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schematic conformations of cyclohexanone labeled (I), (II), (III), and (IV), with axial and equatorial directions a, e, a', and e'

Figure 1: schematic conformations of cyclohexanone labeled (I), (II), (III), and (IV), with axial and equatorial directions a, e, a', and e'

Abstract

Full Text

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OPTICAL STUDY OF THE CONFORMATIONS OF CYCLOHEXANONE AND SOME OF ITS DERIVATIVES

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Cyclohexanone, like cyclohexane (1), at room temperature exists predominantly in the chair form, as follows from an electron-diffraction study of its structure (2). This study establishes the inequality of the angle $\angle C_2C_1C_6$ to the angles $\angle OC_1C_2$ and $\angle OC_1C_6$: the first is determined to be $117 \pm 3°$, the other two $121.5 \pm 1.5°$. If each of these three angles were equal to 120°, or if the sum of all three angles were 360°, the coplanarity of the carbonyl bond with the plane of atoms C_1, C_2, and C_6 would be certain. However, the considerable error limits in the measurement of the angles make it possible to suppose that the indicated coplanarity may be absent; the $C = O$ bond may be somewhat displaced from the plane defined by the carbon atoms C_1, C_2, and C_6, either toward the axial direction (quasi-axial direction a') or the equatorial direction (quasi-equatorial direction e'). In this case one could admit the existence of four conformations of the chair form of cyclohexanone; however, in view of the equivalence of the $C - H$ bonds, conformations (I) and (IV) should be regarded as identical, as should conformations (II) and (III), and therefore one could in fact speak of two conformations of cyclohexanone, differing in the quasi-axial (a') and quasi-equatorial (e') direction of the $C = O$ bond:

The permissibility of this assumption is indicated by optical data: in the combination-scattering spectrum of liquid cyclohexanone (as also of its 12% solution in carbon tetrachloride) the vibrational frequency of the carbonyl group and the frequency of the pulsating vibration of the ring are split into doublets (respectively 1706(7), 1719(5) cm^{-1} and 748(10), 756(8) cm^{-1}); many other frequencies are split into a doublet or have the character of a double line. Judging from the intensities, one of the conformations is present in a somewhat smaller amount (~ 40%) than the other (60%). The foregoing is confirmed by the optical study of other compounds considered in this article.*

According to (^{3}-^{5}), α-chlorocyclohexanone exists in a predominant conformation with an axial position of the $C-Cl$ bond (the so-called a-conformation), since the conformation with an equatorial position of this bond (the so-called e-conformation) proves to be unstable because of the strong mutual repulsion of the dipoles C = O, C—Cl when they are nearly coplanar in the e-conformation. According to infrared absorption spectra ((^5), and also (^3, ^4)), the vibrational frequency of the carbonyl group in the a-conformation of α-chlorocyclohexanone, compared with cyclohexanone (1712 cm^{-1}), is increased (1722 cm^{-1}); in the e-conformation this increase is still more considerable (1740 cm^{-1}). The intensity of the latter frequency is small, which indicates the predominance in α-chlorocyclohexanone of the a-conformation.

Kojima and Yamanuchi, in a recently published work (^6), attempt to refute Corey' s (^5) proposition on the predominance in α-chlorocyclohexanone of the a-conformation, assuming that the e-conformation is predominant. However, this assertion of theirs is in contradiction with their own experimental data, presented in (^6). Indeed, Kojima and Yamanuchi arrived at their conclusion from certain general considerations, relying here on noncharacteristic vibrational frequencies, whose correct assignment is always either difficult or impossible. They completely declined to examine the very characteristic band of the carbonyl group, justifying this, supposedly, by the complexity of its contour (see (^6), p. 4162). Meanwhile, in the same data which they give on the infrared absorption frequencies of the carbonyl group, there are two partially overlapping bands, reported by Corey in (^5), with the same ratio of intensities in the liquid phase and in solutions of CS_2 and CCl_4: a very intense frequency at 1723 cm^{-1} and a weak one at 1743 cm^{-1}. In the gas phase the center of gravity of these overlapping bands shifted to the high frequency (intensity maximum 1739 cm^{-1}), while in the solid state it shifted to the low frequency (1723 cm^{-1}); the second frequency (1743 cm^{-1}) in the solid phase is vanishingly small in intensity (see Table 1 on p. 4160 in (^6)). This means that the conformation characterized by the higher vibrational frequency of the carbonyl group, 1743 cm^{-1}, is energetically more strained, unstable, and predominates only in the gas phase at a higher temperature. With decreasing temperature, on passing to the liquid and solid phases, there must occur, as is known, a "freezing out" of this unstable conformation; under these conditions the more stable conformation, characterized by the carbonyl vibrational frequency 1723 cm^{-1}, is preserved and undoubtedly predominates. The unstable conformation with the carbonyl vibrational frequency 1743 cm^{-1} is the e-conformation; the stable conformation with the carbonyl vibrational frequency 1723 cm^{-1} is the a-conformation, by virtue

