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Structure of 3,6-Bis(4-methoxyphenyl)-1,4,2,5-dithiadiazine, $C_{16}H_{14}N_2O_2S_2$

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Abstract. $M_r = 330{\cdot}42$, orthorhombic, $P2_12_12$, $a = 11{\cdot}260\,(2)$, $b = 17{\cdot}086\,(3)$, $c = 3{\cdot}948\,(1)$ Å, $V = 759{\cdot}6$ Å^3, $Z = 2$, $D_x = 1{\cdot}45$ g cm^{-3}, Mo $K\alpha$(graphite crystal monochromator), $\lambda = 0{\cdot}71069$ Å, $\mu = 3{\cdot}53$ cm^{-1}, $F(000) = 344$, $T = 290$ K, final conventional $R = 0{\cdot}027$, $wR = 0{\cdot}024$ for 839 unique reflections and 121 variables. The title compound was prepared by a new reaction of aminosulfines (thioamide *S*-oxides) and triethyloxonium tetrafluoroborate. The molecule contains the cyclic 1,4,2,5-dithiadiazine system, which is a new heterocycle. The molecule is in the boat conformation. The benzene substituent has a dihedral angle of 31·1 (1)° with the CCSN moiety of the dithiadiazine ring.

Introduction. In exploring the chemistry of sulfines (thioketone *S*-oxides; Zwanenburg, 1982), benzenethioamide *S*-oxides, ArC(=SO)NH$_2$, were treated with triethyloxonium tetrafluoroborate. The resulting iminium salts gave upon reaction with pyridine instead of the expected α-imino sulfoxides novel heterocyclic systems, *viz* 1,4,2,5-dithiadiazines (Lenz & Zwanenburg, 1984). On the basis of the molecular formula and spectroscopic data the arrangement of the N and S atoms in the six-membered heterocyclic ring could not be established unambiguously. Therefore, the present analysis was undertaken.

Experimental. Crystals obtained by recrystallization from toluene/petroleum ether. Crystal approximately 0·25 × 0·07 × 0·07 mm used for measurements. Nonius CAD-4 single-crystal diffractometer. Unit-cell dimensions determined from angular settings of 25 reflections with $20 < \theta < 22°$. Space group $P2_12_12$ from systematic absences: $h00$, $h = 2n + 1$; $0k0$, $k = 2n + 1$. 6914 reflections (full sphere up to $\theta = 27{\cdot}5°$) measured, ω–2θ scan technique, scan angle 1·00°, variable scan rate $\geq 1°$ min^{-1}. Intensity of primary beam checked throughout data collection by monitoring three standard reflections every 30 min. Final drift correction factors between 1·00 and 1·04. On all reflections profile analysis was performed (Lehmann & Larsen, 1974; Grant & Gabe, 1978); empirical absorption correction using ψ scans (North, Phillips & Mathews, 1968) applied (min. transmission 96%, av. 99%). Symmetry-equivalent reflections averaged, $R_{\rm int} = 0{\cdot}033$, 1731 unique reflections of which 840 considered observed with $I > 3\sigma(I)$. Lorentz and polarization corrections, data reduced to $|F_o|$ values. Structure solved using *MULTAN* (Main *et al.*, 1980). Solution was straightforward, using default parameters. Isotropic least-squares refinement (*SHELX*76; Sheldrick, 1976) converged to $R = 0{\cdot}063$. Empirical absorption correction applied (Walker & Stuart, 1983). H atoms located from difference Fourier map. Additional refinement

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

$U_{\rm eq} = \frac{1}{3}$ trace **U**.

	x	y	z	$U_{\rm eq}$(Å^2)
S(1)	0·62427 (6)	0·03816 (4)	0·5970 (2)	0·0537 (3)
N(1)	0·6062 (2)	−0·0545 (1)	0·4439 (6)	0·048 (1)
O(1)	0·5257 (2)	0·4019 (1)	0·0669 (7)	0·063 (1)
C(1)	0·4955 (2)	0·0867 (2)	0·4592 (8)	0·042 (1)
C(2)	0·5090 (2)	0·1692 (2)	0·3541 (7)	0·039 (1)
C(3)	0·6121 (2)	0·1977 (2)	0·2112 (7)	0·045 (1)
C(4)	0·6218 (2)	0·2749 (2)	0·1098 (9)	0·046 (1)
C(5)	0·5266 (2)	0·3249 (2)	0·1532 (8)	0·047 (1)
C(6)	0·4222 (3)	0·2976 (2)	0·3011 (9)	0·050 (2)
C(7)	0·4143 (2)	0·2204 (2)	0·3989 (9)	0·046 (1)
C(8)	0·6311 (3)	0·4332 (2)	−0·085 (1)	0·069 (2)
H(3)	0·678 (2)	0·162 (2)	0·172 (8)	0·07
H(4)	0·695 (2)	0·291 (2)	0·004 (8)	0·07
H(6)	0·362 (3)	0·334 (2)	0·330 (8)	0·07
H(7)	0·346 (2)	0·205 (2)	0·494 (8)	0·07
H(81)	0·641 (3)	0·406 (2)	−0·317 (8)	0·07
H(82)	0·613 (3)	0·484 (2)	−0·124 (9)	0·07
H(83)	0·694 (3)	0·427 (2)	0·056 (9)	0·07

