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CONFORMATION OF NON-AROMATIC RING COMPOUNDS, Part 70 (1)

Electron diffraction investigation on gaseous cyclohexane

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The chair form of cyclohexane was found to be flattened (endocyclic valency angles (ϑ) > 109.5°, torsional angles (φ) < 60°) from an electron diffraction study by Davis and Hassel in 1963 (2). The value of ϑ (111.55°) and the relation between ϑ and φ in chair-shaped cyclohexane (3)

$$\cos\varphi = -\cos\vartheta/(1+\cos\vartheta) \qquad .....(1)$$

yield $\varphi = 54.5^\circ$. This geometrical model of cyclohexane has been used as a basis of theoretical (Westheimer type) calculations of geometries of hydrocarbons (4,5). However, on account of several arguments, the ring puckering should be slightly larger than that concluded from the electron diffraction result:

(i) From X-ray analyses (6) on cyclohexane derivatives (mainly 1-, 1,1-, 1,2- and 1,4-substituted) the average ring torsional angle in most cases appears to exceed 54.5° (observed values for φ_{av} ranging from 53.2 to 57.6°), although substituents are expected to flatten rather than to pucker the ring (7).

(ii) Recent force-field calculations on the geometry of cyclohexane yield for φ :

Allinger et al., 1968 (8)	55.2°
Lifson and Warshel, 1968 (9)	55.8
Schmid et al., 1969 (10)	56
Altona and Sundaralingam, 1970 (7)	56.1

i.e. in all cases $\varphi > 54.5^\circ$.

(iii) The R-value method (11), relating vicinal proton coupling constants to the ring torsional angle, yields $\varphi = 58^\circ$ for cyclohexane, i.e. a much larger deviation from the diffraction result than is found with other six-membered rings investigated.

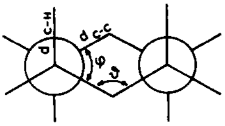
In order to try to solve the discrepancies stated above and to investigate the influence of substitution on the ring puckering, we carried out electron diffraction analyses on cyclohexane and methylcyclohexane. In this paper the geometrical results for cyclohexane are reported (Table 1). Further details concerning the diffraction analysis will be published elsewhere (12), together with the results of methylcyclohexane.

From Table 1 it is seen that our reinvestigation, indeed, yields a higher ring puckering ($\varphi_{II} = 55.9^\circ$) for cyclohexane than that found in ref.2 ($\varphi_I = 54.5^\circ$). As the quantity

$$(\varphi_{II} - \varphi_{I}) \,/\, ((\sigma_\varphi)^2_{I} + (\sigma_\varphi)^2_{II})^{\frac{1}{2}} \cong 2.6 \qquad .....(2)$$

the difference between the two φ values is probably significant (14).

Table 1. Geometrical parameters for cyclohexane from electron diffraction analysis, with estimated standard deviations (esd).

		I. Davis and Hassel (2,13)		II. This work	
			e.s.d.		e.s.d.
	d_{C-H}	1.104 Å	0.005	1.113	0.003
	d_{C-C}	1.528 Å	0.005	1.520	0.003
	ϑ	111.55°	0.15	111.05	0.10-0.15
	φ	54.5°	0.4	55.9	0.3-0.4

The CCH angle is found to be 109°, assuming $CCH_{ax} = CCH_{eq}$. Since (cf.ref.5):

$$\cos \tfrac{1}{2}(\mathrm{CCC}) \cdot \cos \tfrac{1}{2}(\mathrm{HCH}) + \cos(\mathrm{CCH}) = 0 \qquad \ldots\ldots(3)$$

the resulting HCH angle is 110°. However, the reliability of the latter parameter is rather low, as from eq.(3) it follows that $(\delta(\mathrm{HCH})/\partial(\mathrm{CCH}))_{(\mathrm{CCC})} \mathrel{\hat{=}} -4$.

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