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# Bis(benzylsulfanyl)maleonitrile

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**Key indicators**

Single-crystal X-ray study
*T* = 100 K
Mean σ(C–C) = 0.002 Å
*R* factor = 0.035
*wR* factor = 0.089
Data-to-parameter ratio = 20.2

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

The title compound, $C_{18}H_{14}N_2S_2$, crystallizes as a pseudo-merohedral twin, with four independent molecules in the asymmetric unit. The compound shows a combination of π-interactions and close-packing, with the planar maleonitrile and phenyl groups extending into pockets of neighbouring molecules.

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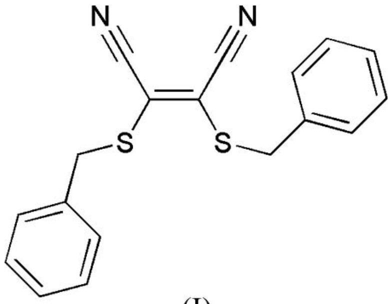
## Comment

Disodium dimercaptomaleonitrile ($Na_2MNT$) (Davison & Holm, 1967; Stiefel *et al.*, 1970) is a common precursor for the synthesis of numerous transition metal compounds with interesting magnetic and electronic properties (Alcácer & Novais, 1983; McCleverty, 1968; Schrauzer, 1969). Bis(benzylsulfanyl)maleonitrile, (I), is readily synthesized by the addition of a slight excess of two equivalents of benzyl bromide to $Na_2MNT$ in alcohols and has been used to prepare star-porphyrazineoctathiolate derivatives (Velázquez *et al.*, 1992). Our interests focus on the preparation of polymeric bis(benzylsulfanyl)maleonitrile derivatives *via* the hydroboration of the nitrile functional groups (Lesley *et al.*, 2003).



(I)

In the course of this work, we were able to isolate single crystals of (I). The solid-state structure was determined by single-crystal X-ray crystallography at 100 K. The compound was found to crystallize in the monoclinic space group $P2_1/c$ with unit-cell dimensions very close to orthorhombic [$\beta$ = 90.138 (1)°]. The initial *R* values after anisotropic refinement were unsatisfactorily high and, after further inspection of the data set, the crystal was found to be pseudo-merohedrally twinned. Introduction of the appropriate twin law ($100\ 0\bar{1}0\ 00\bar{1}$) and a refined twin fraction improved both the *R* values and the general structure quality significantly. The twin components are 12.80 (4)% for the minor and 87.20 (4)% for the major component.

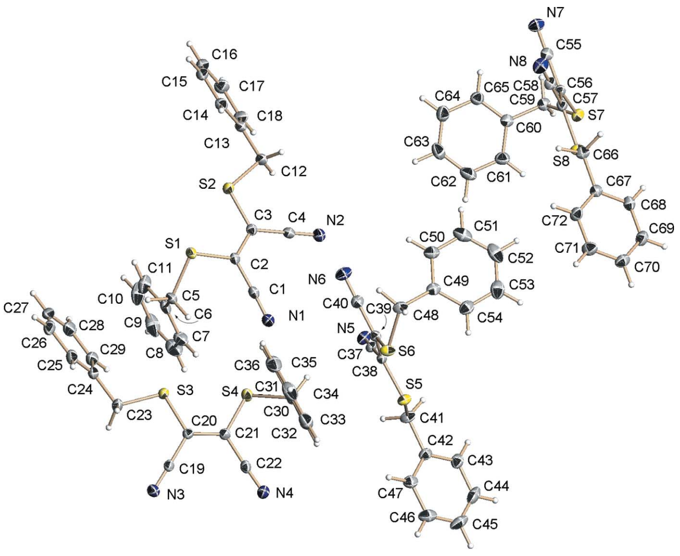


**Figure 1**
The four independent molecules of (I), showing 50% probability displacement ellipsoids and the atom labelling.

