PAULING, L. (1960). *The Nature of the Chemical Bond*, p. 260. Ithaca: Cornell Univ. Press.
RAMAN, S. (1959). *Z. Kristallogr.* **111**, 301.
SCHLEMPER, E. O., HAMILTON, W. C. & LA PLACA, S. J. (1971). *J. Chem. Phys.* **54**, 3990.
SCHOMAKER, V. & TRUEBLOOD, K. N. (1968). *Acta Cryst.* B**24**, 63.
Tables of Interatomic Distances and Configuration in Molecules and Ions, Supplement 1956–59 (1965). Edited by L. E. SUTTON, p. S18. London: The Chemical Society.
WRIGHT, D. A. & MARSH, R. E. (1962). *Acta Cryst.* **15**, 54.
WRIGHT, D. A. & MARSH, R. E. (1963). *Acta Cryst.* **16**, 431.
ZACHARIASEN, W. H. (1967). *Acta Cryst.* **23**, 558.

Acta Cryst. (1972). B**28**, 3214

A Neutron Diffraction Study of the Structure of L-Lysine Monohydrochloride Dihydrate

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The intensities of 1431 (875 independent) neutron Bragg reflexions from a single crystal of L-lysine monohydrochloride dihydrate have been measured at a wavelength of 1·170 Å, using the diffractometer in the symmetrical setting. The structure has been refined by the method of least squares and the final conventional R value is 0·070. An inter-experimental comparison is made with an independent neutron-diffraction study (preceding paper) and with the X-ray results [Wright & Marsh *Acta Cryst.* (1962), **15**, 54].

Introduction

Preliminary studies of the space group and cell constants of L-lysine monohydrochloride dihydrate were carried out by Srinivasan (1956). The structure was first solved using X-ray data by Raman (1959), who suggested that the molecule is in the zwitterion form and also proposed a network of ten hydrogen bonds in the structure. A more accurate X-ray study was reported by Wright & Marsh (1962) whose hydrogen bonding scheme agrees with Raman's except in the bonding of the terminal amino group. The present neutron study was carried out to obtain detailed knowledge of the hydrogen atom positions in this amino acid crystal. A parallel neutron-diffraction study, of which we were unaware until recently, has been carried out independently by Koetzle, Lehmann, Verbist & Hamilton (1972).

Crystal data

L-Lysine monohydrochloride dihydrate, $NH_3^+[CH_2]_4CH(NH_3)^+COO^-.Cl^-.2H_2O$, is monoclinic, $P2_1$, with two molecules per unit cell. The following cell parameters were established from the X-ray study of Wright & Marsh (1962): $a=7{\cdot}492$ (1), $b=13{\cdot}320$ (4), $c=5{\cdot}879$ (1) Å and $\beta=97°47{\cdot}4$ (7)′. The calculated density is 1·249 g.cm^{-3}.

Experimental

Large, clear and well-formed single crystals of L-lysine $HCl.2H_2O$ were easily obtained by slow evaporation from a saturated aqueous solution at room temperature. The crystals were of pyramidal shape with (010) as the basal face and {110} and {011} as the principal side faces, and they were elongated along the **c** direction. The density measured by flotation was 1·246 g.cm^{-3}.

Neutron intensity data were recorded using the four-circle neutron diffractomer 3D-FAD (Momin, Sequeira & Chidambaram, 1969) at the CIRUS reactor in Trombay. The specimen crystal was cut in the shape of a rectangular parallelepiped with a height of 4·94 mm along the b axis and with lateral dimensions of 3·68 and 2·93 mm respectively along and perpendicular to the c axis. The crystal was given a thin coating of an adhesive (brand name Stickfast) to prevent exposure to air, and dipped in liquid nitrogen several times to reduce extinction effects. It was then mounted on the diffractometer with its b axis parallel to the φ-axis of the Eulerian Cradle. The cell parameters and the crystal orientation were refined from the optimised 2θ, χ and φ values for some 30 strong reflexions chosen at random, using the program *REFINE* (Srikanta & Sequeira, 1968). The refined values of the cell parameters were in agreement with the more precise X-ray values listed above to better than two parts per thousand. The systematic absences were checked and found to be consistent with the space group $P2_1$.

