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Structure of 7,12-Dihydrophthalazino[2,3-*b*]phthalazine-5,14-dithione

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Abstract. $C_{16}H_{12}N_2S_2$, $M_r = 296{\cdot}3$, orthorhombic, $P2_12_12_1$, $a = 13{\cdot}064\,(1)$, $b = 13{\cdot}1891\,(7)$, $c = 7{\cdot}756\,(1)$ Å, $V = 1336{\cdot}4\,(2)$ Å^3, $Z = 4$, $D_x = 1{\cdot}473$, $D_m = 1{\cdot}41$ g cm^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71069$ Å, $\mu = 3{\cdot}796$ cm^{-1}, $F(000) = 616$, $T = 293$ K, $R = 0{\cdot}032$, $wR = 0{\cdot}035$ for 1602 reflections. The tetracyclic molecular framework has a non-planar twisted structure bent along the line C(5)···C(14) by 45·0 (1)°. The tetrahydropyridazinedithione heterocycle (*B*) has the conformation of a flattened chair, the tetrahydropyridazine ring (*C*) that of a distorted boat. The average value of the C=S bond length is 1·676 (2) Å.

Introduction. The title compound (I), prepared by the action of phosphorus pentasulfide on 7,12-dihydrophthalazino[2,3-*b*]phthalazine-5,14-dione, can be used for the synthesis of organic dyes and biologically active agents (Lisitsin, Borovkov & Mansur, 1984). The analogous compound 7,14-dihydrophthalazino[2,3-*b*]phthalazine-5,12-dione (II) has high anti-inflammatory activity (Bellasio & Arrigoni-Martelly, 1972; Nardelli & Pelizzi, 1978). For this reason it seemed interesting to study the structure of the dithione (I).

Experimental. Recrystallization from chloroform–benzene mixture yielded colorless prism-like crystals. D_m determined by flotation in $C_2H_2Br_4/CCl_4$. Crystal 0·3 × 0·3 × 0·2 mm. Unit-cell parameters from 12 reflections with $18 < 2\theta < 20°$. Automatic Hilger & Watts four-circle diffractometer, graphite monochromator, $\theta/2\theta$ scan, $2\theta_{\max} = 60°$ ($0 \le h \le 15$, $0 \le k \le 15$, $0 \le l \le 10$). No noticeable changes in intensities of two standard reflections (400 and 004), measured after every 98 reflections. Corrections for absorption and secondary extinction not applied. Structure solved by the direct method using *MULTAN* (Germain, Main & Woolfson, 1971), which revealed all non-hydrogen atoms. Full-matrix least-squares refinement with anisotropic thermal parameters for non-hydrogen atoms using 1602 unique reflections with $I > 2\sigma$, discarding 101 reflections with $I \le 2\sigma$. $R_{\text{int}} \sim 3\%$ for 100 equivalent reflections. Function $\sum w(|F_o| - |F_c|)^2$ minimized, with $w = [\sigma^2(F_o) + |0{\cdot}01F_o|^2]^{-1}$. Atomic scattering factors and corrections for anomalous scattering of the S atoms from *International Tables for X-ray Crystallography* (1974). H atoms located from a difference synthesis and refined isotropically. Final $R = 0{\cdot}0319$, $wR = 0{\cdot}0346$, $S = 1{\cdot}889$, $(\Delta/\sigma)_{\max} = 0{\cdot}5$. Max. and min. peak heights in final difference Fourier synthesis $\pm 0{\cdot}3$ e Å^{-3}. Refinement of inverted structure gave $R = 0{\cdot}0328$, $wR = 0{\cdot}0361$, $S = 1{\cdot}973$. The probability of the validity of the absolute configuration found is 99% (Hamilton, 1965). All calculations carried out with an Eclipse S/200 computer using *INEXTL* programs (Gerr, Yanovsky & Struchkov, 1983).

Discussion. The atomic coordinates are given in Table 1;* the bond angles are listed in Table 2. Fig. 1(*a*) shows bond lengths, and Fig. 1(*b*) the overall conformation of the tetracyclic molecule (I) bent along the line C(5)···C(14) by a large angle of 45·0 (1)°.

