

Structure of 4-Amino-3-hydroxybenzo-1-cycloheptene Hydrobromide

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Abstract. $C_{11}H_{15}NO \cdot HBr$, orthorhombic, $Pbca$, $a = 9.799$ (4), $b = 30.549$ (12), $c = 7.763$ (3) Å, $d_m = 1.45$ (floatation), $d_x = 1.446$ g cm⁻³, $Z = 8$; $\mu(Cu K\alpha) = 54.0$ cm⁻¹. The heptene ring is in the chair conformation. Bond lengths and angles are close to normal values.

Introduction. Crystals were obtained by slow evaporation of an aqueous solution. Unit-cell dimensions were determined from Weissenberg and rotation photographs and later refined with the 2θ values obtained for 40 reflections using the Picker diffractometer available in this laboratory. A crystal $0.035 \times 0.032 \times 0.05$ cm was chosen and the three-dimensional intensity data for 980 reflections were collected with Ni-filtered Cu $K\alpha$ radiation using the multiple-film equi-inclination Weissenberg technique, and were estimated visually by comparison with a standard set of spots prepared from the same crystal. They were then corrected for Lorentz, polarization and spot-shape factors (Phillips, 1954). The absorption correction was applied to the intensities with the assumption that the crystal was cylindrical (*International Tables for X-ray Crystallography*, 1962). Data collected about a and c were brought to a single scale (Rollett & Sparks, 1960). The R factor for the common reflections was 0.105.

From the three-dimensional Patterson synthesis the position of the Br atom was determined and its z coordinate was found to be $\frac{1}{4}$. This introduces for this space group a spurious mirror at $z = \frac{1}{4}$ in the Fourier map with the heavy atom. Two models of the molecules with peaks appearing on either side of the mirror plane were constructed. The structure factor calculations resolved this ambiguity and the correct set of atoms was located. The structure factor calculation with the Br and all the non-hydrogen atoms gave a conventional R factor of 0.42 which after four cycles of block-diagonal least-squares refinement (Shiono, 1968) using isotropic temperature factors followed by two cycles of refinement (Br atom anisotropic) reduced the R factor to 0.13. Four of the fifteen H atoms not revealed in the difference Fourier map were geometrically fixed. All the H atoms were assigned the isotropic temperature factors of the non-hydrogen atoms to which they are bonded. Two cycles of full-matrix least-squares refinement (Gantzel, Sparks & Trueblood,

1961) of the non-hydrogen atoms, with H atoms included only in the structure factor calculations, gave the final R factor of 0.112. The weighting scheme of

Table 1. Final positional and thermal parameters with standard deviations in parentheses

	x	y	z	B (Å ²)
Br	0.0767 (2)	0.0225 (5)	0.2672 (3)	*
N	0.1785 (15)	0.0456 (5)	-0.3443 (20)	3.2 (3)
O	0.0404 (12)	0.0874 (4)	-0.0376 (15)	3.0 (2)
C(1)	0.1988 (17)	0.1748 (5)	-0.0345 (22)	2.4 (3)
C(2)	0.2360 (17)	0.1319 (5)	0.0048 (20)	2.3 (3)
C(3)	0.3277 (20)	0.1243 (6)	0.1334 (26)	3.5 (4)
C(4)	0.3826 (26)	0.1586 (8)	0.2372 (32)	5.3 (5)
C(5)	0.3430 (26)	0.2005 (9)	0.1991 (34)	5.7 (6)
C(6)	0.2448 (23)	0.2094 (7)	0.0594 (27)	4.3 (4)
C(7)	0.0969 (23)	0.1879 (7)	0.1763 (29)	4.4 (4)
C(8)	0.1444 (20)	0.1725 (7)	-0.3621 (27)	2.4 (3)
C(9)	0.1229 (19)	0.1223 (6)	-0.3968 (22)	2.8 (3)
C(10)	0.2110 (15)	0.0920 (5)	-0.2822 (20)	2.2 (3)
C(11)	0.1831 (17)	0.0927 (5)	-0.0953 (21)	3.7 (4)