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The integrated intensities of 875 independent reflexions within the limit $\sin\theta/\lambda \leq 0{\cdot}55$ [$\lambda = 1{\cdot}170$ (1) Å] were recorded in the symmetrical setting using the θ–2θ coupled step-scanning technique. The step size was 0·1° and the range of scan for each reflexion was adjusted so as to have at least ten background points on either side of the peak. Intensities of an additional 556 equivalent reflexions, chosen at random, were also recorded. The mutual agreement factor in the intensities of these 556 pairs of equivalent reflexions was 6·4%. Two standard reflexions were recorded every 20 reflexions so as to keep a check on the stability of the crystal and that of the counting equipment. The reproducibility of the standard intensities was within 5% and there was no perceptible deterioration in the quality of the crystal. The effects of multiple reflexions were found to be negligible for the $0k0$ reflexions ($\chi = 90°$) when their peak intensities were examined as a function of the rotation about their scattering vectors.

The integrated intensities were reduced to F_o^2 by applying the standard Lorentz and absorption corrections using the program *DATARED* (Srikanta, 1968), which includes the absorption correction program *ORABS* (Wehe, Busing & Levy, 1962) as a subroutine. An absorption coefficient of 2·87 cm^{-1} (calculated) was used. The transmission factors ranged from 0·36 to 0·44.

Structure refinement

The positions of the 19 hydrogen atoms in the asymmetric unit were obtained from a Fourier synthesis of the nuclear scattering density computed using the phases calculated from the positions of non-hydrogen atoms obtained in the X-ray study (Wright & Marsh, 1962). The positions and isotropic temperature factors of all atoms were then refined (on F^2) by the method of full-matrix least-squares, using the program *XFLS* (Busing, Martin & Levy, 1962). Refinements using anistropic temperature factors, however, were carried out in three alternate blocks. The function minimized was $\sum w(F_o^2 - |F_c|^2)^2$ with initial weights $w = [\sigma_s^2(F_o^2) + (0{\cdot}1F_o^2)^2]^{-1}$, where $\sigma_s(F_o^2)$ are the standard errors based on counting statistics. In the final stages of the refinement the following weighting scheme based on an error analysis was used:

$$w = (0{\cdot}55 + 0{\cdot}027F_o^2)^{-2}.$$

The intensity data showed moderate extinction effects and a correction for secondary extinction in the form $y = (1 + 2x)^{-1/2}$ (Zachariasen, 1967) was introduced at the start of the refinement and an isotropic extinction parameter G ($= x/Q\bar{T}$) was refined (see, for example, Sequeira, Rajagopal & Chidambaram, 1972;

