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Structure of (2*R*,3*R*,4*S*)-3,4-Dihydroxy-2-hydroxymethyl-8-methyl-6-phenyl-1-oxa-6,8-diazaspiro[4.4]nonane-7-thione, C₁₄H₁₈N₂O₄S

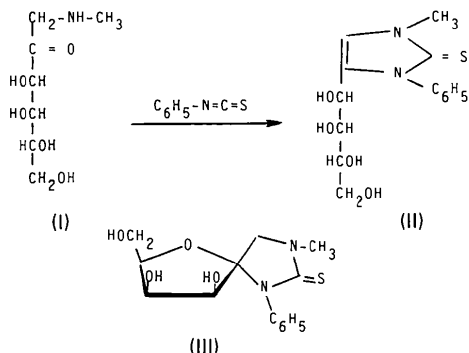
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Abstract. $M_r = 310.37$, tetragonal, $P4_12_12$, $a = 11.255$ (2), $c = 24.829$ (4) Å, $V = 3145.2$ (9) Å³, $Z = 8$, $D_x = 1.31$, $D_m = 1.33$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 0.23$ mm⁻¹, $F(000) = 1312$, $T = 293$ (2) K, $R = 0.077$ for 2023 observed reflections. The molecule consists of three rings: a tetrahydrofuran and an imidazolidine joined by a common spiro C atom and a phenyl group. The furanose ring displays a conformation intermediate between 2T and 3E forms. The imidazolidine ring, significantly non-planar, forms dihedral angles of 90.7 (2)° with the furanose ring and 86.3 (2)° with the phenyl ring. Packing is governed by hydrogen bonds and van der Waals contacts.

Introduction. The title compound (III) has recently been synthesized by Fernandez-Bolaños, Fuentes-Mota, Cert-Ventula & Trujillo (1984) at the Organic Chemistry Department of the University of Seville, Spain, by cyclization of 1,3-dihydro-1-methyl-3-phenyl-4-(*D*-*lyxo*-tetritol-yl)-2-imidazolethione (II) obtained by reaction of 1-deoxy-1-methylamino-*D*-*lyxo*-hexulose (I) and phenyl isothiocyanate.



In the attempt to establish the possible correlations between NMR spectroscopy data and X-ray single-crystal diffraction information the crystal structure of the title compound has been determined. The resolution of the structure confirms the spiranic conformation and the presence of three OH groups as the NMR spectra showed.

Experimental. Sample kindly provided by Professor Fernandez-Bolaños, Organic Chemistry Department, Seville University. Crystal $ca\ 0.3 \times 0.3 \times 0.5$ mm. D_m measured by flotation. Enraf-Nonius CAD-4 diffractometer. Cell dimensions from 2θ angles for 25 reflections ($6 < \theta < 12^\circ$). $h \leq 15$, $k \leq 15$, $l \leq 35$. $2\theta_{\max} = 12^\circ$. 2714 unique reflections, 2023 intensities $\geq 2\sigma(I)$. Intensities of two standard reflections (008 and 008) did not vary significantly. No absorption correction. Structure solved with *MULTAN78* (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978). Trial structure refined with *XRAY* system (Stewart, Kundell & Baldwin, 1970); final cycles of refinement based on F included one scale factor and anisotropic thermal parameters for non-hydrogen atoms; H atoms located in difference electron density map included in refinement with isotropic thermal parameters equal to those of the bonded atoms. Weighting scheme $w = 1/\sigma^2(F)$. Final $R = 0.077$ and $wR = 0.072$ for the observed reflections only. Max. and average Δ/σ in the last refinement cycle 0.033 and 0.006 respectively. Final difference Fourier synthesis showed $\Delta\rho = \pm 0.3 e \text{ \AA}^{-3}$. Scattering factors from *International Tables for X-ray Crystallography* (1962). The absolute configuration was assigned on the basis of the configurations of the products used in the synthesis.

Discussion. The refined atomic coordinates and U_{eq} parameters are listed in Table 1* and the intramolecular bond distances and angles in Fig. 1, which shows a view of the molecule with the numbering of the atoms. The molecules contain a phenyl-substituted imidazolidine ring joined by a spiro C(2) atom to the *lyxo*-tritolol group.

* Lists of structure factors, anisotropic thermal parameters and short contacts involving H atoms have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39875 (21 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Atomic coordinates ($\times 10^4$) and U_{eq} values ($\text{\AA}^2 \times 10^3$) for the title compound

$$U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* a_i a_j \cos(\mathbf{a}_i, \mathbf{a}_j).$$

