

## 3,9-Bis(dicyanomethylene)-2,4,8,10-tetrathiaspiro[5.5]undecane

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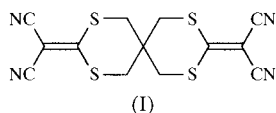
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The title compound, 2,2'-(2,4,8,10-tetrathiaspiro[5.5]undecane-3,9-diylidene)bis(propanedinitrile), C<sub>13</sub>H<sub>8</sub>N<sub>4</sub>S<sub>4</sub>, has been designed and synthesized for use as a potential new organic molecular electronic material. The spiro-annulated structure has twofold symmetry and is formed by two equal push–pull ethylene units, with the cycloalkylthio groups as electron donors and the cyano groups as electron acceptors. The intermolecular S···N non-bonded separation within a layer in the lattice is 3.296 (6) Å, indicating a strong intermolecular interaction between the cyano groups and the S atoms, while the S atoms in two neighbouring molecules have a shortest S···S contact of 3.449 (3) Å. In addition, attractive C—H···N and C—H···S interactions bridge adjacent molecules either within a layer or between layers. In short, these four types of intermolecular interactions combine to form an extended three-dimensional network in the lattice, resulting in a highly ordered array of molecular packing.

## Comment

We have designed and synthesized the title compound, (I), as a potential new organic molecular electronic material with high thermal stability. The compound was synthesized by the reaction of pentaerythrityl iodide and Na<sub>2</sub>[S<sub>2</sub>C=C(CN)<sub>2</sub>], which was prepared from malonitrile and carbon disulfide (Ericsson *et al.*, 1975).



The novel spiro-annulated structure of (I) is formed by two dithiane rings and has a crystallographic twofold rotation axis passing through C2. The molecular structure and atom-labelling scheme are shown in Fig. 1. Each six-membered ring adopts a twisted boat conformation, with a C2—C3—S2—C4 torsion angle of  $-69.5(4)^\circ$  and a C3—S2—C4—C5 torsion angle of  $-146.6(5)^\circ$ . It is noteworthy that the presence of two

equal push–pull ethylene units, with the cycloalkylthio groups as electron donors and the cyano groups as electron acceptors, most probably leads to diverse attractive close interactions in the lattice.

The S···N non-bonded separation is 3.296 (6) Å, which indicates a strong intermolecular interaction between these two atoms. Two of the four cyano groups in each molecule interact with S atoms of the neighbouring molecules in the same layer. Interacting *via* the [S<sub>2</sub>C=C(CN)<sub>2</sub>] moieties, the intermolecular S···N (donor–acceptor) electronic interactions form a series of parallel chains propagating in the *c* direction within each layer (as shown in Fig. 2). Also noteworthy is the existence of a short S···S (donor–donor) contact of 3.449 (3) Å between pairs of adjacent molecules in each layer, which forms a zigzag pattern extending along the *c* axis (as shown in Fig. 2). These types of S···S close contacts are often observed in the unique stacking of TTF-like compounds (TTF is tetrathiafulvalene; Bryce, 1995). In addition, there also exist various weak interlayer S···N interactions [non-bonded separations in the range 3.767 (7)–3.857 (6) Å], as well as S···S short contacts [3.913 (2) Å].

Further examination of the crystal structure of (I) reveals the existence of possible C—H···N and C—H···S interactions, which are either within or between layers (Fig. 2). Using standard criteria for C—H···O hydrogen bonds (Steiner, 1997; Desiraju, 1996), we noticed certain short intermolecular distances between C and N atoms in each layer, which reflect the existence of weak C3—H3B···N2<sup>i</sup> and C1—H1B···N2<sup>ii</sup> hydrogen bonds [symmetry codes: (i)  $2 - x, -y, 1 - z$ ; (ii)  $x, -y, \frac{1}{2} + z$ ]. The C···N separations for these interactions are 3.659 (9) and 3.546 (8) Å, respectively, and the C—H···N angles are 140 and 119°, respectively. In addition, molecules in different layers are bridged by at least three independent weak C—H···N1 interactions, whose C···N separations range from 3.227 (8) to 3.613 (8) Å, and whose C—H···N angles vary from 100 to 141°. Also, short C···S distances between neighbouring layers may be indicative of two independent weak hydrogen bonds formed by C1, S1<sup>iii</sup> and the two H atoms riding on C1 [symmetry code: (iii)  $\frac{3}{2} - x, \frac{1}{2} + y, \frac{3}{2} - z$ ]. The C···S separation is 3.704 (6) Å and the C—H···S angles are 110° and 94°. Full details of the hydrogen-bonding geometry in (I) are given in Table 1.

