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Microwave Spectrum of Cyclohexanone[*1]

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The microwave spectrum of cyclohexanone has been investigated in the frequency region from 7.7 to 23.4 Gc/sec. The R- and Q-branches for both the a- and the c-type have been assigned for the vibrationally ground state. The rotational constants obtained are $A=4195.30$ Mc/sec, $B=2502.57$ Mc/sec, and $C=1754.49$ Mc/sec. From these values it can be concluded that the molecules have the chair form. The value of the component of the dipole moment $|\mu_a|$ is 2.74 ± 0.03 D, and that of $|\mu_c|$ is 0.86 ± 0.03 D. The value of the total dipole moment is 2.87 ± 0.04 D, a value which is in agreement with that obtained by Debye's method. For the structural parameters Romers' data obtained by the electron diffraction seems to be nearly correct.

An electron diffraction investigation of cyclohexanone has been reported by Romers.1) By assuming the chair form for this molecule, the structural parameters obtained in his investigation were as follows: the bond distances were 1.54 ± 0.01 Å, 1.24 ± 0.02 Å, and 1.09 ± 0.02 Å for C–C, C=O, and C–H respectively, and all the carbon bond angles were $109.5°\pm2.5°$, with the exception of the valency angle of the carbonyl carbon atom, which was $117°\pm3°$ for the C–C–C angle. By the study of the microwave spectrum of acetone,2) the ∠C–C–C valency angle has been estimated to be $117°12'\pm20'$. This value is essentially the same as that obtained by Romers. However, no structural investigation of cyclohexanone by microwave spectroscopy has yet been reported. The present work has been carried out in the hope of determining the special ring structure of this molecule.

Experimental

The spectrum was measured over the frequency range from 7700 to 23400 Mc/sec with a conventional Stark modulation microwave spectrometer, employing 100 kc/sec square-wave or sine-wave modulation. All the measurements were made at about −15°C. The frequencies were measured by the method reported in a previous paper.3)

The sample of cyclohexanone, obtained from a commercial source, was distilled twice before use.

Results and Discussion

Microwave Spectrum and Rotational Constants. To obtain an idea of how the spectrum would appear, preliminary rotational constants were calculated by use of the structural parameters obtained by Romers1) for three possible structures, *i. e.*, the chair form, the boat form, and the skew-boat form, as shown in Fig. 1.

It was difficult to assign the spectrum because of its richness, but almost all of the low J transitions for the a-type and some of the low J, c-type transitions were identified by their characteristic Stark effects; these assignments were confirmed by fitting them with rigid-rotor rotational constants. The measured frequencies and the transitions for both a- and c-type are listed in Table 1, together with the rotational constants obtained. In view

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1) C. Romers, *Rec. trav. chim.*, **75**, 956 (1956).

2) R. Nelson and L. Pierce, *J. Mol. Spectry.*, **18**, 344 (1965).

3) A. Hatta, C. Hirose and K. Kozima, This Bulletin, **41**, 1088 (1968).

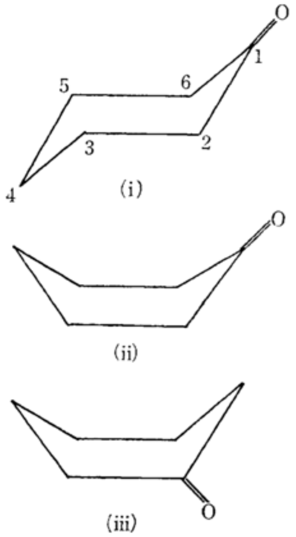

Fig. 1. Possible structures for cyclohexanone ring. (i) chair form, (ii) boat form, and (iii) skew-boat form.

