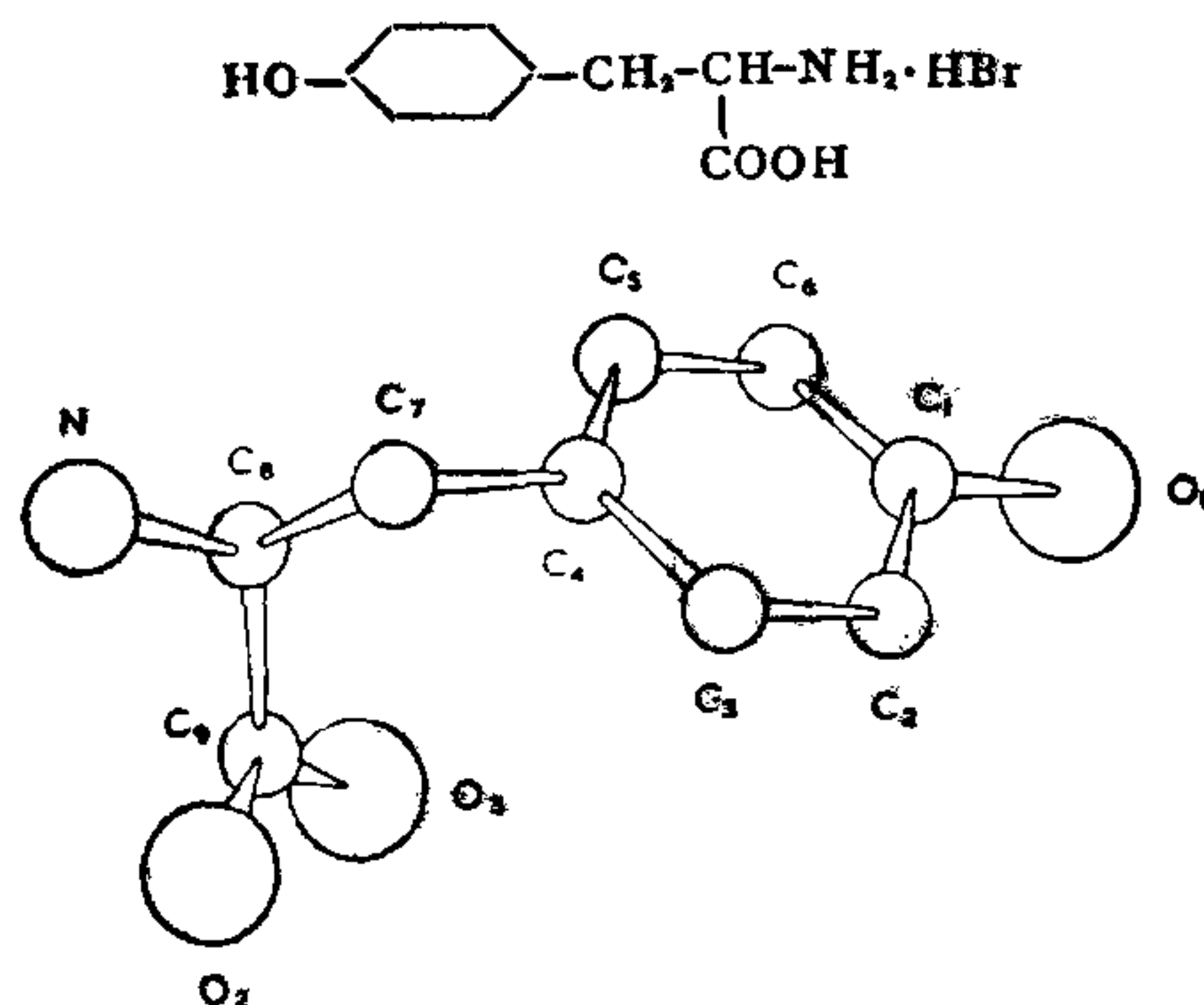# THE CRYSTAL STRUCTURE OF L-TYROSINE HYDROBROMIDE

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CRYSTALS of L-tyrosine hydrobromide,

$$HO-\langle\rangle-CH_2-CH-NH_2\cdot HBr$$
$$\overset{|}{COOH}$$

FIG. 1. View of the molecule of tyrosine projected down the c-axis.

