On the Orientation of the π-Electron Cloud in the Cyclopropane Ring

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Abstract

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V. T. Aleksanyan and Kh. E. Sterin

On the Orientation of the π-Electron Cloud in the Cyclopropane Ring

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In studying the Raman spectra of hydrocarbons in which a three-membered ring is adjacent to a double bond or to a phenyl ring, we found an anomalous enhancement of the intensities of certain lines of the three-membered ring and of the double bond, or of both rings, as compared with the same lines of alkylcyclopropanes, alkylbenzenes, and alkenes, i.e., compounds in which there is only one of the named structural elements (^{1}). An analogous effect, but more strongly expressed, is well known in conjugated systems; therefore the observed phenomenon was attributed to conjugation of the three-membered ring with the double bond (ordinary or aromatic).

As is known, the effect of conjugation of two π-bonds is maximal when their π-electron clouds are parallel, and the greater the departure from parallelism, the weaker the conjugation effect. We studied the Raman spectra of the stereoisomers of 1,2-diphenyl- and 1-phenyl-2-cyclopropylcyclopropane (^{2}). Calculation showed that, in the cis isomers, the mutual orientations of the cyclopropyl and phenyl rings most favorable for conjugation cannot be realized because of steric hindrance. Conversely, in the trans isomers such orientations are permissible. And indeed, comparison of the spectra of each pair of isomers showed unambiguously where conjugation is stronger. On this basis the cis form was assigned to the lower-boiling isomers and the trans form to the higher-boiling ones.*

Of particular interest are the results of studying the stereoisomers of 1-phenyl-2-cyclopropylcyclopropane. In the spectrum of the cis isomer the conjugation effect is practically absent; in the spectrum of the trans isomer, however, the magnitude of the effect is the same as in the case of phenylcyclopropane. Consideration of the configurations of the cis isomer showed that steric hindrance is minimal when the phenyl and cyclopropane rings occupy the mutual position A (Fig. 1); in this case, according to theory (^{5,6}), conjugation should not occur.**

Thus, the data presented testify in favor of the existing ideas concerning the structure of the three-membered ring. But this conclusion could not be considered final, since the difference between the sterically most favorable conformation A of cis-1-phenyl-2-cyclopropylcyclopropane and other possible, but sterically less favorable, conformations—including those in which the phenyl ring occupies position B with respect to the cyclopropane ring—is small. Po-

Fig. 1

Figure 1: Fig. 1

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* The influence of the stereochemical factor on the conditions of conjugation of the three-membered ring with substituents was also studied by Cromwell et al. (3,4) using certain derivatives of ethylenimine as examples. These authors judged conjugation from the behavior of the absorption band in the near ultraviolet region and the C=O absorption band in the infrared spectrum. We believe that, for this purpose, Raman spectra are the most convenient and reliable (see (2)).

** Theory asserts that the π-electron "eights" in the cyclopropane molecule are located in the plane of the ring, perpendicular to the planes of the CH_2 groups (5).

Therefore, for a more reliable judgment about the structure of the three-membered ring, it was necessary to study a compound in which, because of steric features, one of the conformations considered, A or B, is fixed more rigidly.

As such an object of investigation, 1,1-diphenylcyclopropane was chosen, where, according to the assumption, each of the phenyl rings should, owing to stereochemical features, occupy position A with respect to the cyclopropane ring.

Fig. 1

The method for measuring the frequencies and intensities at the maxima of the lines has been described previously (7). The integral intensities were determined by direct measurement along the contour of the line every 1—1.2 cm^{-1}.

1,1-Diphenylcyclopropane

$\Delta\nu$ (cm^{-1}): 150 (60, broad)*, 211 (49), 220(50), 263 (14), 285(6), 302(34), 325(3), 336(3), 375(12), 402(45), 451(8), 479(5), 499(2), 537(14), 551(7, background), 563(13), 582(26), 621(90, sharp), 655(6), 670(6), 692(125, sharp), 708(3), 744(4), 738(3), 763(23), 773(12, background), 808(5), 825(10, broad), 842(17, broad), 875(32), 935(60), 989(15, sharp), 1002(540, sharp), 1026(40), 1032(140), 1053(3), 1085(6), 1129(41), 1157(47), 1179(20), 1192(19), 1265(50), 1280(88), 1298(80), 1313(20), 1328(35), 1342(10), 1359(5, broad), 1404(2), 1426(12), 1444(10), 1460(27), 1476(3, broad), 1496(12), 1580(34), 1601(250, broad), 1634**(3), 1684**(3, broad), 2426(15, background), 2449(5, broad, background), 2495(20, broad), 2524(10, broad), 2560(20, broad), 2842(5, background), 288(110, background), 2909(15, background), 2931(10, background), 2978(50), 3005(190, broad), 3064(470), 3084(70), 7315(30), 3200(20).

Discussion of Results

Table 1 gives the results of measurements of the integral intensities of the $\sim$ 1600 cm^{-1} line of the spectrum of 1,1-diphenylcyclopropane, as well as the spectra of 1-phenyl-2-cyclopropyl- and 1,2-diphenylcyclopropanes studied previously. It can be seen that the intensity of the $\sim$ 1600 cm^{-1} line of 1,1-diphenylcyclopropane is much smaller than in the stereoisomers of 1,2-diphenylcyclopropane. The intensity of this line of 1,1-diphenylcyclopropane, per one phenyl ring, is only twice as large as in various alkylbenzenes, and approximately the same as in the cis isomer of 1-phenyl-2-cyclopropylcyclopropane. Since the orientation of each of the phenyl rings relative to the cyclopropyl ring in the molecule of 1,1-diphenylcyclopropane may be regarded as sufficiently definite (A), it is easy to conclude that in this case the phenyl and the cyclopropyl rings are conjugated relatively weakly. As indicated above, this agrees with the conclusion of the theory that the π-electron cloud is located in the plane of the three-membered ring and thereby, apparently, confirms the correctness of its initial assumptions. It should be noted that the relatively weak conjugation between the cyclopropane and phenyl rings in 1,1-diphenylcyclopropane is also confirmed by chemical data: of all the diphenylcyclopropanes studied, the compound in question is characterized by the lowest rate of hydrogenation with cleavage of the C—C bond of the three-membered ring (^{8}).

Table 1

Integral intensities I_∞ of the line $\sim$ 1600 cm^{-1} for certain aromatic compounds

Compounds	I_∞	I_∞ calculated per one phenyl ring
Toluene	290	290
Isopropylbenzene	330	330
Phenylcyclopropane	1150	1150
cis-1,2-Diphenylcyclopropane	2200	1100
trans-1,2-Diphenylcyclopropane	4100	2050
cis-1-Phenyl-2-cyclopropylcyclopropane	600	600
trans-1-Phenyl-2-cyclopropylcyclopropane	1100	1100
1,1-Diphenylcyclopropane	1300	650

* Designations: broad —broad, sharp —sharp, background —background.
** It is not excluded that these lines belong to impurities.

In conclusion, we note that in the spectrum of 1,1-diphenylcyclopropane there is present a very characteristic, for the cyclopropane ring, intense line of stretching vibrations of C–H bonds near 3005 cm^{-1} (1).

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