TABLE 1. GROUND-STATE ROTATIONAL TRANSITIONS OF CYCLOHEXANONE

	Transitions	Observed* in Mc/sec	$\nu_{obs}-\nu_{calc}$
a-type	$1_{11} \rightarrow 2_{12}$	7766.4	+0.4
	$1_{01} \rightarrow 2_{02}$	8316.0	+0.2
	$1_{10} \rightarrow 2_{11}$	9261.9	−0.3
	$2_{12} \rightarrow 3_{13}$	11537.9	−0.1
	$2_{02} \rightarrow 3_{03}$	12055.6	+0.4
	$2_{21} \rightarrow 3_{22}$	12771.7	+0.5
	$2_{20} \rightarrow 3_{21}$	13487.3	+0.2
	$2_{11} \rightarrow 3_{12}$	13748.5	+0.6
	$3_{13} \rightarrow 4_{14}$	15217.1	−0.3
	$3_{03} \rightarrow 4_{04}$	15553.8	−0.5
	$3_{22} \rightarrow 4_{23}$	16871.0	−0.3
	$3_{31} \rightarrow 4_{32}$	17343.2	+0.3
	$3_{30} \rightarrow 4_{31}$	17537.4	−0.8
	$3_{12} \rightarrow 4_{13}$	18014.5	+0.1
	$3_{21} \rightarrow 4_{22}$	18340.3	0.0
	$5_{15} \rightarrow 5_{14}$	10381.3	−0.7
c-type	$1_{01} \rightarrow 2_{11}$	11702.9	−0.2
	$1_{10} \rightarrow 2_{20}$	14539.0**	+0.3
	$1_{11} \rightarrow 2_{21}$	15088.6	+0.1
	$2_{02} \rightarrow 3_{12}$	17135.5	+0.4
	$2_{11} \rightarrow 3_{21}$	18764.2**	+0.5
	$2_{12} \rightarrow 3_{22}$	20093.6	0.0
	$2_{21} \rightarrow 3_{31}$	23215.8	−0.3
	$4_{22} \rightarrow 4_{32}$	8532.4	−0.9

Rotational constants: $A=4195.30$ Mc/sec
$B=2502.57$ Mc/sec
$C=1754.49$ Mc/sec

* Maximum uncertainty of the observed values is ±0.2 Mc/sec.

** Uncertainty of the observed value is ±0.5 Mc/sec, because of an overlap with other line.

of the relative intensities of the spectrum, it is sure that the frequencies listed in Table 1 are those for the vibrationally ground state. No b-type transitions could be found.

Because the rotational constants thus obtained almost agreed with the preliminary constants of the chair form and differed markedly from the preliminary constants of both the boat and skew-boat forms, it can be concluded that the molecules of cyclohexanone have the chair form, with C_h symmetry.

Dipole Moment. The Stark displacements of the $M=1$ component of the $1_{11}\rightarrow 2_{12}$ transition and of the $M=2$ and $M=3$ components of the $3_{13}\rightarrow 4_{14}$ transition were measured in order to determine the a and c components, μ_a and μ_c, of the electric dipole moment. These lines were nicely fitted to quadratic Stark displacements. The absorption cell was calibrated using the $J=0\rightarrow 1$ transition of OCS, taking the dipole moment of OCS as 0.7124 D.[4] The observed and calculated Stark coefficients are given in Table 2.

TABLE 2. STARK COEFFICIENTS AND DIPOLE MOMENT

Transition,	M	$\Delta\nu/E^2$ (Mc/sec)/(kV/cm)^2 Obsd	Calcd
$1_{11} \rightarrow 2_{12}$	1	645 ±10	640.3
$3_{13} \rightarrow 4_{14}$	2	42.3± 1.0	42.4
	3	96.2± 2.5	98.6

$|\mu_a|=2.74\pm0.03$ D
$|\mu_c|=0.86\pm0.03$ D
$\mu=2.87\pm0.04$ D

The subscripts a and c refer to principal inertial axes of cyclohexanone.

An analysis of these data yields $|\mu_a|=2.74\pm0.03$ D, $|\mu_c|=0.86\pm0.03$ D, and a total dipole moment of 2.87±0.04 D. This value agrees with that of 2.90 D[5] obtained in a 1,4-dioxane solution by Debye's method.