(Fig. 1), obtained by treating the free compound with concentrated hydrobromic acid were found to be isomorphous with the hydrochloride. The preliminary data on these compounds have already been reported (Srinivasan, 1956). Rotation and Weissenberg photographs showed that the lattice was monoclinic with the dimensions:

	a (Å)	b (Å)	c (Å)	(β°)	$V(A^3)$	Z
L-tyrosine HBr	11·41	9·11	5·17	91·0	537·5	2
L-tyrosine HCl	11·03	9·10	5·00	90·7	501·9	2

With $Z = 2$, the calculated density was 1·62 for the hydrobromide and 1·44 for the hydrochloride while the observed value was respectively 1·64 and 1·42 g./cm.^{3}

In the Weissenberg photographs, only $0 k 0$ reflections with k odd were systematically absent. Since the substances are optically active, $P 2_1$ is the only space group possible for both the compounds.

The intensities were estimated visually using the multiple-film technique. They were placed on an absolute scale by Wilson's method and later by comparing $\Sigma|F_0|$ with $\Sigma|F_c|$. The value of B in the isotropic temperature factor $\exp{-(B \sin^2 \theta/\lambda^2)}$ was found to be 2·50 and 2·35 A^2 respectively for the hydrobromide and hydrochloride. The atomic scattering factor values given by Viervoll and Ögrim (1949) were used in structure factor calculations.

DETERMINATION OF THE STRUCTURE

The Difference Patterson (D-P) technique (Kartha and Ramachandran, 1955), was applied to solve the structure. The superposition method of Buerger (1951) was applied on the D-P projected along the c-axis and a satisfactory structure was arrived at. It was further confirmed by obtaining the minimum function (Buerger, 1951), with the ordinary b-axis Patterson function of the hydrobromide. These trial co-ordinates gave values of $R(h k 0) = 33\%$ and $R(h 0 l) = 31\%$ for the hydrobromide, where R is the reliability index defined by

$$R(hkl) = \frac{\sum_{hkl}||F_0|-|F_c||}{\sum_{hkl}|F_0|}$$

The refinement proceeded by Fourier and least squares techniques. An overall anisotropic temperature factor for a particular reflection $h k l$ was taken in the form

$$\exp{-(b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + 2b_{13}hl)}$$

and was applied to the calculated structure factors. The parameters b_{11}, b_{22}, etc., were also refined by the least squares method along with the co-ordinate parameters.

The final values of the reliability indices were : $R(h k 0) = 11·6\%$, $R(h 0 l) = 12·0\%$. If unobserved reflections (*i.e.*, $F_0 = 0$) are omitted, the values are $R(h k 0) = 10·5\%$, $R(h 0 l) = 10·9\%$. These R values are for F_c's without including the hydrogen contributions. Table I gives the atomic co-ordinates while Table II gives intramolecular and intermolecular bond lengths and bond angles.

TABLE I

Atomic co-ordinates in L-tyrosine hydrobromide

	x/a	y/b	z/c	x (Å)	y (Å)	z (Å)
C_1	0·093	0·025	0·361	1·06	0·23	1·87
C_2	·080	·129	·151	0·91	1·18	0·78
C_3	·972	·130	·020	11·09	1·18	0·10
C_4	·880	·028	·084	10·04	0·26	0·44
C_5	·902	·932	·302	10·29	8·49	1·56
C_6	·005	·928	·432	0·07	8·45	2·23
C_7	·760	·033	·938	8·67	0·30	4·85
C_8	·660	·086	·090	7·53	0·78	0·47
C_9	·675	·247	·170	7·70	2·25	0·88
O_1	·195	·028	·518	2·22	0·26	2·68
O_2	·643	·343	·010	7·34	3·13	0·05
O_3	·738	·274	·372	8·42	2·50	1·92
N	·550	·067	·940	6·28	0·61	4·86
Br	·4123	·2500	·4368	4·70	2·28	2·26

TABLE II

(a) Intramolecular bond lengths and bond angles

C_1C_2	1·45 (Å)	$C_1-C_2-C_3$	117° 18′
C_2C_3	1·40	$C_2-C_3-C_4$	122 6
C_3C_4	1·44	$C_3-C_4-C_5$	115 30
C_4C_5	1·45	$C_4-C_5-C_6$	122 20
C_5C_6	1·37	$C_5-C_6-C_1$	117 30
C_6C_1	1·39	$C_6-C_1-C_2$	122 14
C_4C_7	1·57	$O_1-C_1-C_2$	120 0
C_7C_8	1·47	$O_1-C_1-C_6$	116 33
C_8C_9	1·55	$C_3-C_4-C_7$	120 26
C_9O_1	1·42	$C_5-C_4-C_7$	121 54
C_9O_2	1·26	$C_4-C_7-C_8$	115 57
C_9O_3	1·29	$C_7-C_8-C_9$	110 42
C_8N	1·49	C_7-C_8-N	108 6
		$N-C_8-C_9$	109 3
		$C_8-C_9-O_2$	115 50
		$C_8-C_9-O_3$	116 16
		$O_2-C_9-O_3$	124 9

