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The Crystal Structure of L-Leucine Hydriodide

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The crystal and molecular structure of L-leucine hydriodide has been determined by three-dimensional X-ray crystallography using Mo $K\alpha$ radiation. The unit cell is orthorhombic with $a=7\cdot693$, $b=23\cdot38$, $c=5\cdot682$ Å and contains four molecules. The space group is $P2_12_12_1$. The crystal structure was found to be isomorphous with that of L-leucine hydrobromide which provided immediate comparisons between the hydrobromide and the hydriodide ions in a similar environment.

The structure determination of L-leucine hydriodide was undertaken to determine the influence of iodide on the crystal conformations of amino acids, polypeptides, and proteins. This compound is one of a series of iodine-containing amino acid structures currently under investigation in our laboratory (Hamilton & Steinrauf, 1967; Seely, 1966). During our work on this structure, results appeared for the structure of L-leucine hydrobromide (Subramanian, 1967) which permits very direct comparisons to be made for the hydrogen-bond distances and angles around the halide ions, since the two structures are isomorphous.

Poorly formed, flat crystalline plates of L-leucine hydriodide, elongated in the c direction, were obtained from a solution of the free amino acid in 47% hydriodic acid. A crystal with dimensions $0\cdot005 \times 0\cdot01 \times 0\cdot03$ cm was sealed in a thin-walled glass capillary tube and three-dimensional data around the c axis were collected ($l=0-6$) using Zr-filtered Mo $K\alpha$ radiation to record reflections with spacings greater than 0·8 Å. A total of 1205 non-zero, independent reflections were

measured using a Supper–Pace Autodiffractometer. The unit-cell data were obtained from Weissenberg photographs with calibration lines from aluminum ($a_0=4\cdot0489$ Å at 20°C) superimposed:
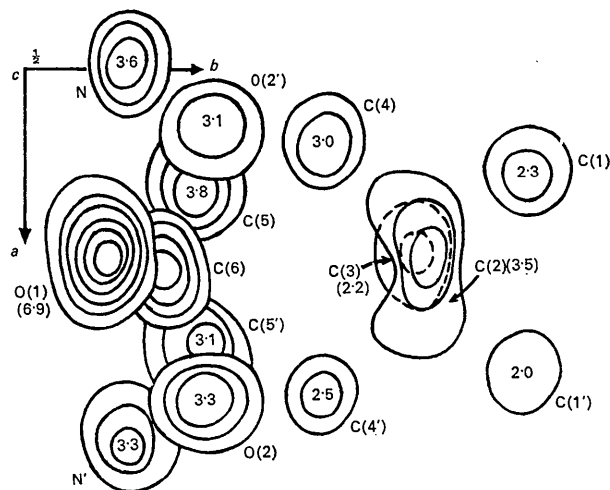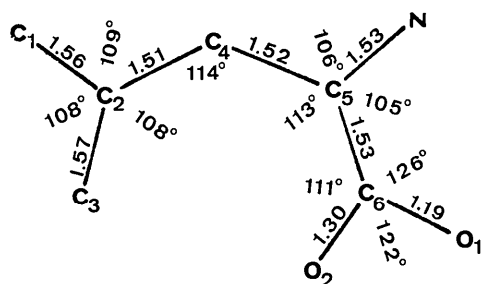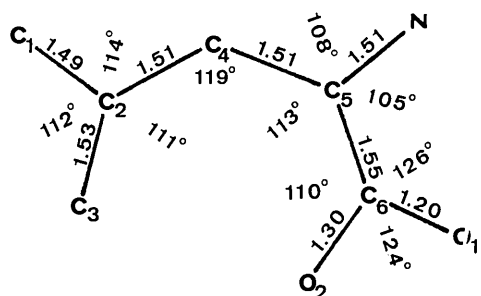

Fig. 1. Heavy-atom Fourier synthesis of L-leucine hydriodide showing pseudo-symmetry and peak heights (e.Å⁻³).