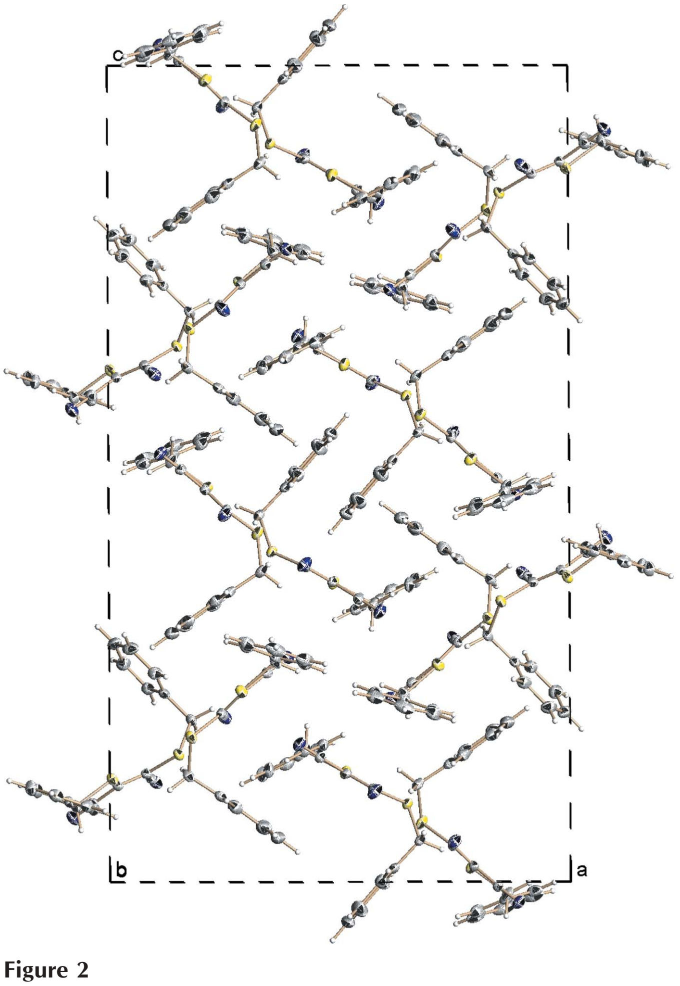


**Figure 2**
The crystal packing viewed along the *b* axis, showing the $\pi$ interactions of the phenyl and maleonitrile groups.

The compound crystallizes with four crystallographically independent molecules in the asymmetric unit (Fig. 1). The equivalent bond distances and angles (Table 1) for all four independent molecules do not differ significantly from each other and all are in the expected ranges. The torsion angles around the sulfur benzyl bonds are approximately either 60 or 180° (*i.e. syn* or *anti* orientation, Table 1) with each of the independent molecules having exactly one benzyl group in the *syn* and one in the *anti* position.

The maleonitrile units are approximately planar, and each unit as well as all but one of the phenyl rings are roughly perpedicular to the (010) plane (see Fig. 2). This allows all the maleonitrile as well as the phenyl groups to be located within a pocket of a neighbouring molecule and being simultaneously parallel to at least one planar maleonitrile or phenyl group. This results in a favourable combination of $\pi$-interactions and close packing of the bis(benzylsulfanyl)maleonitrile molecules in the crystal structure (Fig. 2) and could be the underlying cause for the unusual packing with four independent molecules in the asymmetric unit.

## Experimental

A sample of $Na_2MNT$ (5.000 g, 26.9 mmol) was dissolved in methanol (100 ml) in an ice bath and benzyl bromide (98%, 7.18 ml, 59.1 mmol) was added dropwise *via* a syringe. The solution was stirred gradually, warmed to room temperature for 2 h and the precipitate isolated by vacuum filtration. Recrystallization from a chloroform/hexane mixed-solvent system yielded yellow to colourless crystals of (I) which were collected by filtration and dried in air (yield 7.623 g, 88%; m.p. 344.0–345.4 K).