| | x | y | z | U_{eq} |
|-------|----------|----------|----------|----------|
| S(1) | 5490 (2) | 332 (2) | 4623 (1) | 56 (1) |
| O(1) | 7934 (4) | 2034 (4) | 5943 (2) | 43 (2) |
| O(2) | 7185 (5) | 4388 (4) | 6476 (2) | 48 (2) |
| O(3) | 6652 (5) | 4669 (4) | 5386 (2) | 50 (2) |
| O(4) | 9577 (5) | 1651 (5) | 6865 (2) | 62 (2) |
| N(1) | 6918 (4) | 1924 (4) | 5111 (2) | 33 (1) |
| N(2) | 5269 (5) | 1527 (5) | 5546 (2) | 46 (2) |
| C(1) | 5888 (5) | 1268 (5) | 5110 (2) | 35 (2) |
| C(2) | 7049 (5) | 2584 (5) | 5614 (2) | 29 (2) |
| C(3) | 5808 (6) | 2469 (6) | 5859 (2) | 40 (2) |
| C(4) | 7532 (5) | 3856 (5) | 5540 (2) | 32 (2) |
| C(5) | 8072 (6) | 4123 (6) | 6090 (2) | 38 (2) |
| C(6) | 8662 (6) | 2943 (5) | 6202 (2) | 37 (2) |
| C(7) | 7815 (5) | 1828 (5) | 4699 (2) | 32 (2) |
| C(8) | 8644 (7) | 960 (7) | 4715 (3) | 58 (3) |
| C(9) | 9483 (8) | 887 (8) | 4312 (4) | 74 (3) |
| C(10) | 9473 (9) | 1691 (9) | 3895 (4) | 73 (3) |
| C(11) | 8637 (8) | 2570 (8) | 3870 (3) | 58 (3) |
| C(12) | 7796 (6) | 2647 (6) | 4287 (3) | 44 (2) |
| C(13) | 8811 (8) | 2667 (7) | 6799 (3) | 55 (3) |
| C(14) | 4041 (7) | 1180 (8) | 5638 (3) | 65 (3) |

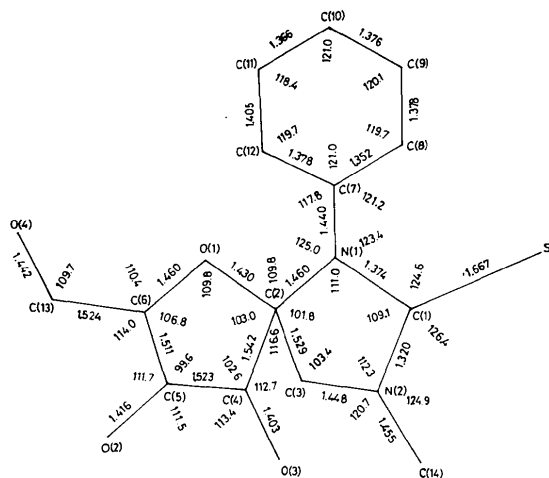


Fig. 1. Interatomic distances (\AA) and angles ($^\circ$) for non-hydrogen atoms. Mean standard deviations 0.007\AA and 0.5° .

The tetrahydrofuran ring of the *lyxo*-tritolol group adopts a conformation intermediate between twist and envelope. In terms of the puckering parameters proposed by Cremer & Pople (1975) for the atomic sequence O(1), C(2), C(4), C(5) and C(6), $Q = 0.419 (6) \text{\AA}$ and $\varphi = -96.4 (7)^\circ$ which correspond to the half-chair conformation.

The imidazolidine group deviates significantly from planarity [maximum deviation $0.106 (7) \text{\AA}$] and the three substituents S, C(7) and C(14) are displaced by $-0.015 (2)$, $0.057 (6)$ and $0.125 (9) \text{\AA}$ respectively from the best least-squares mean plane of the imidazolidine group, atomic sequence N(1), C(1), N(2), C(3) and C(2), which shows a slight half-chair conformation with the pseudo twofold axis through C(1), $Q = 0.148 (6) \text{\AA}$ and $\varphi = 128.9 (21)^\circ$.

The phenyl ring is planar within the errors; maximum deviation from the best least-squares plane $0.008 (9) \text{\AA}$. The substituent N(1) is at $0.021 (5) \text{\AA}$ from this plane.

The dihedral angle between the least-squares planes through the two main rings is $90.7 (2)^\circ$ and the phenyl makes angles of $86.3 (2)$ and $92.2 (2)^\circ$ with the imidazolidine and tetrahydrofuran, respectively. We note that O(2) is in an axial position and O(3) and C(13) in quasi-equatorial positions.

Bond lengths and angles in the tetrahydrofuran ring are similar to those found in the literature (Millan, Conde, Conde & Márquez, 1983). However, the endocyclic C—O bond lengths [C(2)—O(1) $1.430 (6)$ and C(6)—O(1) $1.460 (7) \text{\AA}$] are asymmetric. The average values of the C—C—C, C—C—O and C—O—C endocyclic angles are $101.1 (5)$, $104.9 (4)$ and $109.8 (4)^\circ$, respectively.

