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Studies in molecular structure, symmetry and conformation II

CRYSTAL AND MOLECULAR STRUCTURE OF 1-AMINOCYCLOHEPTANE CARBOXYLIC ACID HYDROBROMIDE MONOHYDRATE*

K. K. CHACKO AND R. SRINIVASAN

Centre of Advanced Study in Physics, University of Madras, Madras-25, India

AND

R. ZAND

Biophysics Research Division, University of Michigan, Ann Arbor, U.S.A.

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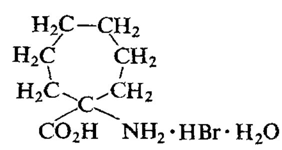
Abstract

1-Aminocycloheptanecarboxylic acid hydrobromide monohydrate crystallizes in space group $P2_12_12_1$ with cell dimensions $a = 25{\cdot}69$, $b = 6{\cdot}85$ and $c = 6{\cdot}61$ Å. The structure was solved in the $hk0$ and $h0l$ projections, and refined with the three-dimensional data to an R factor of 9·86%. The cycloheptane ring is disordered, which leads to 'predominant' and 'alternative' conformations. Both of these conformations correspond to a skew-chair form. The structure is stabilized by a three-dimensional network of hydrogen bonds.

Introduction

A series of crystal and molecular structure determinations of cycloalkane compounds, in particular aminocarboxylic acid derivatives, has been undertaken recently in this laboratory. The interest in these systems is two-fold. Firstly, they are essentially amino acids although not of natural occurence and secondly, they have a cycloalkane ring system, the conformational aspects of which are of interest. In earlier papers from this laboratory, the structures of 1-aminocyclopentane carboxylic acid hydrobromide (Chandrasekharan *et al.*, 1967) and 1-aminocyclooctane carboxylic acid hydrobromide (Srikrishnan *et al.*, 1971) have been presented. In this paper, we present the structure of 1-aminocycloheptanecarboxylic acid hydrobromide monohydrate, (I).



(I)

Experimental

The crystals were needle-shaped, growing along the c axis. Rotation, Weissenberg and precession photographs were taken with Cu $K\alpha$ ($\lambda = 1{\cdot}5418$ Å) radiation. The cell dimensions were calculated from precession photographs, and the crystal data are given below:

Crystal system: orthorhombic

Cell dimensions: $a = 25{\cdot}69 \pm 0{\cdot}03$, $b = 6{\cdot}85 \pm 0{\cdot}01$, $c = 6{\cdot}61 \pm 0{\cdot}01$ Å

* Contribution No. 305 from the Centre of Advanced Study in Physics, University of Madras, Madras-25, India.

Systematic absences: $h00$, $0k0$, $00l$; absent for h, k, l odd, respectively.
Space group: $P2_1 2_1 2_1$
Molecular formula: $C_8H_{15}NO_2.HBr.H_2O$
Z: 4
D_m: 1·47 g cm^{-3}
D_c: 1·46 g cm^{-3}
μ (Cu $K\alpha$): 52 cm^{-1}

A crystal of dimensions 0·05 × 0·015 × 0·02 cm^3 was used to record hkl layers ($l = 0$ to 5), using equi-inclination Weissenberg method for non-zero layers. Another crystal was cut and mounted about the b axis and data for hkl ($k = 0$ to 2) were collected. The dimensions of the crystal used for the b axis data were 0·03 × 0·02 × 0·02 cm^3. The intensities were measured visually, using a calibrated set of intensities recorded from the same specimen, and were corrected for Lorentz and polarization factors and spot shape (Phillips, 1962); absorption corrections were not applied since μr was only about 0·47 for the needle axis data and 0·52 for the b axis data. The data collected about the two axes were correlated with the help of common reflexions collected about both the axes. A total of 1095 reflexions was recorded, 1025 from the c axis photographs and 70 from b axis photographs. Initially, the structure was solved in projection about the c and b axes using the projection data collected about the two axes.

Structure determination and refinement

A two-dimensional Patterson synthesis was computed with the $hk0$ reflexions from which the x and y coordinates of the bromine atom were deduced. The R factor defined by

$$R = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}$$

using only bromine in F_c, was 38 %. A bromine-phased Fourier was computed (Fig. 1) which revealed all the non-hydrogen atoms in the structure. The initial R factor including all the atoms obtained from the bromine phased Fourier was 20 %. Three cycles of block diagonal least-squares refinement with isotropic temperature factors for all atoms reduced the R factor to 13·5 % for this projection.

