CRYSTAL STRUCTURE OF 1-AMINO CYCLOPENTANE CARBOXYLIC ACID HYDROBROMIDE*

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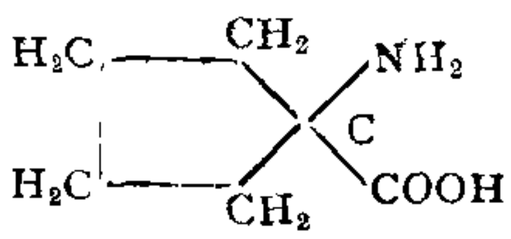
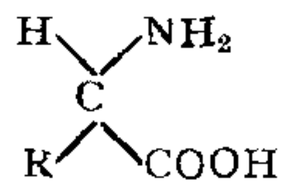
1. INTRODUCTION

STRUCTURAL studies on amino acids and peptides occurring in proteins constitute a major part of the research work in this laboratory. The chemical formula of 1-amino cyclopentane carboxylic acid is



whereas, amino acids of proteins have the chemical formula



R being the side group. The latter have been well studied and the conformational aspects have been widely investigated. In view of the close similarity in the chemical formula between this compound and the amino acids occurring in proteins, the investigation of the crystal structure of 1-amino cyclopentane carboxylic acid hydrobromide has been undertaken by X-ray diffraction methods. The results are described below.

2. EXPERIMENTAL

The crystallographic data are:
Cell dimensions: $a = 10{\cdot}47$; $b = 6{\cdot}09$; $c = 6{\cdot}98$ Å and $\beta = 99{\cdot}7°$;
Space group: $P2_1$
Contents of the unit cell: $2(C_6H_{11}NO_2.HBr)$
Calculated density: 1·61 gm./c.c.
Observed density: 1·615 gm./c.c.
Linear absorption coefficient μ for Cu$K\alpha$ $= 64$ cm.$^{-1}$

Three-dimensional X-ray intensity data were collected using the multiple film equi-inclination Weissenberg technique. 915 reflections were recorded with Cu$K\alpha$ radiation ($\lambda = 1{\cdot}542$ Å) for the layers hKl with $K = 0$ through 5 about the needle axis-b. The intensities were estimated visually by comparison with a graded set of intensities recorded from the same crystal. These were corrected for the Lorentz and polarisation factors and placed on the absolute scale by layerwise Wilson plots. Absorption corrections were not applied.

3. DETERMINATION AND REFINEMENT OF THE STRUCTURE

The LP sharpened Patterson projection down the b-axis yielded the x- and z-co-ordinates of the bromine atom. Using bromine as the known part, a weighted beta synthesis[1] (Fig. 1)

