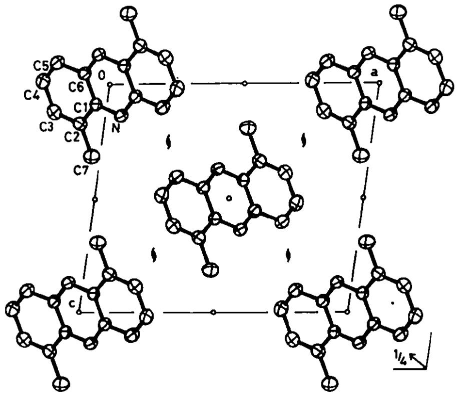

Fig. 2. The molecular arrangements in the crystal viewed along **b**.

with a maximum deviation of 0·007 Å for the C(5) atom. The methyl C atom C(7) attached to the phenazine ring also lies in the same plane with a deviation of 0·026 Å.

The molecular arrangements in the crystal viewed along the *b* axis are shown in Fig. 2. The crystal is built up of individual molecules, with adjacent molecules held together by van der Waals forces.

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(4*R*,5*R*)-1,2-Dithiane-4,5-diol

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Abstract. $C_4H_8O_2S_2$, M_r = 152·24, trigonal, $P3_121$, a = 10·322 (3), c = 10·630 (1) Å, Z = 6, V = 980·2 Å^3, D_c = 1·60, D_m = 1·60 Mg m^{-3}, $F(000)$ = 480, Cu $K\alpha$ radiation. The structure was solved by direct methods and refined by full-matrix least squares to a final R = 0·036 for 73 parameters and 754 observed reflexions. The ring has a chair conformation with a C–S–S–C angle of +58·8°. All molecules are connected by hydrogen bonds.

Introduction. Cyclic disulfides have been extensively used to correlate the chiroptical properties of the disulfide group in the absorption region between 250 and 330 nm with the torsion angle about the S–S bond. 1,2-Dithiane rings, with a fixed asymmetric center near the disulfide group, are sufficiently rigid to allow a direct comparison of the absorption wavelengths and the sign of the CD Cotton effect measured (Carmack & Neubert, 1967; Linderberg & Michl, 1970) in solution with the molecular conformation found in the solid state. In this paper we report the crystal structure of (4*R*,5*R*)-1,2-dithiane-4,5-diol. The compound was prepared by air-oxidation in aqueous solution at pH 8·5 (tris.HCl buffer) and extracted by chloroform. The UV and CD spectra showed the expected absorption band, in the range 280–290 nm, associated with a positive Cotton effect (Carmack & Neubert, 1967; Cleland, 1964).

The crystals were grown from chloroform as transparent prisms elongated along **c**. Systematic absences do not define the space group uniquely and $P3_121$ was established on the basis of the structure determination.

The intensity data were collected on an Enraf–Nonius CAD-4F automatic diffractometer with a crystal approximately 0·10 × 0·11 × 0·30 mm. Unit-cell parameters were refined by the least-squares fit of 18 high-angle reflexions. A $\theta/2\theta$ scanning mode with Ni-filtered Cu $K\alpha$ radiation was used to measure 816 independent reflexions with 2θ values below 135°, 754 of which were considered as observed by the criterion $I > 2{\cdot}5\sigma(I)$, where $\sigma(I)$ was determined from

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counting statistics. The intensity data were reduced to structure amplitudes by the application of Lorentz and polarization factors, and no absorption correction was applied. The structure was solved by direct methods using *MULTAN* 78 (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978).

Full-matrix least-squares refinement with anisotropic thermal parameters yielded an R of 0·055, where $R = \sum||F_o| - |F_c||/\sum|F_o|$. A difference map computed with the phases from the least-squares refinement revealed the positions of all H atoms. Least-squares refinement with isotropic H-atom thermal parameters yielded final R values of 0·036 for the observed reflexions and 0·039 for all measured reflexions. The function minimized was $\sum w(|F_o| - |F_c|)^2$ where $w = 1/\sigma^2(F)$. All parameter shifts during the final cycle were less than $0{\cdot}5\sigma$. Finally, the absolute configuration was confirmed by the diffraction data. Least-squares refinement of the opposite configuration, under the same conditions (space group $P3_221$), gave a final R of 0·047 for the observed reflexions, which is significantly higher than the previous value (Hamilton, 1965). The scattering factors for all atoms were taken from *International Tables for X-ray Crystallography* (1974).