To arrive at the z coordinates of all atoms, a Patterson synthesis was computed with the $h0l$ intensities. The position of the heavy-atom was readily deduced. The R factor using bromine alone in F_c for the $h0l$ projection was 36 %. A bromine-phased Fourier was computed (Fig. 2) for this projection which revealed all the non-hydrogen atoms, and gave an initial R factor of 24 %, with all the atoms included. Three cycles of block diagonal least-squares refinement were carried out and this reduced the R factor to 17 %. The coordinates obtained for the 13 non-hydrogen atoms from the two projections were suitably transformed in three dimensions (Buerger, 1959) and gave an initial R factor of 17 % for the three-dimensional data. Three cycles of full-matrix least-squares refinement, using the program of Gantzel, Sparks and Trueblood, with isotropic temperature factors for all atoms were carried out on the CDC 3600 computer which reduced the R factor to 13·5 %. All atoms except two in the heptane ring had reasonable temperature factors (about 4·5 Å^2 and below) while for C(3) the temperature factor was 8·1 Å^2 and for C(6) it was 7·0 Å^2. This situation led us to suspect possible disorder for these two atoms in the cycloheptane ring. In order to decide this, a difference Fourier was computed leaving out these two atoms from F_c. The difference Fourier showed peaks at the positions C(3) and C(6) given by the earlier refinement with peak heights nearly equal to 2·2 e/Å^3. Apart from these two peaks, peaks of nearly half the height were observed at distances of about 1·4 Å from the corresponding peaks of C(3) and C(6). A composite diagram of the difference Fourier is shown in Fig. 3. An alternative configuration of the cycloheptane ring could be considered with the new positions of C(3′) and C(6′) and the rest of the atoms in the cycloheptane ring unaltered. In

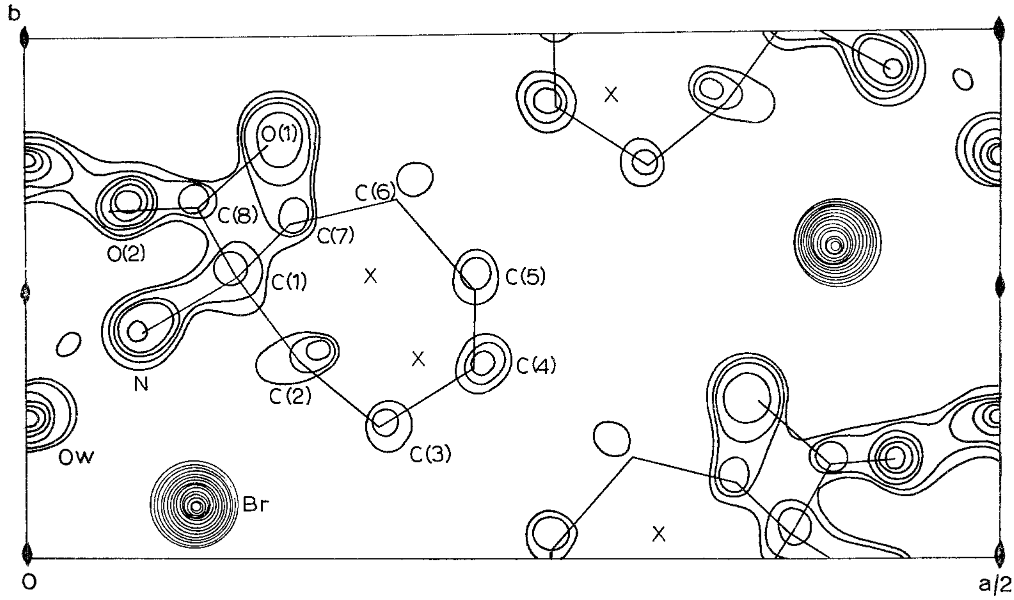


Fig. 1. Bromine phased *hk*0 Fourier projection. Contours are drawn at intervals of 1 e/Å^2 starting from 1 e/Å^2. Contours for bromine are at intervals of 4 e/Å^2 starting from 4 e/Å^2.

fact, this feature could have been suspected in the Fourier projections themselves. For instance, Figs. 1 and 2 show reduced peak heights for C(3) and C(6) compared with those of the other atoms in the cycloheptane ring (the 'alternative' positions C(3′) and C(6′) are marked by crosses in Figs. 1