Table 1. *Final positional and thermal parameters*

All the values are multiplied by 10^4 and their standard deviations (in units of the last digit) are given in parentheses. The form of the anisotropic temperature factor is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cl	2073 (6)	5003 (0)	−1134 (7)	138 (10)	41 (3)	213 (13)	−1 (4)	53 (8)	15 (5)
C	2493 (7)	759 (8)	−2491 (8)	90 (11)	23 (3)	119 (13)	−1 (5)	−7 (9)	1 (6)
C^{α}	3059 (8)	347 (5)	−70 (9)	91 (11)	30 (3)	118 (15)	−8 (5)	14 (9)	10 (6)
C^{β}	2767 (8)	− 793 (5)	− 105 (9)	93 (12)	34 (4)	131 (16)	3 (5)	−9 (10)	6 (6)
C^{γ}	3118 (8)	−1298 (5)	2242 (9)	115 (13)	27 (4)	124 (16)	−4 (4)	−7 (11)	13 (5)
C^{δ}	2919 (10)	−2421 (5)	2051 (11)	198 (16)	26 (4)	196 (21)	17 (6)	108 (14)	11 (6)
C^{ε}	3031 (8)	−2920 (5)	4393 (9)	123 (13)	34 (4)	103 (15)	−8 (55)	−5 (11)	23 (6)
N	1983 (5)	862 (4)	1538 (5)	94 (8)	42 (3)	73 (8)	11 (4)	18 (6)	− 2 (4)
N^{ζ}	2783 (6)	−4017 (4)	4157 (7)	107 (8)	36 (3)	169 (12)	−3 (4)	4 (7)	19 (5)
O^1	1046 (11)	1220 (5)	−2885 (12)	125 (16)	49 (5)	173 (20)	17 (6)	16 (13)	46 (7)
O^2	3585 (10)	602 (6)	−3905 (10)	130 (14)	51 (5)	103 (17)	10 (6)	40 (12)	1 (7)
O^{w1}	1297 (22)	3189 (8)	5358 (20)	597 (45)	41 (6)	416 (36)	−60 (13)	129 (33)	29 (12)
O^{w2}	2948 (19)	2914 (7)	1553 (18)	462 (35)	33 (6)	325 (36)	−6 (10)	122 (27)	17 (10)
H^1	2060 (19)	1600 (11)	1306 (20)	180 (28)	65 (9)	245 (36)	18 (13)	76 (25)	29 (16)
H^2	627 (15)	647 (9)	1281 (18)	106 (22)	60 (8)	241 (32)	10 (10)	60 (19)	− 7 (14)
H^3	2509 (15)	731 (9)	3297 (17)	170 (25)	54 (7)	131 (27)	−7 (12)	− 11 (19)	− 6 (13)
H^{α}	4468 (15)	515 (10)	491 (16)	112 (22)	78 (9)	139 (26)	2 (10)	34 (18)	40 (12)
$H^{\beta 1}$	1315 (20)	− 962 (12)	− 883 (32)	212 (32)	79 (10)	238 (39)	−50 (15)	− 70 (26)	−26 (16)
$H^{\beta 2}$	3609 (26)	−1072 (10)	−1257 (23)	401 (48)	49 (9)	260 (41)	−11 (15)	159 (36)	10 (15)
$H^{\gamma 1}$	4550 (20)	−1110 (12)	2998 (25)	155 (30)	80 (11)	390 (52)	−23 (14)	− 76 (31)	28 (18)
$H^{\gamma 2}$	2170 (27)	−1009 (11)	3397 (26)	393 (48)	49 (9)	368 (51)	40 (16)	163 (36)	26 (17)
$H^{\delta 1}$	1717 (26)	−2581 (12)	1081 (27)	374 (50)	61 (9)	327 (52)	−24 (17)	− 88 (39)	66 (18)
$H^{\delta 2}$	3934 (30)	−2747 (11)	1050 (32)	532 (65)	47 (10)	594 (74)	66 (18)	479 (63)	1 (20)
$H^{\varepsilon 1}$	4363 (24)	−2782 (12)	5471 (26)	285 (40)	69 (11)	332 (46)	−21 (15)	− 18 (32)	39 (17)
$H^{\varepsilon 2}$	2010 (25)	−2646 (11)	5304 (24)	377 (46)	51 (9)	329 (48)	85 (16)	120 (37)	22 (16)
$H^{\zeta 1}$	1753 (24)	−4187 (11)	2968 (24)	353 (44)	49 (9)	360 (47)	−86 (17)	−104 (33)	27 (18)
$H^{\zeta 2}$	3892 (20)	−4336 (11)	3531 (21)	294 (38)	73 (10)	261 (39)	9 (15)	249 (32)	− 9 (16)
$H^{\zeta 3}$	2644 (19)	−4359 (10)	5690 (20)	244 (30)	52 (8)	253 (36)	17 (12)	111 (25)	34 (14)
H^{w11}	1240 (24)	2505 (12)	6107 (29)	272 (40)	72 (11)	422 (57)	21 (16)	64 (35)	86 (19)
H^{w12}	1511 (31)	3672 (11)	6474 (29)	512 (62)	42 (9)	403 (54)	13 (16)	127 (44)	−38 (17)
H^{w21}	2457 (23)	3093 (11)	2977 (27)	306 (43)	47 (8)	385 (51)	15 (15)	− 47 (35)	−20 (17)
H^{w22}	2633 (28)	3472 (14)	634 (28)	309 (46)	88 (12)	380 (56)	−13 (18)	− 67 (38)	23 (21)

Coppens & Hamilton, 1970) along with other structural parameters. The value of G converged to 0·183 × 10^4 giving a minimum extinction correction factor of 0·64 for the 200 reflexion. The final values of the indices are as follows:

Number of observations	1275 ($F_o^2>\sigma$)	1431
$R(F)=\frac{\sum \lvert F_o-\lvert F_c\rvert\rvert}{\sum F_o}$	0·0702	0·0936
$R(F^2)=\frac{\sum \lvert F_o^2-\lvert F_c\rvert^2\rvert}{\sum F_o^2}$	0·0898	0·0975
$R_w(F^2)=\left[\frac{\sum w\lvert F_o^2-\lvert F_c\rvert^2\rvert^2}{\sum wF_o^4}\right]^{1/2}$	0·1174	0·1259

The values of the scattering amplitudes (in units of 10^{-12} cm) used were: H = −0·372, C = 0·663, N = 0·94, O = 0·575 and Cl = 0·958 (Shull, 1971).

The final positional and thermal parameters are listed in Table 1. A stereoscopic picture of the lysine zwitterion with the thermal ellipsoids on a 30 % probability scale is shown in Fig. 1. The bond distances and angles are given in Table 2 and 3 respectively along with values obtained by Koetzle, Lehmann, Verbist & Hamilton (1972) and the X-ray values. A detailed discussion of the molecular structure, hydrogen bonding and thermal motions has been given by Koetzle, Lehmann, Verbist & Hamilton (1972). Since our parameters are in fairly good agreement with theirs, we will not repeat the discussion here.

