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# Bis[*o*-(bromomethyl)benzyl] Disulfide

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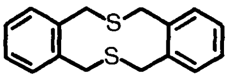
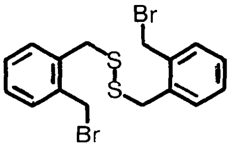
**Abstract.** $C_{16}H_{16}Br_2S_2$, monoclinic, space group $P2_1/c$, $a = 16{\cdot}655$ (5), $b = 4{\cdot}908$ (2), $c = 24{\cdot}024$ (7) Å, $\beta = 120{\cdot}99$ (4)°, $Z = 4$, $D_m = 1{\cdot}695$ (5) (flotation in aqueous KI), $D_x = 1{\cdot}704$ g cm$^{-3}$. The structure was determined from 2591 Cu $K\alpha$ diffractometer data and refined to $R = 0{\cdot}052$.

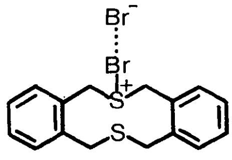
**Introduction.** Recently it has been shown that treatment of 5,7,12,14-tetrahydrodibenzo[*c*,*h*][1,6]dithiecin (I) with an equimolar quantity of pyridinium hydrobromide perbromide in dry tetrahydrofuran at 0 °C yields a major product (II) whose molecular weight by mass spectrometry corresponds to the incorporation of one molar equivalent of $Br_2$ into the starting material (Chan, Au & Mak, 1978). The NMR spectrum of (II) displayed two distinct sets of methylene protons at $\delta$ 3·85 and 4·65, which appeared to indicate complexation at one of the S atoms. Formula (II*b*) seemed reasonable by analogy with the halosulfonium salt structure of the 1 : 1 thiolane–bromine adduct (Allegra, Wilson, Benedetti, Pedone & Albert, 1970), whereas (II*c*) would resemble the sulfurane structure observed for the chlorine complex of bis(*p*-chlorophenyl) sulfide (Baenziger, Buckles, Maner & Simpson, 1969). In the present work, we have established that the correct structure is (II*a*) which arises, surprisingly, from transannular ring-cleavage of the strain-free system (I).



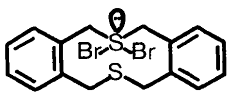
(I)



(II*a*)



(II*b*)



(II*c*)

The title compound (II) was synthesized as described by Chan, Au & Mak (1978) and recrystallized from $CCl_4$ as off-white prisms, m.p. 113–115 °C. Accurate unit-cell parameters were determined by a weighted ($w = \tan\theta$) least-squares fit to the $\theta$ values of 14 reflections. Using a spherical crystal ground to a diameter of 0·3 mm, the intensities of 3062 unique reflections with $\theta \leq 68°$ were collected at the University of Surrey on a Siemens four-circle diffractometer with Cu $K\alpha$ radiation ($\lambda = 1{\cdot}5418$ Å). The data were corrected for Lorentz and polarization factors but not for absorption ($\mu = 88{\cdot}8$ cm$^{-1}$). A total of 471 reflections were classified as unobserved [$I/\sigma(I) \leq 2{\cdot}58$] and omitted from the analysis.

The structure was solved with the heavy-atom method. The two Br atoms in the asymmetric unit were located from a Patterson map. Successive cycles of structure-factor calculations and Fourier syntheses revealed initially the two S atoms and finally the 16 C atoms. Anisotropic refinement of all 20 non-hydrogen atoms gave $R = 0{\cdot}054$. The positions of the methylene

Table 1. *Fractional atomic coordinates with e.s.d.'s in parentheses*

| | *x* | *y* | *z* |
|---|---|---|---|
| Br(1) | 0·12739 (5) | 0·27704 (19) | 0·54067 (3) |
| Br(2) | 0·64671 (4) | 0·20342 (16) | 0·41485 (3) |
| S(1) | 0·24591 (9) | 0·15019 (28) | 0·38658 (6) |
| S(2) | 0·38696 (8) | 0·13292 (28) | 0·44512 (6) |
| C(1) | 0·0519 (3) | 0·2618 (11) | 0·4045 (2) |
| C(2) | −0·0465 (4) | 0·2763 (13) | 0·3672 (3) |
| C(3) | −0·0908 (4) | 0·4536 (15) | 0·3145 (3) |
| C(4) | −0·0382 (4) | 0·6057 (14) | 0·2968 (3) |
| C(5) | 0·0587 (4) | 0·5922 (13) | 0·3328 (3) |
| C(6) | 0·1051 (3) | 0·4188 (11) | 0·3869 (2) |
| C(7) | 0·2106 (3) | 0·4095 (12) | 0·4248 (3) |
| C(8) | 0·0964 (4) | 0·0720 (13) | 0·4617 (3) |
| C(9) | 0·4306 (3) | 0·3889 (11) | 0·4114 (2) |
| C(10) | 0·5315 (4) | −0·0240 (12) | 0·3765 (2) |
| C(11) | 0·4494 (3) | 0·1379 (10) | 0·3262 (2) |
| C(12) | 0·4031 (3) | 0·3311 (10) | 0·3421 (2) |
| C(13) | 0·3275 (4) | 0·4725 (13) | 0·2925 (3) |
| C(14) | 0·2973 (4) | 0·4199 (16) | 0·2274 (3) |
| C(15) | 0·3420 (4) | 0·2286 (15) | 0·2113 (3) |
| C(16) | 0·4186 (4) | 0·0845 (12) | 0·2604 (3) |

