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Structure of Urocanic Acid Dihydrate

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Abstract. $C_6H_6N_2O_2.2H_2O$, orthorhombic, $P2_12_12_1$, $a = 6{\cdot}72$ (1), $b = 9{\cdot}63$ (1), $c = 12{\cdot}89$ (2) Å, $Z = 4$, $d_x = 1{\cdot}393$ Mg m^{-3}. The structure was refined with 1057 observed reflections to a final R of 0·039 ($R_w = 0{\cdot}039$). The structure parameters are compared to those obtained in an independent determination by Hawkinson [*Acta Cryst.* (1977). B**33**, 2288–2291].

Introduction. Crystals of urocanic acid were obtained from a commercial sample (Koch–Light Lab. Ltd) by recrystallization in water. A specimen 0·5 × 0·35 × 0·2 mm was mounted on the goniometer with *a* approximately parallel to the φ axis. Preliminary lattice parameters were obtained from Weissenberg and oscillation photographs and refined by least squares from the setting angles of 24 reflections on a Picker FACS-1 four-circle automatic diffractometer, with Mo $K\alpha$ radiation ($\lambda = 0{\cdot}71069$ Å). Intensities were collected for two equivalent sets of reflections. The lattice dimensions were determined twice before the first data set and once before the second, and a significant shortening of all axes was observed, the shortening being of the order of 0·02 Å (Svinning, 1978). Urocanic acid dihydrate is completely dehydrated at 373 K (Stecher, 1968). Partial dehydration may therefore be a possible cause of the shortening of the axes.

Intensity measurements were made with Nb-filtered Mo $K\alpha$ radiation, a scintillation counter and a pulse-height analyzer. Three standard reflections were remeasured after every 50 reflections, the variations lying within ±1%. Corrections for long-range variations were performed by fitting polynomials of degree 4 and 3, for sets (I) and (II) respectively, to a plot of the normalized average intensity of the standard reflection group as a function of reflection number. The data were corrected for absorption by the analytical method of de Meulenaer & Tompa (1965). The average intensities of the two sets were calculated by the program *MEANER* (Mo, 1977).

The structure was solved by direct methods with *MULTAN* (Germain, Main & Woolfson, 1971), and all other calculations, including the *TANGEN* routine, were performed with XRAY 72 (Stewart, Kruger, Ammon, Dickinson & Hall, 1972). The H atom positions were found from difference maps. Set (I) was used for solving the structure and the average of sets (I) and (II) was used in the last cycles of refinement, giving $R = R_w = 0{\cdot}039$. There were no parameter shifts $>0{\cdot}04\ \sigma$ for the heavy atoms or $>0{\cdot}25\ \sigma$ for the H atoms in the last cycle. The final difference synthesis contained no peaks $>0{\cdot}20$ e Å^{-3}, whereas the most negative value was $-0{\cdot}12$ e Å^{-3}.

Scattering factors for C, N and O were those given by Doyle & Turner (1968), and for H those of Stewart, Davidson & Simpson (1965).

Discussion. When this study was completed in 1977 an independent structure determination was reported by Hawkinson (1977) (hereafter H77). It seems worthwhile to compare these two independent determinations. The latter was based on intensities obtained with Cu $K\alpha$ radiation and was refined to $R = 0{\cdot}038$ for 851 unique reflections with $2\theta < 130°$.

The molecular parameters of urocanic acid obtained in this work are given in Table 1, and are compared with those reported by H77. In addition, corresponding values found in neutron work on L-histidine.HCl.H_2O and average values for eight different studies of the structure of histidine (Fuess, Hohlwein & Mason, 1977) are given for comparison. All angles and bond lengths, except N(2)–C(1), C(7)–C(6) and C(8)–O(10), agree to within 1σ with the values obtained by H77. For the three exceptions the deviations are about 2·3, 1·8 and 1·7σ respectively. The mean bond length in the imidazole ring is 1·351 Å in this work, 1·348 Å in the work of H77, and 1·356 Å for histidine (Fuess *et al.*, 1977). The length of C(8)–C(7) is representative of a C–C bond in the presence of two C=O double bonds (Kennard *et al.*, 1972). Half-normal probability plots (Abrahams & Keve, 1971; Hamilton & Abrahams, 1972; *International Tables for X-ray Crystallography*, 1974) have been prepared in order to compare the refined parameters from this analysis (p_1) with those obtained by H77 (p_2). The measured value of $|p_1 - p_2|/[\sigma^2(p_1)$

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$+ \sigma^2(p_2)]^{1/2}$ is plotted as a function of the value expected if $|p_1 - p_2|$ were normally distributed with a mean of 0 and variance of 1. Calculations and plots were performed by the program *PROB* (Svinning, 1978), and are reproduced in Fig. 1.