Table 2. *Molecular bond distances* (*in* Å)

	Neutron		
	BARC	BNL	X-RAY
$C-O^{1}$	1·240 (10)	1·243 (3)	1·246
$C-O^{2}$	1·260 (9)	1·253 (3)	1·250
$C-C^{\alpha}$	1·531 (7)	1·535 (2)	1·529
$C^{\alpha}-H^{\alpha}$	1·086 (12)	1·090 (3)	0·91
$C^{\alpha}-N$	1·491 (7)	1·487 (2)	1·484
$C^{\alpha}-C^{\beta}$	1·534 (9)	1·525 (3)	1·524
$N-H^{1}$	0·995 (16)	1·034 (4)	0·91
$N-H^{2}$	1·046 (12)	1·028 (4)	0·88
$N-H^{3}$	1·070 (10)	1·059 (4)	1·01
$C^{\beta}-H^{\beta1}$	1·144 (16)	1·093 (5)	1·07
$C^{\beta}-H^{\beta2}$	1·054 (18)	1·097 (5)	1·09
$C^{\beta}-C^{\gamma}$	1·526 (8)	1·530 (3)	1·518
$C^{\gamma}-H^{\gamma1}$	1·132 (15)	1·102 (5)	1·02
$C^{\gamma}-H^{\gamma2}$	1·116 (20)	1·088 (5)	1·11
$C^{\gamma}-C^{\delta}$	1·506 (9)	1·521 (3)	1·526
$C^{\delta}-H^{\delta1}$	1·021 (19)	1·088 (6)	1·07
$C^{\delta}-H^{\delta2}$	1·111 (23)	1·094 (5)	1·18
$C^{\delta}-C^{\varepsilon}$	1·521 (8)	1·514 (3)	1·521
$C^{\varepsilon}-H^{\varepsilon1}$	1·123 (17)	1·082 (5)	1·04
$C^{\varepsilon}-H^{\varepsilon2}$	1·057 (19)	1·090 (5)	1·03
$C^{\varepsilon}-N^{\zeta}$	1·477 (8)	1·485 (2)	1·480
$N^{\zeta}-H^{\zeta1}$	0·995 (16)	1·016 (5)	1·04
$N^{\zeta}-H^{\zeta2}$	1·045 (16)	1·024 (5)	0·82
$N^{\zeta}-H^{\zeta3}$	1·028 (13)	1·026 (4)	0·97
$O^{w1}-H^{w11}$	1·015 (19)	0·960 (9)	1·00
$O^{w1}-H^{w12}$	0·918 (19)	0·953 (11)	0·89
$O^{w2}-H^{w21}$	0·988 (20)	0·957 (11)	1·02
$O^{w2}-H^{w22}$	0·929 (20)	0·936 (9)	1·01

Table 3. *Molecular bond angles* (°)