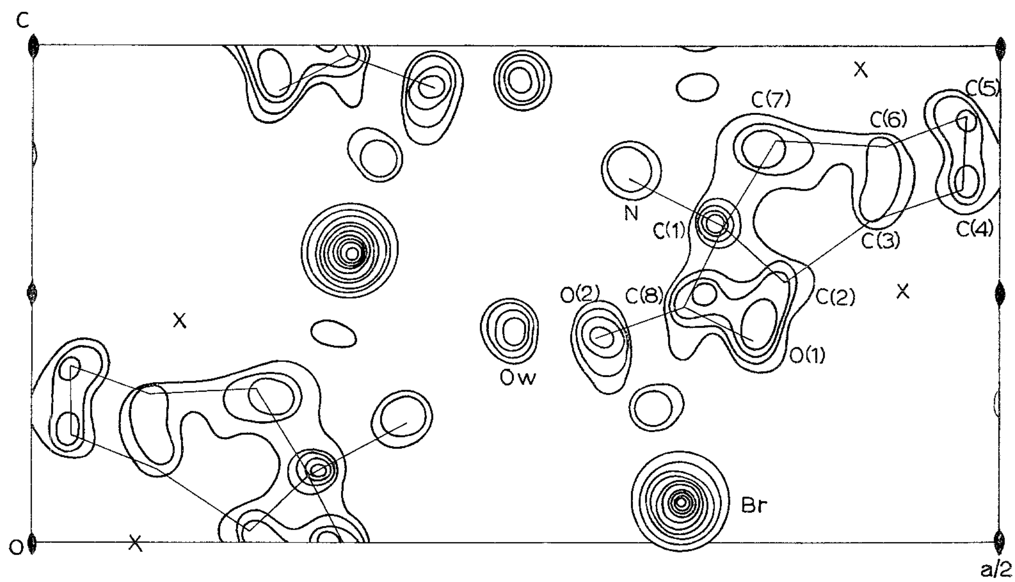


Fig. 2. Bromine phased *h*0*l* Fourier projection. Contours are drawn at intervals of 1 e/Å^2 starting from 1 e/Å^2. Contours for bromine are at intervals of 4 e/Å^2 starting from 4 e/Å^2.

and 2, and have just been missed in contouring because of the low density). Although the peak heights at the 'alternative' positions C(3′) and C(6′) were nearly half the height of the 'predominant' positions C(3) and C(6) of the ring carbon atoms, a structure factor calculation was performed to estimate the occupancy factors of these positions. If $(1-x)F_1$ represents the structure factor for the 'predominant' positions where $(1-x)$ represents its occupancy and if xF_2 represents the structure factor for the 'alternative' positions, the total structure factor F can be written as $F=(1-x)F_1+xF_2+F_3$, where F_3 represents the contribution to the structure factor from the rest of the atoms in the structure. The value of x was varied to find out the minimum R factor. Although a broad minimum was observed for $x = 0{\cdot}30$–$0{\cdot}36$, the value of the occupancy factor x for further cycles of

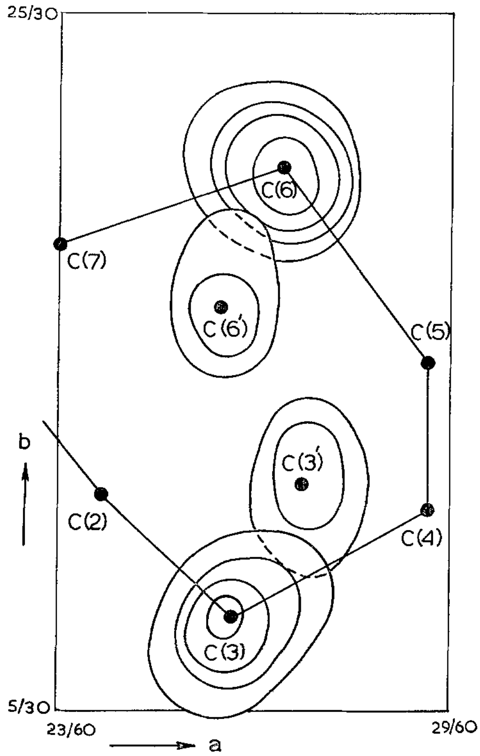


Fig. 3. Composite diagram of the difference Fourier map excluding C(3) and C(6) from F_c. Contours are drawn at intervals of 0·5 e/Å^3 starting with 0·5 e/Å^3.

refinement was taken as the mean $x = 0{\cdot}33$, this gave an R factor of 13·1 %. This procedure for the treatment of disorder was attempted since, with the program available, there is no provision in the full-matrix refinement for the refinement of occupancy factor.

Two further cycles of refinement were carried out with occupancy for the disordered positions as mentioned above and with anisotropic thermal correction for bromine. A weighting scheme of the form $w = (1/a + F_o + cF_o^2)$ was applied (Cruickshank *et al.*, 1961), where the constants a and c were given values equal to 16·0 and 0·02, respectively. The R factor at the end of the refinement was 10·2 %. At this stage the structure factor calculation varying x was repeated with the refined positions of the disordered atoms. This was done to see whether there was any change in the occupancy factors or not. Calculations showed that the R factor was a minimum at x still equal to 0·33. A difference Fourier was computed at this stage for the location of the hydrogen positions in the structure. Peaks at or near the expected hydrogen positions were present for the amino nitrogen, the carboxyl oxygen O(1) and the water molecule Ow. Because of disorder for two of the carbon atoms in the ring system, hydrogen atoms attached to these, as well as the neighbouring carbon atoms, have alternative positions and these hydrogen atoms could not be clearly seen in the difference Fourier. Hydrogen positions were not included for further cycles of refinement.

