

The Crystal and Molecular Structure of 1-Aminocyclohexanecarboxylic Acid*

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1-Aminocyclohexanecarboxylic acid is monoclinic, space group $P2_1/c$, with $a=10.88$, $b=6.54$, $c=11.07$ Å, $\beta=95.8^\circ$, $Z=4$. The structure was solved by symbolic addition and refined by full-matrix least-squares calculations with 1122 visual reflexions to an R of 0.105. The cyclohexane ring exists in the chair conformation.

Introduction

A series of structure determination of aminocycloalkane derivatives has been undertaken in this laboratory (Chandrasekharan, Mallikarjunan, Godavari Chandrasekharan & Zand, 1968; Srikrishnan, Srinivasan & Zand, 1971; Chacko, Srinivasan & Zand, 1971*a,b*; Mallikarjunan, Chacko & Zand, 1972). Their structures are of interest from the point of view of the conformational features of the cycloalkane rings and their nature as amino acids. This paper deals with 1-aminocyclohexanecarboxylic acid; the hydrochloride has been reported by Chacko *et al.* (1971*b*).

Experimental

The crystals were elongated colourless needles. Rotation, Weissenberg and precession photographs were taken with Cu $K\alpha$ ($\lambda=1.5418$ Å) radiation.

Crystal data

Monoclinic, $a=10.88$ (2), $b=6.54$ (1), $c=11.07$ (2) Å, $\beta=95.8$ (2) $^\circ$; space group $P2_1/c$ ($0k0$, k odd and $h0l$, l odd absent), $Z=4$. Molecular formula $C_7NO_2H_{13}$.

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F.W. 142.2, $F(000)=312$ $D_m=1.23$ (by flotation), $D_c=1.21$ g cm $^{-3}$, $\mu(\text{Cu } K\alpha)=7.3$ cm $^{-1}$.

Intensities were collected about \mathbf{b} for hkl (K , 0 through 5) and about \mathbf{c} for hkL (L , 0 through 4) by the multiple-film equi-inclination method. The crystal used for b -axis data had a cross-section of nearly 0.2×0.2 mm and for c -axis data 0.15×0.25 mm. The intensities were measured visually and corrected for Lorentz and polarization factors and for spot shape. No absorption correction was applied. The common reflexions were used to put the data on a common scale (Rollett & Sparks, 1960). 1122 independent reflexions were observed which represent 60% of the total number accessible to the Cu sphere.

Structure determination and refinement

The structure was solved by the symbolic addition method (Karle & Karle, 1963). \sum_2 relations were computed with 147 reflexions with $E > 1.6$. Phases of 138 reflexions could be determined and the resulting E map showed all ten non-hydrogen atoms. Full-matrix least-squares refinement (Gantzel, Sparks & Trueblood, 1961) of these atoms resulted in $R=0.14$ and a subsequent difference synthesis revealed the 13 hydrogens. Further refinement with anisotropic temperature factors for the non-hydrogen atoms gave a final R of 0.105. Hydrogens were included as fixed contributions

Table 1. Fractional atomic coordinates and thermal parameters ($\times 10^4$)

The thermal parameter is of the form $T = \exp [-(b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + b_{12}hk + b_{13}hl + b_{23}kl)]$.

	x	y	z	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
C(1)	6570 (4)	2147 (7)	954 (4)	63 (4)	228 (12)	36 (3)	-14 (11)	10 (5)	-20 (9)
C(2)	7492 (5)	3915 (9)	1105 (4)	107 (5)	316 (17)	58 (4)	-117 (16)	-5 (7)	-50 (13)
C(3)	8747 (6)	3264 (11)	733 (6)	99 (6)	464 (24)	102 (6)	-184 (20)	56 (10)	-109 (19)
C(4)	9262 (5)	1398 (13)	1455 (6)	74 (5)	565 (28)	109 (6)	-28 (20)	6 (9)	79 (22)
C(5)	8354 (5)	-383 (11)	1281 (5)	85 (5)	386 (21)	93 (5)	70 (17)	0 (8)	-31 (16)
C(6)	7072 (4)	228 (8)	1602 (4)	69 (4)	293 (16)	55 (3)	9 (13)	11 (6)	36 (11)
C(7)	6141 (4)	1808 (7)	-418 (4)	78 (4)	220 (13)	40 (3)	-17 (12)	17 (5)	-18 (9)
N	5408 (3)	2812 (7)	1499 (3)	75 (4)	286 (13)	28 (7)	44 (10)	21 (4)	9 (8)
O(1)	5551 (4)	3244 (6)	-952 (3)	132 (4)	324 (12)	41 (2)	44 (12)	-9 (5)	26 (8)
O(2)	6397 (3)	146 (6)	-906 (3)	92 (4)	337 (12)	60 (3)	-22 (11)	11 (5)	-95 (9)

and a Hughes (1941) weighting scheme was employed with weights $1/w^2$ where $w = |F_o|$ for $|F_o| \geq 10$ and $w = 10$ for $|F_o| < 10$.

