BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 42 1263—1265 (1969)

Microwave Spectrum of Cyclohexene*1

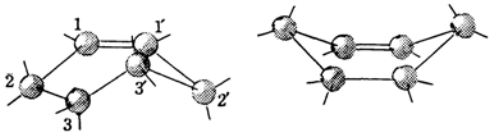
Teruhiko OGATA and Kunio KOZIMA

Laboratory of Molecular Spectroscopy, Tokyo Institute of Technology, Ookayama, Meguro-ku, Tokyo

(Received September 30, 1968)

The microwave spectrum of cyclohexene has been investigated in the frequency region from 7.3 to 27 Gc/sec with a conventional Stark modulation spectrometer, and the spectrum in the ground vibrational state has been assigned. The dipole moment lies entirely along the *b*-principal axis; its value, as obtained from the Stark displacements, is 0.332 ± 0.012D. From the rotational constants and the orientation of the dipole moment, it can be concluded that the equilibrium conformation is a "half-chair" form. Its most probable structure has been determined.

As there are many natural compounds which have a cyclohexene ring, such as terpenes and steroids, it may be considered important to investigate the structure of cyclohexene. Cyclohexene can exist in two conformations without making very great deformations in the normal values of the bond angles, *i.e.*, in a "half-chair" form with C_2 symmetry or in a "half-boat" form with C_s symmetry,[1] as Fig. 1 shows. Beckett, Freeman,



"half-chair" form "half-boat" form

Fig. 1

and Pitzer[2] concluded, by calculating its entropy and gaseous heat capacity, that the "half-chair" form was more stable than the "half-boat" form by about 2.7 kcal/mol. Sakashita[3] reported that no essential difference was observed among the infrared spectra of cyclohexene in the vapor, liquid, and solid states; that the spectrum could be assigned by assuming a single configuration, and that the value of the energy difference estimated by Beckett *et al.*, was reasonable.

X-Ray investigations of pentachlorocyclohexene[4] and naphthalenetetrachloride[5] showed that the molecules have the "half-chair" conformation. However, no detailed structural information is available on cyclohexene.

Experimental

The sample was prepared by dehydrating cyclohexanol.[6] The product was dried over calcium chloride

*1 Presented at the 21st Annual Meeting of the Chemical Society of Japan, Osaka, March, 1968.

1) W. Klyne, "Progress in Stereochemistry," Vol. 1 Butterworths, London (1954), p. 81.

2) C. W. Beckett, N. K. Freeman and K. S. Pitzer, *J. Am. Chem. Soc.*, **70**, 4227 (1948).

3) K. Sakashita, *Nippon Kagaku Zasshi* (*J. Chem. Soc. Japan, Pure Chem. Sect.*), **77**, 1094 (1956).

4) R. A. Pasternak, *Acta Cryst.*, **4**, 316 (1951).

5) M. A. Lasheen, *ibid.*, **5**, 593 (1952).

6) W. M. Dehn and K. E. Jackson, *J. Am. Chem. Soc.*, **55**, 4284 (1933).

and purified by fractional distillation. The infrared spectrum of the sample thus obtained showed no evidence of impurities.

The microwave spectrum was investigated in the frequency region from 7.3 to 27 Gc/sec by using a conventional Stark modulation spectrometer with 110 kc/sec sine- and squar-ewave modulation. All measurements were made at the temperature of dry ice. The frequency measurements were performed with a frequency standard monitored against the standard signals from Station JJY.

Results and Discussion

Microwave Spectrum. The spectrum was found to be quite rich; about 400 sharp and weak lines were observed because of its small dipole moment. No investigation of the electron or X-ray diffraction has yet been made on this molecule. Therefore, the preliminary rotational constants, which were tentatively calculated by assuming the usual values for the bond lengths and the bond angles, were not very useful for the assignments. In order to assign the spectrum, it was necessary to investigate the Stark behavior of many absorption lines.

When the Stark voltage for all the absorption lines in the frequency ranges, which differed by several hundreds Mc/sec from the tentatively-calculated frequencies for the $J=1\rightarrow2$ transitions, were changed, careful examination revealed the lines which were split in two by the Stark effect. By using the three $J=1\rightarrow2$ frequencies thus determined, the rigid-rotor rotational constants were calculated. The assignments of the other transitions, as is shown in Table 2, could be made by the use of these rotational constants. The rotational constants listed in Table 1 were determined so as to get the best fit between these observed and calculated frequencies by assuming a rigid-rotor approximation. In Table 2 the observed frequencies which are marked with * were ascertained by means of their Stark effects. Relative intensity measurements confirmed that these spectrum are due to the vibrational ground state.

The absorption line of the $0_{00}\rightarrow1_{11}$ transtion could not be observed by the spectrometer mentioned above. Therefore, the measurable frequency of the spectrometer was lowered by using 8V69 klystron of the Nippon Elec. Co. and a 6-m J-band absorption cell. As is shown in Table 2, the observed frequency of the $0_{00}\rightarrow1_{11}$ transition is in good agreement with that calculated by the rotational constants.

