

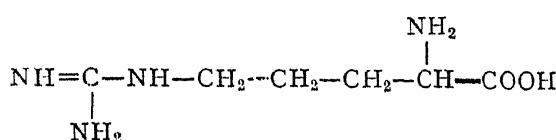
## X-RAY ANALYSIS OF L-ARGININE HYDROHALIDES

S. K. MAZUMDAR AND R. SRINIVASAN

Department of Physics, University of Madras, Madras-25

## 1. INTRODUCTION

THE investigation of the crystal structure of the amino-acid L-arginine



in the form of its hydrohalides was undertaken in this laboratory as part of a major programme of work on compounds related to proteins. Its structure has now been completely established and this is a short preliminary report of the work.

The hydrohalides studied were L-arginine hydrobromide and L-arginine hydrochloride. The latter was found to have two forms differing completely in their crystal data. One of these forms (which we refer to as Form I) was actually found to be isomorphous with the hydrobromide, which existed only in one form. The Form II of the hydrochloride differed from Form I in that the former had no water of crystallization. The crystallographic data of these compounds are given in Table I.

## 2. STRUCTURE DETERMINATION

The work was started first on the hydrobromide since it was hoped that bromine, being heavier than chlorine, could be located easily. Three-dimensional intensity data about the shortest *b*-axis were recorded on equi-inclination Weissenberg photographs with filtered  $\text{CuK}\alpha$  radiation. Data along the *c*-axis were also collected as a subsidiary set of cross-layer data. A similar procedure was adopted for the hydrochloride also. The intensities were estimated visually. The usual corrections for Lorentz and polarisation factors were made and the intensities were placed on the absolute scale by Wilson's method. No correction for absorption was made since the size of the crystal was chosen to be such that the absorption correction was negligible.

The first step in the determination of the structure was to calculate the Patterson function. As might be seen from Table I the asymmetric unit of the cell contains two molecules and hence two bromine atoms. The two bromine positions could be easily located from the Patterson projections on (010) and (001). The position of the two bromine atoms thus

TABLE I  
Crystallographic data for L-arginine hydrohalides

Compound	Space Group	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	$\beta$	Cell contents
L-arginine HBr ..	$P2_1$	11.26	8.65	11.25	91° 30'	4 ( $\text{C}_6\text{H}_{14}\text{O}_2\text{N}_4 \cdot \text{HBr} \cdot \text{H}_2\text{O}$ )
L-arginine HCl (Form I) ..	$P2_1$	11.22	8.50	11.07	91° 00'	4 ( $\text{C}_6\text{H}_{14}\text{O}_2\text{N}_4 \cdot \text{HCl} \cdot \text{H}_2\text{O}$ )
L-arginine HCl (Form II) ..	$P2_1$	5.33	9.46	20.07	90° 30'	4 ( $\text{C}_6\text{H}_{14}\text{O}_2\text{N}_4 \cdot \text{HCl}$ )

Of the three crystals mentioned above the structure analysis of the isomorphous pair was first taken up and completed. The structure was solved essentially by using the beta-synthesis (Ramachandran and Raman, 1959; Raman, 1959 *a, b*; Srinivasan, 1961). It might be mentioned incidentally that this work provided a thorough testing ground for verifying the theoretical prediction of the relative superiority of the beta-synthesis over the usual heavy-atom method (Srinivasan, 1961; Ramachandran and Ayyar, 1963). Details of these and of the complete structure determination will be reported in a separate paper. The present note summarises only the main findings.

obtained were used to calculate a three-dimensional weighted beta-synthesis\* (Ramachandran and Ayyar, 1963) which has coefficients

$$W^2 \beta \equiv W^2 (|F_0|^2 / |F_{Br}|) \exp i\alpha_{Br}$$

where

$$W = \frac{I_1(2X)}{I_0(2X)} \quad \text{with} \quad X = \frac{|F_0|}{L} \frac{|F_{Br}|}{\sum f_j^2}$$

*L* being the number of light atoms in the structure. The resultant three-dimensional map revealed completely the structure which was

\* The calculation of the beta-synthesis was done using the programme written for ELLIOTT-803 by Dr. V. Raghupathy Sarma whom we wish to thank here.

picked out with a ball and spoke model. There were a few spurious peaks in the map but they could be easily eliminated from stereochemical considerations.

