FERRARIS, G., JONES, D. W. & YERKESS, J. (1973). *J. Chem. Soc. Dalton*, pp. 816–121.
GERMAIN, G., MAIN, P. & WOOLFSON, M. M. (1971). *Acta Cryst.* A**27**, 368–376.
HAMILTON, W. C. (1969). *Acta Cryst.* A**25**, 194–206.
International Tables for X-ray Crystallography (1962). Vol. III. Birmingham: Kynoch Press.
JOLY, A. & DUFET, H. (1886). *Bull. Soc. fr. Minér.* **9**, 194–201.
LUNDGREN, I. O. (1974). Acta Univ. Upsala, Dissert. Fac. Sci.
PASCAL, P. (1966). *Nouveau Traité de Chimie Minérale*, Vol. II. Paris: Masson.
PIMENTEL, G. C. & MCCLELLAN, A. L. (1959). *The Hydrogen Bond.* San Francisco: Freeman.
STEWART, J. M., KRUGER, G. J., AMMON, H. L., DICKINSON, C. & HALL, S. R. (1972). The X-RAY System. Univ. of Maryland.
ZIGAN, F. (1974). *Ber. Bunsenges. phys. Chem.* **78**, 403–413.

Acta Cryst. (1976). B**32**, 994

Studies in Molecular Structure, Symmetry and Conformation. XIII. Crystal and Molecular Structure of D-Alloisoleucine Hydrochloride Monohydrate*

BY K. I. VARUGHESE† AND R. SRINIVASAN

Centre of Advanced Study in Physics, University of Madras, Madras-600025, India

(*Received* 1 *May* 1975; *accepted* 7 *August* 1975)

D-Alloisoleucine hydrochloride monohydrate is orthorhombic, space group $P2_12_12_1$, with $a=6{\cdot}13$, $b=24{\cdot}03$, $c=6{\cdot}80$ Å, $Z=4$. The structure was solved by the heavy-atom method and refined to an R of 0·075 with 1054 visual reflexions. The structure is not isomorphous with D-isoleucine hydrochloride monohydrate but has many common structural features.

Introduction

An X-ray crystallographic investigation of D-alloisoleucine.HCl.H_2O was undertaken as part of a series of analyses of stereoisomeric forms of amino acids with more than one asymmetric carbon. The present study forms a parallel with the structure of D-isoleucine.HCl.H_2O (Trommel & Bijvoet, 1954). Results for D-alloisoleucine are reported separately (Varughese & Srinivasan, 1976). Investigation of a number of such crystalline forms leads to information on configurational and conformational variations (Srinivasan, Varughese & Swaminathan, 1973, 1974).

Experimental

D-Alloisoleucine was dissolved in dilute hydrochloric acid and crystals were obtained by slow evaporation of the solution. The crystals were elongated along **a** with well developed {010} faces and exhibited a tendency to cleave perpendicular to **b**. Cell dimensions were measured on $hk0$ and $h0l$ precession photographs. The density was measured by flotation in benzene/bromoform.

Crystal data‡

Orthorhombic, $a=6{\cdot}13$ (1) [6·13], $b=24{\cdot}03$ (2) [25·01], $c=6{\cdot}80$ (1) [6·79] Å. Systematic absences: $h00$, h odd; $0k0$, k odd; $00l$, l odd; space group $P2_12_12_1$, $C_6H_{13}O_2N.HCl.H_2O$, $M=185{\cdot}6$, $D_m=1{\cdot}258$, $D_x=1{\cdot}23$ g cm^{-3}, μ for Cu $K\alpha=33$ cm^{-1}.

Intensities were collected with Ni-filtered Cu $K\alpha$ (1·5418 Å) radiation for layers hkl, $l=1$ to 5 and hkl, $h=1$ to 3 by the equi-inclination Weissenberg technique. The specimen had a cross-section of about 0·15 × 0·15 mm for the c and about 0·15 × 0·25 mm for the a axis data. The intensities were estimated visually and corrected for Lorentz, polarization and spot shape factors (Phillips, 1954). No absorption correction was applied. The two sets were correlated (Rollett & Sparks, 1960) through 521 common reflexions. The discrepancy index was 0·10. 1054 independent reflexions were observed which is about 77% of the reflexions accessible.

