

The Crystal Structure of the Orthorhombic Form of Bis(1-piperidyl) Disulfide

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Bis(1-piperidyl) disulfide and related compounds are well known in the patent literature as anti-oxidants in mineral oils and as additives in polymers.^{1,2} They also possess marked antifungal properties.³

The monoclinic centrosymmetric space group $P2_1/c$ has been reported⁴ for bis(1-piperidyl) disulfide crystallized from petroleum ether (b.p. 90–120 °C). However, crystallization from ethan-

ol gave orthorhombic, somewhat unstable crystals belonging to the non-centrosymmetric space group $P2_12_12_1$.⁵ The origin of the polymorphism may lie in the difference in solvent systems.

Since the crystals showed a marked tendency to decompose in air under X-ray irradiation, the selected crystal was sealed into a two-component epoxy resin and the intensity data were collected rapidly. The intensities of the standard reflections did not decrease by more than about 5% during the data collection and the data were not scaled. No correction for absorption was made. The structure was solved by direct methods⁶ and refined using the X-Ray System programs.⁷ Since the difference Fourier map calculated after anisotropic refinements of the non-hydrogen atoms did not reveal the positions of all hydrogen atoms, these were placed at calculated positions ($C-H = 1.0 \text{ \AA}$ and $U_H = 0.5 \text{ \AA}^2$) and were not refined in the final cycles.

Crystal data and details of the data collection are presented in Table 1 and atomic coordinates in Table 2. The numbering system and the chair conformation of the six-membered rings can be seen in Fig. 1, and bond lengths and angles are shown in Fig. 2.

Comparison of the individual bond lengths and angles and the puckering of the rings revealed only a slight difference in S–S–N angles [110.9(4) and 113.1(3)°] and a considerable difference in S–S–N–C torsion angles (Table 3). Thus, the molecule may have only approximate C_2 symmetry.

Table 1. Crystal data and details of data collection.

Mol. formula	$C_{10}H_{20}N_2S_2$
Mol. weight	232.34
Crystal system	Orthorhombic
$a/\text{\AA}$	10.178(4)
$b/\text{\AA}$	10.614(3)
$c/\text{\AA}$	11.846(3)
Space group	$P2_12_12_1$
$V/\text{\AA}^3$	1279.7(7)
$D_c/\text{g cm}^{-3}$	1.21
Z	4
Crystal dimensions/mm	0.2×0.3×0.4
Diffractometer	Nicolet P3
Radiation	$MoK\alpha$ ($\lambda = 0.71069 \text{ \AA}$)
Absorption coefficient/ cm^{-1}	3.7
Scan type	ω
2θ limits	$5^\circ < 2\theta < 47^\circ$
Scan rate/ $^\circ \text{ min}^{-1}$	5–30
No. of collected reflections	1060
No. of observed reflections	873 ($F_o > 5\sigma F_o $)
R	0.058
R_w	0.070

Table 2. Fractional atomic coordinates and thermal parameters.

Atom	x	y	z	$U_{eq}/\text{\AA}^2$
S(1)	0.4795(3)	0.1888(3)	0.2095(2)	0.051(2)
S(2)	0.5216(3)	0.1728(3)	0.0402(2)	0.048(2)
N(1)	0.3376(9)	0.1175(8)	0.2406(8)	0.046(6)
N(2)	0.6281(8)	0.0583(8)	0.0119(7)	0.041(6)
C(1)	0.3405(12)	-0.0237(11)	0.2436(12)	0.059(9)
C(2)	0.2191(12)	-0.0717(11)	0.3087(11)	0.062(9)
C(3)	0.0934(12)	-0.0258(13)	0.2461(12)	0.065(9)
C(4)	0.0955(11)	0.1179(12)	0.2357(13)	0.064(9)
C(5)	0.2215(11)	0.1645(10)	0.1777(9)	0.048(7)
C(6)	0.5840(11)	-0.0725(11)	0.0322(11)	0.056(8)
C(7)	0.6758(13)	-0.1611(11)	-0.0387(14)	0.076(10)
C(8)	0.8167(14)	-0.1436(12)	-0.0026(13)	0.077(11)
C(9)	0.8580(12)	-0.0054(12)	-0.0176(13)	0.070(10)
C(10)	0.7645(11)	0.0787(11)	0.0532(10)	0.048(8)

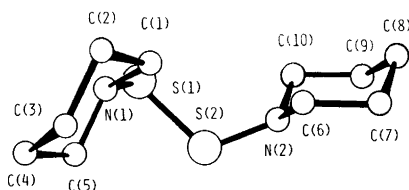


Fig. 1. Numbering system and conformation of the six-membered rings in the orthorhombic form of bis(1-piperidyl) disulfide.

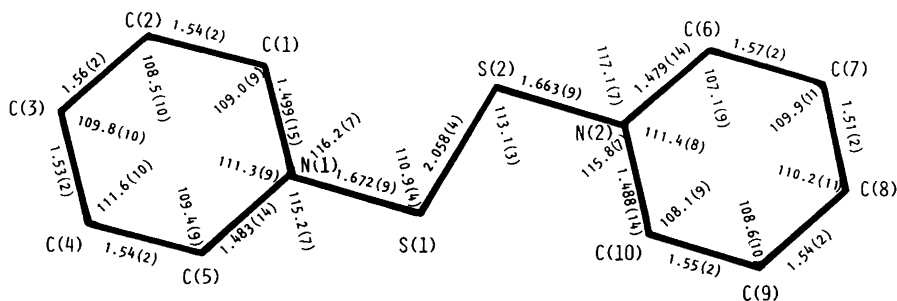
The bond lengths and angles, the puckering of the rings and the torsion angles of the orthorhombic form of bis(1-piperidyl) disulfide do not deviate significantly from the values for the monoclinic form. The bond lengths and angles in the orthorhombic form are also comparable to those

Table 3. Selected torsion angles ($^\circ$).

N(1)–S(1)–S(2)–N(2)	-99.1(5)
S(1)–S(1)–N(1)–C(1)	74.7(9)
S(2)–S(1)–N(1)–C(5)	-58.0(8)
S(1)–S(2)–N(2)–C(6)	66.8(8)
S(1)–S(2)–N(2)–C(10)	-68.1(8)
S(1)–N(1)–C(1)–C(2)	162.2(8)
S(1)–N(1)–C(5)–C(4)	-164.9(8)
S(2)–N(2)–C(6)–C(7)	160.1(8)
S(2)–N(2)–C(10)–C(9)	-158.2(8)

in bis(4-morpholinyl) disulfide,^{8,9} but the N–S–S–N torsion angle in the latter is smaller (84.2 $^\circ$).⁸

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Fig. 2. Bond lengths (\AA) and angles ($^\circ$) in the orthorhombic form of bis(1-piperidyl) disulfide.

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