It has been observed in polar space groups, that the imaginary component of anomalous dispersion often produces significant errors in coordinates in polar directions. (Ueki *et al.*, 1966; McDonald & Cruickshank, 1967). Further cycles of refinement were therefore carried out with the form factor of bromine corrected for the real and imaginary components of anomalous scattering (International Tables for X-ray Crystallography, Vol. III, 1962). Collection of the experimental data for different layers were done systematically from layer to layer such that they were all either *hkl* or $hk\bar{l}$ type of

Table 1. *Atomic coordinates, occupancies and thermal parameters*

Atom	*x*	*y*	*z*	Occupancy	*B* (Å²)
Br	0·3348(1)	0·0944(2)	0·3256(2)	1·00	*
C(1)	0·3560(5)	0·5349(22)	−0·1182(24)	1·00	2·21
C(2)	0·3886(6)	0·3751(25)	−0·2217(27)	1·00	3·22
C(3)	0·4270(11)	0·2583(48)	−0·1036(54)	0·67	4·11
C(4)	0·4789(8)	0·3609(30)	−0·0475(34)	1·00	4·18
C(5)	0·4780(8)	0·5138(34)	0·1057(36)	1·00	4·45
C(6)	0·4390(10)	0·6826(42)	0·0436(48)	0·67	3·63
C(7)	0·3835(6)	0·6403(23)	0·0592(27)	1·00	2·82
C(8)	0·3373(6)	0·6731(22)	−0·2767(24)	1·00	2·62
N	0·3080(5)	0·4341(20)	−0·0241(22)	1·00	2·79
O(1)	0·3722(5)	0·7929(18)	−0·3430(23)	1·00	5·16
O(2)	0·2921(6)	0·6699(23)	−0·3396(28)	1·00	3·72
Ow	0·2491(4)	0·2419(16)	−0·3341(20)	1·00	3·12
C(3′)	0·4459(14)	0·3828(59)	−0·2426(65)	0·33	1·63
C(6′)	0·4246(18)	0·5445(75)	0·2032(86)	0·33	3·00

* Temperature factor:

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

b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
0·00149	0·01170	0·01526	−0·00025	0·00049	0·00418

reflexions. This would mean that the $\Delta f''$ correction for the data could be either positive or negative, depending on whether they are *hkl* or $hk\bar{l}$ reflexions, respectively. Consequently, two sets of two cycles of refinement each with the form factor of bromine corrected for the $\Delta f'$ component and with the $\Delta f''$ correction positive and negative respectively were carried out. The *R* factor at the end of these two cycles of refinement with $\Delta f''$ correction positive was 10·02%, and with $\Delta f''$ correction negative was 9·86%. On applying the Hamilton (1965) significance test it was found out that lowering of *R* factor was in fact significant at the 0·005 level, indicating that the data are $hk\bar{l}$ rather than *hkl*. Thus the absolute configuration of the structure would be the one with the *z* coordinates of atoms reversed in sign for the final coordinates given in Table 1. The shifts in the positional parameters in the last cycle of refinement were of the order of one-fifth to one-tenth of the estimated standard deviation.

Discussion of the structure

Intramolecular features. The bond distances and bond angles calculated from coordinates listed in Table 1 are given in Fig. 4(1) and (b) and are listed in Table 2. In view of the relatively large standard deviations due to disorder in the structure, it is perhaps not worthwhile to undertake a detailed discussion of bond lengths and angles. Only a brief discussion is given. The mean standard deviation of the bond lengths not involving the disordered atoms is 0·02 Å, while that involving disordered atoms is 0·04 Å. The mean values of the C—C bond lengths for the 'predominant' and 'alternative' conformations of the cycloheptane ring are 1·518 and 1·524 Å, respectively, which are in reasonable agreement with the mean value of 1·533 Å found in *n*-alkanes by Bartell & Kohl (1963). Deviations from this value occur mainly for C(4)—C(5), C(5)—C(6) and C(6)—C(7) bonds which have lengths 1·457, 1·584 and 1·459 Å, respectively. Considering the standard deviations of these bonds, the deviations of the bond lengths are within the 3σ level and need not therefore be taken as significant. Similar comments apply to bond angles in the ring. The average C—C—C bond angle in the cycloheptane ring for the 'predominant' and 'alternative' conformations are 116·9 and 118·1°, respectively, with a mean value of 117·5°, and are larger than the mean value of 114·1° obtained by the theoretical

