L. V. VILKOV, N. I. SADOVA

CHEMISTRY

1965

SovietRxiv

Fig. 1. Configurations of rotational isomers of the phenylcyclopropane molecule

Figure 1: Fig. 1. Configurations of rotational isomers of the phenylcyclopropane molecule

Abstract

Full Text

L. V. VILKOV, N. I. SADOVA

ELECTRON-DIFFRACTION STUDY OF THE STRUCTURE OF PHENYLCYCLOPROPANE MOLECULES

(Presented by Academician B. A. Kazanskii, November 9, 1964)

CHEMISTRY

The physical and chemical properties of compounds containing a cyclopropane ring adjacent to a multiple bond indicate the presence of conjugation in them ([1–3]).

Theoretical concepts of the structure of cyclopropane ([1,4]) make it possible to explain conjugation in such compounds and provide a means of predicting the configurations of the corresponding molecules. In particular, for the phenylcyclopropane molecule, in accordance with these concepts, configuration I (Fig. 1) is the most probable, in which the plane of the phenyl ring is perpendicular to the plane of the three-membered ring, whereas configuration II is less probable. However, in configuration I, as compared with II, there are significant steric interactions that are not taken into account by the indicated concepts.

Fig. 1. Configurations of rotational isomers of the phenylcyclopropane molecule

In a number of works ([1,3]), attempts were made to determine the configuration of the phenylcyclopropane molecule. Aleksanyan and Sterin ([3]) studied regularities in the intensities of the lines of combination scattering of a series of aromatic compounds including the cyclopropane ring. On the basis of stereochemical concepts and changes in conjugation effects determined from the intensities of the spectra, the authors concluded that the phenylcyclopropane molecule has a configuration of type I, consistent with the concept of conjugation.

Nevertheless, it is undoubtedly of interest to determine directly the structure of the phenylcyclopropane molecule. The present work gives the results of such a study, performed by the method of electron diffraction in the gas phase.

Electron diffraction patterns of phenylcyclopropane vapor (b.p. 172—173°; n_D^{20} 1.5336) were obtained by the previously described procedure ([5]) with an r^3

sector at two distances between the nozzle and the plate (140 and 260 mm). It was assumed that the blackening density is directly proportional to the intensity in accordance with the calibration curve for the given series of plates.

To separate the molecular component of the scattering intensity $M(s)$, smooth background lines were drawn on the averaged intensity curves. In doing so, we were guided by the region of background lines calculated theoretically for various trial models of the phenylcyclopropane molecule.

The experimental curve $sM(s)$, into which a correction for nonnuclear scattering had been introduced, was used to calculate two radial distribution curves $f(r)$, differing from one another in the method of extrapolating the curve $sM(s)$ into the region from 0 to 3 $Å^{-1}$. In curve a (Fig. 2) the extrapolation was carried out with the theoretical curve $sM(s)$, calculated for isomer I; in curve b, for isomer II. The two curves practically completely coincide with one another. After correcting the error wave in the initial region of curve a (Fig. 2), the final experimental radial distribution curve was obtained (Fig. 2, v).

Fig. 2. Experimental and theoretical curves $f(r)$

The first two peaks of the curve $f(r)$ have maxima at $r = 1.085$ Å and $r = 1.423$ Å and correspond to the internuclear distances of the C-H and C-C bonds, respectively. Since the geometrical parameters of the benzene molecule are well known, the theoretical curve $f(r)$ for the phenyl radical was subtracted from the experimental radial distribution curve. On the resulting difference curve there are two symmetrical peaks at $r = 1.08$ Å and $r = 1.50$ Å. The first peak corresponds to the internuclear distances C-H in cyclopropane; the second peak includes the three C-C bonds of the three-membered ring and the C_1—C_7 bond between the rings. The symmetrical form of the second peak indicates that r(C—C) in cyclopropane and $r(C_1—C_7)$ are close to one another; therefore all of them were taken to be equal to 1.50 Å.

From the peaks of the difference curve at 1.08 Å and 1.50 Å, the root-mean-square amplitudes of vibration of the C-H and C-C bonds in cyclopropane and of the C_1—C_7 bond were also determined by the least-squares method. l(C—C) proved to be 0.055 Å, and l(C—H) = 0.039 Å, on the assumption that for benzene $l(\mathrm{C}\cdots\mathrm{C}) = 0.045$ Å, l(C—H) = 0.073 Å.