Scattering factors are those listed in *International Tables for X-ray Crystallography* (1962). The final positional and thermal parameters are given in Table 1.* Table 2 gives the coordinates of the hydrogen atoms.

Table 2. Coordinates of the hydrogen atoms from the difference synthesis

	x	y	z	B (Å ²)	Bonded to
H(1)	0.461	0.203	0.158	1.8	N
H(2)	0.561	0.294	0.219	1.8	N
H(3)	0.500	0.433	0.119	1.8	N
H(4)	0.722	0.506	0.069	2.1	C(2)
H(5)	0.758	0.431	0.211	2.1	C(2)
H(6)	0.872	0.289	-0.019	4.0	C(3)
H(7)	0.911	0.444	0.086	4.0	C(3)
H(8)	1.011	0.097	0.111	4.9	C(4)
H(9)	0.961	0.156	0.239	4.9	C(4)
H(10)	0.872	-0.164	0.178	3.8	C(5)
H(11)	0.833	-0.089	0.039	3.8	C(5)
H(12)	0.656	-0.097	0.133	2.6	C(6)
H(13)	0.717	0.069	0.261	2.6	C(6)

Description of the structure

The bond lengths and angles are listed in Table 3. The average standard deviations of the C-C and C-O

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30761 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

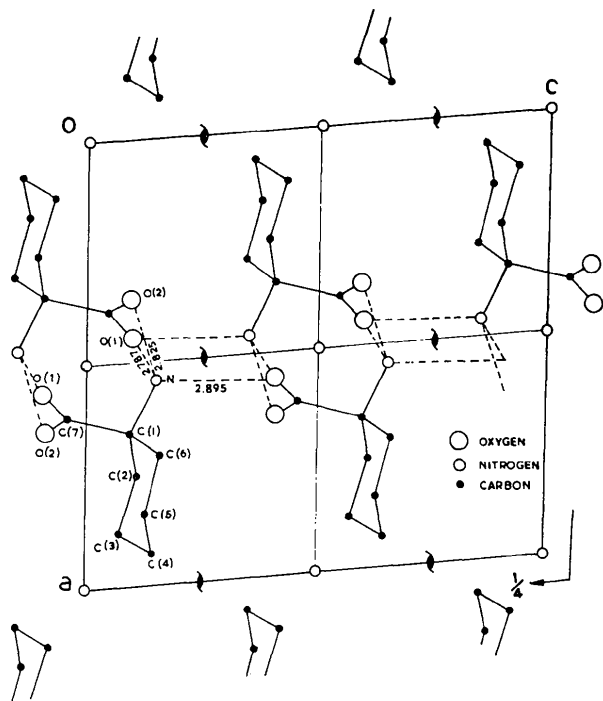


Fig. 1. Molecular packing viewed down b.

bonds are 0.008 and 0.006 Å respectively. The average standard deviation of a C-C angles is 0.8°. The average C-C length in the ring is 1.527, close to the value of 1.533 Å obtained for n-alkanes by Bartell & Kohl (1963). The corresponding mean value for the chlorine derivative of 1-aminocyclohexanecarboxylic acid (Chacko *et al.*, 1971*b*) is 1.530 and for cyclohexane II (Kahn, Fourme, André & Renaud, 1973) 1.523 Å. The average C-C-C angle of 111.6° for the ring is, as expected, greater than the tetrahedral value and agrees well with the theoretically predicted value of 111.5° (Bixon & Lifson, 1967) and 111.34° for cyclohexane II (Kahn *et al.*, 1973). The C(1)-N distance of 1.518 is significantly greater than the mean value of 1.487 Å found in amino acids (Marsh & Donohue, 1967). However, in other aminocarboxylic acids of cycloalkanes, this length is systematically greater than the above expected value. The C-N distances are 1.51 in 1-aminocyclopentanecarboxylic acid hydrobromide (Chandrasekharan *et al.*, 1968), 1.527 in 1-aminocyclohexanecarboxylic acid hydrochloride (Chacko *et al.*, 1971*b*), 1.542 in 1-aminocyclooctanecarboxylic acid hydrobromide (Srikrishnan *et al.*, 1971), 1.544 in 1-aminocycloheptanecarboxylic acid hydrobromide (Chacko *et al.*, 1971*a*) and 1.516 Å in 1-aminocyclopentanecarboxylic acid monohydrate (Mallikarjunan *et al.*, 1972). The C(1)-C(7) bond of 1.559 is significantly longer than the average value of