Structural determination and refinement

This structure has the same space group and very nearly the same cell dimensions as D-isoleucine.HCl–H_2O, suggesting that the two structures could be isomorphous. A test for isomorphism (Srinivasan & Ramachandran, 1965*a*, *b*) was performed and found to be

---

[*] Contribution No. 413 from the Centre of Advanced Study in Physics, Madras, India.

[†] Present address: Indian Institute of Science, Bangalore 560012, India.

[‡] Values given in brackets are for D-isoleucine.HCl.H_2O (Trommel & Bijvoet, 1954).

poor (Srinivasan, Varughese & Swaminathan, 1974). Hence the structure was solved by the heavy-atom method. The Cl coordinates were obtained from the three Harker sections. A structure factor calculation with Cl alone gave an *R* of 0·48. All nonhydrogen atoms were located from a Fourier map phased on Cl: *R* for the total structure was 0·27.

Three cycles of full-matrix least-squares refinement with the program of Gantzel, Sparks & Trueblood (1961) reduced *R* to 0·15. For further refinement the quantity minimized was $\sum w(|F_o|-|F_c|)^2$ where *w* was $1/F^2_{\min}$ for $|F_o| \le 10$ and $1/|F_o|^2$ for $|F_o| \ge 10$. Two more cycles of refinement with isotropic temperature factors for all atoms reduced *R* to 0·125. The H atoms were located from a difference map. They appeared with heights varying from 0·12 to 0·48 e Å^{-3} [Table 3(*a*)]. They were included in the structure factor calculation for further refinement with the isotropic temperature factor of the atom to which each is bonded.

Anomalous dispersion corrections for Cl were $\Delta f''=0·702$ and $\Delta f'=0·348$ (Cromer & Liberman, 1970). Even though the absolute configuration of the molecule was known to be D and the indexing done consistently (Peerdeman & Bijvoet, 1956; Vaidya & Ramaseshan, 1963), two sets of refinements (with anisotropic thermal parameters) were carried out for both L and D configurations. Three cycles for the D configuration gave an *R* of 0·075 while for L configuration *R* was 0·082. This difference is significant at the 0·005 level according to Hamilton's (1965) statistical test.

The shifts in the parameters in the last cycle of refinement were less than one fifth the estimated standard deviations. The final positional and thermal parameters are listed in Tables 1 and 2. Table 3 gives the positional and thermal parameters of the H atoms. Scattering factors for Cl$^-$, O, N, C and H were those listed in *International Tables for X-ray Crystallography* (1962).*

Table 1. *Positional parameters of non-hydrogen atoms and their standard deviations*

	x	*y*	*z*
Cl	0·2330 (3)	0·1661 (1)	0·0739 (2)
O*W*	0·6225 (8)	0·2386 (2)	0·2343 (7)
O(1)	0·6251 (9)	0·1274 (2)	0·8504 (7)
O(2)	0·5730 (10)	0·2000 (2)	0·6531 (10)
N	0·9547 (9)	0·1885 (2)	0·4708 (8)
C(1)	0·6781 (10)	0·1604 (2)	0·7051 (9)
C(2)	0·8911 (11)	0·1441 (2)	0·6123 (9)
C(3)	0·8842 (11)	0·0855 (2)	0·5248 (10)
C(4)	1·1182 (12)	0·0650 (3)	0·4838 (12)
C(5)	1·1239 (18)	0·0032 (3)	0·4365 (16)
C(6)	0·7410 (16)	0·0831 (3)	0·3426 (13)

The description of the structure, bond lengths and angles

The bond lengths and angles are given in Table 4(*a*) and (*b*) with the weighted averages found in amino acid structures with un-ionized carboxyl groups (Sundaralingam & Putkey, 1970). Only C(3)–C(2)–N [114·6 (6)°] shows a large deviation from the expected value. C(2)–C(1), 1·502 (9) Å, is close to 1·50 Å expected for a C(sp^2)–C(sp^3) bond; the average value in amino acids is 1·524 (7) and the present value is within the 3σ level.