Table 2. *Bond lengths and angles and their standard deviations*

Bond	Length (Å)	Bond	Angle (deg)
C(1)—C(2)	1·539(23)	C(1)—C(2)—C(3)	120·6(1·7)
C(2)—C(3)	1·491(37)	C(2)—C(3)—C(4)	116·8(3·0)
C(3)—C(4)	1·552(38)	C(3)—C(4)—C(5)	118·5(2·4)
C(4)—C(5)	1·457(30)	C(4)—C(5)—C(6)	110·8(2·2)
C(5)—C(6)	1·584(37)	C(5)—C(6)—C(7)	117·1(2·8)
C(6)—C(7)	1·459(34)	C(6)—C(7)—C(1)	119·0(2·0)
C(7)—C(1)	1·548(22)	C(7)—C(1)—C(2)	114·9(1·5)
C(1)—C(8)	1·492(21)	C(7)—C(1)—C(8)	112·5(1·5)
C(1)—N	1·544(20)	C(2)—C(1)—C(8)	108·3(1·7)
C(8)—O(1)	1·292(20)	C(2)—C(1)—N	107·2(1·5)
C(8)—O(2)	1·234(19)	C(7)—C(1)—N	105·5(1·6)
C(2)—C(3′)	1·479(43)	C(8)—C(1)—N	108·0(1·5)
C(3′)—C(4)	1·551(45)	C(1)—C(8)—O(1)	114·7(1·7)
C(5)—C(6′)	1·530(56)	C(1)—C(8)—O(2)	121·9(1·6)
C(6′)—C(7)	1·566(54)	O(1)—C(8)—O(2)	123·4(1·7)
		C(1)—C(2)—C(3′)	123·9(1·7)
		C(2)—C(3′)—C(4)	117·6(3·6)
		C(3′)—C(4)—C(5)	120·0(2·6)
		C(4)—C(5)—C(6′)	113·9(2·2)
		C(5)—C(6′)—C(7)	114·0(4·6)
		C(6′)—C(7)—C(1)	125·0(2·8)

calculations of Bixon & Lifson (1967) and 114·7° by Hendrickson (1967) for pure cycloheptane skew-chair conformation.

The carboxyl group in this structure exists as —CO_2H itself, while the amino nitrogen is in the NH_3^+ form, protonated with the hydrogen of the HBr. The C(1)—N distance of 1·544 Å is fairly large compared with the average value of 1·487 Å for the C—N distance in amino acids and peptides (Marsh & Donohue, 1967). It is to be mentioned that in the case of other analogues of 1-aminocycloalkanecarboxylic acids the C—N distances are found to be larger than the average value of 1·487 Å given by Marsh & Donohue (1967). Thus in the case of 1-aminocyclooctanecarboxylic acid hydrobromide, the C—N distance is 1·542 Å (Srikrishnan *et al.*, 1971) and for 1-aminocyclohexanecarboxylic acid hydrochloride it is 1·527 Å. The carboxyl group of atoms C(8), O(1) and O(2) and the C(1) atom are planar, with a deviation of 0·31 Å from the least-squares plane for the nitrogen atom. The equation of the least-squares plane is given by $0{\cdot}261\,X + 0{\cdot}656\,Y + 0{\cdot}708Z + 0{\cdot}531$, where X, Y and Z are given in Å. The deviation of atoms from the least-squares plane are given in Table 3.