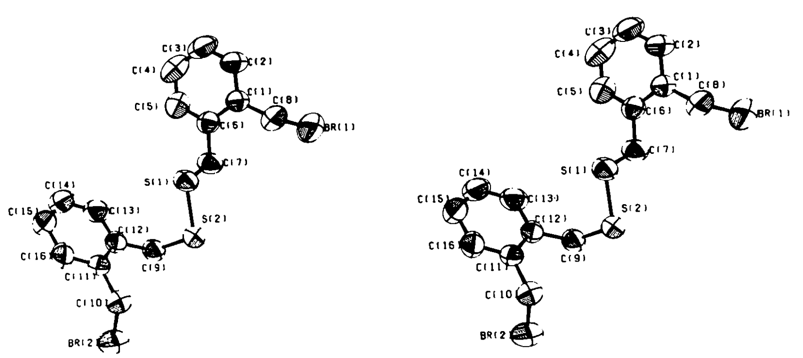


Fig. 1. A stereoview with atom numbering of the bis[*o*-(bromomethyl)benzyl] disulfide molecule.

Table 2. *Bond lengths* (Å) *and angles* (°) *and their e.s.d.'s*

| | | | | | |
|---|---|---|---|---|---|
| Br(1)–C(8) | 1·967 (6) | Phenyl ring 1 | | Phenyl ring 2 | |
| Br(2)–C(10) | 1·989 (6) | | | | |
| S(1)–S(2) | 2·025 (2) | C(1)–C(2) | 1·408 (7) | C(16)–C(11) | 1·413 (7) |
| S(1)–C(7) | 1·834 (6) | C(2)–C(3) | 1·394 (9) | C(11)–C(12) | 1·394 (6) |
| S(2)–C(9) | 1·836 (5) | C(3)–C(4) | 1·374 (9) | C(12)–C(13) | 1·394 (7) |
| C(1)–C(8) | 1·502 (8) | C(4)–C(5) | 1·386 (8) | C(13)–C(14) | 1·398 (9) |
| C(6)–C(7) | 1·507 (6) | C(5)–C(6) | 1·406 (8) | C(14)–C(15) | 1·372 (10) |
| C(9)–C(12) | 1·509 (6) | C(6)–C(1) | 1·394 (7) | C(15)–C(16) | 1·403 (9) |
| C(10)–C(11) | 1·503 (7) | | | | |
| C(1)–C(8)–Br(1) | 109·0 (4) | C(1)–C(2)–C(3) | 120·5 (5) | C(11)–C(12)–C(13) | 119·2 (4) |
| C(11)–C(10)–Br(2) | 109·7 (4) | C(2)–C(3)–C(4) | 119·8 (5) | C(12)–C(13)–C(14) | 120·7 (5) |
| C(7)–S(1)–S(2) | 103·8 (2) | C(3)–C(4)–C(5) | 120·3 (6) | C(13)–C(14)–C(15) | 120·4 (6) |
| S(1)–S(2)–C(9) | 104·3 (2) | C(4)–C(5)–C(6) | 121·0 (5) | C(14)–C(15)–C(16) | 119·9 (6) |
| C(6)–C(7)–S(1) | 107·1 (4) | C(5)–C(6)–C(1) | 118·8 (4) | C(15)–C(16)–C(11) | 119·8 (5) |
| S(2)–C(9)–C(12) | 113·2 (3) | C(6)–C(1)–C(2) | 119·5 (4) | C(16)–C(11)–C(12) | 120·0 (4) |

and aromatic H atoms were then generated using program *GHMC* (Mak, Mok & Tse, 1977). Inclusion of these H atoms with $B = 5{\cdot}0$ Å$^2$ gave a final $R$ of 0·052 and a featureless difference map.

Scattering factors for non-hydrogen atoms were taken from *International Tables for X-ray Crystallography* (1974), and for H from Stewart, Davidson & Simpson (1965). Computations were performed on an ICL-1904A system in the Hong Kong Universities and Polytechnic Computing Centre with *ORFLS* (Busing, Martin & Levy, 1962). The function minimized was $\sum w(|F_o| - |F_c|)^2$, the weighting scheme being that of Cruickshank (1961) with $w = (2F_{\min} + |F_o| + 2|F_o|^2/F_{\max})^{-1}$, where $F_{\min}$ and $F_{\max}$ were 4·0 and 250·0 respectively. The final atomic coordinates are listed in Table 1.*