Conformation of the molecule

The conformation of the backbone can be described by the deviation of the N atom from the plane containing C(2) and the carbonyl atoms. The equation of the plane is $0·4941x+0·58514y+0·6431z=7·4004$ with respect to the crystallographic axes where *x*, *y* and *z* are in Å. The deviations of the atoms are O(1), 0·003; O(2), −0·008; O(2), 0·003; O(2), 0·002; and N, 0·200 Å. The backbone conformation can also be described by the torsion angles ψ_1 and ψ_2 (Lakshminarayanan, Sasisekharan & Ramachandran, 1967) which are 188·6 and 7·0° respectively with $\psi_1-\psi_2=181·6°$. The χ_{11} and χ_{12} angles (Lakshminarayanan *et al.*, 1967) are 71·4 and 306·4° respectively. The χ_{21} angle is 168·4° showing that C$^\delta$ is *trans* to C$^\alpha$.

Crystal packing and hydrogen bonding

The packing of the structure viewed along **c** is shown in Fig. 1. The structure is stabilized by a network of

Table 2. *The final thermal parameters and their standard deviations*

The values are multiplied by 10^4. The temperature factor is of the form $T=\exp[-(B_{11}h^2+\cdots+B_{12}hk+\cdots)]$.

	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Cl	280 (4)	28 (0)	190 (3)	3 (2)	100 (7)	12 (2)
O*W*	344 (14)	22 (1)	197 (10)	−12 (6)	−19 (24)	6 (5)
O(1)	405 (16)	23 (1)	232 (10)	25 (7)	278 (25)	41 (5)
O(2)	463 (22)	27 (1)	407 (18)	90 (8)	484 (35)	93 (8)
N	285 (15)	18 (1)	203 (12)	−8 (6)	150 (24)	−1 (5)
C(1)	307 (18)	17 (1)	202 (13)	1 (7)	130 (27)	11 (6)
C(2)	254 (16)	18 (1)	193 (14)	4 (7)	95 (28)	8 (6)
C(3)	274 (17)	19 (1)	219 (15)	−14 (8)	65 (29)	3 (7)
C(4)	294 (19)	20 (1)	313 (19)	21 (9)	71 (36)	25 (8)
C(5)	629 (39)	23 (1)	425 (29)	66 (13)	241 (66)	−16 (11)
C(6)	381 (25)	31 (2)	336 (21)	−23 (12)	−128 (48)	−51 (10)

---

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31320 (13 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

hydrogen bonds. There are six protons which can take part and all are involved in intermolecular hydrogen bonding. Table 5 gives the relevant lengths and angles. The protonated NH_3^+ has four neighbours O*w*(ii), O(2)(ii), Cl(iv) and O*w*(i) at distances of 2·854, 2·899, 3·238 and 2·860 Å respectively. The possibility of O*w*(ii) and O(2) (ii) forming a bifurcated hydrogen bond was investigated. However, the angles C(2)–N···O(2) (ii) (156·2) and H(6)–N···O(2) (ii) (47°) suggest that N···O(2) (ii) is only an ionic contact. O*w* donates two protons for hydrogen bonding with Cl(i) and Cl(iii) and the hydrogen-bond distances are 3·150 and 3·178 Å respectively. The water molecule accepts two protons in the direction of the lone pairs. The four neighbours of O*w* are approximately tetrahedrally disposed. O(1) of the carboxyl group donates its proton to form a strong hydrogen bond with Cl(v), O(i)···Cl(v) 2·992 Å. The molecules are arranged in hydrogen-bonded double

Table 3. *Positional and thermal parameters of hydrogen atoms and their peak heights as obtained from the difference map*

	Bonded to atom	*x*	*y*	*z*	*B*(Å)^2	Peak height
H(1)	C(2)	1·014	0·144	0·728	4·42	0·48
H(2)	C(3)	0·817	0·061	0·628	4·12	0·29
H(3)	C(4)	1·203	0·078	0·347	4·53	0·23
H(4)	C(4)	1·225	0·075	0·599	4·53	0·28
H(5)	O(1)	0·470	0·136	0·911	5·47	0·24
H(6)	N	1·014	0·225	0·550	4·07	0·12
H(7)	N	1·067	0·178	0·367	4·07	0·41
H(8)	N	0·850	0·197	0·356	4·07	0·37
H(9)	C(5)	1·072	−0·008	0·292	7·00	0·33
H(10)	C(5)	1·278	−0·008	0·419	7·00	0·21
H(11)	C(5)	1·033	−0·002	0·536	7·00	0·23
H(12)	C(6)	0·800	0·111	0·228	6·56	0·21
H(13)	C(6)	0·733	0·042	0·300	6·56	0·22
H(14)	C(6)	0·589	0·094	0·367	6·56	0·29
H(15)	O*W*	0·667	0·258	0·122	4·72	0·38
H(16)	O*W*	0·497	0·222	0·183	4·72	0·23