For the complete set of parameters the plot deviates somewhat from a straight line, indicating that the differences are not strictly normally distributed. The average slope of the plot is also seen to be larger than one; thus the standard deviations are apparently underestimated by a factor of approximatley 1·5. Fig. 1(*b*) and (*c*) show that, when considered individually, both positional and thermal parameters are normally distributed. The standard deviations of the U_{ij} values are, however, underestimated by a factor of 1·75, Fig. 1(*d*). Hamilton & Abrahams (1970) suggest that the standard deviations from least-squares refinements are on average too small by factors of 1·4 for positional and 2·2 for thermal parameters. A comparison of the thermal parameters shows that the values obtained in this work* are systematically lower than those found by H77. In this connection it should be noted that apparently no absorption correction was made by H77 ($\mu_{\mathrm{Cu}\,K\alpha}$ = 0·971 mm^{-1}). This may account for the observed differences.

Table 1. *Molecular parameters of urocanic acid dihydrate and histidine*

Estimated standard deviations are given in parentheses.

	S*	H†	FHM‡	AV§
N(2)–C(3)	1·370 (4) Å	1·368 (3) Å	1·376 (3) Å	1·371 (8) Å
N(2)–C(1)	1·319 (4)	1·310 (3)	1·326 (4)	1·337 (14)
N(5)–C(4)	1·384 (4)	1·382 (3)	1·383 (4)	1·385 (6)
N(5)–C(1)	1·327 (4)	1·326 (3)	1·328 (3)	1·324 (10)
C(4)–C(3)	1·353 (2)	1·354 (3)	1·368 (3)	1·370 (11)
C(6)–C(4)	1·451 (4)	1·450 (3)		
C(7)–C(6)	1·323 (4)	1·316 (3)		
C(8)–C(7)	1·494 (4)	1·497 (3)		
C(8)–O(9)	1·251 (4)	1·249 (3)	1·264 (3)	
C(8)–O(10)	1·251 (3)	1·246 (3)	1·237 (3)	
C(3)–N(2)–C(1)	108·7 (3)°	108·7 (2)°	109·1 (2)°	
C(4)–N(5)–C(1)	108·6 (3)	108·4 (2)	109·0 (1)	
N(5)–C(4)–C(3)	106·2 (3)	106·1 (2)		
N(2)–C(3)–C(4)	107·6 (3)	107·5 (2)	106·9 (2)	
N(2)–C(1)–N(5)	109·0 (3)	109·2 (2)	108·7 (1)	
N(5)–C(4)–C(6)	124·5 (3)	124·6 (2)	122·6 (1)	
C(6)–C(4)–C(3)	129·3 (3)	129·3 (2)	131·0 (2)	
C(7)–C(6)–C(4)	126·3 (3)	126·3 (2)		
C(8)–C(7)–C(6)	123·1 (3)	123·5 (2)		
O(9)–C(8)–C(7)	115·8 (2)	116·0 (2)		
O(10)–C(8)–C(7)	120·0 (2)	119·7 (2)		
O(9)–C(8)–O(10)	124·1 (3)	124·3 (2)		

* Present work: urocanic acid dihydrate.

† Hawkinson (1977): urocanic acid dihydrate.

‡ Fuess, Hohlwein & Mason (1977): L-histidine.HCl.H_2O, neutron.

§ Average values for eight different works on histidine (Fuess, Hohlwein & Mason, 1977).