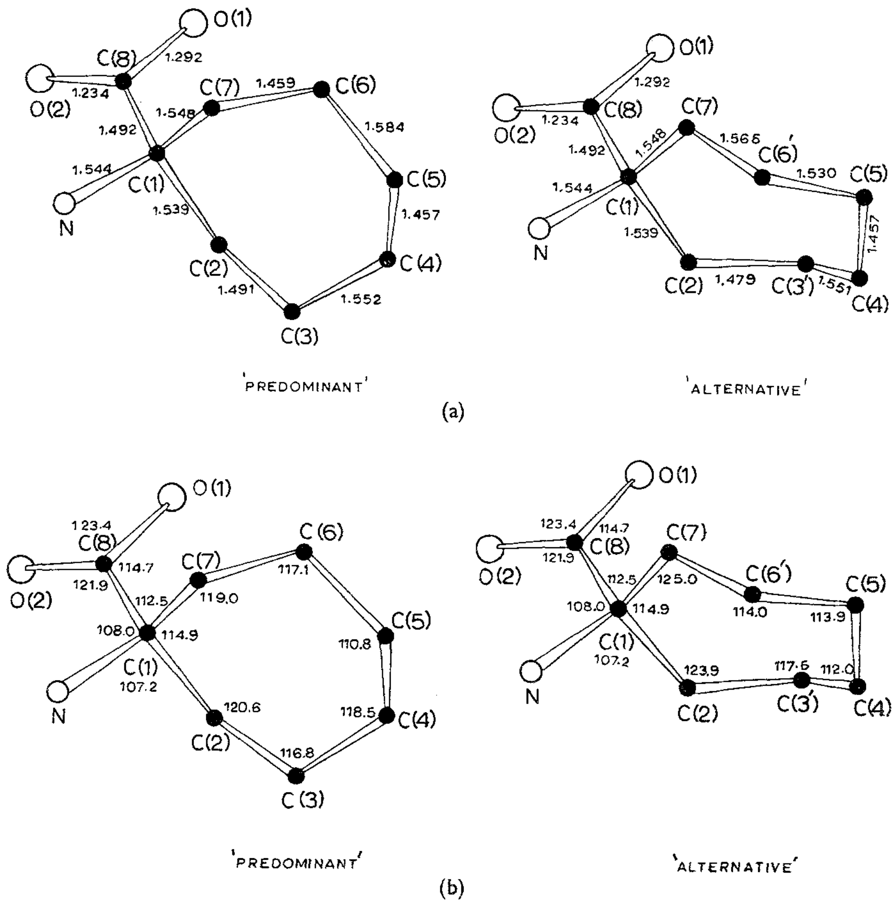


Fig. 4(a). Bond lengths for the 'predominant' and 'alternative' conformations. (b) Bond angles for the 'predominant' and 'alternative' conformations.

Table 3. *Deviations from least-squares planes for the carboxyl group and the heptane ring*

Plane 1 Passing through C(1), C(8), O(1) and O(2)		Plane 2 Passing through C(1), C(2), C(4), (5) and C(7)	
Atom	Deviation (Å)	Atom	Deviation (Å)
C(1)	0·001	C(1)	0·013
C(8)	−0·004	C(2)	0·003
O(1)	0·001	C(4)	−0·019
O(2)	0·001	C(5)	0·024
N	0·31	C(7)	−0·021
		C(3)	−0·71
		C(6)	0·73
		C(3′)	0·63
		C(6′)	−0·72

A method of describing the conformation of the carboxyl group has been given from this laboratory (Ramachandran & Lakshminarayanan, 1966). The notation followed is that of Edsall *et al.* (1966). The angles ψ_1 and ψ_2 describe the disposition of the two C—O bonds of the carboxyl group and measure the clockwise rotation of these two bonds about the C_α—C′ bond with respect to the C_α—N bond. These angles are usually 180° and 0°, respectively; in this structure ψ_1 and ψ_2 are 168° and 347°. Other features common to amino acids are found to exist in this structure also. For instance, the shorter C—O bond [namely, C(8)—O(2)] is *cis* with respect to the amino nitrogen about the C(1)—C(8) bond (Lakshminarayanan *et al.*, 1967). Correspondingly, the angle C(1)—C(8)—O(2) (121·9°) is larger than the other C(1)—C(8)—O(1) angle (114·7°).

Five of the atoms in the cycloheptane ring [namely, C(1), C(2), C(4), C(5) and C(7)] lie very nearly in a plane. The equation of the least-squares plane through these atoms is given by $0{\cdot}342X + 0{\cdot}677Y - 0{\cdot}651Z = 6{\cdot}108$. The deviations of these atoms from the least-squares plane are given in Table 4. The

Table 4. *Comparison of torsion angles observed for the two conformations of the cycloheptane ring with that of dimeric cycloheptanone peroxide and the theoretically predicted values of Bixon and Lifson and Hendrickson for the skew-chair conformation*

Torsion angle	'Predominant' conformation (°)	'Alternative' conformation (°)	Dimeric cycloheptanone peroxide (°)	Bixon & Lifson (1967) (°)	Hendrickson (1967) (°)
C(7)—C(1)—C(2)—C(3)	32·0(2·4)	32·6(2·8)	24·9	−40	39·1
C(1)—C(2)—C(3)—C(4)	−75·7(2·9)	69·2(3·6)	−79·5	90	−88·1
C(2)—C(3)—C(4)—C(5)	71·6(3·1)	−68·1(3·6)	105·4	−70	72·3
C(3)—C(4)—C(5)—C(6)	−57·3(2·8)	63·3(3·5)	−55·6	51	−54·3
C(4)—C(5)—C(6)—C(7)	73·3(2·7)	−70·8(3·8)	69·6	−74	72·3
C(5)—C(6)—C(7)—C(1)	−84·4(2·5)	74·0(3·9)	−90·8	94	−88·1
C(6)—C(7)—C(1)—C(2)	37·9(2·3)	−31·3(3·0)	49·8	−40	39·1
Mean absolute deviation:	6·1	12·4	13·8		
Root mean squared deviation (taking Bixon and Lifson value as standard):	7·6	12·6	15·7		