By taking into account the fact that the vector of the dipole moment should be nearly parallel to the C=O bond, the directions of the vectors of μ_a and μ_c can be determined; from this, the angle, α, made by the vector of the total dipole moment and the a axis can then be determined to be 17.5°± 1°.

Structural Calculations. Since the experimental results provide only three moments of inertia and the orientation of the dipole moment vector, a number of assumptions are required in order to extract any structural information. It may be assumed that (i) all C–H bonds are of equal length; (ii) the oxygen atom is coplanar with the three

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[4] S. A. Marshall and J. Weber, *Phys. Rev.*, **105**, 1502 (1957).

[5] I. F. Halverstadt and W. D. Kumler, *J. Am. Chem. Soc.*, **64**, 1982 (1942).

carbon atoms of C_6, C_1, and C_2; (iii) the internuclear distance, r_{2-3}, between C_2 and C_3 is equal to that, r_{3-4}, between C_3 and C_4; (iv) the HC_iH angle bisector is located along the $C_{i-1}C_iC_{i+1}$ angle bisector; (v) the HC_iH plane is perpendicular to the $C_{i-1}C_iC_{i+1}$ plane, and (vi) all of the HCH angles are the same. We then find that there are still nine undetermined structural parameters: r_{1-2}, r_{2-3}, r_{C-H}, $r_{C=O}$, $\angle C_1C_2C_3$, $\angle C_2C_3C_4$, $\angle C_3C_4C_5$, $\angle C_6C_1C_2$, and $\angle HCH$, where the numbers denote the positions of the carbon atoms in the ring, as shown in Fig. 1, and where r denotes the internuclear distance between the atoms shown in the subscripts. Therefore, we have to make six additional assumptions.

In our calculations the four internuclear distances and the two angles of $\angle C_6C_1C_2$ and $\angle HCH$ were assumed, and the remaining three angles were determined so as to get agreement between the observed and the calculated rotational constants. For the set I of the structural parameters, the assumed values are those(1) obtained by the electron diffraction. For the set II, the assumed values are those found in the microwave studies of acetone(2) and propane,(6) except that $\angle HCH$ is assumed to be a tetrahedral angle. The values of $r_{C=O}$, r_{1-2}, and $\angle C_6C_1C_2$ are those of acetone, and the values of r_{2-3} and r_{C-H} are those of propane. The angles of the ring obtained are listed in Table 3. Since, for the set II, the angle, β, made by the C=O bond and the a axis is considerably larger than the value of α, the set II seems to be inadequate. With an increase in the values of r_{2-3} or r_{1-2}, or with a decrease in the value of $C_6C_1C_2$, the value of β decreases. By the use of these facts, the sets III and IV, shown in Table 3, are tentatively calculated.

TABLE 3. STRUCTURAL PARAMETERS OF CYCLOHEXANONE

	Set I	Set II	Set III	Set IV
r_{1-2}*	1.54	1.507	1.507	1.516 Å
r_{2-3}*	1.54	1.526	1.535	1.535 Å
r_{C-H}*	1.09	1.096	1.096	1.096 Å
$r_{C=O}$*	1.24	1.222	1.222	1.222 Å
$\angle C_6C_1C_2$*	117°	117°12′	117°12′	116°12′
$\angle$HCH*	109°30′	109°28′	109°28′	109°28′
$\angle C_1C_2C_3$	109°35′	109°25′	109°31′	110°27′
$\angle C_2C_3C_4$	107°48′	119°31′	116°34′	114°39′
$\angle C_3C_4C_5$	106°34′	110°19′	109°40′	110°41′
β	17°05′	23°33′	22°28′	21°55′

β: The angle between the C=O bond and the a axis.

* These values were assumed for each set.

The agreement between the angle of α and that of β is satisfactory in the case of the set I; this favors Romers' data.

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6) D. R. Lide, Jr., *J. Chem. Phys.*, **33**, 1514 (1960).