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* We note that there is no basis for attributing the splitting of the vibration frequency of the $C=O$ bond of cyclohexanone observed by us to Fermi resonance; it occurs in monosubstituted cyclohexanones, in cyclopentanone and its substituted derivatives, in most of which there is not even a hint of the possibility of the appearance of Fermi resonance.

of the following circumstances. In aliphatic ketones a halogen in the α-position relative to the carbonyl always raises the frequency of its vibrations (see, for example, (ˆ7)); the interaction of the C—Cl and C=O bonds, and consequently the frequency-raising effect of the former on the latter, is more considerable when both bonds are in an equatorial position (ˆ1, ˆ8), i.e., in the e-conformation, and not in the a-conformation, in which the C—Cl bond is axial; hence it follows directly that the conformation with the carbonyl vibrational frequency 1723 cm^{-1} is the stable a-conformation of α-chlorocyclohexanone, predominating in the liquid and solid phases, as well as in solutions of this substance in CS_2 and CCl_4; the conformation with the higher carbonyl vibrational frequency 1743 cm^{-1} is the unstable e-conformation, predominating only in the gas phase of α-chlorocyclohexanone. These conclusions of ours from the analysis of the experimental data (ˆ6) are in complete agreement with the data presented in the present article and with Corey’ s data in (ˆ5), and do not confirm the conclusions of Kojima and Yamanuchi in (ˆ6), which do not correspond to reality. We note that the Raman spectrum of α-chlorocyclohexanone given in (ˆ6) is unsatisfactory; for example, in it the structurally complex carbonyl band is designated by only a single frequency (1721 cm^{-1}), whereas in fact four frequencies are observed in this region; the region of stretching vibrations of C—H bonds is designated in (ˆ6) by only two frequencies (2899, 2949 cm^{-1}), whereas in fact ...

in fact there are thirteen frequencies (including component frequencies) in this region, etc.

The combination scattering spectrum of α-chlorocyclohexanone studied by us, while confirming the above-mentioned statement of Corey (5) on the predominantly axial position of the C—Cl bond in the liquid phase of this substance and in its solution in CCl_4, at the same time indicates a greater variety of conformations in which α-chlorocyclohexanone exists than is represented in (5). Indeed, in the region of the carbonyl-group vibration frequencies an intense doublet 1719(7), 1729(5) and a weaker doublet 1734(2), 1746(2) cm^{-1} are observed, i.e., not two, but four frequencies in all. In agreement with the results of our previous investigations (1, 8) and with what was said above concerning cyclohexanone and α-chlorocyclohexanone (in particular, concerning the possible quasi-axial (a') and quasi-equatorial (e') positions of the carbonyl), it may be assumed that for the latter substance four conformations are possible, the most predominant of which is trans-1a'2a (V); together with (V), the conformation cis-1e'2a (VII) is evidently present in appreciable amount; conformations (VI) and (VIII) are also present in the equilibrium mixture, but in considerably smaller amount:

	(V) trans-1a'2a	(VI) trans-1e'2e	(VII) cis-1e'2a	(VIII) cis-1a'2e
C –Cl	539(9)	552(2)	533(6)	544(3)
C = O	1719(7)	1734(2)	1729(5)	1746(2)

conformations V–VIII

Figure 2: conformations V–VIII

conformations XIII–XVI

Figure 3: conformations XIII–XVI

	(V) trans-1$a'2a$	(VI) trans-1$e'2e$	(VII) cis-1$e'2a$	(VIII) cis-1$a'2e$
Ring	713(5)	722(2)	694(3)	705(2)

In the case of α- and still more of β-methylcyclohexanone there is no factor which forces the C—Cl bond in α-chlorocyclohexanone (strong repulsion of the $C = O$ and C—Cl dipoles when the C—Cl bond is in an equatorial position) to occupy predominantly an axial position, contrary to the rules of Hassel and Barton. In these compounds the methyl group, in agreement with the indicated rules (1, 8), occupies chiefly the equatorial position. Therefore, in α-methylcyclohexanone the predominant conformation is trans-1$e'2e$ (IX); along with it there is present in appreciable amount the conformation cis-1$e'2a$ (XI), with an axial methyl group and a quasi-equatorial carbonyl group:

	(IX)	(X)	(XI) cis-1$e'2a$	
	trans-1$e'2e$	trans-1$a'2a$		(XII) cis-1$a'2e$
$C = O$	1709(8)	1695(0)	1720(5)	1703(1)
Ring	721(8)	716(0)	727(3)	733(0)

In β-methylcyclohexanone the predominant conformations are cis-1$e'3e$ (XIII), and also trans-1$a'3e$ (XVI), with equatorial positions of the methyl group in them:

	(XIII) cis-1$e'3e$	(XIV) cis-1$a'3a$	(XV) trans-1$e'3a$	(XVI) trans-1$a'3e$
$C = O$	1708(8)	1692(0)	1700(1)	1721(6)
Ring	754(8)	740(0)	747(1)	763(6)

The combination scattering spectra were recorded on a domestic ISP-51 spectrograph with a medium camera and on a Hilger E612 spectrograph.