The electron-withdrawing effect of the [S<sub>2</sub>C=C(CN)<sub>2</sub>] moiety induces a partial positive charge on the adjacent C atoms and on the H atoms to which they are bonded. This would support our contention that the short C—H···N and

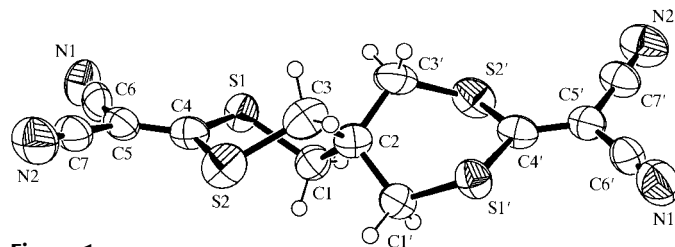
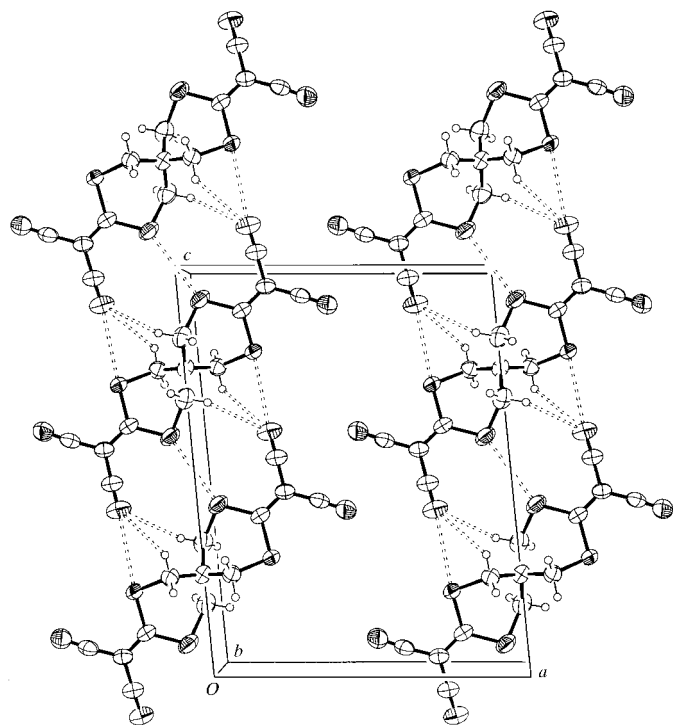


Figure 1

The molecular structure of (I), with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.



**Figure 2**  
The crystal structure of (I), viewed along the *b* axis. Dashed lines indicate intralayer S...N intermolecular interactions, shortest S...S contacts and C—H...N hydrogen bonds.

C—H...S interactions could be considered attractive interactions in the lattice.

In conclusion, the strong S...N interactions, shortest S...S contacts and weak C—H...N hydrogen bonds form isolated repeating belts within each layer, while the interlayer contacts, such as S...N, S...S, C—H...N and C—H...S, bridge these interlayer belts. As a result, all four types of interaction together weave an extended three-dimensional network in the lattice of (I), resulting in a highly ordered array of molecular packing.