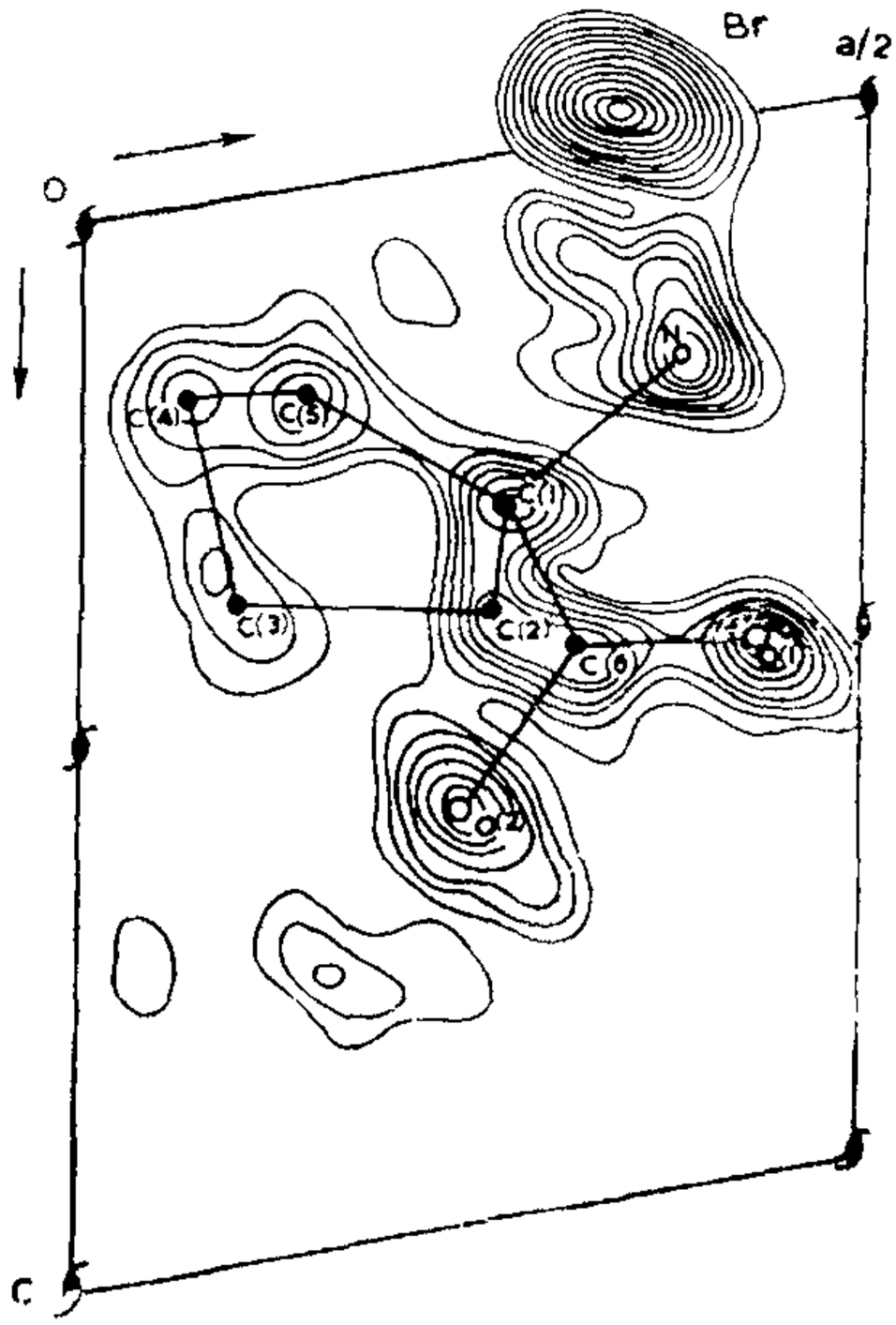


FIG. 1. Projection beta synthesis map down the b axis. Contours from zero level at intervals of 2e/Å^2 except near bromine where the interval is 5e/Å^2

for this projection was computed. The structure could be easily fitted with the map and the R-index for the trial structure was 0·170 for the $h0l$ reflections. Two cycles of difference-Fourier synthesis were carried out and the structure refined to $R = 0{\cdot}163$. These maps

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indicated anisotropic thermal vibrations for the bromine atom.

A three-dimensional model of the structure was constructed from stereochemical considerations with the y-co-ordinate of the bromine atom at the origin. The y-co-ordinates of the rest of the atoms were taken from this model. The structure was then refined using the three-dimensional data by the method of least-squares. Two cycles of refinement were carried out on CDC 3600 with the program of Busing, Martin and Levy.[2] The positional and isotropic thermal parameters of all the atoms and the layerwise scale factors were varied in the refinement and the R-index dropped to 0·173 from the initial value of 0·210. It was then noticed that the atoms C(3) and C(4) were showing large thermal parameters ($B \simeq 9$ Å^2) while the rest were having much less values ($B \simeq 3{\cdot}9$ Å^2). In addition the bond lengths C(2) — C(3) and C(3) — C(4) were not of standard value, the former being much longer (1·61 Å) and the latter being much shorter (1·39 Å).