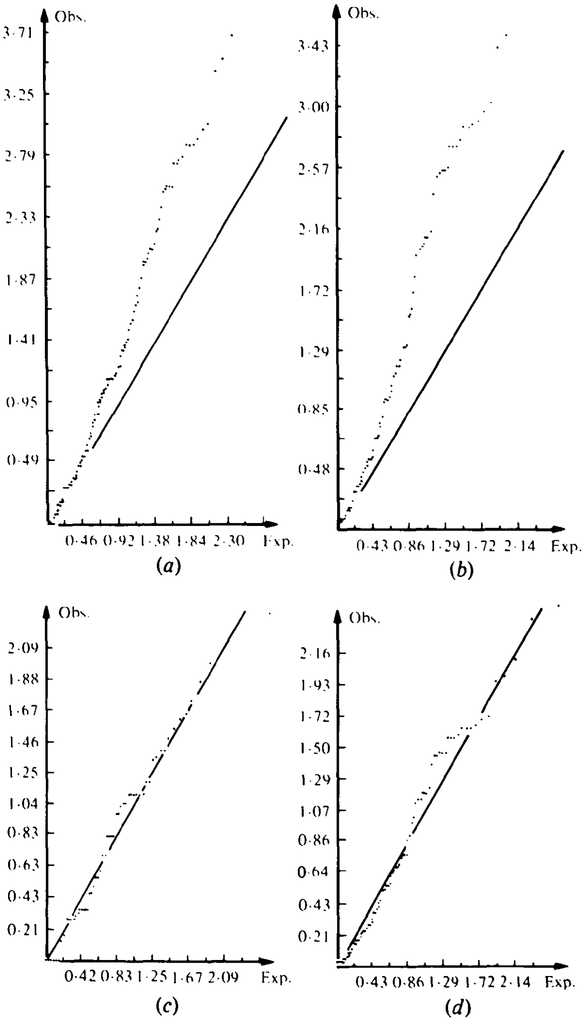

Fig. 1. Half-normal probability plots of urocanic acid dihydrate (see text). (*a*) Positional and thermal parameters with σ from least-squares refinement. (*b*) Thermal parameters with σ from least-squares refinement. (*c*) Positional parameters with σ from least-squares refinement. (*d*) Thermal parameters, σ multiplied by 1·75.

The imidazole ring (using the numbering of H77) C(4)–N(5)–C(1)–N(2)–C(3) is planar to within 0·002 Å. The chain C(4)–C(6)–C(7)–C(8) is also planar to within 0·0002 Å. The angle between the least-squares planes through the imidazole ring plus C(6) and through the carboxyl group is 7·5° compared to the 7·3° found by H77. The torsion angle C(8)–C(7)–C(6)–C(4) is found here to be 180° compared to 177·2° found by H77. A recalculation of the torsion angle from data reported by H77 in fact gave a value of 179·8° instead of 177·2°, the calculations being made by the *LSQPL* routine of XRAY 76 (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976). None of these atom groups is found to be strictly planar, even at a significance level of 2%. Hydrogen-bonding data of

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* Lists of structure factors, positional and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34654 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

this work on average agree with those reported by H77 to within 0·005 Å for the D(donor)—A(acceptor) distance, 0·06 Å for the H—A distances, and 5° for the D—H—A angle.

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The Absolute Configuration of (2*R*)-2-(Benzyloxycarbonylamino)-3-hydroxypropyl Chloromethyl (*R*)-Sulphoxide

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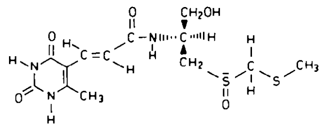
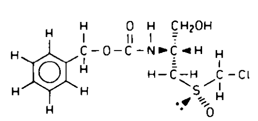
Abstract. $C_{12}H_{16}ClNO_4S$, monoclinic, $P2_1$, $a = 4{\cdot}829\,(1)$, $b = 10{\cdot}402\,(2)$, $c = 14{\cdot}174\,(4)$ Å, $\beta = 97{\cdot}95\,(2)°$, $Z = 2$, $V = 705$ Å^3, $D_c = 1{\cdot}44$ Mg m^{-3}. The structure was solved by routine direct methods and refined to $R = 0{\cdot}033$ for 2901 observed reflections. Determination of the absolute configuration, based upon the anomalous scattering of S and Cl, using Mo $K\alpha$ and Cu $K\alpha$ radiations, showed R chirality at the S atom and the asymmetric C atom.

Introduction. The structure of the antibiotic sparsomycin (I) was suggested mainly on the basis of spectroscopic and degradation studies (Wiley & MacKellar, 1976). The chiral C atom has the *S* configuration as depicted. The configuration of the sulphoxide S atom is unknown. Recently, a total synthesis of the enantiomer and a diastereomer of sparsomycin, both having *R* chirality at the C atom, was reported (Ottenheijm, Liskamp & Tijhuis, 1979). One of the intermediates in the synthesis of the diastereomeric compound is (II). The chirality of the C atom is *R*, whereas that of the S atom is unknown, but is identical with that of the S atom in the natural product (I). To determine the stereochemistry of the sulphoxide S atom in (II), we subjected (II) to an X-ray study.


(I)


(II)

A crystal (0·1 × 0·1 × 0·5 mm) was used for data collection on a Nonius CAD-4 diffractometer with a graphite monochromator (Mo $K\alpha$, $\lambda = 0{\cdot}71069$ Å). Systematic absences ($0k0$, k odd) are consistent with space group $P2_1$. Unit-cell parameters were obtained by least-squares treatment of 25 reflections with $38° < 2\theta < 42°$. Intensities were collected in the ω–2θ scan mode with a scan width of $\Delta\theta = (0{\cdot}95 + 0{\cdot}35 \tan\theta)°$ 4090 independent reflections with $2\theta < 60°$ were measured of which 2901 with $I > 3\sigma(I)$ were considered observed. The intensities of three standard reflections, monitored every 100 reflections, showed no

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