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8,9-Dimethyl-1,6-benzodithiocin, a Heterocyclic 10-π-Electron System

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Abstract. $C_{12}H_{12}S_2$, triclinic, $P\bar{1}$, $a = 6{\cdot}850\,(6)$, $b = 11{\cdot}225\,(10)$, $c = 8{\cdot}053\,(10)$ Å, $\alpha = 92{\cdot}04$, $\beta = 96{\cdot}91$, $\gamma = 113{\cdot}76°$, $Z = 2$, $D_x = 1{\cdot}30$ g cm^{-3}, $\lambda(\mathrm{Cu}\,K\alpha) = 1{\cdot}5418$ Å, $\mu = 38$ cm^{-1}. The isolated molecules show no evidence of aromatic character in the heterocycle.

Introduction. The title compound includes a 1,4-dithiocin system formally containing 10 π electrons. The $(4n + 2)$ rule would predict aromaticity but proton NMR studies on this and related compounds (Schroth & Moegel, 1977; Moegel, Schroth & Werner, 1978) detected no aromatic character. However, the UV spectrum of the title compound shows an absorption at 360 nm suggesting some planarity in the heterocycle, possibly by conjugation stabilization.

Crystals were available from the previous studies as white rhombs mostly split. Since these were known to be of low stability in air at room temperature, data were collected from crystals sealed in capillaries. Equi-inclination Weissenberg photographs of the levels *h*0–9*l* and 0–6*kl* were scanned by a microdensitometer (SRC service, Daresbury Laboratory). Absorption corrections were not applied. All calculations were carried out with *SHELX* 76 (Sheldrick, 1976).

The structure was solved by direct methods. This revealed the S atoms and the benzene ring. Successive Fourier syntheses combined with full-matrix least-squares refinement revealed the remaining C atoms. With all atoms isotropic $R = 0{\cdot}133$. Refinement continued with anisotropic thermal parameters for the C and S atoms; isotropic H atoms were inserted in calculated positions except for those of the methyl groups which were located on a difference map and refined with C–H = 1·01 Å. Six planes with $F_o \geq 2F_c$ were omitted in the final refinement which terminated at $R = 0{\cdot}057$. The weighting scheme was $w = 1{\cdot}00/[\sigma^2(F) + 0{\cdot}019598F^2]$. Scattering factors were taken from *International Tables for X-ray Crystallography* (1974).†

Discussion. The results presented in Tables 1–3 and Figs. 1 and 2 show that the heterocycle is far from a flat aromatic ring. The group C(2), C(3), C(4), C(5) is best regarded as a 1,4-substituted 1,3-butadiene. The bond lengths and angles in this fragment (1·344 and 1·449

Table 1. *Final atomic coordinates* (×10^4, *for* H ×10^3) *and hydrogen thermal parameters* (×10^3), *with e.s.d.'s in parentheses*

	x	*y*	*z*
S(1)	7708 (2)	8500 (1)	3961 (2)
S(6)	2722 (2)	7294 (1)	1236 (2)
C(2)	7841 (9)	9535 (4)	2338 (7)
C(3)	6471 (9)	10115 (5)	2053 (7)
C(4)	4522 (10)	9779 (6)	2808 (7)
C(5)	2948 (9)	8569 (6)	2685 (8)
C(7)	3078 (7)	5027 (4)	1643 (6)
C(8)	3981 (7)	4164 (4)	2039 (5)
C(9)	6057 (7)	4638 (4)	2994 (6)
C(10)	7109 (6)	5982 (4)	3456 (6)
C(11)	6196 (6)	6862 (4)	3051 (5)
C(12)	4120 (7)	6383 (4)	2121 (6)
C(13)	2732 (11)	2708 (5)	1486 (9)
C(14)	7165 (10)	3764 (6)	3463 (9)

	x	*y*	*z*	*U* (Å^2)
H(2)	907 (1)	971 (1)	154 (1)	134 (31)
H(3)	685 (1)	1088 (1)	121 (1)	116 (25)
H(4)	432 (1)	1055 (1)	351 (1)	62 (15)
H(5)	176 (1)	837 (1)	352 (1)	53 (15)
H(131)	141 (16)	263 (9)	95 (12)	119 (29)
H(132)	362 (15)	244 (10)	114 (12)	126 (36)
H(133)	246 (14)	235 (9)	254 (12)	114 (31)
H(141)	877 (11)	438 (6)	385 (8)	70 (18)
H(142)	694 (15)	322 (9)	224 (13)	131 (30)
H(143)	704 (14)	333 (8)	430 (11)	98 (27)

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† Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33855 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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