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L-leucine hydriodide

L-leucine hydrobromide

Fig. 2. Comparison of covalent bond lengths and angles for L-leucine hydriodide and L-leucine hydrobromide (Subramanian, 1967). The estimated standard deviations of bond lengths and bond angles for atoms C(1), C(2), C(3), C(4) are 0·03 Å and 2° respectively. The standard deviations for the remaining atoms are 0·02 Å and 1°.

$C_6H_{13}NO_2I$ F.W. 258·08
Leucine . HI

Leucine . HBr
(Subramanian, 1967)

$a=$ 7·693 (0·01) Å $a=$ 7·29 Å
$b=23\cdot38$ (0·02) $b=24\cdot51$
$c=$ 5·682 (0·008) $c=$ 5·54
$\varrho_{calc}=1\cdot685$ (0·007) g.cm^{-3}
$\varrho_{obs}=1\cdot68$ (0·01) g.cm^{-3}
μ(Mo $K\alpha$)=32 g.cm^{-1} .

The space group was determined as $P2_12_12_1$ ($h00$, $0k0$, $00l$ absent for h, k, $l=2n+1$). All reflections were corrected for Lorentz and polarization effects. Absorption corrections were not made.

The positions of the iodine atoms were determined from the three-dimensional Patterson synthesis; unfortunately, they appeared to lie on special positions at $x=\frac{1}{4}$ and $x=\frac{3}{4}$. If the iodine atoms were exactly on special positions, additional symmetry would be found in a Fourier synthesis using the iodine positions for phasing. The unwanted symmetry was broken by examing the position of the iodine atom in several small steps between $x=0\cdot20$ to 0·30. The best position was found by least-squares refinement to be $x=0\cdot256$. This was far enough from its special position to produce differences (0·3 to 0·6 e.Å^{-3}) in the relative peak heights of a light atom and its mirror image. The mirror symmetry and peak-height differences are shown by the

Table 1. *Final positional and thermal parameters*

(a) Atomic positions

Estimated standard deviations times 10^4 are in parentheses.

	x/a	y/b	z/c
I	0·2469 (2)	0·0822 (1)	0·0660 (2)
O(1)	0·7291 (19)	0·0408 (5)	0·2655 (24)
O(2)	0·5587 (25)	0·0941 (8)	0·4802 (39)
N	0·9968 (18)	0·0467 (6)	0·5691 (33)
C(1)	0·8651 (33)	0·2526 (11)	0·6093 (53)
C(2)	0·7829 (32)	0·1926 (8)	0·6569 (46)
C(3)	0·7527 (57)	0·1873 (13)	0·9294 (66)
C(4)	0·9110 (22)	0·1469 (7)	0·5849 (39)
C(5)	0·8432 (21)	0·0865 (7)	0·6176 (37)
C(6)	0·7067 (20)	0·0699 (6)	0·4348 (36)

(b) Thermal parameters

Estimated standard deviations are in parentheses.

Anisotropic $T=\exp[-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+2\beta_{12}hk+2\beta_{13}kl+2\beta_{23}kl)]$.

	$10^4\beta_{11}$	$10^4\beta_{22}$	$10^4\beta_{33}$	$10^4\beta_{12}$	$10^4\beta_{13}$	$10^4\beta_{23}$
I	165 (2)	21 (1)	163 (31)	8 (1)	53 (4)	2 (1)

Isotropic $T=\exp[-B(\sin\theta/\lambda)]$

	B
O(1)	3·2 (0·3)
O(2)	6·2 (0·4)
N	2·4 (0·3)
C(1)	5·1 (0·6)
C(2)	4·1 (0·5)
C(3)	8·3 (0·8)
C(4)	2·4 (0·3)
C(5)	2·4 (0·3)
C(6)	2·1 (0·3)

heavy-atom Fourier synthesis in Fig. 1. A choice could now be made between two positions for each light atom. In every case the correct choice was the peak with the greater electron density.