At this stage a three-dimensional difference-Fourier synthesis was computed leaving these two atoms. The map showed significant anisotropic thermal vibration for the heavy atom bromine. Peaks had developed at the expected atomic sites of C(3) and C(4) with strengths of only 1·8e/Å.[3] These peaks were extended along the y-direction over a spread of about 1 Å. Evidence for stereochemically feasible alternate sites for these atoms were not found in this map. Further refinement was now carried out using a suitable weighting scheme by minimising the function $\Sigma W(|F_o|-|F_c|)^2$ where W is the weighting function adopted following Cruickshank *et al.*[3] Anisotropic thermal parameters were used for the heavy atom and three cycles of refinement using the full-matrix least-squares program of Gantzel, Sparks and Trueblood[4] brought down the R-index to 0·109.

4. Discussion of the Structure

The atomic parameters at the end of the refinement are given in Table I. The atoms C(3) and C(4) continue to have large thermal parameters. The bond lengths and bond angles in the molecule are shown in Fig. 2 and listed in Table II.

But for the short bond length C(4) — C(5) (1·44 Å), the other bond lengths and bond angles in the molecule agree well with the standard values. This anomaly in the bond length, together with the large B values for

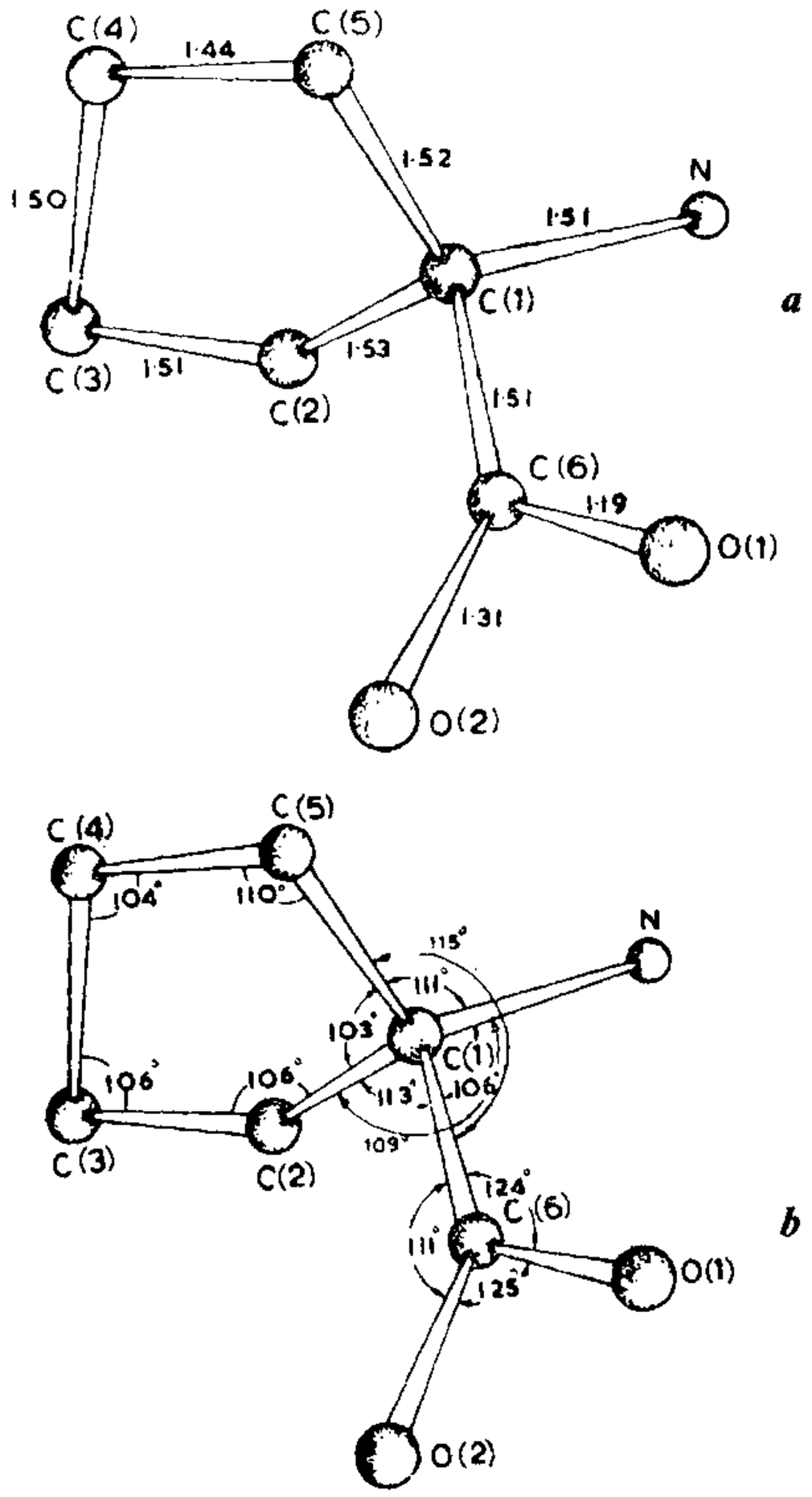

FIG. 2. (*a*) Bond lengths and (*b*) bond angles in the molecule.

TABLE I

The final atomic co-ordinates (fractional) and thermal parameters

Atom	x	y	z	B (Å^2)
Br	0·3444	0·0000	−0·0242	*
O (1)	0·4271	0·7628	0·5102	3·7
