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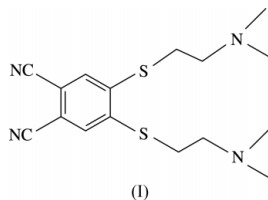
## Key indicators

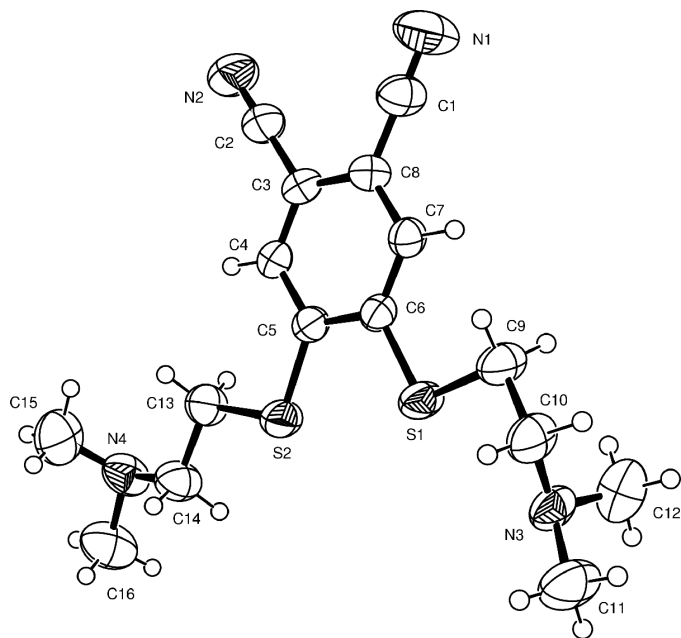
Single-crystal X-ray study  
 $T = 293\text{ K}$   
Mean  $\sigma(\text{C}-\text{C}) = 0.004\text{ \AA}$   
 $R$  factor = 0.045  
 $wR$  factor = 0.095  
Data-to-parameter ratio = 21.9For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

## 4,5-Dicyano-1,2-bis(2-dimethylaminoethylsulfanyl)benzene

The title compound,  $\text{C}_{16}\text{H}_{22}\text{N}_4\text{S}_2$ , contains a dicyanobenzene ring and two 2-dimethylaminoethylsulfanyl substituents that have a twist conformation. The crystal structure is stabilized by  $\text{C}-\text{H}\cdots\text{N}$  and  $\text{C}-\text{H}\cdots\pi$  interactions.

## Comment

Phthalonitriles have been used as starting materials for the synthesis of phthalocyanines (*Pc*) and their derivatives, which have been extensively studied and have found wide applications (Leznoff & Lever, 1996). The introduction of sulfanyl (Tian *et al.*, 2000), carboxyl (Kobayashi *et al.*, 1984) or amino (Derkacheva *et al.*, 1981) groups, or diazadithia macrocycles bearing sulfanyl groups (Yılmaz & Bekaroğlu, 1996) into peripheral position of phthalocyanines leads to water solubility over a wide pH range. Water solubility and aggregation properties of phthalocyanine derivatives are important and may have a strong influence on the bioavailability, the *in vivo* distribution and the singlet production efficiency. Quaternary ammonium groups are especially useful, providing solubility over wide pH ranges for phthalocyanine derivatives which are considered the best target molecules as photosensitizers for photodynamic therapy.For these reasons, the structures of 4,5-dicyanobenzene derivatives with different substituents have been of much interest in our laboratory (Çoruh, Akdemir, Ağar, Kim & Erdönmez, 2002; Çoruh, Akdemir, Ağar, Vázquez-López & Erdönmez, 2002; Çoruh, Işık *et al.*, 2002). The molecular structure of the title compound, (I), is shown in Fig. 1. Tables 1 and 2 list selected molecular and hydrogen-bonding geometry. The molecule consists of a benzene ring substituted by two 2-dimethylaminoethylsulfanyl moieties at positions 1 and 2, and substituted by two cyano groups at positions 4 and 5. The  $\text{N}\equiv\text{C}$  distances of 1.138 (4) and 1.141 (3) Å are similar to values reported in the literature (Çoruh, Akdemir, Ağar, Kim & Erdönmez, 2002; Çoruh, Akdemir, Ağar, Vázquez-López & Erdönmez, 2002; Çoruh, Işık *et al.*, 2002; Karadayı *et al.*, 2003). The  $\text{S}1-\text{C}6$  and  $\text{S}2-\text{C}5$  distances are 1.752 (3) and 1.742 (3) Å, respectively, and also show good agreement with corresponding distances reported previously (Çoruh, Akdemir, Ağar, Kim & Erdönmez, 2002). While the bond lengths at sulfur are essentially equal, the  $\text{C}5-\text{S}2-\text{C}13-\text{C}14$ Received 28 October 2003  
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**Figure 1**  
The structure of (I), with the atomic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

and C6—S1—C9—C10 torsion angles of  $-179.3(2)$  and  $165.6(2)^\circ$ , respectively, are different. This destroys any molecular symmetry.