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

S(1)–N(1)	1·707 (2)	C(5)–C(6)	1·393 (4)
S(1)–C(1)	1·756 (3)	C(6)–C(7)	1·377 (4)
O(1)–C(5)	1·359 (3)	C(3)–H(3)	0·97 (3)
O(1)–C(8)	1·434 (4)	C(4)–H(4)	0·96 (3)
C(1)–C(2)	1·477 (4)	C(6)–H(6)	0·93 (3)
C(2)–C(3)	1·380 (3)	C(7)–H(7)	0·90 (3)
C(2)–C(7)	1·391 (4)	C(8)–H(81)	1·03 (3)
C(3)–C(4)	1·383 (4)	C(8)–H(82)	0·90 (3)
C(4)–C(5)	1·381 (4)	C(8)–H(83)	0·91 (3)
N(1)–S(1)–C(1)	103·3 (1)	C(2)–C(3)–H(3)	119 (2)
C(5)–O(1)–C(8)	117·4 (2)	C(4)–C(3)–H(3)	119 (2)
S(1)–C(1)–C(2)	116·9 (2)	C(3)–C(4)–H(4)	118 (2)
C(1)–C(2)–C(3)	122·5 (2)	C(5)–C(4)–H(4)	122 (2)
C(1)–C(2)–C(7)	119·1 (2)	C(5)–C(6)–H(6)	117 (2)
C(3)–C(2)–C(7)	118·4 (3)	C(7)–C(6)–H(6)	124 (2)
C(2)–C(3)–C(4)	121·4 (3)	C(2)–C(7)–H(7)	122 (2)
C(3)–C(4)–C(5)	119·6 (3)	C(6)–C(7)–H(7)	117 (2)
O(1)–C(5)–C(4)	125·0 (3)	O(1)–C(8)–H(81)	107 (2)
O(1)–C(5)–C(6)	115·0 (3)	O(1)–C(8)–H(82)	104 (2)
C(4)–C(5)–C(6)	120·0 (3)	H(81)–C(8)–H(82)	108 (3)
C(5)–C(6)–C(7)	119·6 (3)	O(1)–C(8)–H(83)	110 (2)
C(2)–C(7)–C(6)	121·1 (3)	H(81)–C(8)–H(83)	114 (3)
		H(82)–C(8)–H(83)	113 (3)

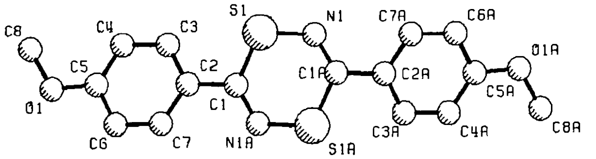

Fig. 1. Crystallographic atomic numbering scheme. (Molecule in minimum overlap position.)

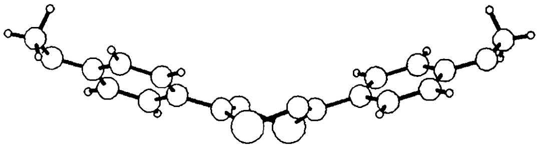

Fig. 2. Side-on view of the molecule.

with all non-H atoms anisotropic and fixed thermal parameters for H atoms ($U = 0{\cdot}07$ Å^2) converged to $R = 0{\cdot}027$ and $wR = 0{\cdot}024$ for 839 observed reflections and 121 variables. Function minimized $\sum w(F_o - F_c)^2$ with $w = 1/[\sigma^2(F_o) + 0{\cdot}00010F_o^2]$, $\sigma(F_o)$ from counting statistics. Max. Δ/σ in last least-squares cycle (full matrix) $<0{\cdot}012$. Final difference Fourier map showed no peaks higher than 0·22 e Å^{-3}. Atomic scattering factors from *SHELX*. Calculation of the Bijvoet coefficient (Beurskens, Noordik & Beurskens, 1980) showed that the absolute structure is correct.

Discussion. The molecular structure clearly reveals the 1,4-positions of the two sulfur atoms and rules out the alternative 1,2,3,4-dithiadiazine structure. Final positional and thermal parameters are given in Table 1.* Molecular geometry data are collected in Table 2. A stereoview of the molecule in minimum overlap position, showing the molecular configuration has been deposited. The crystallographic atomic numbering scheme is given in Fig. 1.

The heterocyclic system has not been reported previously. The side-on view (Fig. 2) shows that the molecule is not planar but is in the boat conformation. The lack of coplanarity of the benzene ring with the C(2)C(1)S(1)N(1′) moiety [dihedral angle = 31·1 (1)°] is probably due to some steric hindrance as indicated by the contacts S(1)···C(3) = 3·125 (3) and S(1)···H(3) = 2·77 (3) Å.

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* Lists of structure factors, anisotropic thermal parameters and a stereoview showing the molecule in minimum overlap position have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42136 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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