TABLE 1. ROTATIONAL CONSTANTS AND MOMENT OF INERTIA OF CYCLOHEXENE IN THE GROUND VIBRATIONAL STATE*

Rotational constant Mc/sec		Moments of inertia amu·Å²	
A	4739.148±0.01	I_a	106.6387
B	4544.406±0.02	I_b	111.2086
C	2562.402±0.02	I_c	197.2278

* Conversion factor 5.05377×10^5 amu·Å²·Mc/sec is used to caclulate moments of inertia, corresponding to $^{12}C=12$ atomic weight scale.

TABLE 2. GROUND-STATE ROTATIONAL TRANSITIONS OF CYCLOHEXENE (in Mc/sec)

Transition	Observed[a]	Calculated	$\nu_{calc}-\nu_{obs}$
$0_{00}\rightarrow1_{11}$	7301.56	7301.55	−0.01
$1_{01}\rightarrow2_{12}$	12426.36*	12426.35	−0.01
$1_{11}\rightarrow2_{02}$	12218.00*	12217.95	−0.05
$1_{10}\rightarrow2_{21}$	16779.80*	16779.84	+0.04
$2_{02}\rightarrow3_{13}$	17459.19*	17459.18	−0.01
$2_{12}\rightarrow3_{03}$	17444.86*	17444.93	+0.07
$2_{11}\rightarrow3_{22}$	21904.66*	21904.64	−0.02
$2_{21}\rightarrow3_{12}$	21252.62*	21252.58	−0.04
$2_{20}\rightarrow3_{31}$	26350.00*	26350.10	+0.10
$3_{03}\rightarrow3_{12}$	10337.85	10337.88	+0.03
$3_{13}\rightarrow3_{22}$	10405.23	10405.12	−0.11
$3_{03}\rightarrow4_{14}$	22576.76*	22576.80	+0.04
$3_{13}\rightarrow4_{04}$	22576.18*	22576.19	+0.01
$3_{12}\rightarrow4_{23}$	26771.22*	26771.32	+0.10
$3_{22}\rightarrow4_{13}$	26699.18*	26699.29	+0.11
$4_{04}\rightarrow4_{13}$	14528.38	14528.24	−0.14
$4_{13}\rightarrow4_{22}$	10224.93	10225.04	+0.11
$4_{14}\rightarrow4_{23}$	14532.39	14532.40	+0.01
$4_{04}\rightarrow5_{15}$	27701.08*	27701.22	+0.14
$4_{14}\rightarrow5_{05}$		27701.20	+0.12
$5_{14}\rightarrow5_{23}$	14505.18	14505.31	+0.13
$5_{24}\rightarrow5_{33}$	14521.72	14521.78	+0.06
$5_{23}\rightarrow5_{32}$	10073.90	10074.04	+0.14
$5_{33}\rightarrow5_{42}$	10512.43	10512.65	+0.22
$5_{42}\rightarrow5_{51}$	7745.10	7745.36	+0.26

a) ±0.1 Mc/sec

Dipole Moment. The dipole moment for the ground vibrational state was determined from the Stark displacements of the $1_{10}\rightarrow2_{21}$ and $1_{01}\rightarrow2_{12}$ transitions. The observed and calculated Stark coefficients are given in Table 3. The absorption cell was calibrated using the $J=1\rightarrow2$ transition of OCS, taking the dipole moment of OCS as 0.7124.[7]

TABLE 3. STARK COEFFICIENTS AND DIPOLE MOMENT

Transition	M	$\Delta\nu/E^2$ (Mc/sec)/(kV/cm)²	
		Observed	Calculated
$1_{10}\rightarrow2_{21}$	0	0.402	0.405
	1	−2.852	−2.826
$1_{01}\rightarrow2_{12}$	0	0.556	0.547
	1	3.400	3.455
$\mu=0.332\pm0.012$D			

7) S. A. Marshall and I. Weber, *Phys. Rev.*, **105**, 1502 (1957).

The value of the dipole moment of 0.332 D obtained by us is considerably lower than those of 0.75D[8] (in a hexane solution), 0.63 D[8] (in a CCl_4 solution), and 0.61 D[9] (in vapor) obtained by Debye's method. Our value supports Smyth's suggestion[10] that the value of 0.61 D is too high. Kumler *et al.*[11] obtained the value of 0.21 D (in a heptane solution) for this molecule by Debye's method. This value is a little lower than ours. However, their value of the atomic polarization, as estimated from those of analogous compounds, seems to be nearly correct.

A possible upper limit for the μ_c component of the dipole moment could be estimated from the Stark effect of the $1_{01}\rightarrow 2_{12}$ transition, since the effect of μ_c on the observed Stark effect would be to alter the Stark effect of the μ_b component. By assuming the error in the frequency measurement to be ± 0.1 Mc/sec, it could be estimated that the possible upper limit of the value of μ_c is 5.84×10^{-3}D. Therefore, it is very probable that the value of μ_c is zero within the limits of exprimental error.

