Electron Diffraction Investigation of Molecules Containing a Cyclohexane Type Six-membered Ring

M. DAVIS and O. HASSEL

Universitetets Kjemiske Institutt,
Blindern-Oslo, Norway

Studies of the molecular structures of cyclohexane and some of its derivatives and analogues has contributed considerably to the elucidation of the stereochemistry and conformational behaviour of these substances. Accurate values of bond distances and valency angles are mostly lacking, however, and it appears rather important to determine such values for at least some typical compounds. Results of electron diffraction studies carried out in this laboratory during the last years will therefore be reported here. The new Oslo diffraction unit was employed and the computations carried out as described in previous publications [1].

Data are given for the following substances: Cyclohexane, 1,4-dioxan, piperazine and N,N′-dimethylpiperazine (Table 1). In a forthcoming communication results related to hydrocarbons containing fused cyclohexane rings will be reported.

In the case of cyclohexane the experimental material obtained by Cand.real. A. Almenningen had previously been analysed by Mrs. E. Björnsborg and Mrs. L. Fernholt. In no case could the presence of conformations be traced which cannot be described as having the six-membered ring in the chair form. For dimethylpiperazine it was found that both methyl groups are in "equatorial" positions and that the positions of the methyl hydrogens are probably "eclipsed" rather than "staggered" relative to the bonds between the nitrogen atom and the two nearest ring carbons.

For obvious reasons the bond angles including hydrogen atoms must necessarily be somewhat less accurate than those involving only heavier atoms and such angles have therefore not been listed in Table 1.

From the figures given it follows that in each of the rings investigated the C-C bond distance was found to be slightly shorter than in diamond. The CXC angle (X = C, N, O) is equal to, or larger than the "tetrahedral" angle (109°28′), the value for cyclohexane being 111.55°. In view of the results generally obtained for "open" chain this finding was not surprising. It leads to a cyclohexane ring which is slightly "flatter" than that based on the classical tetrahedral angle. When methylene carbon atoms are being replaced by oxygen or nitrogen the CCX angle is nearly tetrahedral, but a certain flattening of the ring still occurs because the angle at the "hetero atom" is significantly larger than the tetrahedral angle.

We wish to express our sincere gratitude to Cand.real. A. Almenningen who has taken all the diagrams on which the determinations reported in this communication were based.

1. Bastiansen, O., Hassel, O. and Risberg, E. *Acta Chem. Scand.* **9** (1955) 232 and a series of later publications from our institute.

Received April 16, 1963.

Table 1.

Bond length (Å)		Bond angle (°)	
Cyclohexane			
C−C	1.528 ± 0.005	CCC	111.55 ± 0.15
C−H	1.104 ± 0.005		
1,4-Dioxan			
C−C	1.523 ± 0.005	CCO	109.2 ± 0.5
C−O	1.423 ± 0.003	COC	112.45 ± 0.5
C−H	1.112 ± 0.010		
Piperazine			
C−C	1.527 ± 0.005	CCN	109.8 ± 0.5
C−N	1.471 ± 0.005	CNC	112.6 ± 0.5
C−H	1.112 ± 0.010		
N−H	1.030 ± 0.015		
N,N′-Dimethylpiperazine			
C−C	1.521 ± 0.010	CCN	110.3 ± 1
C−N(ring)	1.457 ± 0.010	CNC(ring)	114.4 ± 1
C(methyl)-N	1.461 ± 0.010	CNC(methyl)	110.0 ± 1
C−H(mean value)	1.097 ± 0.010		