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2,3-Bis(4-nitrobenzylthio)maleonitrile

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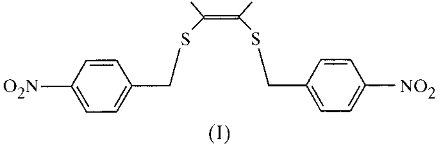
The maleonitrile moiety of the title compound, (2*Z*)-2,3-bis[(4-nitrobenzyl)sulfanyl]but-2-enedinitrile, $C_{18}H_{12}N_4O_4S_2$, is almost planar. The two benzene rings are nearly parallel to each other and perpendicular to the maleonitrile plane. Intermolecular S···S and π–π interactions are observed in the crystal structure.

Comment

New materials with useful properties (*e.g.* catalytic properties) may be afforded by infinite networks constructed from building blocks of various connectivities and geometries (Venkataraman *et al.*, 1995; Fujita *et al.*, 1994). Generally, the building blocks are ligands which are polydentate or which have groups that can be combined by weak interactions, namely hydrogen-bond, S···S or π–π interactions. Maleonitrile–dithiacrown ethers are a class of polydentate ligand whose S and nitrile N atoms are capable of bonding to metals, thus allowing the construction of self-assembling materials with new properties (Drexler *et al.*, 1999) and, as a result of this, they have attracted the interest of chemists. Maleonitrile–dithioethers, on the contrary, have been studied relatively little and they are expected to construct infinite network structures in combination with transition metals. We have recently synthesized the title compound, (I), which can act as a tetradentate ligand. The nitro group is capable of acting as a hydrogen-bond acceptor forming hydrogen bonds with hydrogen-bond donors. Intermolecular π–π interactions are also possible and the title compound is therefore a potential supramolecular building block.



(I)

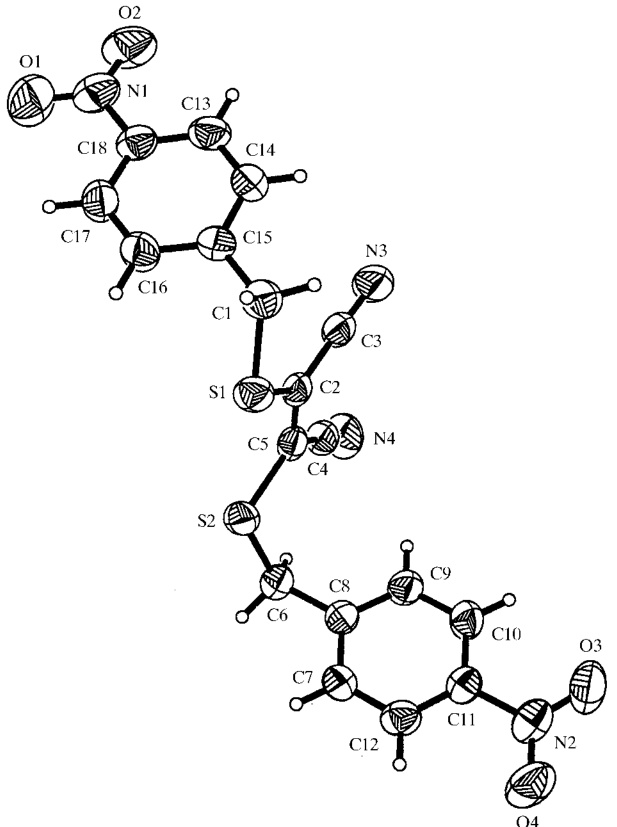


Figure 1
The molecular structure of the title compound. Displacement ellipsoids are shown at the 30% probability level.

The molecular structure of (I) is shown in Fig. 1. The maleonitrile moiety is almost planar, and the bond lengths and angles are consistent with those of an analogous compound (Spannenberg *et al.*, 1996). It is worth noting that the average C—S bond length linking to maleonitrile [1.750 (2) Å] is shorter than that linking to benzyl [1.820 (2) Å]; this arises from the *p*–π conjugation effect between the S atom and conjugated maleonitrile system. The two benzene rings adopt conformations which are away from the maleonitrile moiety, with a dihedral angle of 7.5 (3)° between them, almost parallel to one another, and nearly perpendicular to the maleonitrile plane; the dihedral angles between the benzene rings and maleonitrile plane are 88.6 (3) and 88.1 (3)°. The intramolecular S1···S2 distance is 3.110 (2) Å and the intermolecular S2···S2$(-x+\frac{1}{2}, -y+\frac{1}{2}, -z)$ distance is 3.272 (2) Å, which is