Molecular Structure. The possibility of the "half-boat" form can be excluded in view of the fact that the value of μ_c is zero or nearly zero. As a possible structure, a planar cyclohexene ring might be considered, because the μ_c value of the molecule with this ring should be zero. In this case, as the molecule has C_{2v} symmetry, the quantity of $(I_c-I_a-I_b)/2$ is given approximately by $8mr^2\sin^2(\theta/2)$, where θ is the valency angle of $\angle$H–C_i–H and where r is the bond length of the C_i–H bond ($i=2$, 2′, 3, and 3′; see Fig. 1). By assuming that θ is 109°28′ and that r is 1.10Å, we can obtain $(I_c-I_a-I_b)/2=-6.687$ amu·Å^2. Since this value is quite different from the observed value of -10.3098 amu·Å^2, the possibilities of a planar ring and of a nearly planar ring can be eliminated. Therefore, as a remaining possibility we have to check whether or not the molecule has the "half-chair" form.

As the molecule of the "half-chair" form should have C_2 symmetry, the value of μ_c is zero, in agreement with the experimental fact. Next we have to obtain a reasonable set of structural parameters so as to get the best fit between the observed and the calculated principal moments of inertia. However, as there are many structural parameters to be determined, a number of assumptions or approximations are necessary. It is reasonable to consider that the ethylene group of $\overset{H}{C}\!>\!C=C\!<\!\overset{H}{C}$ has a planar structure. Furthermore, the following assumptions may be safely made:

(1) the C–H bond of the ethylene group is located along the angle bisector of $\angle$C=C–C;

(2) the angle bisector of $\angle$H–C_i–H is that of $\angle$C–C_i–C ($i=2$, 2′, 3, and 3′);

(3) the angles of $\angle$H–C_i–H are tetrahedral;

(4) the internuclear distance, r_{2-3}, between C_2 and C_3 is equal to that, $r_{3-3'}$ between C_3 and $C_{3'}$ and

(5) all aliphatic C–H bonds are of equal length.

When taking into account the relation that only two of three $\angle$CCC bond angles are independent, there are still seven structural parameters to be determined.

By calculating the value of $\partial I_i/\partial X_j$, where I_j is the jth moment of inertia and X_i is the ith structural parameter, we can see that the angles of $\angle$C=C–C and $\angle$C–C–C and the bond length of C=C and C–C are highly sensitive to the values of the moment of inertia. By assuming the values of the aliphatic and the olefinic C–H bond lengths, r_{C-H} and $r_{=C-H}$; the double bond length, $r_{1-1'}$, and either r_{1-2} or r_{2-3}, the values of the two $\angle$CCC bond angles and either r_{1-2} or r_{2-3} were determined so as to get a good fit for the observed moments of inertia. For each set of structural parameters the value of $r_{1-1'}$ was assumed to be that of propylene.[12] For the set I, all the assumed values are those of propylene. For the set II, the assumed values of r_{2-3} and r_{C-H} are those of ethane,[13] while $r_{=C-H}$ is that of ethylene.[14] For the set III, the values of r_{2-3}, r_{C-H}, and $r_{=C-H}$ are those of propane,[15] ethane, and ethylene respectively.

The calculated values of the set III do not seem reasonable, because the r_{1-2} value is almost the same to that of r_{2-3}. The values of the sets I and II are not so different from each other. The values of both sets are very probable for the structural parameters of this molecule.

TABLE 4. STRUCTURAL PARAMETERS OF CYCLOHEXENE

	Set I	Set II	Set III
$r_{1-1'}$	1.336*	1.336*	1.336Å*
r_{1-2}	1.501*	1.495	1.523Å
$r_{2-3}=r_{3-3'}$	1.541	1.543*	1.526Å*
$r_{=C-H}$	1.090*	1.086*	1.086Å*
r_{C-H}	1.098*	1.102*	1.102Å*
$\angle C_1'C_1C_2$	123°48′	123°51′	123°22′
$\angle C_1C_2C_3$	111°32′	111°46′	111°08′
$\angle C_2C_3C_3'$	110°22′	110°19′	110°55′

* These values were assumed.

8) M. Puchalik, *Acta Phys. Polon.*, **4**, 145 (1935).
9) M. Kubo, *Sci. Pap. Inst. Phys. Chem. Res. Tokyo*, **32**, 26 (1937).
10) C. P. Smyth, "Dielectric Behavior and Structure," McGraw-Hill Book Co., New York (1955), p. 263.
11) W. D. Kumler, R. Boikess, P. Bruck and S. Winstein, *J. Am. Chem. Soc.*, **86**, 3126 (1964).
12) D. R. Lide, Jr., and D. Christensen, *J. Chem. Phys.*, **35**, 1374 (1961).
13) G. E. Hansen and D. M. Dennison, *ibid.*, **20**, 313 (1952).
14) H. C. Allen, Jr., and E. K. Plyler, *J. Am. Chem. Soc.*, **80**, 2673 (1958).
15) D. R. Lide, Jr., *J. Chem. Phys.*, **33**, 1514 (1960); Note added in proof–*cf. ibid.*, **49**, 2368 (1968).