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## Key indicators

Single-crystal X-ray study

T = 293 K

Mean  $\sigma(\text{C}-\text{C}) = 0.005 \text{ \AA}$ 

R factor = 0.046

wR factor = 0.134

Data-to-parameter ratio = 14.9

For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.Dimethyl 2,2'-(4,5-dicyano-*o*-phenylenedithio)-  
diacetate

The title compound, 4,5-di(mercaptoacetic acid methyl ester)-phthalonitrile,  $\text{C}_{14}\text{H}_{12}\text{N}_2\text{O}_4\text{S}_2$ , exhibits five intermolecular hydrogen bonds, four of them  $\text{C}-\text{H}\cdots\text{O}$  bonds and the other a  $\text{C}-\text{H}\cdots\text{N}$  bond. The molecule contains three different molecular planes, two of which pass through the ester groups, while the other includes the aromatic ring. The dihedral angles between the ester-group planes and the aromatic ring plane are  $74.98(1)$  and  $58.55(1)^\circ$ , while the dihedral angle between the two ester-group planes is  $63.55(1)^\circ$ .

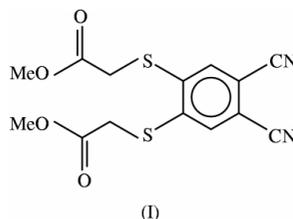
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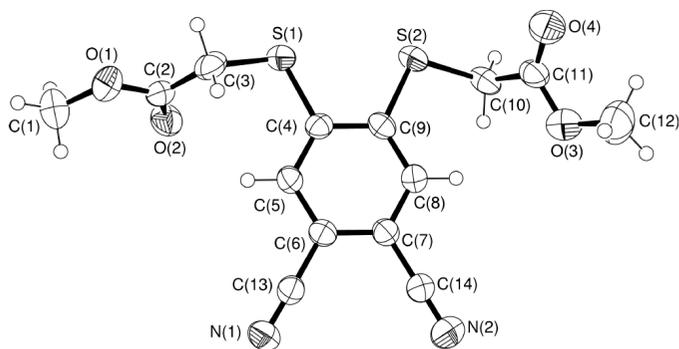
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## Comment

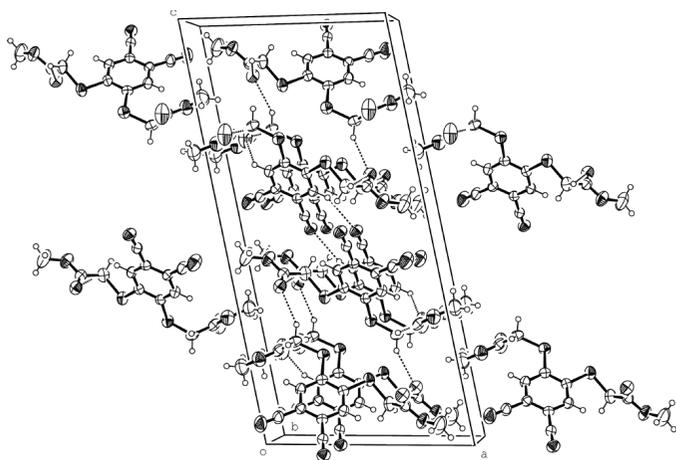
Phthalonitriles have been used as starting materials for phthalocyanines (Leznoff & Lever, 1996), which are important components for dyes, pigments, gas sensors, optical limiters and liquid crystals, and which are also used in medicine, as singlet oxygen photosensitisers for photodynamic therapy (PDT) (McKeown, 1998). Some phthalocyanines have been used by the petroleum industry as catalysts for the oxidation of sulfur compounds in the gasoline fraction. Applications as photoconductors in the xerographic double layers of laser printers and copy machines, and as active materials in writable disks, are also known (Wöhrle, 2001).



The title molecule, (I), is shown in Fig. 1, with selected bond angles and hydrogen-bond parameters in Tables 1 and 2, respectively. The structure shows that the  $\text{N1}\equiv\text{C13}$  and  $\text{N2}\equiv\text{C14}$  distances of  $1.143(4)$  and  $1.128(4) \text{ \AA}$ , respectively, correspond to literature values (Öztürk *et al.*, 2000). All bond lengths in the ester groups of (I) are similar to those in recently reported structures containing ester groups (Armelin, Urpi *et al.*, 2001; Armelin, Escudero *et al.*, 2001; Bujak *et al.*, 2002). The  $\text{C3}-\text{S1}-\text{C4}$  and  $\text{C9}-\text{S2}-\text{C10}$  angles of  $103.62(16)$  and  $103.82(15)^\circ$ , respectively, show good agreement, whereas the  $\text{C2}-\text{C3}-\text{S1}-\text{C4}$  and  $\text{C9}-\text{S2}-\text{C10}-\text{C11}$  torsion angles of  $-90.1(3)$  and  $-92.1(3)^\circ$ , respectively, show a small difference. The ester groups and the aromatic ring are planar to within experimental error, with a maximum deviation of  $0.0152 \text{ \AA}$  from the mean planes defined by the ester groups,  $\text{O1/O2/C1/C2/C3}$  and  $\text{O3/O4/C10/C11/C12}$ , and a maximum deviation of  $0.0202(1) \text{ \AA}$  from the best plane defined by the aromatic ring.