(b) Intermolecular distances and angles
(See Fig. 3)

Hydrogen bonds			Angles			Short contacts		
$N(M')H$ · · Br'	..	3·46 (Å)	$C_8-N(M')-Br'_{(001)}$	..	136°	$Br-C_9(M_{100})$	..	3·30 (Å)
$N(M')H$ · · $Br'_{(001)}$	..	3·46	$C_8-N(M')-Br'$	..	102	$N(M')-O_2(M_{101})$	..	3·01
$N(M')H$ · · $Br'_{(001)}$	..	3·50	$C_8-N(M')-Br_{(001)}$	..	107	$Br-O_2(M_{100})$	..	3·55
$O_3(M')H$ · · $O_1(M)$	..	2·50	$C_9-O_3(M')-O_1(M)$	..	112			
$O_1(M)H$ · · Br	··	3·23	$C_1-O_1(M)-Br$	..	132			

DISCUSSION OF THE STRUCTURE

The standard deviations of atomic co-ordinates were estimated using the least squares formula and were found to be almost the same for the three directions, x, y, z for any particular atom. The average values are 0·036 Å for
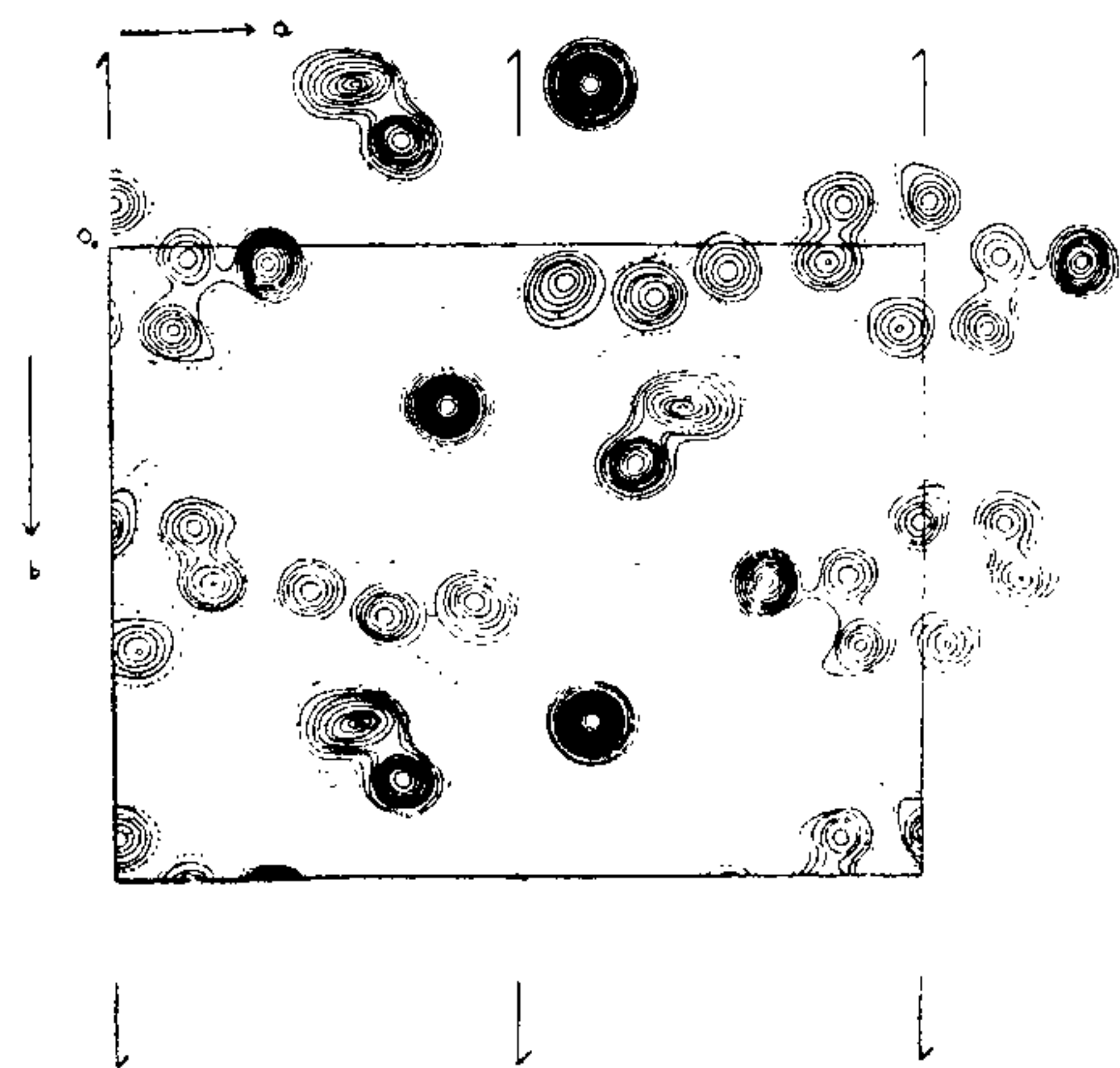