* Anisotropic temperature factors in the form:

$$T = \exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + hk\beta_{12} + hl\beta_{13} + kl\beta_{23}) \times 10^{-4}]$$

β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
133 (3)	8 (2)	119 (4)	5 (11)	7 (6)	4 (2)

Table 2. Positional and thermal parameters of the hydrogen atoms as obtained from the difference electron density map

Bonded to	x	y	z	B (Å ²)	
H(1)	C(3)	0.331	0.084	0.225	2.47
H(2)	C(4)	0.450	0.154	0.417	5.34
H(3)	C(5)	0.361	0.250	0.297	5.71
H(4)	C(6)	0.204	0.240	-0.026	4.23
H(5)	C(7)	0.104	0.225	-0.172	4.36
H(6)	C(7)	0.027	0.179	-0.147	4.36
H(7)	C(8)*	0.328	0.175	-0.396	2.45
H(8)	C(8)*	0.122	0.208	-0.511	2.45
H(9)	C(9)	0.134	0.132	-0.560	2.79
H(10)	C(9)	0.047	0.121	-0.391	2.79
H(11)	N	0.195	0.021	-0.486	3.22
H(12)	N	0.100	0.044	-0.325	3.22
H(13)	N	0.225	-0.003	-0.250	3.22
H(14)	O	0.067	0.078	-0.083	3.50
H(15)	C(10)*	0.318	0.101	-0.301	2.19
H(16)	C(11)*	0.229	0.063	-0.039	3.71

* Contribution No. 472.

* Geometrically fixed positions.

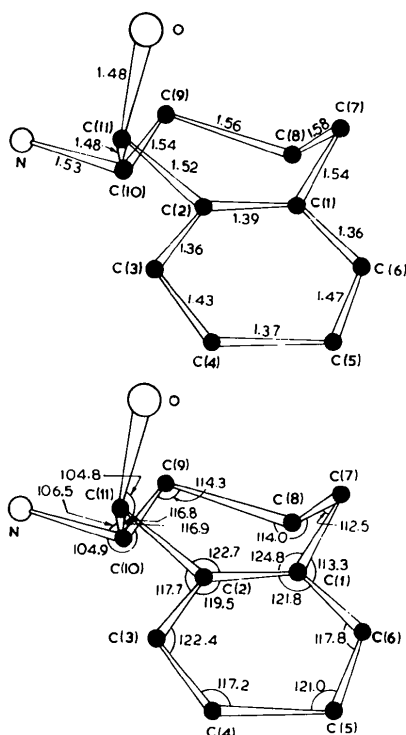


Fig. 1. Bond lengths (Å) and angles (°).

Table 3. Least-squares plane and atomic deviations (Å) from it

The equation to the plane is $AX + BY + CZ = D$ with respect to the crystallographic axes a , b and c , where X , Y , Z and D are in Å.

Equation to the plane

$$0.7618X + 0.0856Y - 0.6421Z = 2.0924$$

Deviations

C(1)	0.020	C(5)	0.000
C(2)	-0.010	C(6)	-0.014
C(3)	0.014	C(7)	0.001
C(4)	-0.004	C(11)	-0.008

Cruikshank, Bujosa, Lovell & Truter (1961), viz $w = (a + |F_o| + b|F_o|^2)^{-1}$ with $a = 6.0$ and $b = 0.009$, was used. Anomalous-dispersion corrections were applied to the scattering factor of the Br atom (Cromer & Liberman, 1970). The scattering factors used were taken from *International Tables for X-ray Crystallography* (1962). The final positional and thermal parameters for the non-hydrogen atoms are given in Table 1, and Table 2 gives those for the H atoms.*

Discussion. The bond lengths and angles are shown in Fig. 1. The average standard deviation in C—C bonds is 0.03 Å and that in bond angles is 1.4°. The bond lengths and angles in the heptene ring, excluding those involving the atoms in the fused part, agree with the corresponding values for a free heptane ring. The N atom is protonated and the C—N bond has a length of 1.53 (2) Å, which is larger than the value of 1.47 Å reported for monocarboxylic acids; however, such lengths have been observed in other cycloalkanes where the N atom is protonated (Chacko, Srinivasan & Zand, 1971*a,b*; Chandrasekharan, Mallikarjunan, Chandrasekharan & Zand, 1968; Srikrishnan, Srinivasan & Zand, 1971).