**Figure 1**  
A view of (I) with the atomic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.



**Figure 2**  
The hydrogen-bond network observed in (I), viewed approximately along the [010] axis of the monoclinic cell.

In the molecule of (I), the  $S1 \cdots S2$  distance is 3.003 Å. Repulsion between  $C5-H5$  and  $C3-H3A$  leads to an enlargement of the  $S1-C4-C5$  angle. While the  $S1-C4-C5$  angle is  $123^\circ$ , the  $S1-C4-C9$  angle is  $117^\circ$ . Similarly, the  $S2-C9-C8$  angle is  $129^\circ$ , whereas the  $S2-C9-C4$  angle is  $117^\circ$ .

In the case of (I), the ester groups and the phenyl ring are able to form hydrogen bonds with the ester moieties and phenyl ring of a symmetry-related molecule. All details of the  $C-H \cdots O$  and  $C-H \cdots N$  types of intermolecular interaction found in the crystal, by which the crystal structure is stabilized, can be seen in Table 2. These contacts generate infinite chains along the [010] axis (Fig. 2) and seem to force the molecule to adopt a twisted conformation, with the dihedral angle between ester groups being far from  $0^\circ$ . This arrangement also explains the absence of intramolecular hydrogen bonds in (I). Considering atoms O2 and O4 as potential acceptors, the observed contacts are  $C1-H1C \cdots O2$  and  $C12-H12A \cdots O4$ , with angles of 84.4 and  $97.1^\circ$ , respectively, *i.e.* with electrostatic interaction energies approaching zero.

## Experimental

Mercaptoacetic acid methyl ester and 1,2-dichloro-4,5-dicyanobenzene were dissolved in anhydrous dimethylformamide under an

$N_2$  atmosphere, and then dry fine-powdered potassium carbonate was added in several portions over a period of 2 h with efficient stirring. The product was then recrystallized from ethanol and dried. Single crystals of (I) were obtained *via* slow evaporation from absolute ethanol.

### Crystal data

$C_{14}H_{12}N_2O_4S_2$   
 $M_r = 336.38$   
Monoclinic,  $P2_1/c$   
 $a = 12.1201$  (1) Å  
 $b = 5.148$  (1) Å  
 $c = 24.944$  (1) Å  
 $\beta = 101.20$  (1) $^\circ$   
 $V = 1526.8$  (3) Å $^3$   
 $Z = 4$

$D_x = 1.463$  Mg m $^{-3}$   
Mo  $K\alpha$  radiation  
Cell parameters from 25 reflections  
 $\theta = 8.2$ – $12.2^\circ$   
 $\mu = 0.37$  mm $^{-1}$   
 $T = 293$  (2) K  
Plate, dark yellow  
 $0.45 \times 0.25 \times 0.10$  mm

### Data collection

Enraf–Nonius CAD-4 MACH-3 diffractometer  
 $\omega/2\theta$  scans  
3152 measured reflections  
3004 independent reflections  
1853 reflections with  $I > 2\sigma(I)$   
 $R_{int} = 0.072$

$\theta_{max} = 26^\circ$   
 $h = 0 \rightarrow 14$   
 $k = 0 \rightarrow 6$   
 $l = -30 \rightarrow 30$   
3 standard reflections  
frequency: 60 min  
intensity decay: negligible

### Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.046$   
 $wR(F^2) = 0.134$   
 $S = 1.03$   
3004 reflections  
201 parameters  
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0586P)^2 + 0.7252P]$   
where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{max} = 0.001$   
 $\Delta\rho_{max} = 0.36$  e Å $^{-3}$   
 $\Delta\rho_{min} = -0.30$  e Å $^{-3}$

**Table 1**

Selected geometric parameters (Å,  $^\circ$ ).

C13–N1	1.143 (4)	C14–N2	1.128 (4)
C4–S1–C3	103.62 (16)	C9–S2–C10	103.82 (15)
O2–C2–C3–S1	14.5 (5)	C10–C11–O3–C12	177.6 (3)
S2–C10–C11–O4	−57.3 (5)	C2–C3–S1–C4	−90.1 (3)
C3–C2–O1–C1	−178.8 (3)	C11–C10–S2–C9	−92.1 (3)

**Table 2**

Short  $C-H \cdots O$  and  $C-H \cdots N$  contacts (Å,  $^\circ$ ).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
$C10-H10B \cdots O2^i$	0.97	2.44	3.32 (1)	151
$C8-H8 \cdots O4^{ii}$	0.93	2.57	3.14 (1)	120
$C10-H10A \cdots O4^{ii}$	0.97	2.45	3.41 (1)	168
$C5-H5 \cdots N1^{iii}$	0.93	2.57	3.42 (1)	153
$C3-H3B \cdots O2^{iv}$	0.98	2.42	3.34 (1)	160

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

H atoms were positioned geometrically and then refined isotropically with fixed displacement parameters.

Data collection: *CAD-4-PC Software* (Enraf–Nonius, 1992); cell refinement: *CAD-4-PC Software*; data reduction: *XCAD4/PC* (Harms, 1997); 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*.

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