Table 3. *Torsion angles* (°)

| | |
|---|---|
| Br(1)–C(8)–C(1)–C(2) | −95·1 |
| Br(1)–C(8)–C(1)–C(6) | 86·1 |
| C(8)–C(1)–C(6)–C(7) | −0·7 |
| C(1)–C(6)–C(7)–S(1) | 92·3 |
| C(5)–C(6)–C(7)–S(1) | −88·5 |
| C(6)–C(7)–S(1)–S(2) | −175·6 |
| C(7)–S(1)–S(2)–C(9) | −89·4 |
| S(1)–S(2)–C(9)–C(12) | −60·4 |
| S(2)–C(9)–C(12)–C(13) | 100·1 |
| S(2)–C(9)–C(12)–C(11) | −78·5 |
| C(9)–C(12)–C(11)–C(10) | −1·4 |
| C(12)–C(11)–C(10)–Br(2) | −78·8 |
| Br(2)–C(10)–C(11)–C(16) | 102·2 |

**Discussion.** An *ORTEP* (Johnson, 1965) plot of the molecular structure with atom numbering is shown in Fig. 1. The molecular dimensions of bis[*o*-(bromomethyl)benzyl] disulfide (Table 2) closely match corresponding ones in dibenzyl disulfide (Lee & Bryant, 1969; van Dijk & Visser, 1971). The average S–S, S–$C_{sp^3}$, Br–$C_{sp^3}$, $C_{ar}$–$C_{sp^3}$ (ar = aromatic) and $Cr_{ar}$–$C_{ar}$ bonds of 2·025 (2), 1·835 (5), 1·978 (6), 1·505 (6) and 1·395 (6) Å respectively are all normal. Torsion angles are given in Table 3. The angle C(7)–S(1)–S(2)–C(9) of 89·4° agrees closely with the theoretical value of 90° for optimum $\pi$ overlap between filled $p$ orbitals on one S atom with empty $d_{x^2-y^2}$ and $d_{z^2}$ orbitals on the other (Hordvik, 1966). It lies in the middle of the range of 90 ± 10° found in most organic disulfides (Shefter,

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* Lists of anisotropic temperature factors, generated hydrogen positions, and structure factors have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33647 (21 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 4. *Equations to planes*

Plane equations are expressed in the form $AX + BY + CZ = D$, where $X$, $Y$, $Z$ are atomic coordinates in Å referred to **a***, **b**, **c**, and $D$ is the origin-to-plane distance in Å.

| Plane | Atoms | *A* | *B* | *C* | *D* |
|---|---|---|---|---|---|
| 1 | C(1), C(2), C(3), C(4), C(5), C(6), C(7), C(8) | 0·3270 | −0·7377 | −0·5908 | −7·2195 |
| 2 | Br(1), C(1), C(8) | −0·9666 | −0·2139 | −0·1416 | 2·5467 |
| 3 | C(9), C(10), C(11), C(12), C(13), C(14), C(15), C(16) | −0·7045 | −0·7090 | −0·0331 | −3·1223 |
| 4 | Br(2), C(10), C(11) | 0·6341 | −0·3220 | −0·7031 | −2·7538 |

Angles between planes (°): 1–2, 94·3; 3–4, 101·3; 1–3 71·9

Distances of atoms from planes ($\times 10^3$ Å)

Plane 1: C(1), −3; C(2), 13; C(3), −15; C(4), 7; C(5), 0; C(6), 3; C(7), −2; C(8), −1; Br(1), −1855; S(1), 1747

Plane 2: C(9), 21; C(10), −5; C(11), −10; C(12), −11; C(13), −14; C(14), 0; C(15), 11; C(16), 8; Br(2), −1840; S(2), 1694

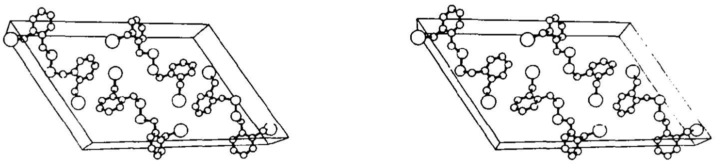

Fig. 2. A stereoscopic drawing showing the molecular packing viewed approximately along **b** towards the origin of the unit cell at the lowest left corner.

1970; Raghavan & Seff, 1977). Both phenyl rings, each with their two exocyclic C atoms, are planar within experimental error (Table 4). Unlike dibenzyl disulfide, which possesses a twofold rotation axis (van Dijk & Visser, 1971; Einspahr & Donohue, 1971; Lee & Bryant, 1971; Srinivasan & Vijayalakshmi, 1972), the two substituted benzyl groups in the present molecule are oriented very differently with respect to the disulfide linkage. As expected from steric repulsion, each *o*-bromomethyl group lies in a plane approximately perpendicular to its phenyl ring. The S(2)—C(9)—C(12) angle of 113·2° is unusually large and may be partly accounted for by the adopted molecular conformation (Fig. 1). It is interesting to note that the C(3)—C(4) and C(14)—C(15) bonds, which are farthest from the ring substituents, have significantly shorter lengths.

A stereoplot of the molecular packing viewed along **b** is shown in Fig. 2. All intermolecular contacts correspond to the normal van der Waals separations.

The bromination of (I) provided the first example of a ring-opening reaction involving the participation of two transannular S atoms. The mechanism and utility of this reaction will be discussed elsewhere.

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