Table 4. *Bond lengths and angles*

(*a*) Intramolecular bond lengths (Å) with their standard deviations

		Average *
C(1)–O(1)	1·307 (8)	1·306 (11)
C(1)–O(2)	1·203 (9)	1·203 (9)
C(1)–C(2)	1·502 (9)	1·524 (7)
C(2)–N	1·490 (8)	1·482 (4)
C(2)–C(3)	1·530 (9)	1·523 (13)
C(3)–C(4)	1·541 (10)	
C(3)–C(6)	1·520 (12)	
C(4)–C(5)	1·520 (11)	

(*b*) Intramolecular bond angles with their standard deviations

		Average *
O(1)–C(1)–O(2)	124·7 (7)	126·1 (9)
O(1)–C(1)–C(2)	112·0 (6)	111·1 (10)
O(2)–C(1)–C(2)	123.3 (7)	122·8 (15)
C(1)–C(2)–C(3)	112·3 (6)	110·2 (21)
C(1)–C(2)–N	108·2 (6)	108·4 (12)
C(3)–C(2)–N	114·6 (6)	110·4 (6)
C(2)–C(3)–C(4)	109·8 (6)	
C(2)–C(3)–C(6)	111·5 (6)	
C(4)–C(3)–C(6)	112·2 (7)	
C(3)–C(4)–C(5)	111·8 (7)	

* Sundaralingam & Putkey (1970).

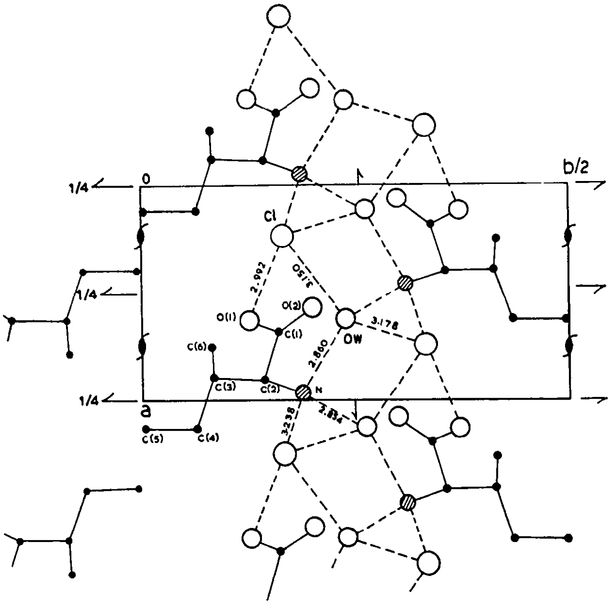

Fig. 1. Packing diagram of the structure viewed along **c**.

Table 5. *Hydrogen-bond lengths and angles*

Donor	Acceptor	*D*···*A* (Å)	H···*A* (Å)	*D*–H···*A* (Å)	C–*D*···*A* (°)	H–*D*···*A* (°)
C(2)–N——H(6)	O*W*(ii)	2·854	1·83	154	94·6	16
C(2)–N——H(6)	O(2) (ii)*	2·899	2·30	113	156·2	47
C(2)–N——H(7)	Cl (iv)	3·238	2·25	162	123·9	13
C(2)–N——H(8)	O*W*	2·860	1·90	153	118·6	18
C(1)–O(1)—H(5)	Cl (v)	2·992	1·97	162	113·3	12
O*W*–H(16)	Cl	3·150	2·23	168		9
O*W*–H(15)	Cl (iii)	3·178	2·29	158		16

Symmetry code

(i)	$\frac{3}{2}-x$	$-y$	$\frac{1}{2}+z$
(ii)	$\frac{1}{2}+x$	$\frac{1}{2}-y$	$1-z$
(iii)	$\frac{1}{2}+x$	$\frac{1}{2}-y$	$-z$
(iv)	$1+x$	y	z
(v)	x	y	$1+z$