	Neutron		
	BARC	BNL	X-RAY
$O^{1}-C-O^{2}$	126·0 (6)	126·2 (2)	125·5
$O^{1}-C-C^{\alpha}$	118·4 (6)	117·9 (2)	117·7
$O^{2}-C-C^{\alpha}$	115·6 (5)	115·9 (2)	116·8
$C^{\alpha}-N-H^{1}$	108·7 (9)	109·1 (2)	113
$C^{\alpha}-N-H^{2}$	112·3 (7)	111·3 (2)	103
$C^{\alpha}-N-H^{3}$	112·2 (7)	112·4 (2)	108
$H^{1}-N-H^{2}$	108·9 (11)	109·4 (4)	106
$H^{1}-N-H^{3}$	105·9 (10)	105·9 (4)	103
$H^{2}-N-H^{3}$	108·5 (9)	108·6 (3)	124
$C-C^{\alpha}-C^{\beta}$	108·7 (4)	109·3 (2)	109·8
$C-C^{\alpha}-N$	108·6 (4)	109·2 (1)	109·7
$N-C^{\alpha}-C^{\beta}$	112·1 (5)	111·7 (2)	111·8
$C-C^{\alpha}-H^{\alpha}$	110·1 (7)	109·9 (2)	118
$N-C^{\alpha}-H^{\alpha}$	107·4 (7)	107·9 (2)	104
$C^{\beta}-C^{\alpha}-H^{\alpha}$	109·9 (8)	109·8 (3)	104
$C^{\alpha}-C^{\beta}-C^{\gamma}$	114·7 (5)	114·1 (2)	114·6
$C^{\alpha}-C^{\beta}-H^{\beta1}$	109·0 (9)	109·5 (3)	106
$C^{\alpha}-C^{\beta}-H^{\beta2}$	105·1 (9)	106·6 (3)	109
$C^{\gamma}-C^{\beta}-H^{\beta1}$	108·3 (9)	108·4 (3)	116
$C^{\gamma}-C^{\beta}-H^{\beta2}$	112·4 (9)	109·0 (3)	104
$H^{\beta1}-C^{\beta}-H^{\beta2}$	107·1 (12)	109·1 (5)	108
$C^{\beta}-C^{\gamma}-C^{\delta}$	111·6 (5)	111·4 (2)	111
$C^{\beta}-C^{\gamma}-H^{\gamma1}$	107·2 (9)	110·2 (3)	113
$C^{\beta}-C^{\gamma}-H^{\gamma2}$	110·6 (9)	111·0 (4)	117
$C^{\delta}-C^{\gamma}-H^{\gamma1}$	109·2 (9)	109·6 (4)	108
$C^{\delta}-C^{\gamma}-H^{\gamma2}$	108·9 (10)	108·3 (3)	105
$H^{\gamma1}-C^{\gamma}-H^{\gamma2}$	109·4 (13)	106·2 (5)	101
$C^{\gamma}-C^{\delta}-C^{\varepsilon}$	112·0 (5)	112·2 (2)	111·5
$C^{\gamma}-C^{\delta}-H^{\delta1}$	108·6 (11)	109·6 (3)	116
$C^{\gamma}-C^{\delta}-H^{\delta2}$	111·1 (10)	109·5 (3)	110
$C^{\varepsilon}-C^{\delta}-H^{\delta1}$	110·5 (11)	108·3 (3)	105
$C^{\varepsilon}-C^{\delta}-H^{\delta2}$	110·6 (10)	109·3 (4)	105
$H^{\delta1}-C^{\delta}-H^{\delta2}$	103·8 (15)	107·9 (6)	108
$C^{\delta}-C^{\varepsilon}-N^{\zeta}$	110·9 (4)	110·6 (2)	110·9
$C^{\delta}-C^{\varepsilon}-H^{\varepsilon1}$	112·0 (10)	111·5 (3)	114
$C^{\delta}-C^{\varepsilon}-H^{\varepsilon2}$	110·7 (9)	110·2 (3)	112
$N^{\zeta}-C^{\varepsilon}-H^{\varepsilon1}$	107·8 (9)	108·1 (3)	106
$N^{\zeta}-C^{\varepsilon}-H^{\varepsilon2}$	107·4 (10)	106·5 (3)	115
$H^{\varepsilon1}-C^{\varepsilon}-H^{\varepsilon2}$	107·8 (13)	109·8 (5)	98
$C^{\varepsilon}-N^{\zeta}-H^{\zeta1}$	111·5 (9)	110·4 (4)	112
$C^{\varepsilon}-N^{\zeta}-H^{\zeta2}$	109·9 (9)	109·5 (3)	107
$C^{\varepsilon}-N^{\zeta}-H^{\zeta3}$	112·5 (8)	111·6 (3)	108
$H^{\zeta1}-N^{\zeta}-H^{\zeta2}$	103·9 (12)	111·9 (5)	120
$H^{\zeta1}-N^{\zeta}-H^{\zeta3}$	110·7 (12)	106·6 (4)	111
$H^{\zeta2}-N^{\zeta}-H^{\zeta3}$	108·0 (11)	107·1 (4)	97
$H^{w11}-O^{w1}-H^{w12}$	109·4 (18)	107·1 (7)	103
$H^{w21}-O^{w2}-H^{w22}$	101·9 (18)	102·7 (7)	102