## Experimental

Compound (I) was synthesized by reacting pentaerythrityl iodide and  $\text{Na}_2[\text{S}_2\text{C}=\text{C}(\text{CN})_2]$ , which was prepared *in situ* by a modification of the literature method of Ericsson *et al.* (1975), in dry benzene and dimethylformamide (1:1) at 333 K for about 20 h. Work-up gave the crude product (yield 60%) which was purified by recrystallization from hot acetonitrile and dimethylformamide (1:2) to obtain pale-yellow prisms of (I) (m.p. >573 K). Analysis calculated for  $\text{C}_{13}\text{H}_8\text{N}_4\text{S}_4$ : C 44.80, H 2.31, N 16.08%; found: C 44.87, H 2.40, N 15.90%;  $^{13}\text{C}$  NMR (DMSO-*d*<sub>6</sub>,  $\delta$ , p.p.m.): 38.3, 40.5, 73.9, 112.5, 188.7.

### Crystal data

$\text{C}_{13}\text{H}_8\text{N}_4\text{S}_4$   
 $M_r = 348.47$   
 Monoclinic, *C*2/*c*  
 $a = 12.596$  (8) Å  
 $b = 7.157$  (2) Å  
 $c = 16.498$  (3) Å  
 $\beta = 95.53$  (3)°  
 $V = 1480.4$  (11) Å<sup>3</sup>  
 $Z = 4$

$D_x = 1.564$  Mg m<sup>-3</sup>  
 Mo *K* $\alpha$  radiation  
 Cell parameters from 20 reflections  
 $\theta = 6.90$ – $12.25$ °  
 $\mu = 0.638$  mm<sup>-1</sup>  
 $T = 293$  (2) K  
 Prism, pale yellow  
 $0.3 \times 0.2 \times 0.2$  mm

### Data collection

Rigaku AFC-7R diffractometer  
 $\omega/2\theta$  scans  
 Absorption correction: empirical (North *et al.*, 1968)  
 $T_{\min} = 0.832$ ,  $T_{\max} = 0.883$   
 1370 measured reflections  
 1307 independent reflections  
 872 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.039$   
 $\theta_{\text{max}} = 24.99$ °  
 $h = 0 \rightarrow 14$   
 $k = 0 \rightarrow 8$   
 $l = -19 \rightarrow 19$   
 3 standard reflections  
 every 200 reflections  
 intensity decay:  $-1.18\%$

### Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.057$   
 $wR(F^2) = 0.177$   
 $S = 1.036$   
 1307 reflections  
 96 parameters  
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0659P)^2 + 6.8039P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\text{max}} < 0.001$   
 $\Delta\rho_{\text{max}} = 0.674$  e Å<sup>-3</sup>  
 $\Delta\rho_{\text{min}} = -0.346$  e Å<sup>-3</sup>

**Table 1**  
Hydrogen-bonding and short contact geometry (Å, °).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
C3—H3B...N2 <sup>i</sup>	0.97	2.86	3.659 (9)	140
C1—H1B...N2 <sup>ii</sup>	0.97	2.97	3.546 (8)	119
C1—H1B...N1 <sup>iii</sup>	0.97	2.81	3.613 (8)	141
C3—H3A...N1 <sup>iv</sup>	0.97	2.78	3.227 (8)	109
C3—H3B...N1 <sup>iv</sup>	0.97	2.91	3.227 (8)	100
C1—H1B...S1 <sup>iii</sup>	0.97	3.26	3.704 (6)	110
C1—H1A...S1 <sup>iii</sup>	0.97	3.50	3.704 (6)	94

Symmetry codes: (i)  $2-x, -y, 1-z$ ; (ii)  $x, -y, \frac{1}{2}+z$ ; (iii)  $\frac{3}{2}-x, \frac{1}{2}+y, \frac{3}{2}-z$ ; (iv)  $\frac{1}{2}+x, y-\frac{1}{2}, z$ .

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1992); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *TEXSAN* (Molecular Structure Corporation, 1985); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* (Farrugia, 1999); software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BJ1015). Services for accessing these data are described at the back of the journal.

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