Ring Puckering of Azetidine: an Electron Diffraction Study

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Summary The ring configuration of azetidine is characterized by a 37° dihedral angle as found by gas-phase electron diffraction.

While several *X*-ray diffraction studies have been performed on azetidine derivatives,[1,2] no structural data are available on azetidine itself. The biological activity of these compounds is supposed to be related to their molecular conformation.[3] As small strained rings are often characterized by unusual parameters, the azetidine ring geometry cannot be predicted by analogy with other four-membered ring molecules.

Table

	Barrier to inversion (kcal/mol)	Dihedral angle (°)
Cyclobutane ..	1·44 (ref. 9)	35 (ref. 11)
Azetidine	1·26 (ref. 6)	37 (present work)
Oxetan	0·044 (ref. 10)	~4 (ref. 10 and ref. 13)

A nozzle temperature of about 60° was used in the electron scattering experiments.[4,5] Intensity data have been utilized in the interval $1{\cdot}80 \leqslant s \leqslant 27{\cdot}4$ Å^{-1}.

A molecular model (see Figure) with C_s symmetry for the whole and local C_{2v} symmetry for the CH_2 groups has been applied in the structure analysis. Both forms with axial (*a*) and equatorial (*e*) imine hydrogen atom positions, respectively, were assumed to be present according to a far-i.r. spectroscopy study[6] which has also established a potential function corresponding to a puckered equilibrium structure for this molecule.

The structure analysis showed that the azetidine ring is non-planar and the least-squares refinement based on the molecular intensities[7] yielded the values for the main geometrical parameters shown in the Figure (the uncertainties given include also the experimental scale error).

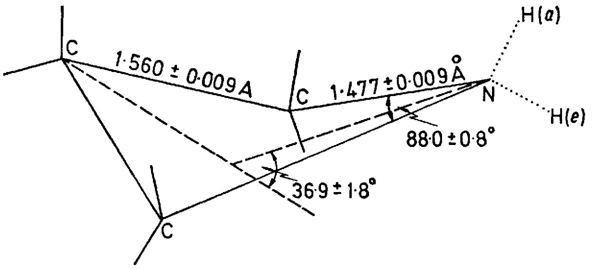

Figure. The model of azetidine with two alternate imine hydrogen positions. The geometrical parameters determined are shown.

The bonds seem to be 0·01—0·02 Å longer than those in related non-cyclic molecules indicating a strain in the ring. As for the ring conformation, both planar and puckered analogues are known in the solid state[2] where packing forces may exercise significant influence. Recent n.m.r. investigation[8] indicates non-planarity of the ring in several azetidine derivatives.

The Table shows a comparison of the barriers to inversion and the dihedral angles of four-membered rings.

Our electron diffraction result can also be compared with the average dihedral angle calculated to be 32° by Brunvoll[12] for azetidine at 300 K on the basis of population distribution among vibrational levels.

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