Bond lengths and angles in the phenyl and imidazolidine rings are in the range often observed for these groups. The average C—C distance and angle of the phenyl ring are $1.377 (7) \text{\AA}$ and $119.9 (7)^\circ$,

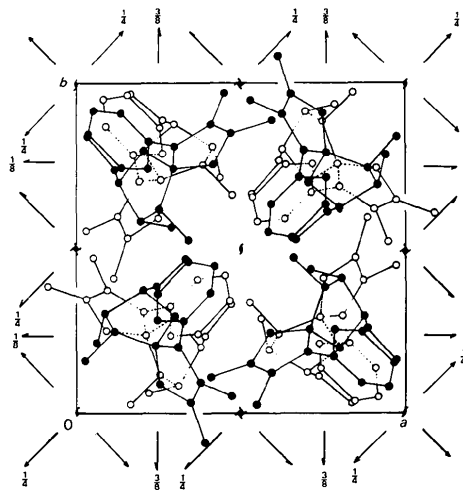


Fig. 2. The molecular packing viewed along the z axis.

respectively. The S(1)–C(1), C(1)–N(1) and C(1)–N(2) distances of 1.667 (6), 1.374 (7) and 1.320 (7) Å, respectively, for the imidazolidine ring indicate the effect of the thiourea resonance system.

There are three intermolecular hydrogen bonds: O(3)–H...O(4)($\frac{1}{2}+y, \frac{3}{2}-x, -\frac{1}{4}+z$) = 2.673 (7), and H...O(4) = 1.72 (5) Å; O(2)–H...O(1)($\frac{3}{2}-x, \frac{1}{2}+y, \frac{5}{4}-z$) = 2.988 (6) and H...O(1) = 1.97 (5) Å; O(4)–H...O(3)($\frac{3}{2}-x, -\frac{1}{2}+y, \frac{5}{4}-z$) = 2.697 (7) and H...O(3) = 1.63 (5) Å. All other intermolecular contacts are van der Waals interactions. The molecular packing is shown in Fig. 2.

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Structure of 25-Ethoxycarbonyl-2,3,7,8,12,13,17,18-octaethyl-21,22-methano-21*H*,22*H*-porphyrin Hydrobromide, C₄₀H₅₁N₄O₂⁺.Br⁻. The First Example of a *cis*-*N,N*-Bridged Porphyrin

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Dedicated to Professor Dorothy Hodgkin on the occasion of her 75th birthday

Abstract. $M_r = 699.79$, monoclinic, $C2/c$, $a = 20.324$ (3), $b = 19.947$ (3), $c = 18.976$ (3) Å, $\beta = 98.31$ (5)°, $V = 7612.07$ Å³, $Z = 8$, $D_m = 1.21_8$, $D_x = 1.221$ Mg m⁻³, graphite-monochromatized Cu $K\alpha$ radiation, $\lambda = 1.54178$ Å, $\mu(\text{Mo } K\alpha) = 10.51$, $\mu(\text{Cu } K\alpha) = 16.23$ mm⁻¹, $T = 295$ K, $F(000) = 2960$, $R = 0.073$ for 1811 observed reflections. The porphyrin macroring is considerably folded as illustrated by the angles the pyrrole rings form with the mean N(21)–N(24) plane: -9.8 , -3.9 , 12.8 and 6.1 ° (e.s.d.'s ca 0.9 °) respectively. The ethoxycarbonylmethylene group and Br are disordered. The H atom bonded to N(23) deviates -0.22 (9) Å from the plane of the macroring in the opposite direction from the side chain.

Introduction. Reactions of cobalt(II) octaethylporphyrin and corresponding cobalt(III) complexes with ethyl diazoacetate were investigated to ascertain the possibility that a cobalt carbene complex is an intermediate in the reactions of biochemical rearrangements controlled by cobalamin-containing enzymes (Batten, Hamilton, Johnson, Shelton & Ward, 1974; Johnson, Ward, Batten, Hamilton, Shelton & Elson, 1975). The title hydrobromide and a number of metalloporphyrins obtained in the course of this work

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were the first examples of a *cis*-*N,N*-substituted porphyrin and of metalloporphyrins.

The present work was undertaken to investigate the geometry of the octaethylporphyrin (OEP) nucleus when the neighboring N atoms are bridged by ethoxycarbonylmethylene. The introduction of a C atom between N(21) and N(22) completes a new six-membered ring within the porphyrin macrocycle. This was expected to cause considerable difference in the stereochemistry of the N atoms present in the structure. Additionally, the position of the inner proton was of interest. It was postulated (Johnson, 1976) that this proton should be at equal distances from the N atoms and deviate from the plane of these N atoms in the opposite direction from the bridging methine group. The crystals of the hydrobromide were kindly supplied by the late Professor A. W. Johnson of Sussex University, England.

Experimental. Deep-purple prisms grown by slow evaporation from acetone–aqueous NaBr solution. D_m by flotation in aqueous KI. CAD-4 automated four-circle diffractometer. Crystal $0.10 \times 0.18 \times 1.30$ mm; 15 reflections in the θ range 25 – 35 ° used for refinement of the unit-cell parameters; graphite-monochromatized