The six-membered tetrahydropyridazinedithione heterocycle (*B*) has the conformation of a considerably flattened half-chair: N(6) and N(13) deviate from plane (1) through the other four atoms of the ring by −0·069 (2) and 0·070 (2) Å, respectively.

The tetrahydropyridazine heterocycle (*C*) has the conformation of a twisted boat: C(5) and C(14) deviate from plane (2) of the bottom of the boat by −0·641 (3) and −0·388 (3) Å, respectively. The angle of the heterocycle bending along the line C(5)···C(14) is 46·1 (1)°.

Benzene ring (*A*) [C(7a)···C(11a), plane (3)] is, in fact, coplanar with the flat part of ring (*B*) [planes (1) and (3) form a dihedral angle of 1·3 (1)°]. At the same time, benzene ring (*D*) [C(4a)···C(14a)], owing to considerable twisting of ring (*C*), forms a dihedral angle of 22·9 (1)° with plane (2).

The pseudo-torsional angles C(11a)C(7a)N(6)N(13) and N(13)N(6)C(4a)C(14a) are −6·9 (3) and −11·0 (3)°, respectively, confirming the twisting of the heterocycles which causes an overall twisting of the

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* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42328 (14 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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molecule (I) and a distortion from its ideal C_s symmetry [pseudo-torsional angles C(11a)C(7a)C(4a)C(14a) and C(10)C(9)C(3)C(2) are −18·0 (3) and −17·2 (4)°, respectively]. The dihedral angle formed by planes (1) and (2) of the heterocycles is 22·2 (1)°.

S(1) and S(2) are almost in plane (1). The average $C{=}S$ bond length of 1·676 (2) Å is somewhat increased as compared with the length [1·610 (9) Å] of this bond in the molecule of thioacetaldehyde in the vapor phase (Kroto & Landsberg, 1976) and coincides with the bond length of 1·671 (3) Å found in *N*,*N*-dimethylthiobenzamide (Walter, Harto & Voss, 1976).

In molecule (I), conjugation in the planar moieties C(7a)C(7)S(1)N(6) and C(11a)C(12)S(2)N(13), bonded to benzene (*A*), is observed. In fact, the coordination planes of the planar trigonal N(6) and N(13) atoms (the sums of the bond angles at these atoms are 359·7 and 360·0°, respectively) are almost coplanar with the planar part of heterocycle (*B*), which is favorable for π interaction of the lone electron pairs of the N atoms with the π systems of the $C{=}S$ bonds. Accordingly, the average value of the $C(sp^2)$—N bond lengths in (I) is 1·348 (2) Å, which is considerably shorter than the standard length of this bond [1·426 (12) Å] (*International Tables for X-ray Crystallography,* 1968). The average value of the $C(sp^2)$—$C(sp^2)$ bond lengths [1·462 (5) Å] is close to the standard value of 1·476 Å (Kitaigorodsky, 1973).

There is no conjugation through the N—N bond: its length of 1·406 (2) Å actually coincides with the value of 1·410 (4) Å in molecule (II) with a distorted sp^2 hybridization of the N atoms and is also close to the value of 1·403 (6) Å found in the molecule of 2-chloro-8,9,10,11-tetrahydro-6*H*,11a*H*-pyridazino[1,2-*a*]cinnoline-1,4-dione (Vegas, Perez-Salazar, Martínez-Ripoll & García-Blanco, 1982). In both of these molecules the $N(sp^2)$—$N(sp^2)$ bond is ordinary (Chang, Porter & Bauer, 1970). The absence of a π interaction through the N—N bond is also indicated by the twisting around it [torsional angle C(7)N(6)N(13)C(12) 13·7 (3)°].

The average values of the $C(sp^3)$—N and $C(sp^2)$—$C(sp^3)$ bond lengths in (I) of 1·479 (3) and 1·490 (2) Å, respectively, are close to the values of the corresponding single bonds [1·456 (7) and 1·504 (1) Å] in molecule (II).

In the crystal intermolecular contacts between the benzene rings of the molecules related by twofold screw axes parallel to [100] (Fig. 2) are observed: C(3)···C(8′) 3·393 (4), C(4)···C(11a′) 3·345 (4) and C(4)···C(12′) 3·373 (3) Å [atoms C(8′), C(11a′) and C(12′) are derived by the symmetry transformations $\frac{1}{2}+x$, $\frac{1}{2}-y$, $\bar{z}$ and $\frac{1}{2}+x$, $\frac{1}{2}-y$, $1-z$, respectively]. These distances are comparable with the doubled van der Waals radius of the C atom (3·40 Å) (Bondi, 1966). The molecules, forming these contacts, make up infinite chains along the *a* axis.