O (2)	0·2404	0·7026	0·6114	5·4
N	0·3810	0·4872	0·2166	3·2
C (1)	0·2771	0·5054	0·3410	3·1
C (2)	0·2555	0·2788	0·4254	4·5
C (3)	0·1129	0·2311	0·3713	9·0
C (4)	0·0669	0·3644	0·1917	9·0
C (5)	0·1472	0·5584	0·2179	4·1
C (6)	0·3249	0·6744	0·4954	2·9

B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
0·0150	0·0198	0·0183	−0·0026	0·0143	−0·0112

The temperature factor is of the form

$$\exp\,[-(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + B_{12}hk + B_{13}hl + B_{23}kl)]$$

TABLE II
Bond lengths and bond angles

Bond length (Å)		Bond angle (°)	
C (6)–O (1)	1·19	O (1)–C (6)–O (2)	125
C (6)–O (2)	1·31	O (1)–C (6)–C (1)	124
C (6)–C (1)	1·51	O (2)–C (6)–C (1)	111
C (1)–N'	1·51	N-C (1)–C (2)	109
C (1)–C (2)	1·53	N–C (1)–C (5)	111
C (2)–C (3)	1·51	N–C (1)–C (6)	106
C (3)–C (4)	1·50	C (5)–C (1)–C (6)	115
C (4)–C (5)	1·44	C (2)–C (1)–C (6)	113
C (5)–C (1)	1·52	C (1)–C (2)–C (3)	106
		C (2)–C (3) C (4)	106
		C (3)–C (4)–C (5)	104
		C (4)–C (5)–C (1)	110
		C (5)–C (1)–C (2)	103

the atoms C(3) and C(4) suggests the possibility of disorder existing in this part of the molecule. In connection with this, it may be mentioned that conformational energy calculations[5,6] for the cyclopentane ring have indicated that different conformers having the same minimum energy are possible. Further work taking into account these anomalies are in progress and will be reported elsewhere.

The two C—O distances of the carboxyl group are distinctly different and are in agreement with the values reported in structures where the carboxyl group exists as –COOH in the ionised form.