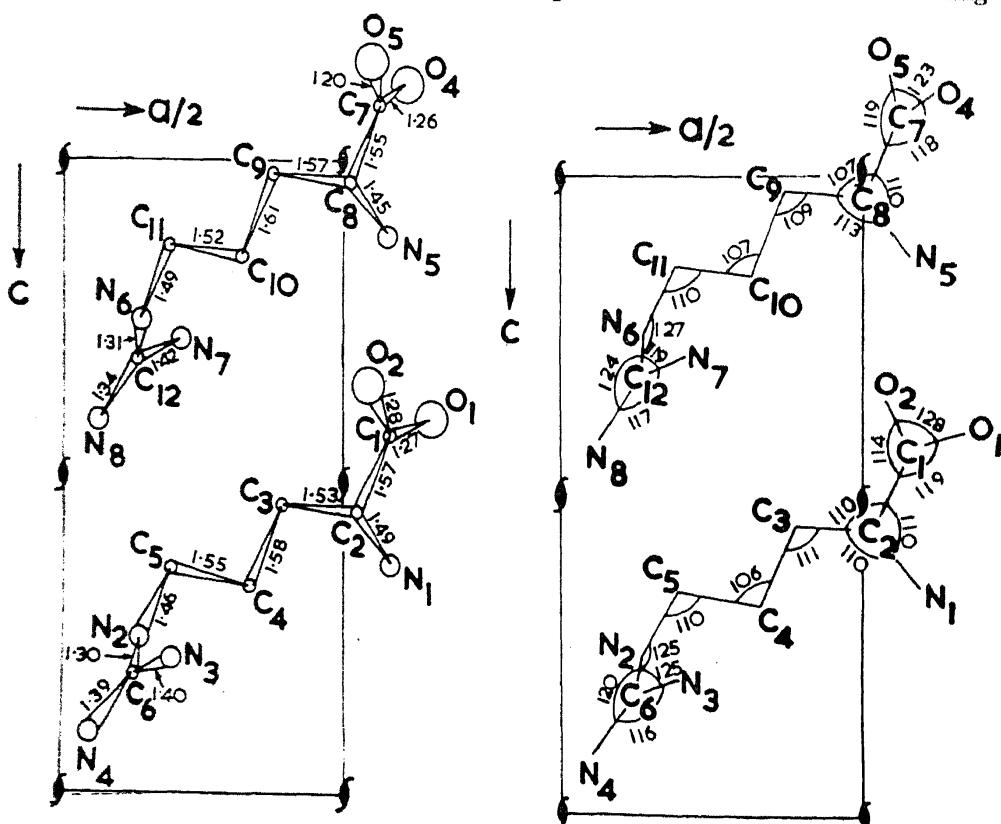
The refinement of the structure proceeded at first by difference-Fourier syntheses on projections and later by three-dimensional least-squares methods. The value of the reliability index  $R$  for three-dimensional data has been brought down to 10.4%. In the case of the hydrochloride, the corresponding value of  $R$  is 13.9%. While both structures may require a few more cycles of refinement for complete convergence, the results, nevertheless, seem to be sufficient to reveal the main features and to confirm the general agreement between the structures. We give here the molecular structure and dimensions as obtained for the hydrobromide, since this corresponds to a lower  $R$ -value. Table II lists the fractional atomic parameters and the individual isotropic temperature factors of the various atoms. The interatomic distances and angles are shown in Fig. 1 which shows the two non-equivalent molecules in their relative positions as seen projected down the  $b$ -axis.

The interatomic distances and bond angles are all satisfactory. Corresponding bond angles and bond distances in the two molecules of the asymmetric unit also agree well with each other.