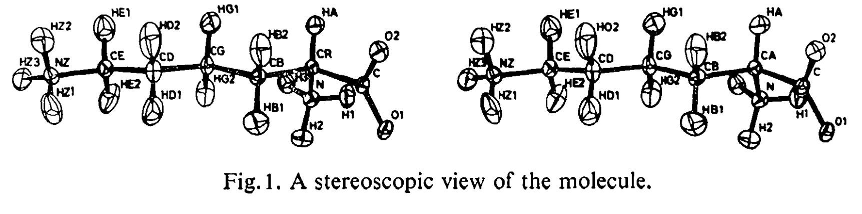
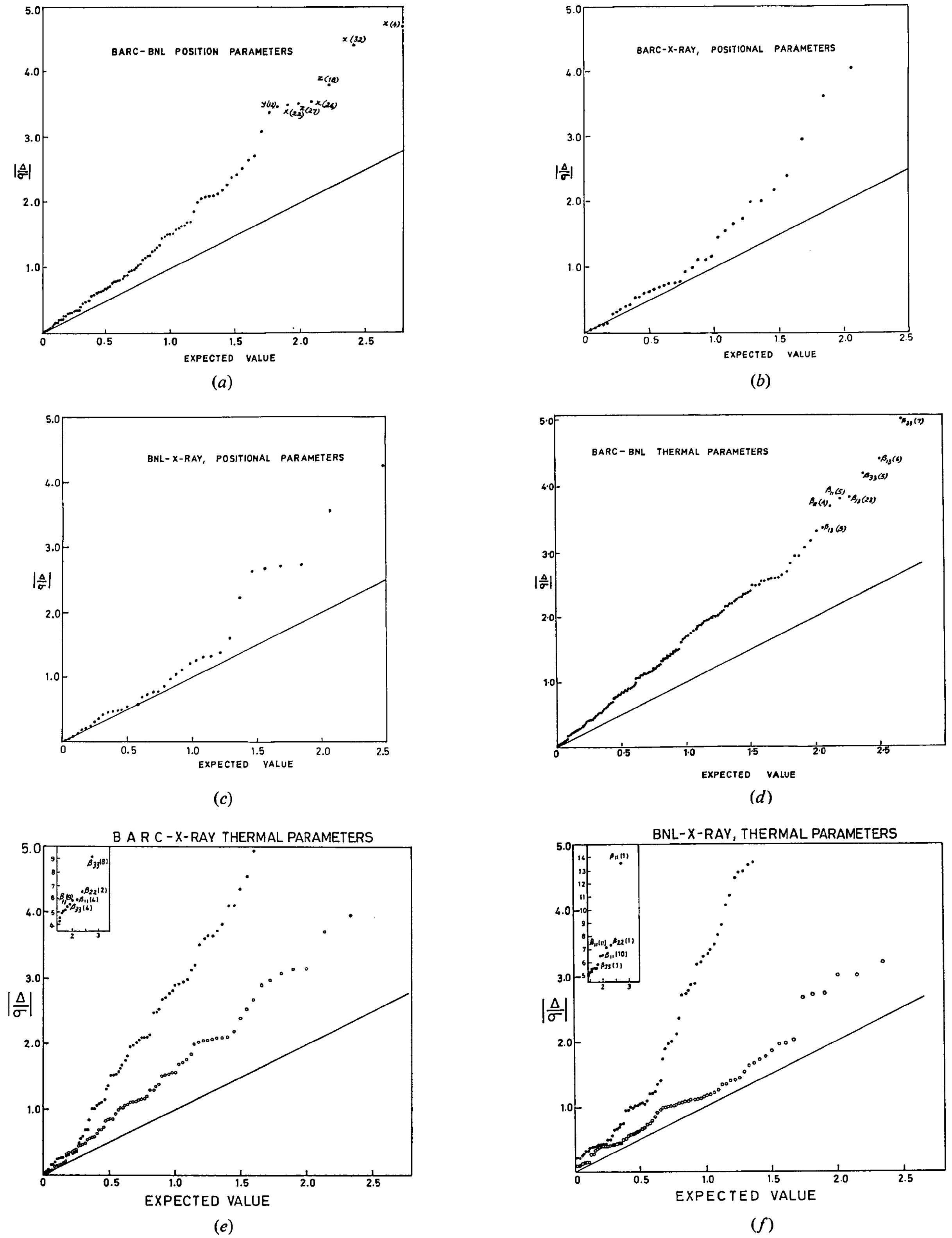


Fig. 1. A stereoscopic view of the molecule.



(*a*) (*b*)

(*c*) (*d*)

(*e*) (*f*)

Fig. 2. Half-normal probability plots for inter-experimental comparison of parameters. The number in parentheses in the labelling of some of the points corresponds to the sequence number of the atoms in the parameter list. In (*e*) and (*f*) the upper plots are based on X-ray thermal parameters as reported by Wright & Marsh (1962); for the lower plots, isotropic temperature factors of 0·93 and 0·70 Å^2 respectively have been deducted from the X-ray thermal parameters as explained in the text.

Inter-experimental comparison

The availability of another set of neutron parameters (Koetzle, Lehmann, Verbist & Hamilton, 1972) and a set of X-ray parameters (Wright & Marsh, 1962) has given us a good opportunity for inter-experimental comparison by the use of the half-normal probability plots (Abrahams & Keve, 1971) and the χ^2 tests (Hamilton, 1969). We will hereafter identify the two parameter sets mentioned above as BNL and X-RAY and the present parameter set as BARC.