The 4,5-dicyanobenzene moiety and the 2-dimethylaminoethylsulfanyl moieties form weak hydrogen bonds, details of which are in Table 2; these contribute to the stability of the crystal structure.

The structure of (I) also shows an intermolecular C—H $\cdots\pi$  contact involving the benzene ring of a symmetry-related molecule (Table 2).

## Experimental

The title compound was synthesized according to a reported procedure (Gürsoy *et al.*, 2001). 1,2-Dichloro-4,5-dicyanobenzene and 2-dimethylaminoethanethiol hydrochloride were dissolved in dry DMF at 293 K under a nitrogen atmosphere. Finely ground anhydrous  $K_2CO_3$  was added in portions over 2 h. The reaction mixture was stirred under nitrogen at 293 K for 30 h, then poured into ice-water. The resulting solid was collected by filtration and washed with water. It was recrystallized from *n*-hexane and then from an ethanol/water mixture. Single crystals of (I) were obtained *via* slow evaporation of the solvent from a solution in *n*-hexane/ $CH_2Cl_2$ .

### Crystal data

$C_{16}H_{22}N_4S_2$	Mo $K\alpha$ radiation
$M_r = 334.50$	Cell parameters from 7087 reflections
Orthorhombic, <i>Pbca</i>	$\theta = 2.1\text{--}25.8^\circ$
$a = 9.5897(6) \text{ \AA}$	$\mu = 0.29 \text{ mm}^{-1}$
$b = 27.024(2) \text{ \AA}$	$T = 293(2) \text{ K}$
$c = 14.3392(14) \text{ \AA}$	Lath, pale yellow
$V = 3716.1(5) \text{ \AA}^3$	$0.80 \times 0.34 \times 0.08 \text{ mm}$
$Z = 8$	
$D_x = 1.196 \text{ Mg m}^{-3}$	

### Data collection

Stoe IPDS2 diffractometer	4367 independent reflections
$\omega$ scans	1651 reflections with $I > 2\sigma(I)$
Absorption correction: by integration ( <i>X-RED32</i> ; Stoe & Cie, 2002)	$R_{\text{int}} = 0.092$
$T_{\text{min}} = 0.802$ , $T_{\text{max}} = 0.977$	$\theta_{\text{max}} = 27.8^\circ$
26348 measured reflections	$h = -12 \rightarrow 11$
	$k = -35 \rightarrow 35$
	$l = -18 \rightarrow 18$

### Refinement

Refinement on $F^2$	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.045$	$w = 1/[\sigma^2(F_o^2) + (0.0239P)^2]$
$wR(F^2) = 0.096$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 0.72$	$(\Delta/\sigma)_{\text{max}} = 0.001$
4367 reflections	$\Delta\rho_{\text{max}} = 0.18 \text{ e \AA}^{-3}$
199 parameters	$\Delta\rho_{\text{min}} = -0.32 \text{ e \AA}^{-3}$

**Table 1**

Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ ).

C11—N3	1.457(4)	C2—N2	1.141(3)
C12—N3	1.452(4)	C14—N4	1.462(3)
S1—C6	1.752(3)	C14—C13	1.505(3)
S1—C9	1.806(3)	N3—C10	1.439(3)
S2—C5	1.742(3)	N4—C16	1.444(4)
S2—C13	1.818(3)	N4—C15	1.447(4)
C3—C2	1.431(4)	C1—N1	1.138(4)
C8—C1	1.423(4)	C10—C9	1.527(4)
C6—S1—C9	103.37(12)	C6—C5—S2	117.66(19)
C5—S2—C13	103.21(12)	C7—C6—S1	124.77(19)
C4—C5—S2	124.6(2)	C5—C6—S1	115.40(19)
C13—S2—C5—C4	5.3(3)	C13—C14—N4—C15	-66.0(3)
C8—C7—C6—C5	2.1(4)	C12—N3—C10—C9	65.4(3)
S2—C5—C6—S1	-3.0(3)	N3—C10—C9—S1	53.2(3)
C9—S1—C6—C7	7.6(3)	C6—S1—C9—C10	165.6(2)

**Table 2**

Hydrogen-bonding geometry ( $\text{\AA}$ ,  $^\circ$ ).