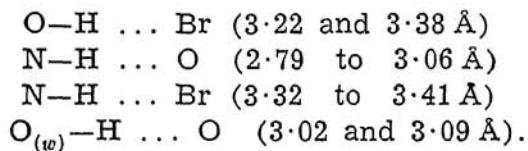
TABLE II  
Fractional atomic co-ordinates and individual temperature factors

Atom	$x/a$	$y/b$	$z/c$	$B (\text{\AA}^2)$
Br <sub>1</sub>	0.1679	0.2474	0.8726	1.91
O <sub>3(w)</sub>	0.1198	0.1341	0.5890	2.83
O <sub>2</sub>	0.5415	0.0654	0.3578	1.88
O <sub>1</sub>	0.6491	0.4493	0.4095	2.09
N <sub>4</sub>	0.0422	0.7509	0.9054	1.95
N <sub>3</sub>	0.1826	0.8771	0.7878	2.80
N <sub>2</sub>	0.1320	0.6117	0.7500	1.64
N <sub>1</sub>	0.5758	0.4511	0.6357	1.36
C <sub>6</sub>	0.1221	0.7405	0.8141	1.59
C <sub>5</sub>	0.1943	0.5955	0.6441	1.55
C <sub>4</sub>	0.3288	0.5681	0.6702	1.63
C <sub>3</sub>	0.3876	0.5510	0.5452	1.89
C <sub>2</sub>	0.5225	0.5719	0.5501	1.35
C <sub>1</sub>	0.5789	0.5610	0.4302	1.45
Br <sub>2</sub>	0.1284	0.8902	0.3623	1.53
O <sub>6(w)</sub>	0.1199	0.9724	0.0827	2.80
O <sub>5</sub>	0.5458	0.7647	0.8506	2.45
O <sub>4</sub>	0.6093	0.5324	0.8850	2.59
N <sub>8</sub>	0.0607	0.3048	0.4089	2.67
N <sub>7</sub>	0.2098	0.2665	0.2875	1.97
N <sub>6</sub>	0.1371	0.5186	0.2580	1.43
N <sub>5</sub>	0.5724	0.5601	0.1226	1.53
C <sub>12</sub>	0.1321	0.3888	0.3170	1.43
C <sub>11</sub>	0.1922	0.5435	0.1406	1.86
C <sub>10</sub>	0.3138	0.6172	0.1576	1.64
C <sub>9</sub>	0.3722	0.6213	0.0285	1.43
C <sub>8</sub>	0.5072	0.6632	0.0424	1.40
C <sub>7</sub>	0.5601	0.6569	0.9163	1.74

The two molecules are arranged parallel to the  $ac$  plane with their chains running diagonally.



the exception being in the orientation of the guanidine groups. In one molecule the guanidine group ( $C_6N_2N_3N_4$ ) points upward along the positive direction of the  $b$ -axis, while in the other molecule this group ( $C_{12}N_6N_7N_8$ ) points downward along the negative direction of the  $b$ -axis. The two molecules when projected onto the  $ac$  plane are found to be separated by a translation of roughly  $c/2$ . The two molecules are linked together by a system of hydrogen bonds and also to the halogen ions and water molecules. The hydrogen bonds are of the types



### 3. ACKNOWLEDGEMENTS

We wish to thank the California Corporation for Biochemical Research, Los Angeles, for sup-

plying us a sample of L-arginine as a gift. The author's wish to thank Professor G. N. Ramachandran for his interest and encouragement during the course of this work. Our thanks are due to the Director of the Royal Institution for permitting us to carry out some calculations on the ELLIOTT-803 computer, and to Dr. V. Raghupathy Sarma for helping us to carry out the calculations with his programme. One of us (S. K. M.) wishes to thank the Council of Scientific and Industrial Research, India, for the financial help during the tenure of which this work was carried out.

1. Ramachandran, G. N. and Ramachandra Ayyar, R., In *Crystallography and Crystal Perfection*, Ed. G. N. Ramachandran, Academic Press, London, 1963, p. 25.
2. — and Raman, S., *Acta Cryst.*, 1959, **12**, 957.
3. Raman, S., *Ibid.*, 1959, **12**, 964.
4. —, *Ibid.*, 1961, **14**, 148.
5. Srinivasan, R., *Ibid.*, 1961, **14**, 607.