The theoretical curve $f(r)$, calculated for the parameters: $r(\mathrm{C}\cdots\mathrm{C}) = 1.40$ Å, $l(\mathrm{C}\cdots\mathrm{C}) = 0.045$ Å, r(C—H) = 1.083 Å, l(C—H) = 0.073 Å, in benzene; r(C—C) = 1.50 Å, l(C—C) = 0.050 Å, r(C—H) = 1.08 Å, l(C—H) = 0.075 Å, in cyclopropane; $r(C_1—C_7) = 1.50$ Å and $l(C_1—C_7) = 0.050$ Å, agrees well with the experimental one in the region of the first two peaks. Thus the relative error $\sigma(f)/f_{\max} = 0.01$ for the C-H peak, and $\sigma(f)/f_{\max} = 0.02$ for the C-C peak. The position of the C-H peak in the theoretical curve $f(r)$ coincides, to within approximately 0.001 Å, with the experimental one, while the position of the C-C peak differs from the experimental one by approximately 0.005 Å (see the note to Table 1).

Fig. 3. Experimental and best theoretical curve $sM(s)$

Figure 2: Fig. 3. Experimental and best theoretical curve $sM(s)$

Table 1

Basic parameters and positions of the peaks of the radial distribution curve (Figs. 1, 2)

Curve $f(r)$	Isomer	α°	Position of maximum (in Å), 4	Position of maximum (in Å), 5	Position of maximum (in Å), 7	Position of maximum (in Å), 8
Exp. *			3.14	3.38	4.43	5.14
(c)						
Theor. 1 **	I	125	3.07	3.41	4.36	5.01
2	I	127	3.09	3.40	4.38	5.03
3	I	128.5	3.11	3.38	4.39	5.07
4	I	130	3.13	3.38	4.45	5.26
5	I	133	3.18	3.34	4.55	5.26
6	II	127	3.18	–	–	–
7	II	130	3.28	–	–	–
8	II	133	3.31	–	–	–
9	free rotation	130	3.40	–	–	–

* Peaks 1, 2, 3, and 6 are located at $r = 1.085$; 1.432; 2.44 and 3.82 Å, respectively.
** Peaks 1, 2, 3, and 6 are located at $r = 1.085$; 1.427; 2.44 and 3.82 Å, respectively.
(c) Parameters not varied in calculating the theoretical curves are given in the text.

The mutual spatial arrangement of the benzene and cyclopropane rings is characterized by the valence angles $C_1C_7C_8$ and by the angle φ, which determines the rotational isomerism (Fig. 1). Instead of the valence angles $C_1C_7C_{8(9)}$, it is convenient to introduce the angle α, formed by the bond C_1—C_7 with the plane of the cyclopropane ring (Fig. 1).

To determine these parameters from the experimental curve $f(r)$, theoretical radial-distribution curves were calculated for the phenyl and cyclopropyl radicals. On the resulting difference curve, two peaks at $r = 3.12$ Å and

Fig. 3. Experimental and best theoretical curve $sM(s)$

Fig. 4. Potential curves for the phenylcyclopropane molecule

Fig. 4. Potential curves for the phenylcyclopropane molecule

Figure 3: Fig. 4. Potential curves for the phenylcyclopropane molecule

3.81 Å were analyzed in greatest detail. The peak at 3.12 Å for isomer I can be assigned to $r(C_6 \ldots C_{8(9)})$, which leads to $\alpha = 129.5^\circ$; for isomer II it can be assigned to $r(C_6 \ldots C_8)$, $r(C_2—C_9)$, and then $\alpha = 121^\circ$. The second peak includes $r(C_7 \ldots C_{3(5)})$, which does not depend on the angles α and φ and is equal to 3.79 Å, as well as $r(C_2 \ldots C_{8(9)})$ for isomer I or $r(C_2 \ldots C_8)$, $r(C_6 \ldots C_9)$ for isomer II. In the analysis of the peak this second distance is found to be approximately 3.83 Å, whence in the case of isomer I $\alpha = 131^\circ$, and in the case of isomer II $\alpha = 139^\circ$.

Comparison of the results of analyzing the peaks at $r = 3.12$ Å and $r = 3.81$ Å shows that for isomer I the values of the angle α agree well, whereas for isomer II there are substantial discrepancies. This is one of the arguments in favor of isomer I.

Refinement of the sought parameters and of the form of the rotational isomer was carried out by comparing the experimental curves $sM(s)$ and $f(r)$ with theoretical curves calculated for several models. Thus, for isomer I, the following values were assigned for α: 120; 122.5; 125; 127; 128.5; 130, and 133°; the last five curves $f(r)$ are shown in Fig. 2 (curves 1-5). For isomer II, α took the values 122.5; 127; 130; 133°; the last three curves $f(r)$ are depicted in Fig. 2 (curves 6-8). In addition, curves $sM(s)$ and $f(r)$ were calculated for free rotation at $\alpha = 130^\circ$ (Fig. 2, curve 9).