### *Crystal data*

$C_{18}H_{14}N_2S_2$
$M_r = 322.43$
Monoclinic, $P2_1/c$
$a = 18.1665\ (13)$ Å
$b = 11.0409\ (8)$ Å
$c = 32.197\ (2)$ Å
$\beta = 90.138\ (1)°$
$V = 6457.9\ (8)$ Å$^3$
$Z = 16$
$D_x = 1.327$ Mg m$^{-3}$
Mo $K\alpha$ radiation
Cell parameters from 9419 reflections
$\theta = 2.2$–$28.3°$
$\mu = 0.33$ mm$^{-1}$
$T = 100\ (2)$ K
Chunk (cut from larger crystal), colourless
0.50 × 0.40 × 0.40 mm

### *Data collection*

Bruker AXS SMART APEX CCD diffractometer
$\omega$ scans
Absorption correction: multi-scan (*SADABS* in *SAINT-Plus*; Bruker, 2003)
$T_{\min} = 0.722$, $T_{\max} = 0.877$
67954 measured reflections
16071 independent reflections
15009 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.034$
$\theta_{\max} = 28.3°$
$h = -24 \rightarrow 24$
$k = -14 \rightarrow 14$
$l = -42 \rightarrow 42$

### *Refinement*

Refinement on $F^2$
$R[F^2 > 2\sigma(F^2)] = 0.035$
$wR(F^2) = 0.089$
$S = 1.03$
16071 reflections
794 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0471P)^2 + 2.229P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.002$
$\Delta\rho_{\max} = 0.55$ e Å$^{-3}$
$\Delta\rho_{\min} = -0.27$ e Å$^{-3}$

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**Table 1**
Selected geometric parameters (Å, °).

| | | | |
|---|---|---|---|
| S1—C2 | 1.7489 (14) | N5—C37 | 1.144 (2) |
| S1—C5 | 1.8219 (15) | N6—C40 | 1.149 (2) |
| S2—C3 | 1.7466 (15) | S5—C38 | 1.7383 (15) |
| S2—C12 | 1.8280 (15) | S5—C41 | 1.8207 (16) |
| N1—C1 | 1.148 (2) | S6—C39 | 1.7497 (15) |
| N2—C4 | 1.148 (2) | S6—C48 | 1.8233 (16) |
| C1—C2 | 1.430 (2) | C37—C38 | 1.436 (2) |
| C2—C3 | 1.360 (2) | C38—C39 | 1.359 (2) |
| C3—C4 | 1.428 (2) | C39—C40 | 1.428 (2) |
| S3—C20 | 1.7401 (15) | S7—C56 | 1.7528 (14) |
| S3—C23 | 1.8195 (16) | S7—C59 | 1.8283 (15) |
| S4—C21 | 1.7483 (15) | S8—C57 | 1.7434 (15) |
| S4—C30 | 1.8253 (16) | S8—C66 | 1.8278 (15) |
| N3—C19 | 1.146 (2) | N7—C55 | 1.146 (2) |
| N4—C22 | 1.147 (2) | N8—C58 | 1.150 (2) |
| C19—C20 | 1.428 (2) | C55—C56 | 1.431 (2) |
| C20—C21 | 1.358 (2) | C56—C57 | 1.363 (2) |
| C21—C22 | 1.429 (2) | C57—C58 | 1.433 (2) |
| | | | |
| C2—S1—C5—C6 | −66.94 (12) | C38—S5—C41—C42 | −177.29 (11) |
| C3—S2—C12—C13 | 168.11 (11) | C39—S6—C48—C49 | −64.92 (13) |
| C20—S3—C23—C24 | −176.02 (11) | C56—S7—C59—C60 | −67.55 (12) |
| C21—S4—C30—C31 | −62.35 (13) | C57—S8—C66—C67 | 179.70 (10) |

The crystal was identified to be pseudo-merohedrally twinned with the unit-cell dimensions being very close to an orthorhombic setting. The twin law was found to be $(100\ 0\bar{1}0\ 00\bar{1})$, and the minor twin fraction refined to 0.1280 (4). The H atoms were geometrically positioned and refined with a C—H distance of 0.95 (phenyl) or 0.99 Å (methylene) and with $U_{\rm iso} = 1.2U_{\rm eq}({\rm C})$. The s.u. values of the cell parameters are taken from the software, recognizing that the values are unreasonably small (Herbstein, 2000).

Data collection: *SMART* (Bruker, 2002); cell refinement: *SAINT* (Bruker, 2003); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 2000); software used to prepare material for publication: *SHELXTL*.

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