Block-diagonal least-squares refinement was stopped at an R index of 0·098 with the iodine atom anisotropic and all other atoms isotropic. Final refinement was accomplished by Busing, Martin & Levy's (1962) full-

Table 2. *Final observed and calculated structure factors obtained with the atomic parameters in Table 1*

F_o, F_c and $\alpha(°)$ are multiplied by a factor of 10.

matrix least-squares program modified for mixed temperature factors. The quantity minimized was $\sum w(|F_o| - |F_c|)^2$. A unitary weighting scheme was used and refinement was completed when the parameter shifts were within 0·1 of their estimated standard deviations. Another R index $(R = \sum ||F_o - F_h| - F_l|/\sum |F_o - F_h|$, where F_h is the iodide contribution and F_l is the light-atom contribution) was calculated in order to determine the extent of refinement for the light atoms. The value obtained was 0·480. The magnitude of the agreement factor is indicative of the extent to which the refinement is controlled by the iodine atom.

The final positional and thermal parameters are given in Table 1 and the final observed and calculated structure factors in Table 2. The positions of the hydrogen atoms were not determined and therefore not included in the structure factor calculations.

The similarity between the cell parameters and atomic coordinates for L-leucine hydriodide and L-leucine hydrobromide (Fig. 2) (Subramanian, 1967) shows that the two structures are indeed isomorphous. Intermolecular distances for both, along with expected van der Waals values (Bondi, 1964), are listed in Table 3. It appears that for both derivatives the hydrogen atoms are important in controlling the packing of the side chains in the crystal. Only one intermolecular contact distance between side chains [C(1)–C(2) (I)] is less than its expected van der Waals value. The atoms at the end of the side chain [in particular, C(1), C(2) and C(3)] are observed to have a higher degree of thermal motion than the interior atoms. Qualitatively, the molecular packing for both derivatives is similar. Minor differences in packing arise when the iodide is substituted for bromide, since certain atoms must shift in position

Table 3. *Intermolecular contacts* 4 Å *or less*

Roman numerals indicate the relation of atom 2 to atom 1 at position x, y, z.

I	$x + \frac{1}{2}$	$-y + \frac{1}{2}$	$-z + 1$
II	$-x + \frac{3}{2}$	$-y$	$z + \frac{1}{2}$
III	x	y	$z + 1$
IV	$x + 1$	y	$z + 1$
V	$x - 1$	y	z

Estimated standard deviations are in parentheses.

Atom 1	Atom 2	Leucine.HI distance	Leucine.HBr distance (Subramanian, 1967)	Van der Waals contact distance†
C(1)	O(2) (I)	3·92 (0·01) Å	> 4·00 Å	3·57 Å
C(1)	C(2) (I)	3·78 (0·04)	3·82	3·90
C(3)	O(1) (III)	3·93 (0·03)	3·97	3·55
C(3)	C(6) (III)	4·00 (0·04)	> 4·00	3·90
C(5)	O(1) (II)	3·14 (0·02)	3·16	3·55
C(5)	O(1) (III)	3·93 (0·02)	3·75	3·55
C(6)	O(1) (II)	3·24 (0·02)	3·20	3·55
O(1)	O(1) (II)	3·44 (0·02)	3·39	3·20
O(2)	O(1) (II)	3·90 (0·02)	3·94	3·22
N	C(6) (II)	3·77 (0·02)	3·71	3·70
N	X(II)*	3·60 (0·01)	3·38	3·81 (HI), 3·70 (HBr)
X	O(1) (V)	4·00	3·93	3·66 (HI), 3·55 (HBr)

* X represents halogen atom.
† Values taken from Bondi (1964) and Brant & Flory (1965) and augmented by 0·1 Å.