S(1)–C(2)	1·765 (5)	C(8)–C(9)	1·412 (6)
C(2)–C(3)	1·345 (8)	C(8)–C(13)	1·526 (6)
C(3)–C(4)	1·449 (9)	C(9)–C(10)	1·397 (6)
C(4)–C(5)	1·343 (8)	C(9)–C(14)	1·497 (7)
C(5)–S(6)	1·758 (6)	C(10)–C(11)	1·394 (6)
S(6)–C(12)	1·775 (4)	C(11)–S(1)	1·783 (4)
C(12)–C(7)	1·410 (5)	C(11)–C(12)	1·404 (5)
C(7)–C(8)	1·372 (6)		

C(11)–S(1)–C(2)	107·2 (2)	C(13)–C(8)–C(9)	120·7 (4)
S(1)–C(2)–C(3)	122·6 (5)	C(8)–C(9)–C(10)	117·7 (4)
C(2)–C(3)–C(4)	124·0 (5)	C(8)–C(9)–C(14)	122·3 (5)
C(3)–C(4)–C(5)	124·0 (5)	C(14)–C(9)–C(10)	119·9 (4)
C(4)–C(5)–S(6)	123·6 (5)	C(9)–C(10)–C(11)	123·4 (4)
C(5)–S(6)–C(12)	110·9 (2)	C(10)–C(11)–S(1)	115·5 (3)
S(6)–C(12)–C(7)	114·1 (3)	C(10)–C(11)–C(12)	118·7 (4)
S(6)–C(12)–C(11)	127·9 (3)	C(11)–C(12)–C(7)	117·6 (3)
C(12)–C(7)–C(8)	123·6 (4)	C(12)–C(11)–S(1)	125·4 (3)
C(7)–C(8)–C(9)	119·0 (4)		
C(7)–C(8)–C(13)	120·3 (4)		

Table 3. *Distances* (Å) *of atoms from the mean plane of the benzene ring*

Equation of mean plane

$$-3\cdot3242X - 0\cdot0192Y + 7\cdot3750Z = 0\cdot1782$$

S(1)	0·165	C(4)	0·368
S(6)	−0·186	C(5)	0·808
C(2)	−1·080	C(13)	0·006
C(3)	−0·0837	C(14)	−0·007

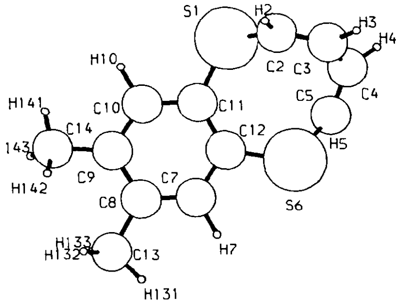

Fig. 1. 8,9-Dimethyl-1,6-benzodithiocin: view perpendicular to the plane of the benzene ring, showing numbering scheme.

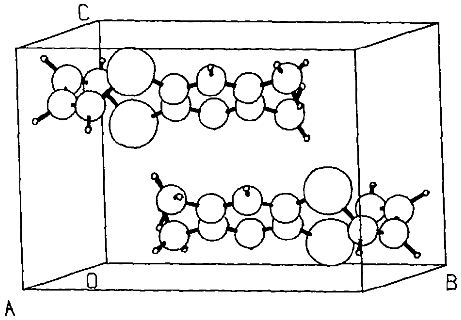

Fig. 2. Unit cell of 8,9-dimethyl-1,6-benzodithiocin.

Å, 124·0°) are not significantly different from those in butadiene itself (1·337 and 1·476 Å, 122·9°) (Marais, Sheppard & Stoicheff, 1962), in spite of the very different conformation, and are similar to those in 1,3-cyclooctadiene (1·3474 and 1·4750 Å, 129·0°) (Trætteberg, 1970). In the title compound the torsion angle C(2)–C(3)–C(4)–C(5) is 55·8°, implying much less ring strain than the 37·8° for the corresponding angle in 1,3-cyclooctadiene where additional constraints are imposed by H···H contacts between methylene groups, particularly those on C(1) and C(6).

The C–S bonds (1·770 Å, average) are all typical of single bonds to sp^2 C atoms. The C–S–C angles (109° average) confirm the expectation that each S atom carries two lone pairs of electrons not involved in π bonding.

The eight-membered ring is composed of three approximately planar groups: *A* [S(1), C(2),C(3),C(4)], *B* [S(6),C(5),C(4),C(3)] and *C* [S(1),C(11),C(12), S(6)]. The angles between the normals to these planes are *AB* 71·7, *AC* 73·3 and *BC* 69·8°; C(3)–C(4) makes an angle of 29° with plane *C*. This is close to the ideal geometry for a 1,3,6-cyclooctatriene.

There is no chemical reason for the substantial deviation from the possible molecular twofold axis bisecting C(8)–C(9) and C(3)–C(4) (Fig. 2, Table 3). However, the shortest C···C intermolecular contacts are C(4)···C(4)′ (3·49 Å) and C(3)···C(3)″ (3·60 Å) to molecules in the diagonally adjacent cells. This suggests packing constraints on the relatively flexible heterocycle. There are no other C···C contacts <3·75 Å.

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