All crystallographic calculations were carried out on the PDP11/34 computer with the Enraf–Nonius structure determination package.

Discussion. Final atomic positions are given in Table 1.* The molecule with the numbering scheme is shown in Fig. 1. Bond lengths and angles are in Table 2. The six-membered dithiane ring has a regular chair conformation with the OH groups as equatorial substituents (Table 3). The torsion angle about the S–S bond is +58·8 ± 0·5°, as found in other dithiane rings (Foss, Johnsen & Reistad, 1964; Debaerdemaeker, 1975). This positive value agrees with the rule which associates a positive rotatory strength for the first UV transitions with a twisting of the disulfide chromophore in the sense of a right-handed helix (Linderberg & Michl, 1970).

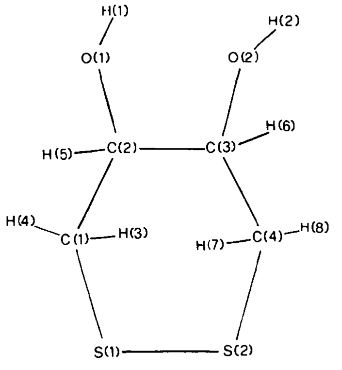

Fig. 1. Numbering scheme.

Table 1. *Atomic coordinates* (× 10⁴, × 10³ *for* H) *with their estimated standard deviations and temperature factors* (× 10⁴, × 10³ *for* H)

	x	y	z	U_{eq}*/U (Å²)
S(1)	737 (1)	1881 (1)	3415·6 (9)	495
S(2)	1491 (1)	4014 (1)	4003·3 (9)	511
O(1)	4446 (3)	3085 (2)	1428 (2)	424
O(2)	4237 (3)	5635 (2)	1004 (2)	385
C(1)	2484 (4)	2073 (3)	2881 (3)	413
C(2)	3155 (3)	3160 (3)	1787 (3)	303
C(3)	3584 (3)	4771 (3)	2113 (3)	285
C(4)	2269 (4)	4949 (4)	2529 (4)	435
H(1)	475 (3)	352 (3)	86 (3)	29
H(2)	473 (4)	661 (5)	111 (4)	67
H(3)	320 (4)	250 (4)	354 (3)	27
H(4)	240 (5)	118 (5)	258 (4)	69
H(5)	233 (4)	280 (4)	109 (3)	42
H(6)	448 (5)	518 (4)	279 (4)	56
H(7)	136 (4)	444 (5)	185 (4)	58
H(8)	266 (4)	614 (4)	261 (4)	33

* These values are the arithmetic averages of the principal components of the anisotropic temperature factors.

Table 2. *Bond distances* (Å) *and bond angles* (°) *with estimated standard deviations in parentheses*

S(1)–S(2)	2·032 (1)	O(1)–H(1)	0·72 (3)
S(1)–C(1)	1·804 (3)	O(2)–H(2)	0·88 (4)
S(2)–C(4)	1·805 (3)	C(1)–H(3)	0·96 (3)
C(1)–C(2)	1·520 (3)	C(1)–H(4)	0·94 (4)
C(2)–C(3)	1·532 (3)	C(2)–H(5)	1·04 (3)
C(3)–C(4)	1·523 (3)	C(3)–H(6)	1·08 (3)
O(1)–C(2)	1·425 (3)	C(4)–H(7)	1·09 (3)
O(2)–C(3)	1·427 (3)	C(4)–H(8)	1·09 (3)

S(2)–S(1)–C(1)	99·0 (1)	C(3)–C(4)–S(2)	111·9 (2)
S(1)–S(2)–C(4)	98·0 (1)	O(1)–C(2)–C(3)	110·4 (2)
S(1)–C(1)–C(2)	112·6 (2)	O(1)–C(2)–C(1)	105·0 (2)
C(1)–C(2)–C(3)	113·9 (2)	O(2)–C(3)–C(2)	106·3 (2)
C(2)–C(3)–C(4)	113·9 (2)	O(2)–C(3)–C(4)	109·6 (2)

Table 3. *Torsion angles* (°)