Table 4. *Hydrogen-bonding contacts*

Roman numerals indicate the relation of atom 2 to atom 1 at position x, y, z.

I	x	y	z
II	$x + 1$	y	z
III	$x + 1$	y	$z + 1$
IV	$-x + \frac{3}{2}$	$-y$	$z + \frac{1}{2}$

Estimated standard deviations are in parentheses.

Atom 1	Atom 2	Leucine.HI distance	Leucine.HBr distance (Subramanian, 1967)
N	X(II)*	3·54 (0·02) Å	3·36 Å
N	X(III)	3·52 (0·02)	3·32
N	O(1) (IV)	2·91 (0·02)	2·91
O(2)	X(I)	3·37 (0·02)	3·16

* X represents halogen atom.

to incorporate the larger iodide ion. The y coordinates for the C(1), C(2), C(3) side-chain atoms are quite different in the two derivatives. When the cell parameters for both derivatives are compared, it is observed that the iodide substitution causes the molecules to move apart in the **a** and **c** directions (along which the hydrogen bonds to the halide are directed) and together in the **b** direction.

Because of the difference in polarizability between the side chain and glycine-like group, the number of efficient packing arrangements for the leucine molecule in a crystal is limited. The molecules are observed to pack in sheets extending perpendicular to the b axis. The sheets are layered so that the hydrophobic side chains are held together by van der Waals forces and the polar glycine-like groups by hydrogen-bonding forces. The molecular packing arrangement of L-leucine.HI is observed to be similar to that of L-leucine.HBr (Figs. 6 and 7, Subramanian, 1967).

Like the HBr derivative, the charged amino nitrogen atom of L-leucine.HI undergoes what is probably rather weak hydrogen bonding with the two iodide ions, I(II) and I(III), and one oxygen atom O(1) (IV). A third iodide ion, I(IV), directly faces the amino nitrogen atom and does not participate in hydrogen bonding. Hydrogen bonding also occurs between the O(2) oxygen atom and the I(I) iodide ion. Hydrogen-bond distances for both the HI and HBr derivatives are given in Table 4.

The equation of the mean plane passing through atoms C(5), C(6), O(1) and O(2) is $0.258X+0.800Y-0.541Z+1.37$ Å $=0$. The maximum deviation of the above atoms from the calculated mean plane is 0.014 Å. The amino nitrogen atom, which was not used in the meanplane calculation, deviates by -0.29 Å.

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The Crystal and Molecular Structure of 2,2',4,4',6,6'-Hexamethyldiphenyl Sulphone (Dimesityl Sulphone)

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Crystals of 2,2',4,4',6,6'-hexamethyldiphenyl sulphone are orthorhombic, space group *Pbca*, with eight molecules in a unit cell of dimensions $a=24.45$, $b=15.90$, $c=8.15$ Å. The structure has been determined using photographically recorded X-ray data and refined to an R value of 0.115 for 1349 observed reflexions. Steric interactions between the sulphone and methyl groups lead to abnormal bond lengths, bond angles and non-bonded intramolecular atomic separations.

Introduction

2,2',4,4',6,6'-Hexamethyldiphenyl sulphone,

$$[C_6H_2(CH_3)_3]_2, SO_2,$$
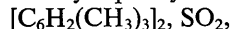
usually called dimesityl sulphone, is a very unstable compound chemically. The 2,4,6- and 2,4,5-trimethyldiphenyl sulphones convert easily to the 3,4,5 isomer when fused with aluminum chloride (Holt & Pagdin, 1961) but dimesityl sulphone disintegrates totally when

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treated with aluminum chloride (Holt, 1970). The instability of dimesityl sulphone is no doubt closely linked with strain in the molecule caused by steric interactions between the sulphone and methyl groups, and the crystal structure has been determined to investigate the nature of these strains.

Experimental

Crystals of dimesityl sulphone were grown from ethyl alcohol as long, orthorhombic needles for which the needle axis has been chosen as the c axis.