FIG. 2. Final Fourier projection of L-tyrosine hydrobromide along the *c*-axis. Contours at intervals of 0·5 e/Å². For bromine the interval is 2·0 e/Å². Dotted contour corresponds to 2·5 e/Å².

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carbon, 0·030 Å for nitrogen, 0·023 Å for oxygen and 0·007 Å for bromine atoms. The standard deviation in bond lengths using the above values are found to be 0·05 Å for C-C, 0·047 Å for C-N, 0·045 Å for C-O, and 0·034 Å for O-O distance. The error in bond angles is about 3°.

The Fourier projection along the *c*-axis is shown in Fig. 2 and can be compared with the molecule projected along the same axis (Fig. 3).

The bond lengths and angles are quite normal, judged from the values of the standard deviations. The benzene ring is planar, the largest deviation from the plane being 0·028 Å. The group $C_8C_9O_2O_3$ is also planar as found in other amino acids. The distance of nitrogen from this plane is 0·62 Å.

The molecules are arranged in sheets parallel to (0 1 0) (Fig. 3). They are held together by a system of hydrogen bonds of the type
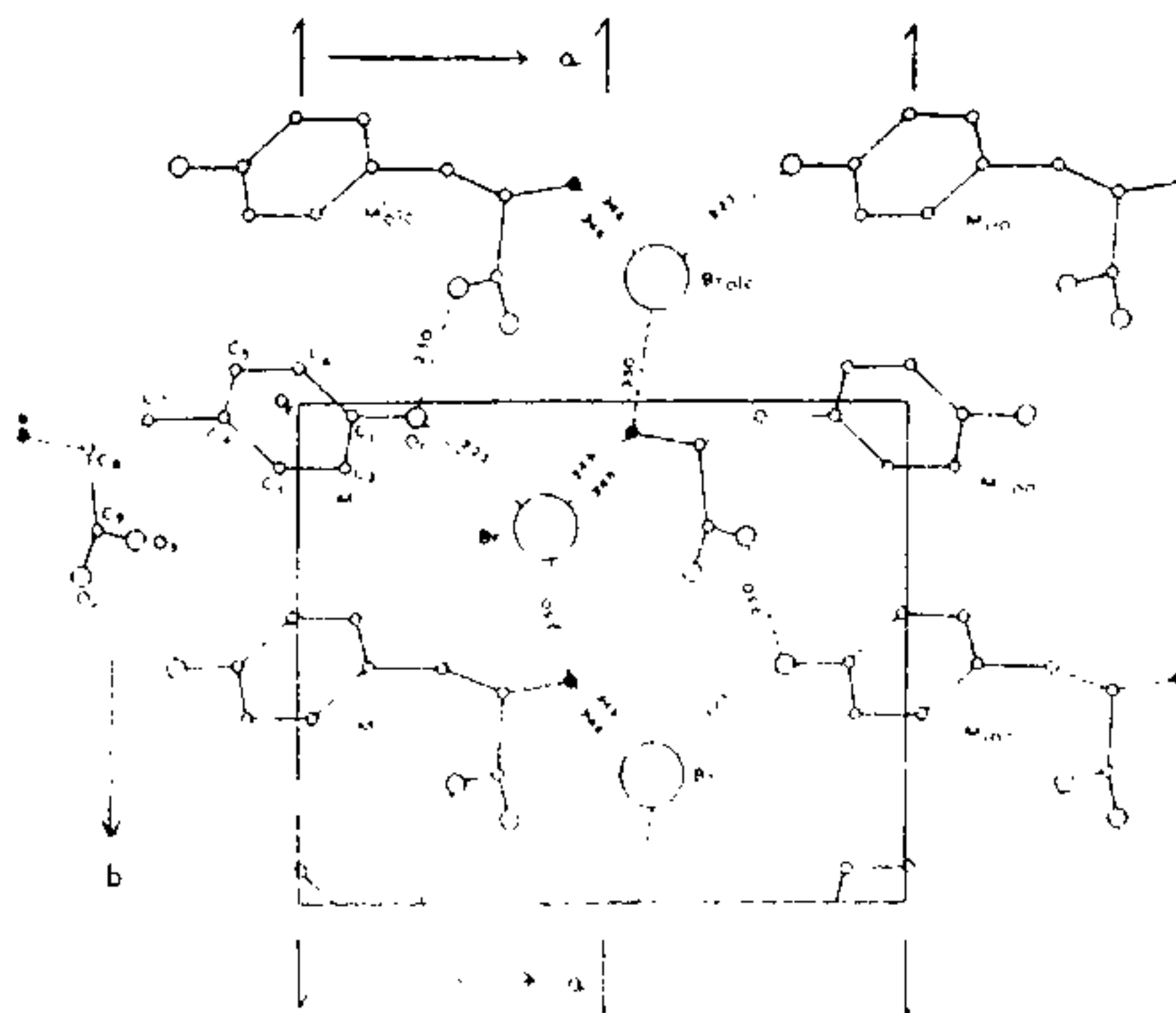