The positions of the peaks depending on the angles α and φ are given in Table 1. The best agreement of the theoretical curves $f(r)$ and $sM(s)$ with the experimental ones, both in shape and in the positions of the maxima, is obtained for isomer I with $\alpha = 128.5^\circ$. Figure 3 shows the theoretical curve $sM(s)$, calculated for this model, and the experimental curve.

Thus, as a result of the investigation of the structure of the phenylcyclopropane molecule, in agreement with $r(C{=}C) = 1.40 \pm 0.01$ Å and $r(C—H) = 1.08 \pm 0.02$ Å for the benzene ring, it was found: $r(C—C) = 1.50 \pm 0.02$ Å, $r(C—H) = 1.08 \pm 0.02$ Å in the cyclopropane ring; $r(C_1—C_7) = 1.50 \pm 0.03$ Å; $\alpha = 128.5 \pm 3^\circ$, correspondingly the valence angle $C_1C_7C_{8(9)} = 122.5 \pm 3^\circ$; the predominant isomer is isomer I. In this case, the errors in the bond lengths were calculated from the approximate equation 12a (6)

taking into account the scale error ($\sim 0.2\%$). The error in α was estimated from variation of this parameter.

The values obtained for $r(\mathrm{C-C})$ and $r(\mathrm{C-H})$ in cyclopropane agree with the data of other authors. Thus, in cyclopropane $r(\mathrm{C-C}) = 1.510 \pm 0.002$ Å, $r(\mathrm{C-H}) = 1.089 \pm 0.003$ Å ([7]).

The length of the $\mathrm{C_1-C_7}$ bond may, as a convention, be compared with the

bond length in propylene, equal to 1.501 ± 0.004 Å ([8]).

One of the most interesting questions concerning the structure of the phenylcyclopropane molecule is the rotational isomerism about the central $C_1 - C_7$ bond. The configuration of the rotational isomer of phenylcyclopropane agrees with that previously predicted on the basis of the concept of conjugation. It was of interest to determine the form of the rotational potential about the $C_1 - C_7$ bond, caused by the interaction of nonbonded atoms. For this purpose, of the numerous semiempirical equations, the following were used ([9,10]):

$$U = Ae^{-\beta r} - Be^{-2\beta r}, \tag{1}$$

$$U = Ce^{-\alpha r} - \frac{D}{r^6}. \tag{2}$$

where A, B, C, D, α, and β are constants for the C—C, C—H, and H—H bonds.

Both methods led to substantially different quantitative, but qualitatively similar, results (Fig. 4). In this case the difference in the energies of the two isomers according to equation (1) is ~ 20 kcal/mol, and according to equation (2) ~ 0.3 kcal/mol; correspondingly, the barrier of rotation from isomer II to I is 23 kcal/mol (substantially hindered rotation) and 0.4 kcal/mol (free rotation).

Despite the approximate nature of the calculations carried out, it may be concluded that the interaction only of nonbonded atoms in the phenylcyclopropane molecule does not determine the configuration of the rotational isomer. Establishing the nature of the interaction of bonds in various rotational isomers is an important problem in the theory of chemical structure ([11,12]).

The authors express their deep gratitude to Yu. S. Shabarov and V. K. Potapov for providing the phenylcyclopropane sample and for extremely useful discussions of the questions addressed.

Moscow State University
named after M. V. Lomonosov

Received
4 XI 1964

CITED LITERATURE

[1] J. F. Music, F. A. Matsen, J. Am. Chem. Soc., **72**, 5256 (1950).
[2] R. Ya. Levina, Yu. S. Shabarov et al., Vestn. Moskovsk. univ., No. 5, 145 (1957).
[3] V. T. Aleksanyan, Kh. E. Sterin, DAN, **131**, 1373 (1960).
[4] M. E. Dyatkina, Ya. K. Syrkin, DAN, **122**, 837 (1958).
[5] L. V. Vilkov, V. S. Mastryukov, P. A. Akishin, Zhurn. strukturn. khim., **4**, 323 (1963).

[6] R. A. Bonham, L. S. Bartell, J. Chem. Phys., **31**, 702 (1959).
[7] O. Bastiansen, F. N. Fritsch, K. Hedberg, Acta crystallogr., **17**, 538 (1964).
[8] D. R. Lide, D. Christensen, J. Chem. Phys., **35**, 1374 (1961).
[9] V. Magnasco, Nuovo Cimento, **24**, No. 3, 425 (1962).
[10] N. P. Borisova, M. V. Vol' kenshtein, Zhurn. strukturn. khim., **2**, 346 (1961).
[11] E. B. Wilson, Proc. Nat. Acad. Sci. U.S.A., **43**, 816 (1957).
[12] N. P. Borisova, M. V. Vol' kenshtein, Zhurn. strukturn. khim., **2**, 469 (1961).

Note: Figure translations are in progress. See original paper for figures.