S(1)–S(2)–C(4)–C(3)	−64·9 (3)
S(2)–C(4)–C(3)–C(2)	66·0 (3)
C(4)–C(3)–C(2)–C(1)	−61·2 (4)
C(3)–C(2)–C(1)–S(1)	63·4 (3)
C(2)–C(1)–S(1)–S(2)	−63·2 (3)
O(1)–C(2)–C(3)–O(2)	60·1 (3)

The geometry of the C–S–S–C fragment has been shown to depend on the value of the disulfide torsion angle (Jones, Bernal, Frey & Koetzle, 1974; Neubert, Carmack & Huffman, 1977). The values found for the present compound compare well with those expected for a dihedral angle close to 60°.

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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 35768 (16 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

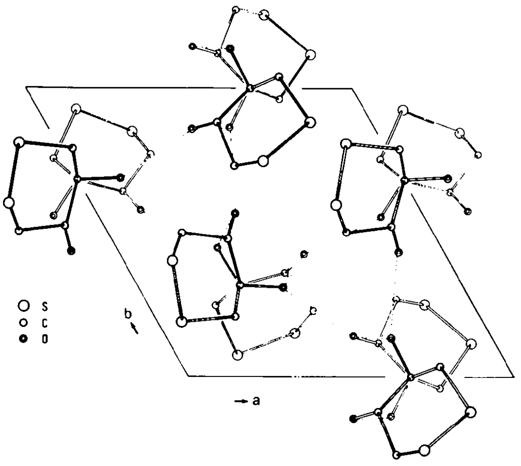

Fig. 2. Projection of the crystal structure along the c axis. Broken lines indicate hydrogen bonds.

The positions of the H atoms do not allow the formation of an intramolecular hydrogen bond between the two OH groups in the *cis* position.

In the crystal (Fig. 2), the molecules are fully hydrogen bonded. Each hydroxyl group is involved in two linear hydrogen bonds to symmetry-related molecules. O(1) is the donor to O(2) across the diad axis [O(1)···O(2) 2·85, H(1)···O(2) 2·15 Å, O(1)···H(1)···O(2) 163°], giving rise to dimeric molecules which are bonded helically, *via* the O(2) donor bonds, along the screw axes [O(1)···O(2) 2·86, H(2)···O(1) 2·00 Å, O(1)···H(2)···O(2) 162°]. The packing distances fall within the normal range except for the S(1) atom which is involved in a rather short intermolecular contact [S(1)(x,y,z); S(1)($x-y, -y, \frac{2}{3}-z$)] of 3·37 Å, which is well below the sum of the van der Waals radii (3·7 Å).

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Structure of *p*-Hydroxyephedrine Hydrochloride

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Abstract. $C_{10}H_{15}NO_2.HCl$, $M_r = 217·7$, orthorhombic, $P2_12_12_1$, $a = 6·388\,(3)$, $b = 7·555\,(3)$, $c = 23·854\,(5)$ Å, $V = 1151·23$ Å^3, $Z = 4$, $D_m = 1·26$, $D_c = 1·26$ Mg m^{-3}, $\lambda(\text{Cu }K\alpha) = 1·5418$ Å, $\mu(\text{Cu }K\alpha) = 2·773$ mm^{-1}. The structure was solved by direct methods and refined to an R value of 0·047 for 1088 diffractometer data using block-diagonal least-squares methods. The ethylamine side chain is in the extended form, the C—C—C—N$^+$ torsion angle being 178·1°. The mean plane through these atoms makes an angle of 81·1° with the plane of the phenol ring. The distance of the amino N atom from the centre of the phenyl ring is 5·16 Å. The crystal structure is stabilized by a network of N—H···Cl, O—H···Cl and O—H···O hydrogen bonds.

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Introduction. *p*-Hydroxyephedrine, *p*-hydroxy-α-[1-(methylamino)ethyl]benzyl alcohol, a sympathomimetic amine, pharmacologically resembles *p*-aminoephedrine which is about twice as active, and half as toxic, as ephedrine (McLean, 1960). Since such biogenic amines are found to assume a favoured conformation (Carlström, Bergin & Falkenberg, 1973), it was thought worthwhile to determine the crystal structure of *p*-hydroxyephedrine hydrochloride.