Table 1. *Atomic coordinates* (×10⁵ *for* S, ×10⁴ *for* N, C) *and equivalent isotropic thermal parameters*

$$B_{\rm eq} = \tfrac{1}{3}\textstyle\sum_i\sum_j B_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$B_{\rm eq}$(Å²)
S(1)	21602 (5)	8926 (4)	17540 (10)	4·31 (2)
S(2)	18738 (5)	53420 (5)	44116 (9)	4·03 (1)
N(6)	2763 (1)	2539 (1)	3399 (3)	3·08 (4)
N(13)	2745 (1)	3573 (1)	3838 (2)	2·95 (4)
C(1)	5535 (2)	3976 (2)	3432 (3)	3·90 (6)
C(2)	6384 (2)	3442 (2)	2908 (4)	4·42 (7)
C(3)	6339 (2)	2383 (2)	2801 (3)	4·28 (7)
C(4)	5455 (2)	1876 (2)	3218 (3)	3·84 (6)
C(4a)	4606 (2)	2421 (2)	3765 (3)	3·21 (5)
C(5)	3600 (2)	1971 (2)	4240 (3)	3·68 (6)
C(7)	2034 (2)	2090 (2)	2439 (3)	2·92 (5)
C(7a)	1124 (2)	2703 (2)	2078 (3)	2·71 (5)
C(8)	299 (2)	2284 (2)	1167 (3)	3·51 (6)
C(9)	−571 (2)	2841 (2)	877 (3)	3·62 (6)
C(10)	−637 (2)	3831 (2)	1484 (3)	3·58 (6)
C(11)	153 (2)	4250 (2)	2392 (3)	3·39 (5)
C(11a)	1054 (2)	3697 (2)	2704 (3)	2·81 (5)
C(12)	1905 (2)	4155 (2)	3639 (3)	2·94 (5)
C(14)	3711 (2)	3999 (2)	4530 (3)	3·85 (6)
C(14a)	4642 (2)	3473 (2)	3868 (3)	3·23 (5)

Table 2. *Bond angles* (°)

C(2)C(1)C(14a)	120·4 (2)	C(7a)C(8)C(9)	120·6 (2)
C(1)C(2)C(3)	119·7 (3)	C(8)C(9)C(10)	119·9 (2)
C(2)C(3)C(4)	120·5 (3)	C(9)C(10)C(11)	120·5 (2)
C(3)C(4)C(4a)	119·5 (2)	C(10)C(11)C(11a)	120·8 (2)
C(4)C(4a)C(14a)	120·5 (2)	C(11)C(11a)C(7a)	118·7 (2)
C(4C(4a)C(5)	125·1 (2)	C(11)C(11a)C(12)	120·6 (2)
C(5)C(4a)C(14a)	114·4 (2)	C(7a)C(11a)C(12)	120·7 (2)
C(4a)C(5)N(6)	110·0 (2)	C(11a)C(12)N(13)	116·2 (2)
C(5)N(6)N(13)	113·4 (2)	C(11a)C(12)S(2)	123·1 (2)
C(5)N(6)C(7)	123·0 (2)	S(2)C(12)N(13)	120·7 (2)
C(7)N(6)N(13)	123·3 (2)	C(12)N(13)N(6)	122·5 (2)
N(6)C(7)C(7a)	115·9 (2)	C(12)N(13)C(14)	121·3 (2)
N(6)C(7)S(1)	121·4 (2)	N(6)N(13)C(14)	116·2 (2)
S(1)C(7)C(7a)	122·7 (2)	N(13)C(14)C(14a)	113·2 (2)
C(7)C(7a)C(11a)	120·2 (2)	C(14)C(14a)C(4a)	117·1 (2)
C(7)C(7a)C(8)	120·2 (2)	C(14)C(14a)C(1)	123·3 (2)
C(8)C(7a)C(11a)	119·6 (2)	C(1)C(14a)C(4a)	119·5 (2)

