A Comparison of Solid- and Liquid-phase Conformations; 4,4-Diphenylcyclohexanone, a Flattened Chair

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COMPARATIVE studies of molecular shapes in solution and in the solid phase have been lacking because of insufficient tools for examining liquid-phase structures. A qualitative method for the determination of the shapes of saturated six-membered rings by means of n.m.r. spectroscopy[1,2] has recently made predictions concerning distortions in cyclohexanones. Our aim was to obtain detailed structural information on a cyclohexanone from *X*-ray crystallographic and n.m.r. data and thence to compare the solid- and liquid-phase geometries. We report the first crystal structure of a simple, light-atom cyclohexanone.† The distortions predicted for the molecule in solution are found to carry over into the solid state.

Of the molecules previously studied by n.m.r.,[1]

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† Structures have been reported for a highly substituted cyclohexanone (L. C. G. Goaman and D. F. Grant, *Tetrahedron*, 1963, **19**, 1531) and for cyclohexane-1,4-dione (P. Groth and D. Hassel, *Acta Chem. Scand.*, 1964, **18**, 923; A. Mossel and C. Romers, *Acta Cryst.*, 1964, **17**, 1217). The probable structure of cyclohexanone has been discussed (W. Moffitt, A. Moscowitz, R. B. Woodward, W. Klyne, and C. Djerassi, *J. Amer. Chem. Soc.*, 1961, **83**, 4013), and an electron-diffraction study has been reported (C. Romers, *Rec. Trav. chim.*, 1956, **75**, 950).

4,4-diphenylcyclohexanone was chosen for X-ray crystallographic analysis. The molecule crystallizes in space group $P2_1/c$, monoclinic, $a = 7{\cdot}09$, $b = 16{\cdot}16$, $c = 12{\cdot}38$ Å, $\beta = 105^\circ\ 40'$, $Z = 4$, $D_m = 1{\cdot}213$, $D_c = 1{\cdot}216$ g./cm.^{3}. The 1219 independent non-zero reflections were obtained with Mo-K_α radiation, by use of both precession and Weissenberg equi-inclination photographs, which were analysed visually. Signs for the 300 strongest electron densities were determined by reiterative application of Sayre's equation.[3] The resulting Fourier electron-density map readily showed the positions of the 19 non-hydrogen atoms. During the last few refinement cycles, the phenyl rings were treated as ideal, rigid hexagons. The temperature factors for the seven non-hydrogen atoms in the cyclohexanone ring were allowed to vary anisotropically. The hydrogen atoms were included at their calculated positions. The discrepancy factor is at present 10·6.

In the solid state the molecule assumes a chair conformation in which the carbonyl end of the ring is severely flattened (Figure 1). The angle between the planes formed by C(6)–C(1)–C(2) and C(3)–C(4)–C(5) is 13·7 ± 0·5° (Figure 2). In cyclohexane, this angle is required by symmetry to be 0°. The angle (γ) between the C(6)–C(1)–C(2) plane and the C(2)–C(3)–C(5)–C(6) plane is 38°, indicative of flattening, whereas the angle (ϵ) between the C(3)–C(4)–C(5) plane and the C(2)–C(3)–C(5)–C(6) plane is 52° (Figure 2). In a cyclohexane ring with C–C–C angles of 111·55°,[4] the angles between these planes would both be about 49°. Thus, most of the ring distortion is localized around the carbonyl group. The geometry in the vicinity of the C(4) atom, to which the phenyl groups are attached, is altered much less (ϵ 52° *cf.* 49° in cyclohexane). Although the C(3)–C(4)–C(5) angle is small (105·9°), the normal external angle between the substituents (110·5°) demonstrates the absence of a substantial "geminal" effect.[5] Most likely, the C(3)–C(4)–C(5) angle is reduced in order to compensate for the enlarged C(6)–C(1)–C(2) angle. The geometry in the solid state is thus best described as a chair, flattened around one three-atom segment and very slightly puckered at the other end.