We have prepared half-normal probability plots for each of the three pairs of parameter sets (BARC–BNL, BARC–X-RAY and BNL–X-RAY). These plots are shown in Fig. 2(*a*)–(*f*). The positional and thermal parameters have been compared separately. For the former, approximate straight line distributions are obtained in all the cases, indicating that the errors are normally distributed. The slopes of these lines, however, deviate from unity, indicating that the estimated standard deviations are underestimated as usual (Abrahams & Keve, 1971). The observed slopes are given in Table 4. The pooled errors defined by $\sigma=(\sigma_1^2+\sigma_2^2)^{1/2}$ for the BARC–BNL and BARC–X-RAY comparisons of positional parameters appear to be underestimated by about 1·6 and 1·3 respectively. Since the pooled errors are dominated by the BARC σ's (which are on an average three times as large as the BNL σ's and twice as large as the X-RAY σ's), the estimated standard deviations of the BARC parameters may be underestimated by about 1·6 or less.

The BARC–BNL comparison of thermal parameters again shows the pooled σ's to be underestimated by about 1·6. But the BARC–X-RAY comparison of the thermal parameters indicates the pooled σ's to be underestimated by as much as 2·8. If we accept that the BARC σ's are underestimated by 1·6, the estimated standard deviations for the X-ray thermal parameters would, at first sight, appear to be highly underestimated. This is also borne out by the BNL–X-RAY comparison of the thermal parameters. However, comparison of the equivalent isotropic temperature factors (defined as $B_{\rm eq}=8\pi^2(u_1^2+u_2^2+u_3^2)/3$, where u_1, u_2, u_3 are r.m.s. amplitudes of vibration along the principal axes) of the non-hydrogen atoms in the three sets showed a systematically higher value for the X-ray data compared with the BARC and BNL data. This average excess was 0·93 Å relative to BARC and 0·70 Å^2 relative to BNL.* When this isotropic excess was deducted from the X-ray thermal parameters, the half-normal probability plots for both the BARC–X-RAY and the BNL–X-RAY comparison of thermal parameters became reasonable, as shown in Fig. 2(*e*) and (*f*). The values of $R^2\left(=\sum\left|\frac{\Delta}{\sigma}\right|^2\right)$ and the weighted mean Δ/σ listed in Table 4 for various classes of parameters also show that the BARC, BNL and X-RAY results (the latter after changing the thermal parameters as explained above) agree fairly well.

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Table 4. *Summary of statistical comparisons between the BARC, BNL and X-RAY parameter sets for lysine*.HCl.2H$_2$O

Half normal probability plot slopes

	BARC–BNL (all atoms)	BARC–X-RAY (non-hydrogen atoms)	BNL–X-RAY (non-hydrogen atoms)
Position	1·6	1·3	1·2
Thermal	1·6	2·8 (1·6)	3·2 (1·3)

Values of $R^2\left(=\sum^N\left|\frac{\Delta}{\sigma}\right|^2\right)$; $\chi^2_{32,0.01}=53$; $\chi^2_{13,0.01}=28$

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
BARC–BNL ($N=32$)	118	69	73	98	77	147	58	110	51
BARC–X-RAY ($N=13$)	45	39	16	163 (30)	152 (44)	248 (44)	30	54 (48)	17
BNL–X-RAY ($N=13$)	49	5	31	446 (30)	218 (25)	223 (48)	20	11 (6)	12

Values of weighted mean $\frac{\Delta}{\sigma}$

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
BARC–BNL	1·0	4·0	−2·6	− 3·0	− 2·5	− 8·6	0·8	−1·5	0·8
BARC–X-RAY	1·3	4·1	−1·7	−12 (−1·0)	−11 (1·0)	−14 (−1·3)	−0·1	−2·5 (−0·5)	1·9
BNL–X-RAY	−1·2	1·2	−0·1	−21 (−4·2)	−14 (2·3)	−14 (3·6)	0·2	−2·3 (1·0)	1·2

The numbers in parentheses correspond to values of X-RAY thermal parameters corrected as described in the text.

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* This was pointed out to us by R. E. Marsh who ascribes it to the use of a smaller, more imperfect crystal in X-ray work or partly due to increased heating of the crystal by X-rays. The former is perhaps unlikely owing to the reasonably good agreement between the BARC and BNL thermal parameters obtained from extinction-corrected neutron data from two different crystals.

References

Abrahams, S. C. & Keve, E. T. (1971). *Acta Cryst.* A**27**, 157.

Busing, W. R., Martin, K. O. & Levy, H. A. (1962). *ORFLS*. Report ORNL-TM-305. Oak Ridge National Laboratory, Oak Ridge, Tennessee. The CDC 3600 version incorporates modifications by W. C. Hamilton, J. A. Ibers, C. K. Johnson & S. Srikanta.