Table 1

Physical properties of the compounds investigated (synthesis (9))

Compounds	M.p., °C	B.p., °C/mm	n_D^{20}	Compounds	B.p., °C/mm	n_D^{20}
Cyclohexanone	–	52°/20	1.4507	α-Methylcyclohexanone	47°/10	1.4480
α-Chlorocyclohexanone	23	57°/3.5	1.4835	β-Methylcyclohexanone	56°/15	1.4454

from the exciting blue line 4358 Å of a mercury lamp (notations for intensities see in (1,8).

Cyclohexanone, $\Delta\nu$ cm^{-1}: 190(1), 314(3 dw), 412(6), 480(1), *492(4* dw), 655(7 sh, dw), 748(10* r), 756(8* r), 783(0), 842(7), 895(2* dw), 910(3* dw), 995(2), 1021(9), 1057(1), *1075(5* dw), 1118(5), 1224(5), 1250(4), 1268(3), 1318(6 dw), 1350(2), 1422(4), *1431(3)*, 1451(6), **1463(2)**, 1706(7), *1719(5)*, 2668(2), **2686(2)**, 2827(2), *2861(10* dw), 2895(7* r), 2906(7* r), 2930(5* r), 2941(10 r), *2954(10* r), 2967(5), *2980(1)*.

α-Chlorocyclohexanone, $\Delta\nu$ cm^{-1}: 200(3sh), 235(5), 261(2), 312(3), 335(9), 409(2), *425(3)*, 533(6), **539(9p)**, 544(3p), **552(2)**, 659(4), *668(4)*, 694(3), **705(2)**, 713(5), *722(2)*, 756(3), 800(3), 824(2), *835(3)*, 842(3), *856(4)*, *895(3)*, *939(2)*, *973(7)*, *1022(5)*, 1032(4), *1071(7)*, *1102(2)*, *1128(3 sh)*, *1195(4)*, *1230(1)*, 1249(5), *1266(4)*, 1302(1), **1316(6)**, 1335(5), 1396(1 sh), 1424(3), *1434(4)*, 1454(9), **1467(1)**, 1719(7), *1729(5)*, 1734(2), *1746(2)*, 2643(0), **2662(1)**, 2687(1**), 2810(1), 2839(1), 2870(10), *2901(8)*, 2914(8), *2919(3* r), 2948(10), *2960(10)*, 2974(7), *2990(2)*.

α-Methylcyclohexanone, $\Delta\nu$ cm^{-1}: 242(0), 290(2), 327(2), 394(4), 427(5), 504(3), 576(6), 632(0), 662(6 sh, dw), 716(0), 721(8* r), 727(3* r), 733(0), *840(5)*, *868(4)*, *966(3)*, *993(6 dw)*, *1054(3)*, *1070(2)*, *1084(2 dw)*, *1121(6 dw)*, *1147(4 dw)*, *1164(1)*, *1219(4)*, *1239(1)*, *1256(6)*, *1286(1) 1316(7)*, *1347(1)*, 1361(2), *1432(3)*, ***1454(9)***, *1467(1)*, ***1695(0)***, ***1703(1)***, ***1709(8)***, **1720(5)**, ***2653(0)***, *2671(1)*, ***2690(0)***, *2732(1 dw)*, *2761(0)*, *2807(2)*, 2827(2), *2854(10)*, 2869(6), *2930(10)*, 2942(8), *2965(4)*, 2982(2), *2995(1)*.

β-Methylcyclohexanone, $\Delta\nu$ cm^{-1}: 249(1), *266(1)*, 302(1 sh), 388(3), *399(5)*, 426(0), 439(3), 491(3), 517(3), 644(8 sh), 672(1), 740(0), *747(1* r), 754(8* r), 763(6* r), 786(0), 822(3), *832(3)*, 864(0), **874(1)**, 890(3), 948(4), 963(5), *973(4)*, 1047(5), **1060(1)**, 1084(7), 1109(1), 1123(8), 1207(5), 1229(7), 1266(4), *1276(4)*, 1306(4), **1319(4)**, 1328(4), **1339(6)**, 1361(3), 1425(6), 1460(9), 1692(0), *1700(1)*, 1708(8* r), 1721(6* r), 2630(0), 2652(1), *2679(0)*, 2716(1), **2737(1)**, 2817(3), *2831(3)*, 2847(4), *2867(10)*, 2881(3), *2930(6)*, 2954(10), *2971(5)*.

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