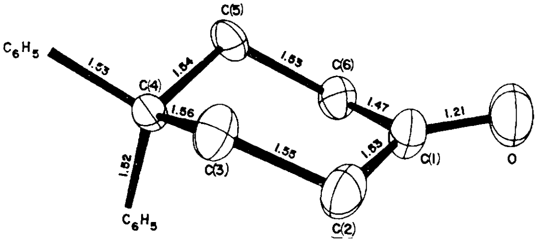

FIGURE 1. *The geometry of 4,4-diphenylcyclohexanone in the crystal. Standard deviations for the bond lengths and bond angles are not larger than* 0·01 Å *and* 0·6°, *respectively.*

Bond Angles

C(6)–C(1)–C(2)	116·8	C(3)–C(4)–C(5)	105·9
C(1)–C(2)–C(3)	110·5	C(4)–C(5)–C(6)	113·8
C(2)–C(3)–C(4)	112·6	C(5)–C(6)–C(1)	115·2
O–C(1)–C(2)	118·8	C(6)–C(1)–O	124·4
Ph–C(4)–Ph	110·5		

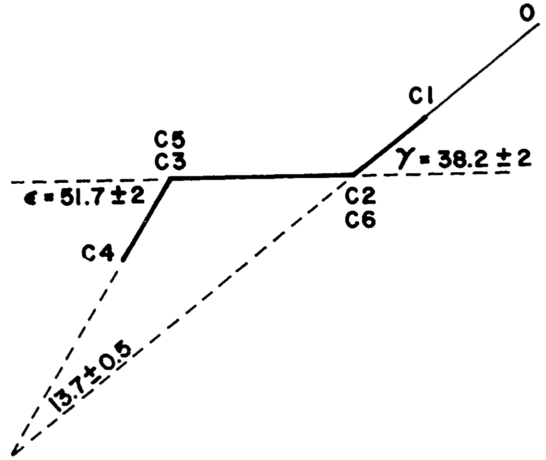

FIGURE 2. *Projection of the cyclohexanone ring on the* O–C(1)–C(4) *plane.*

The n.m.r. spectra of 4,4-diphenylcyclohexanone in carbon disulphide at 60 and 100 MHz were analyzed by the method of Swalen and Reilly.[6] The vicinal coupling constants between the protons on C(2) and C(3) [or C(5) and C(6)], averaged by ring inversion, were found to be 8·45 (J_{trans}) and 5·1 Hz (J_{cis}).‡ The ratio ($R = 1{\cdot}65$) between these averaged coupling constants corresponds to a conformation with neighbouring protons more nearly eclipsed than in cyclohexane.[1,2] The only reasonable conformations that fulfil this requirement are the flattened chair and certain members of the flexible (boat) family. The

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‡ Allowance in the present analysis for a long-range coupling of about 2 Hz between the equatorial protons on C(2) and C(6) accounts for the small variation with respect to the numbers reported previously.[1] The spectra were taken on Varian T 60 and HA 100 spectrometers. The CDC 3400 and 6400 computers were used for the analysis.

original analysis[1] did not attempt to choose between these two alternatives. The perfect chair (R *ca.* 2·0; γ, ϵ *ca.* 49°) and the puckered chair ($R > 2{\cdot}4$; γ, $\epsilon > 49°$) are specifically excluded. The crystal structure, which corresponds to the flattened chair, eliminates flexible forms from further consideration. In confirmation of the similarity of conformation in the liquid and solid states, the i.r. spectrum of 4,4-diphenylcyclohexane has band for band coincidences in Nujol, KBr (pellet), chloroform, and carbon disulphide, and as a solid film.

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[1] J. B. Lambert, *J. Amer. Chem. Soc.*, 1967, **89**, 1836.
[2] J. B. Lambert and R. G. Keske, *Tetrahedron Letters*, 1967, 4755.
[3] D. Sayre, *Acta Cryst.*, 1952, **5**, 60.
[4] M. Davis and O. Hassel, *Acta Chem. Scand.*, 1963, **17**, 1181.
[5] E. L. Eliel, "Stereochemistry of Carbon Compounds," McGraw-Hill, New York, 1962, pp. 197—8.
[6] J. D. Swalen and C. A. Reilly, *J. Chem. Phys.*, 1962, **37**, 21.