Coppens. P. & Hamilton, W. C. (1970). *Acta Cryst.* A**26**, 71.

Hamilton, W. C. (1969). *Acta Cryst.* A**25**, 194.

Koetzle, T. F., Lehmann, M. S., Verbist, J. J. & Hamilton, W. C. (1972). *Acta Cryst.* B**28**, 3207.

Momin, S. N., Sequeira, A. & Chidambaram, R. (1969). Abstract of Seminar on Crystallography, Centre of Advanced Study in Physics, Madras.

Raman, S. (1959). *Z. Kristallogr.* **111**, 301.

Sequeira, A., Rajagopal, H. & Chidambaram, R. (1972). *Acta Cryst.* B**28**, 2860.

Shull, C. G. (1971). Private communication.

Srikanta, S. (1968). *DATARED*: A Fortran program for data reduction (unpublished).

Srikanta, S. & Sequeira, A. (1968). *REFINE*: A Fortran program for refining crystal orientation and cell parameters (unpublished).

Srinivasan, R. (1956). *Acta Cryst.* **9**, 1039.

Wehe, D. J., Busing, W. R. & Levy, H. A. (1962). *ORABS*: A Fortran program for calculating single crystal absorption corrections. The CDC 3600 version incorporates modifications by S. Srikanta & A. Sequeira.

Wright, D. A. & Marsh, R. E. (1962). *Acta Cryst.* **15**, 54.

Zachariasen, W. H. (1967). *Acta Cryst.* **23**, 558.

Acta Cryst. (1972). B**28**, 3219

The Crystal and Molecular Structure of Bufotenine, 5-Hydroxy-(*N*,*N*)-dimethyltryptamine

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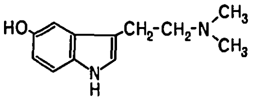
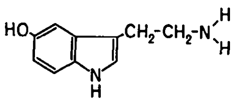
Bufotenine, or 5-hydroxy-(*N*,*N*)-dimethyltryptamine, crystallizes as a base in the monoclinic space group $P2_1/a$ with $a=17{\cdot}95$, $b=11{\cdot}52$, $c=14{\cdot}24$ Å; $\beta=131{\cdot}29°$; $Z=8$. Data were collected on a PAILRED automatic linear diffractometer. The structure was determined by the symbolic addition procedure and refined by the method of full-matrix least-squares to $R=0{\cdot}054$ for 1748 observed reflexions. The molecular structures of the two molecules in the asymmetric unit are almost identical. The indole nucleus of the *A*-molecule is planar; in the *B*-molecule there is a small angle of 1·5° between the pyrrole and benzene portions of the ring system. The ethylamine chain is almost fully extended, and lies approximately in a plane which is nearly perpendicular to the indole nucleus. This conformation is defined by the torsion angles τ_1, which is 87 and 72° for molecules *A* and *B* respectively, and τ_2 (175 and 170°). There are normal O–H···N hydrogen bonds linking the *A*-molecules (2·68 Å) and the *B*-molecules (2·72 Å) separately in two similarly arranged hydrogen-bonding systems.

Introduction

Bufotenine, or 5-hydroxy-(*N*,*N*)-dimethyltryptamine, is an indolealkylamine with a somewhat controversial pharmacology regarding its effects on the central nervous system. It was first isolated from toad venom, hence its name, and studied for its circulatory effects (Handovsky, 1920). Stromberg (1954) found bufotenine in seeds of *Piptadenia peregrina*, which were used by South American Indians for intoxicating purposes. Since then, it has been isolated from several hallucinogenic drugs of plant origin. Bufotenine was reported to be psychoactive in humans after intravenous injection (Hawkins & Fabing, 1956) but these results were not confirmed by further studies (Turner & Merlis, 1959). Later, bufotenine was claimed to occur in blood and urine of both normal and schizophrenic patients. The occurrence of bufotenine is of great interest, and Brune & Himwich (1962) suggested that it might be the psychotomimetic substance active in schizophrenia. The recent discovery of an enzyme, indolealkylamine-*N*-methyltransferase, in the human brain (Mandell & Morgan, 1971), shows that methylated indole derivatives really can be produced in the central nervous system. The differences in receptor activity between these compounds and serotonin may be due to steric factors, and an X-ray crystallographic study of bufotenine was undertaken accordingly.



Bufotenine



Serotonin

Experimental

Bufotenine base was kindly supplied by Professor Bo Holmstedt, Department of Toxicology, Karolinska