FIG. 3. One unit cell of L-tyrosine hydrobromide projected down the *c*-axis. Hydrogen bonds are shown by dotted lines. The bond lengths are in Å.

NH....Br, OH....Br and OH....O. The three NH....Br bonds from the nitrogen of the NH_3 group are of lengths 3·46, 3·46 and 3·50 Å and are also making approximately tetrahedral angles with C-N (101°, 136° and 107°). The OH....O bond (2·50 Å) is short compared with that found in other amino acids. There is also an OH....Br bond of length 3·23 Å. The

hydrogen bond distances and angles are listed in Table II.

Details of the investigations will be published elsewhere in due course.

The author wishes to acknowledge his grateful thanks to Professor G. N. Ramachandran

for helpful guidance during these investigations.

1. Buerger, M. J., *Acta Cryst.*, 1951, **4**, 531.
2. Kartha. G. and Ramachandran, G. N., *Ibid.*, 1955, **8**, 1955.
3. Srinivasan, R., *Ibid.*, 1956, **9**, 1039.
4. Viervoll, H. and Ögrim, O., *Ibid.*, 1949, **2**, 277.

MARINE BIOLOGICAL STATION, PORTO NOVO (S. INDIA)

A BIOLOGICAL STATION on the banks of Vellar estuary at Porto Novo had been the dream of the Zoology Department of the Annamalai University ever since its inception in 1931. The station however came into being only in 1951 with some improvised equipment, and was located in a tenanted building, situated close to the foreshore at Porto Novo, which was transferred later to the University, as a generous gift by the South Arcot District Board for the development of a marine biological station. Financial aid came first from the Ministry of Education, New Delhi, and later from the Madras State Government for the development of the station.

This enabled the University to adequately equip the station with oceanographic instruments, cruising boats including a sturdy seaworthy 35 ft. research vessel equipped with apparatus for investigations in fundamental as well as applied aspects of marine and estuarine biology.

A newly constructed annex to the building, which was recently declared open by Dr. C. D. Deshmukh, provides moderate accommodation for a hydrobiological laboratory, an aquarium, ichthyological museum, and also for certain lines of biochemical and biophysical work.

With its proximity to the sea, the estuary, the fresh-water head, and the backwaters connecting with the Coleroon, the Porto Novo Biological Station has especially good opportunities for distinctive lines of work relating to the evolution of biochemical adaptations in organisms, and for gaining a comparative picture of the basic factors that control the productivity of different waters.

The work at the biological station has so far been in what may be termed 'hobby spirit', and as a side activity of the Zoology Department, without any special and permanent staff. However, several cruises have been conducted in the sea as well as in the estuary, and valuable data systematically recorded. Planktonic studies, faunistic surveys, observations on tidal cycles and transmission of different wavelengths of radiant energy in the neritic and estuarine waters have been a routine aspect of the work of the Porto Novo Biological Station. The bottom fauna of the estuary and the inshore waters has been dredged and its ecology is under investigation. The consolidation of the results of all these studies is in progress.

Apart from the routine lines of work, the investigation of the biochemical aspects of the reproductive cycles of certain estuarine fish and the quantitative study of the amino acids of the fishes of Porto Novo have been in progress for some time, and the role of some trace elements in estuarine ecology and the ionic regulation in some of the estuarine molluscs and fish are on the current programme of study.

With generous and substantial encouragement from the University Grants Commission, with the keen interest evinced by the authorities of the Annamalai University, and also with a capital of zeal, industry and spirit of intellectual enterprise, the Porto Novo Biological Station hopes to soon augment its facilities, and intensify its research activities.