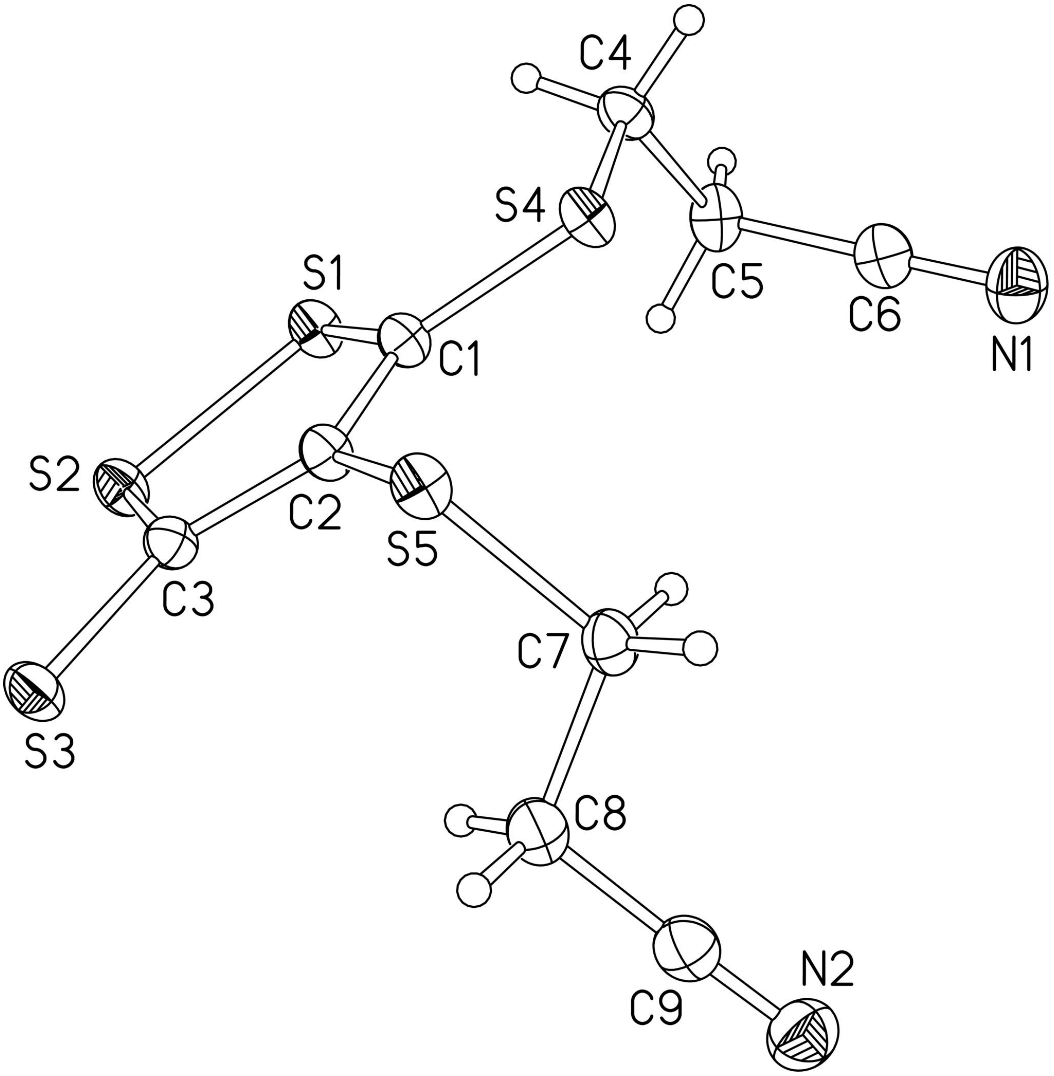

Fig. 3