deviations of the disordered atoms C(3) and C(6) ('predominant' positions) from this plane are −0·71 and +0·73 Å, respectively, while the deviations of atoms C(3′) and C(6′) ('alternative' positions) from the plane are +0·63 and −0·72 Å, respectively. The situation of disorder in the heptane ring system is thus clearly understood from the deviations of the disordered positions from the least-squares plane described above, while for the 'predominant' conformation, the atom C(3) is below the mean plane by 0·71 Å and the atom C(6) is above it by 0·73 Å. This situation reverses in the case of the 'alternative' conformation with C(3) and C(6) replaced by C(3′) and C(6′). Both these conformations correspond to the skew-chair conformation of Bixon & Lifson (1967) and Hendrickson (1967). Table 4 gives the torsion angles about the C—C bonds for the two conformations of the cycloheptane ring; the standard deviations of the torsion angles (given in parentheses) are calculated from the expression given by Huber-Buser & Dunitz (1961). The values predicted theoretically for a pure cycloheptane ring are given for comparison. The mean absolute deviation $\langle|\theta - \theta_0|\rangle$ and the root mean square deviation $\langle|\theta - \theta_0|^2\rangle^{1/2}$ of the 'predominant' conformation of the cycloheptane ring (where θ_0 corresponds to the value from Bixon and Lifson) are 6·1° and 7·6°, respectively, while for the 'alternative' conformation they are 12·4° and 12·6°, respectively. There is only one other cycloheptane structure reported in the literature, which is the structure of dimeric cycloheptanone peroxide (Groth, 1967). The conformation of the cycloheptane ring in this structure is also a skew-chair. The torsion angles for this structure are given in Table 4 for comparison. The mean absolute

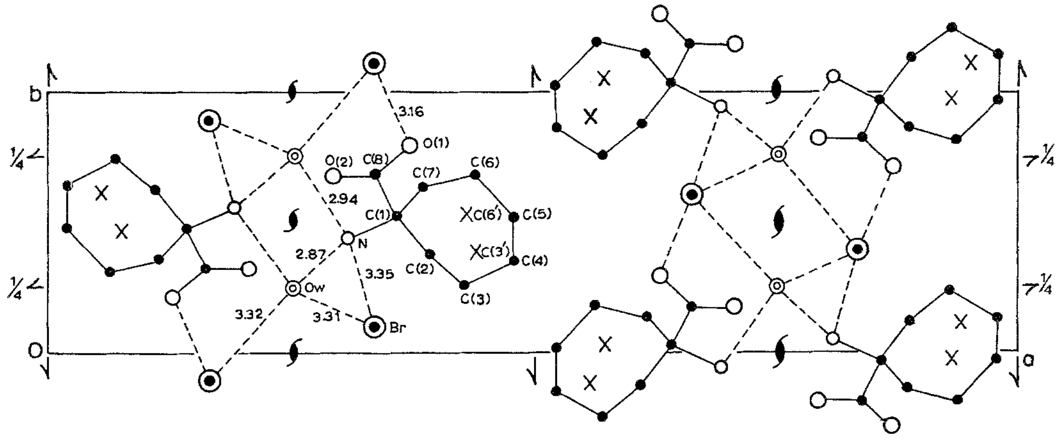


Fig. 5. View of the structure projected down *c* axis drawn with respect to the 'predominant' conformation. The 'alternative' positions C(3′) and C(6′) are indicated by X.

deviation and the root mean squared deviation for this structure are 13·8° and 15·7°, respectively. Judging from the deviations from the theoretical value of the torsion angle for a pure cycloheptane ring for the above three cases, we can state that the 'predominant' conformation is here more close to the skew-chair form than in the other two compounds which appear to show slightly distorted skew-chair conformations.

Intermolecular features. The crystal structure is stabilized by a three-dimensional network of hydrogen bonds. A view of the structure down the *c* axis is given in Fig. 5. There are six hydrogen atoms in the molecule which can take part in hydrogen bonding, and all of them are involved in intermolecular hydrogen bonds. The nitrogen atom has three hydrogens for hydrogen-bonding and all of them form strong bonds with Ow(i), Ow(ix) and Br(i) at distances of 2·87, 2·94 and 3·35 Å, respectively. In addition, it has what appears to be an ionic contact with O(2)(ix) at a distance of 2·93 Å. The