A view of the structure projected on (010) is shown in Fig. 3. There are four protons available for intermolecular hydrogen bonding and all of them take part in a three-dimensional network of hydrogen bonds. The hydrogen bond lengths and bond angles are given

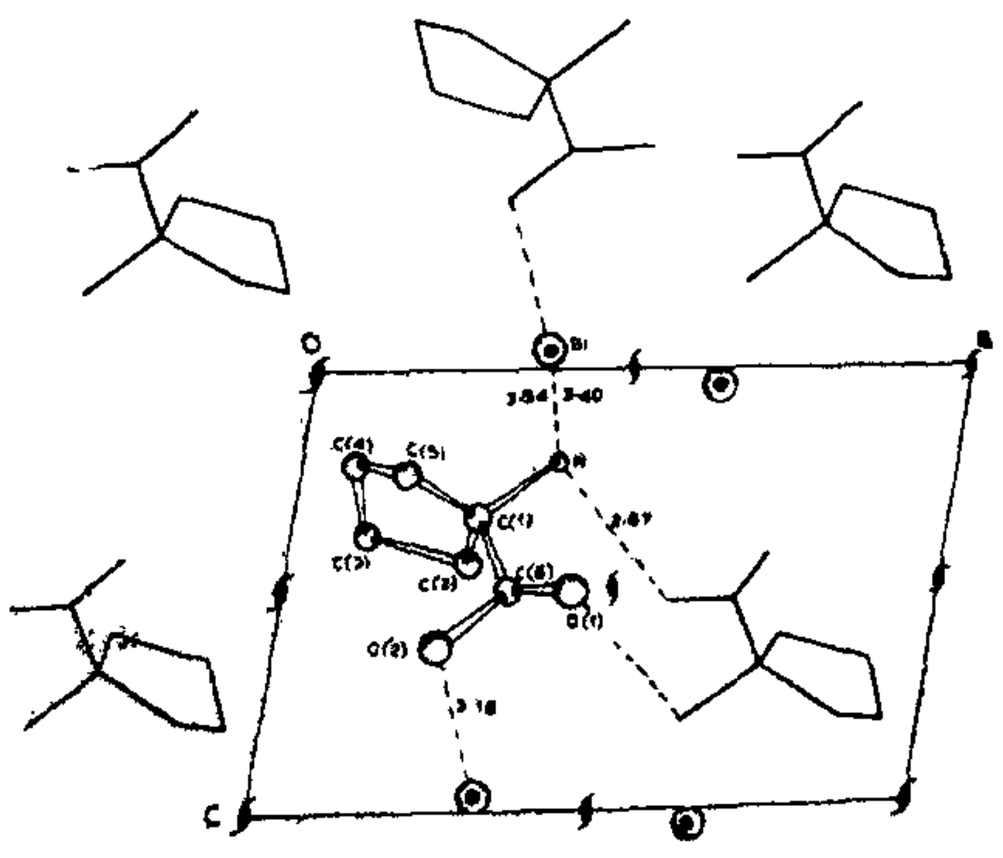

Fig. 3. View of the structure projected on (010).

TABLE III
Hydrogen bond lengths and angles

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

Bond length (Å)		Bond angle (°)	
O (2)–H...Br (II)	3·16	C (6)-O (2)...Br (II)	113
N–H...Br	3·40	C (1)–N...Br	109
N–H...O (1) (IV)	2·87	C (1)–N...O (1) (IV)	98
N–H...Br (I)	3·54	C (1)–N...Br (1)	100

in Table III. In the carboxyl group, O(2) is hydrogen-bonded to Br(II) and the distance O(2)–H ... Br(II) is 3·16 Å. The hydrogen attached to the bromine atom has been transferred to the nitrogen forming a charged group $-NH_3^+$ and Br^-. The nitrogen takes part in three hydrogen bonds of the types N–H ... Br, N–H ... O(1)(IV) and N–H ... Br(I) of lengths 3·4, 2·87 and 3·54 Å respectively. In addition, there is a short ionic contact between the amino nitrogen and Br(III) of length 3·37 Å. Similar examples of four negatively charged atoms approaching a protonated amino group within hydrogen bond distances while only three of them are hydrogen-bonded are available in the literature.

5. ACKNOWLEDGEMENT

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