* Ionic contact

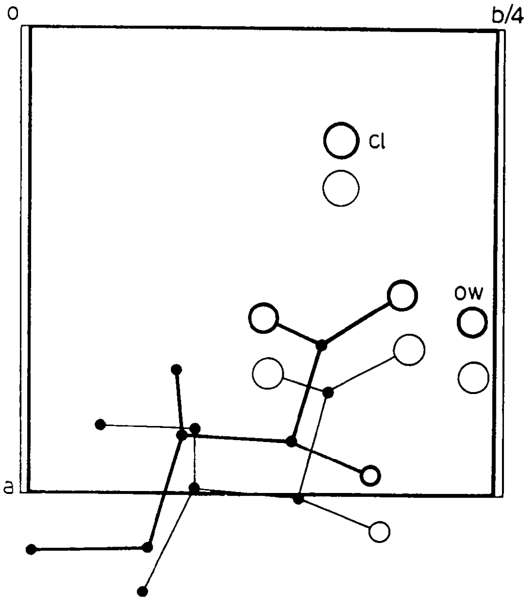

Fig. 2. Projections of the structures of D-alloisoleucine-HCL.H_2O (thick line) and D-isoleucine.HCL.H_2O(thin line).

layers so that the terminal groups of the side chain face each other. Between the double layers only van der Waals forces act which explains the cleavage perpendicular to **b**.

The packing of the structure is very nearly the same as in D-isoleucine.HCl.H_2O. Fig. 2 shows the projection of both structures down **c**. The origin is translated by $x/2$ for D-isoleucine.HCl.H_2O for easy comparison. The change in configuration at C^{β} can be readily seen from this diagram. It also indicates an overall shift between the two structures by about 0·7 Å along x which is responsible for the lack of isomorphism between the two structures.

It is thus seen that the crystal forms of different isomers of the same compound need not be isomorphous even though they may have almost identical cell dimensions and the same space group. A more detailed comparison of different isomeric forms of isoleucine and threonine is made elsewhere (Srinivasan *et al.*, 1974).

References

CROMER, D. T. & LIBERMAN, D. (1970). Los Alamos Scientific Laboratory, Univ. of California Report, LA-4403 UC-34.

GANTZEL, P. K., SPARKS, R. A. & TRUEBLOOD, K. N. (1961). Univ. of California Program, *UCLALS*1.

HAMILTON, W. C. (1965). *Acta Cryst.* **18**, 502–510.

International Tables for X-ray Crystallography (1962). Vol. III. Birmingham: Kynoch Press.

LAKSHMINARAYANAN, A. V., SASISEKHARAN, V. & RAMACHANDRAN, G. N. (1967). In *Conformation of Biopolymers*, edited by G. N. RAMACHANDRAN, Vol. 1, p. 61. London: Academic Press.

PEERDEMAN, A. F. & BIJVOET, J. M. (1956). *Acta Cryst.* **9**, 1012–1015.

PHILLIPS, D. C. (1954). *Acta Cryst.* **7**, 746–751.

ROLLETT, J. S. & SPARKS, R. A. (1960). *Acta Cryst.* **13**, 273–274.

SRINIVASAN, R. & RAMACHANDRAN, G. N. (1965*a*). *Acta Cryst.* **19**, 1003–1007.

SRINIVASAN, R. & RAMACHANDRAN, G. N. (1965*b*). *Acta Cryst.* **19**, 1008–1014.

SRINIVASAN, R., VARUGHESE, K. I. & SWAMINATHAN, P. (1973). Stockholm Symposium on Structure of Biological Molecules, Abstracts, p. 70.

SRINIVASAN, R., VARUGHESE, K. I. & SWAMINATHAN, P. (1974). *Acta Cryst.* **B30**, 2270–2271.

SUNDRALINGAM, M. & PUTKEY, E. F. (1970). *Acta Cryst.* **B26**, 790–800.

TROMMEL, J. & BIJVOET, J. M. (1954). *Acta Cryst.* **7**, 703–709.

VAIDYA, S. N. & RAMASESHAN, S. (1963). In *Crystallography and Crystal Perfection*, edited by G. N. RAMACHANDRAN, p. 243. London: Academic Press.

VARUGHESE, K. I. & SRINIVASAN, R. (1976). *J. Cryst. Mol. Struct.* To be published.