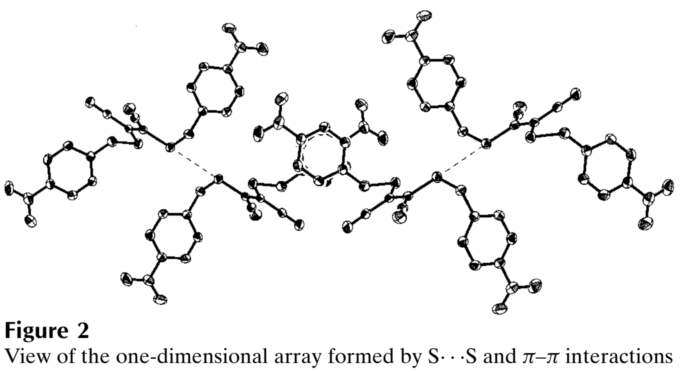


Figure 2
View of the one-dimensional array formed by S···S and π–π interactions in the structure of (I).

shorter than that of the dmit derivative 4,5-(2-hydroxypropylenedithio)-1,3-dithiolethione (Marshallsay *et al.*, 1993). An intermolecular π–π interaction occurs between the C13–C18 and C13–C18($-x$, y, $\frac{1}{2} - z$) benzene rings in (I). For an overlapping pair of benzene rings, the centroid–centroid distance is 4.086 (2) Å (Spek, 1990), the shortest atom–atom distance is 3.577 (2) Å, being larger than the distance of 3.48 Å in the TCNQ (tetracyanoquinodimethane) complex (Nakasuji *et al.*, 1987), and the dihedral angle between the two benzene rings is 13.2 (3)°. Infinite molecular chains are formed through intermolecular S···S and π–π interactions (Fig. 2).

Experimental

The title compound was prepared by refluxing a 2:1 molar ratio of 4-nitrobenzyl chloride and disodium maleonitriledithiolate in methanol. The precipitated product was filtered off, washed with methanol and dried under vacuum. Yellow crystals were recrystallized from an acetone–*n*-butanol solution of the compound (m.p. 419–421 K).

Crystal data

$C_{18}H_{12}N_4O_4S_2$
$M_r = 412.44$
Monoclinic, $C2/c$
$a = 29.456$ (6) Å
$b = 15.440$ (3) Å
$c = 8.1900$ (16) Å
$\beta = 99.52$ (3)°
$V = 3673.6$ (13) Å^3
$Z = 8$
$D_x = 1.491$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 1.68$–8.79°
$\mu = 0.324$ mm^{-1}
$T = 293$ (2) K
Block, yellow
0.32 × 0.26 × 0.24 mm

Data collection

FR590 CAD-4 diffractometer
$2\theta/\omega$ scans
3491 measured reflections
3237 independent reflections
2227 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.016$
$\theta_{\rm max} = 25°$
$h = -34 \rightarrow 34$
$k = 0 \rightarrow 18$
$l = 0 \rightarrow 9$
3 standard reflections every 97 reflections intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.033$
$wR(F^2) = 0.100$
$S = 1.012$
3237 reflections
254 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0454P)^2 + 2.8648P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.16$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.18$ e Å^{-3}
Extinction correction: *SHELXL*
Extinction coefficient: 0.0017 (2)

Table 1
Selected geometric parameters (Å, °).

S1—C2	1.743 (2)	C5—C4	1.431 (3)
S1—C1	1.816 (2)	C3—N3	1.137 (3)
S2—C5	1.750 (2)	C3—C2	1.426 (3)
S2—C6	1.820 (2)	N4—C4	1.137 (3)
C5—C2	1.351 (3)		
C2—S1—C1	103.48 (12)	N3—C3—C2	178.2 (3)
C5—S2—C6	103.65 (11)	C5—C2—C3	119.3 (2)
C2—C5—C4	120.9 (2)	C5—C2—S1	120.32 (17)
C2—C5—S2	120.13 (17)	C3—C2—S1	120.35 (19)
C4—C5—S2	118.79 (19)	N4—C4—C5	177.0 (3)

The H atoms were placed in geometrically calculated positions (C—H = 0.93 Å and N—H = 0.86 Å), with $U_{\rm eq}(H) = 1.2U_{\rm eq}$(parent atom).

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989); cell refinement: *CAD*-4 *Software*; data reduction: *CAD*-4 *Software*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 1997); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1375). Services for accessing these data are described at the back of the journal.

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