$D\text{---}H\cdots A$	$D\text{---}H$	$H\cdots A$	$D\cdots A$	$D\text{---}H\cdots A$
C11—H11A $\cdots$ N1 <sup>i</sup>	0.96	2.83	3.768(5)	166
C12—H12C $\cdots$ N1 <sup>ii</sup>	0.96	2.86	3.731(5)	152
C7—H7 $\cdots$ N3 <sup>iii</sup>	0.93	2.83	3.737(3)	165
C13—H13A $\cdots$ N2 <sup>iv</sup>	0.97	2.69	3.597(4)	155
C15—H15B $\cdots$ N2 <sup>iv</sup>	0.96	2.84	3.779(5)	166
C10—H10B $\cdots$ N1 <sup>v</sup>	0.97	2.90	3.789(5)	154
C13—H13B $\cdots$ N4 <sup>vi</sup>	0.97	2.89	3.738(4)	147
C16—H16B $\cdots$ N2 <sup>vii</sup>	0.96	2.99	3.899(5)	159
C11—H11C $\cdots$ Cg1 <sup>viii</sup>	0.96	2.90	3.738(4)	147

Symmetry codes: (i)  $1+x, \frac{3}{2}-y, \frac{1}{2}+z$ ; (ii)  $\frac{1}{2}+x, \frac{3}{2}-y, 1-z$ ; (iii)  $x-\frac{1}{2}, y, \frac{3}{2}-z$ ; (iv)  $-x, 1-y, 1-z$ ; (v)  $\frac{1}{2}+x, y, \frac{3}{2}-z$ ; (vi)  $1-x, 1-y, 1-z$ ; (vii)  $\frac{1}{2}-x, 1-y, \frac{1}{2}+z$ ; (viii)  $x, \frac{1}{2}-y, \frac{1}{2}+z$ . Cg1 is the centroid of the benzene ring at  $x, \frac{1}{2}-y, \frac{1}{2}+z$ .

All H atoms were positioned geometrically and treated as riding atoms, with C—H distances in the range 0.93–0.97  $\text{\AA}$  and  $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$  for methyl groups and  $1.2U_{\text{eq}}(\text{C})$  for others.

Data collection: *X-AREA* (Stoe & Cie, 2002); cell refinement: *X-AREA*; data reduction: *X-RED* (Stoe & Cie, 2002); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *SHELXL97* and *WinGX* (Farrugia, 1999).

## References

- Çoruh, U., Akdemir, N., Açar, E., Kim, Y. & Erdönmez, A. (2002). *Acta Cryst.* **E58**, o994–o996.
- Çoruh, U., Akdemir, N., Açar, E., Vázquez-López, E. M. & Erdönmez, A. (2002). *Acta Cryst.* **E58**, o896–o897.
- Çoruh, U., Işık, Ş., Akdemir, N., Açar, E., Vázquez-López, E. M. & Erdönmez, A. (2002). *Acta Cryst.* **E58**, o953–o955.
- Derkacheva, V. M., Bundina, N. I., Mekhyakova, N. G., Kaliya, O. L., Gulinat, T. Y. & Lukyanets, E. A. (1981). *Russ. J. Inorg. Chem. (Engl. Ed.)*, **26**, 911–913.
- Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
- Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.
- Gürsoy, S., Cihan, A., Koçak, M. B. & Bekaroğlu, Ö. (2001). *Monatsh. Chem.* **132**, 813–819.
- Karadayı, N., Akdemir, N., Açar, E., Gümrükçüoğlu, İ.E. & Büyükğüngör, O. (2003). *Acta Cryst.* **E59**, o945–o946.
- Kobayashi, N., Shirai, H. & Hojo, N. (1984). *J. Chem. Soc. Dalton Trans.* pp. 2107–2110.
- Leznoff, C. C. & Lever, A. B. P. (1996). *Phthalocyanines, Properties and Applications*. Vols. 1–4. Weinheim: VCH.
- Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
- Stoe & Cie (2002). *X-Area* (Version 1.18) and *X-RED32* (Version 1.04). Stoe & Cie, Darmstadt, Germany.
- Tian, H., Ali, H., Johan, E. & Van Lier, J. E. (2000). *Tetrahedron Lett.* **41**, 2435–2438.
- Yılmaz, İ. & Bekaroğlu, Ö. (1996). *Chem. Ber.* **129**, 967–971.