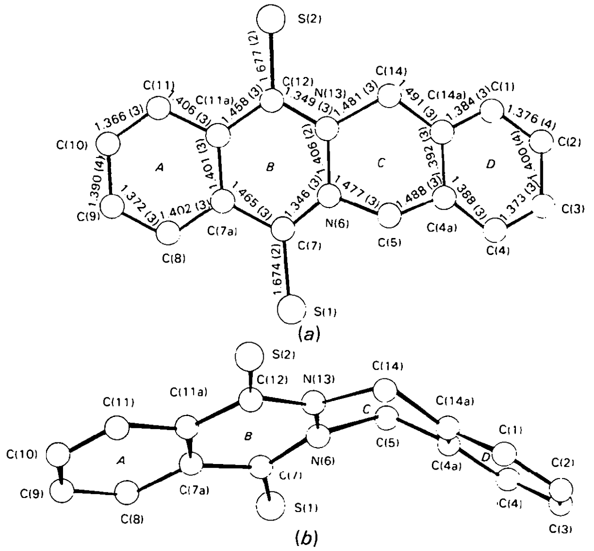

Fig. 1. (*a*) Bond lengths (Å) and (*b*) overall conformation of (I).

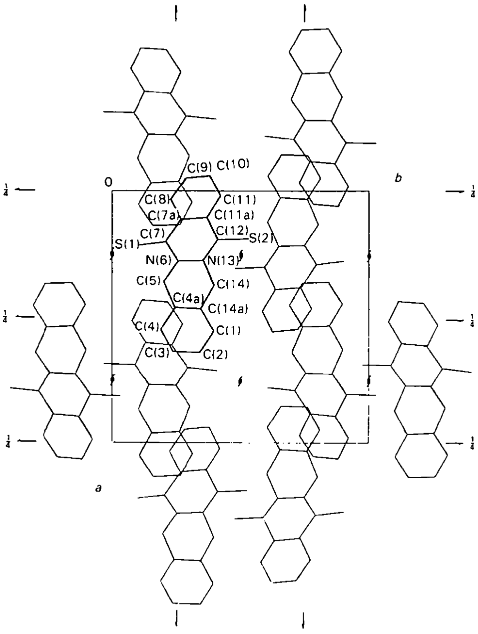

Fig. 2. Crystal packing viewed down **c**.

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Structure of (*S*)-2-Methyl-1-[(*R*)-1-phenylethylamino]-1-propanephosphonic Acid Monohydrate

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Abstract. $C_{12}H_{20}NO_3P.H_2O$, $M_r = 275{\cdot}3$, orthorhombic, $C222_1$, $a = 10{\cdot}167\,(3)$, $b = 18{\cdot}970\,(10)$, $c = 15{\cdot}580\,(7)$ Å, $U = 3005$ Å^3, $Z = 8$, $D_m = 1{\cdot}22\,(1)$, $D_x = 1{\cdot}22$ Mg m^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}71069$ Å, $\mu = 0{\cdot}19$ mm^{-1}, $F(000) = 1184$, $T = 293$ K, $R = 0{\cdot}06$ for 1617 nonzero independent amplitudes. The title compound exists as a zwitterion, Ph—CHMe—NH_2^+—CH(CHMe$_2$)—PO_3H^-. The conformation of the molecule is *gauche–gauche*, angles χ^1 [P—C(1)—N—C] and χ^2 [C(1)—N—C—C(phenyl)] being 68·3 (4) and 60·9 (5)°, respectively. Two short P—O···H···O—P hydrogen bonds of 2·554 (5) and 2·526 (4) Å occur between molecules related by a twofold rotation axis. The absolute configuration of the molecule was assigned as *S,R* with reference to the known *R* configuration of (+)-(*R*)-1-phenylethylamine.

Introduction. The determination of the molecular structure and absolute configuration of 1-aminoalkanephosphonic acids (1) is of considerable importance in view of the established inhibition of enzymes involved in the metabolism of amino acids by the phosphonic acid analogues of substrates (Neuzil & Cassaigne, 1980; Adams, Mukherjee & Dunathan, 1974; Brand & Lowenstein, 1978; Neale, 1970; LaCoste, Cassaigne & Neuzil, 1972; Lejczak, Starzemska & Mastalerz, 1981).

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