Table 3. Bond lengths and angles with their estimated standard deviations

C(1)-C(2)	1.529 (7) Å	C(1)-C(2)-C(3)	110.8 (8)°
C(1)-C(6)	1.519 (7)	C(2)-C(1)-C(6)	111.9 (7)
C(1)-C(7)	1.559 (6)	C(1)-C(6)-C(5)	113.5 (7)
C(2)-C(3)	1.526 (9)	C(2)-C(1)-C(7)	110.0 (7)
C(3)-C(4)	1.533 (10)	C(6)-C(1)-C(7)	113.6 (6)
C(4)-C(5)	1.527 (10)	C(2)-C(3)-C(4)	111.8 (9)
C(5)-C(6)	1.527 (8)	C(3)-C(4)-C(5)	110.1 (9)
C(1)-N	1.518 (6)	C(4)-C(5)-C(6)	111.4 (8)
C(7)-O(1)	1.252 (6)	C(2)-C(1)-N	107.7 (6)
C(7)-O(2)	1.257 (6)	C(6)-C(1)-N	108.8 (6)
		C(7)-C(1)-N	104.4 (6)
		C(1)-C(7)-O(1)	116.2 (6)
		C(1)-C(7)-O(2)	118.9 (6)
		O(1)-C(7)-O(2)	124.8 (6)

Table 4. Torsion angles of the cyclohexane ring and their standard deviations

C(1)-C(2)-C(3)-C(4)	-56.8 (6)°
C(2)-C(3)-C(4)-C(5)	57.7 (7)
C(3)-C(4)-C(5)-C(6)	-54.6 (7)
C(4)-C(5)-C(6)-C(1)	52.5 (6)
C(5)-C(6)-C(1)-C(2)	-51.4 (5)
C(6)-C(1)-C(2)-C(3)	52.8 (5)

Table 5. Equation of and deviation from the best plane passing through the atoms C(1), C(7), O(1) and O(2)

0.8863x + 0.3942y - 0.2430z = 6.5393			
C(1)	0.000 Å	O(2)	-0.001 Å
C(7)	0.002	N	-1.149
O(1)	-0.001		

Table 6. *Hydrogen-bond lengths and angles*

Donor	Acceptor	$D \cdots A$	$H \cdots A$	$D-H \cdots A$	$C-D \cdots A$	$H-D \cdots A$
C(1)-N	$\cdots O(2^{ii})$	2.787 Å	1.900 Å	143.4°	107.6°	24.0°
C(1)-N	$\cdots O(1^{iii})$	2.895	2.200	147.8	110.7	23.9
C(1)-N	$\cdots O(1^i)$	2.825	1.710	170.9	108.7	5.5

Symmetry code: (i) $1-x, 1-y, -z$; (ii) $1-x, -y, -z$; (iii) $x, \frac{1}{2}-y, \frac{1}{2}+z$.

1.527 Å found in amino acids (Marsh & Donohue, 1967). The C(7)-C(1)-N angle of 104.4° is significantly smaller than the tetrahedral value. The corresponding value in the hydrochloride (Chacko *et al.*, 1971*b*) is 104.3°. The mean C-H and N-H bond lengths are 1.04 and 0.98 Å respectively.

Molecular conformation

The cyclohexane ring exists in the chair conformation. The torsion angles about the C-C bonds are given in Table 4 and agree closely with the theoretically predicted value of $\pm 54.7^\circ$ (Bixon & Lifson, 1967). The conformation of the cyclohexane ring is a slightly distorted chair and the absolute mean deviation of a torsion angle from the theoretical value of Bixon & Lifson is 1.9°. Compared with this structure, the conformation of the cyclohexane ring is more a distorted chair in the case of the hydrochloride of 1-aminocyclohexanecarboxylic acid (Chacko *et al.*, 1971*b*) where the mean absolute deviation in torsion angle from the chair conformation is 7°. The carboxyl group is oriented axially to the cyclohexane ring in the present structure while in the hydrochloride it is equatorial.

The carboxyl group atoms C(7), O(1) and O(2) and C(1) form a plane with N deviated from the mean plane by 1.149 Å. The equation of the plane and the deviations of atoms are given in Table 5.

Molecular packing and hydrogen bonding

The packing of the molecule viewed down **b** is shown in Fig. 1. The molecule exists as a zwitterion. The nitrogen is hydrogen bonded to O(1ⁱ), O(2ⁱⁱ) and O(1ⁱⁱⁱ) at distances of 2.825, 2.787 and 2.895 Å respectively (Table 6). Fig. 2 shows the projection down C(1)-N. The hydrogen-bond directions are staggered to the bonds covalently linked to C(1).

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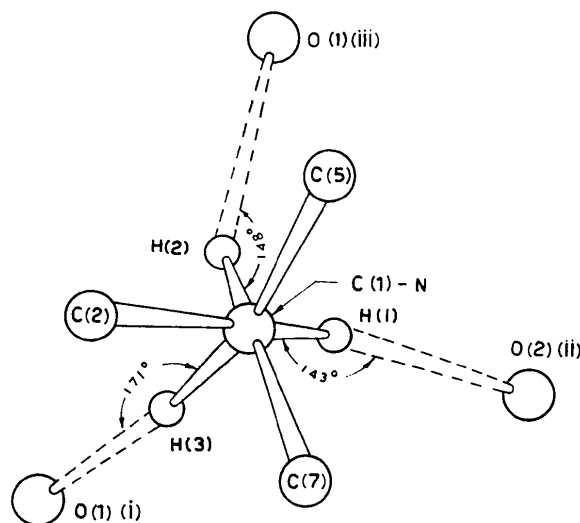


Fig. 2. Projection down C(1)-N.

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