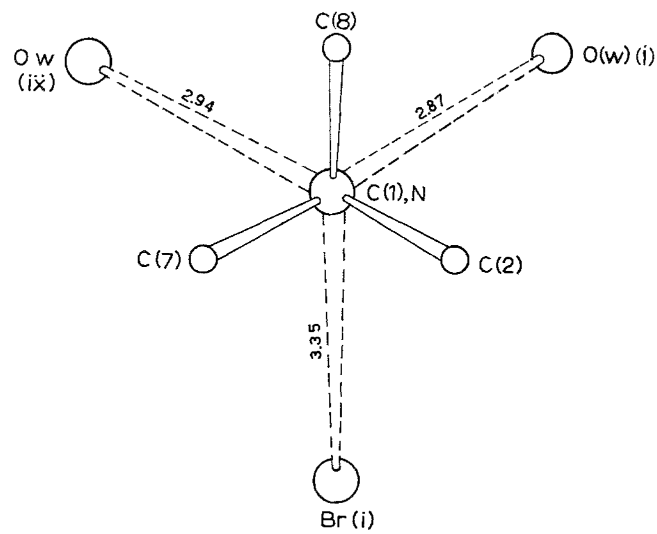


Fig. 6. Environment of amino nitrogen atom (projection down C(1)—N bond).

projection down C(1)—N bond is given in Fig. 6 which shows the three hydrogen bond directions are staggered with respect to the bonds covalently linked to the C(1) atom. The carboxyl oxygen atom O(1) forms a hydrogen bond of length 3·16 Å with Br(v). The environment of the water molecule

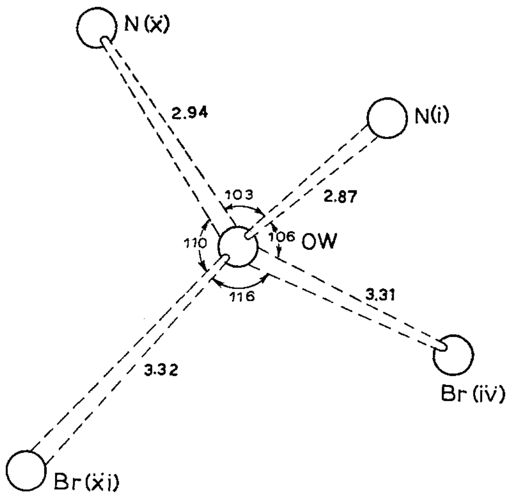


Fig. 7. Environment of the water molecule Ow as seen along *c* axis.

Ow is shown in Fig. 7; it has four nearest neighbours, each in a distorted tetrahedral configuration. The two hydrogen atoms associated with the water molecule form hydrogen bonds with Br(iv) and Br(xi) at distances 3·31 and 3·32 Å, respectively. The oxygen atom in the water molecule also acts as

Table 5. *Hydrogen bond lengths and angles*

Bond	Length (Å)	Bond	Angle (deg)
N—H···Br(i)	3·35	C(1)—N···Br(i)	115
N—H···Ow(i)	2·87	C(1)—N···Ow(i)	110
N—H···Ow(ix)	2·94	C(1)—N···Ow(ix)	103
O(1)—H···Br(v)	3·16	C(8)—O(1)···Br(v)	116
Ow···Br(iv)	3·31	Br(iv)···Ow···Br(xi)	116
Ow···Br(xi)	3·32		

Symmetry code:

(i) x, y, z	(vi) $1-x, \frac{1}{2}+y, \frac{1}{2}-z-1$
(ii) $x, 1+y, z$	(vii) $1-x, \frac{1}{2}+y-1, \frac{1}{2}-z$
(iii) $x, y, 1+z$	(viii) $1-x, \frac{1}{2}+y, \frac{1}{2}-z+1$
(iv) $x, y, z-1$	(ix) $\frac{1}{2}-x, 1-y, \frac{1}{2}+z$
(v) $x, 1+y, z-1$	(x) $\frac{1}{2}-x, 1-y, \frac{1}{2}+z-1$
	(xi) $\frac{1}{2}-x, -y, \frac{1}{2}+z-1$

an acceptor for two hydrogen bonds, as is shown in Fig. 7. The symmetry code of the atoms as well as the hydrogen bond distances and angles are given in Table 5. Intermolecular non-bonded contacts less than 4 Å are listed in Table 6; there are no unusual short contacts in the structure.

Table 6. *Intermolecular contacts less than* 4·0 Å

Atom i	Atom j	Distance d_{ij} (Å)
C(7)	Br(ii)	3·79
O(1)	C(3)(ii)	3·83
Br	C(2)(iii)	3·82
C(6′)	O(1)(iii)	3·70
C(6′)	C(3′)(iii)	3·87
C(4)	O(1)(vi)	3·92
C(5)	C(6)(vii)	3·88
C(4)	C(5)(vii)	3·93
C(5)	C(3′)(viii)	3·99
C(6)	C(3′)(viii)	3·82
Br	O(2)(ix)	3·80
C(7)	Ow(ix)	3·57
O(2)	Ow(x)	3·49
C(1)	Ow(ix)	3·63
C(8)	Ow(ix)	3·72
N	O(2)(ix)	2·93
O(2)	Ow(ix)	3·56

See Table 5 for symmetry code.

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