The benzene ring is planar and the equation to the least-squares plane passing through the atoms in the benzene ring and C(7) and C(11) of the heptene ring is

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33229 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

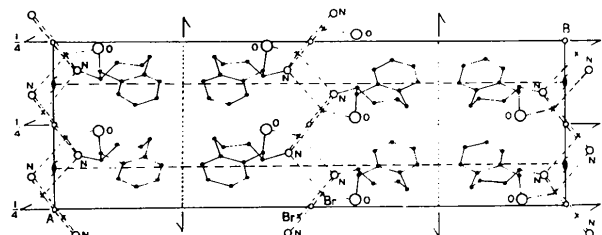
Fig. 2. The contents of the unit cell viewed down c .

Table 4. Hydrogen-bond lengths and angles

Donor (D)	Acceptor (A)	$D \cdots A$	$H \cdots A$	$\angle D-H \cdots A$	$\angle C-D \cdots A$	$\angle H-D \cdots A$
C(11)—O—H(14)	Br ^I	3.25 Å	2.19 Å	142.2°	94.6°	14.4°
C(10)—N—H(12)	Br ^{II}	3.28	2.03	121.4	111.3	26.3
C(10)—N—H(11)	Br ^{III}	3.33	2.70	136.6	132.1	9.7
C(10)—N—H(13)	Br ^{IV}	3.30	2.28	129.1	123.8	16.8

Symmetry code

(i)	x ,	y ,	z	(iii)	$-x$,	$-y$,	$-z$
(ii)	$\frac{1}{2} - x$,	$-y$,	$\frac{1}{2} + z$	(iv)	x ,	y ,	$z - 1$

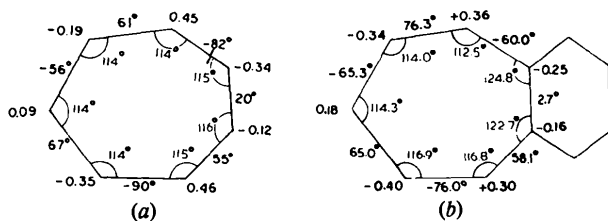


Fig. 3. Torsion angles of (a) Bixon & Lifson (1967) for cycloheptane and (b) the title compound. Deviations (Å) of atoms from a plane through the cycloheptane(ene) ring are also shown.

given in Table 3 with the deviations of individual atoms from this plane.

The arrangement of the molecules in the unit cell is shown in Fig. 2. The structure is stabilized by a three-dimensional network of hydrogen bonds of N—H...Br and O—H...Br types. Three of the four protons available for the hydrogen bonding take part in hydrogen bonding of the former type and the fourth in that of the latter. The hydrogen-bond lengths and angles are given in Table 4. The torsion angles around various bonds of the heptene ring shown in Fig. 3 agree closely with those of Bixon & Lifson (1967) for the chair conformation.

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The Optically Active Form of the Alkaloid Jamine

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Abstract. $C_{21}H_{35}N_3$, $M_r = 329.5$, orthorhombic, $a = 6.367$ (3), $b = 12.730$ (7), $c = 23.106$ (8) Å, $Z = 4$, $P2_12_12_1$. The X-ray analysis ($R = 0.055$ on 1315 reflections) of an alkaloid obtained from *Ormosia costulata* showed it to be the optically active form of jamine which has previously been reported as a racemate.

Introduction. In the course of an extended investigation of the *Ormosia* genus, a large number of alkaloids have been isolated from numerous species of this genus (Rinehart *et al.*, 1978). In particular, an alkaloid, $[\alpha]_D^{26} = -8.7^\circ$ (c 1.0 g/100 ml, $CHCl_3$), was obtained from *Ormosia costulata* and was crystallized from acetone to give colorless crystals (m.p. 120–122°C). The same compound was isolated during an investigation of the alkaloidal extract of the bark of

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