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Abstract

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VIBRATIONAL SPECTRA OF CYCLOPENTADIENE AND MONODEUTEROCYCLOPENTADIENES

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Recently ([1]) it was shown that substituted cyclopentadienes are characterized by an equilibrium between isomers differing in the positions of the intracyclic double bonds. As a probable transition state in the mutual transformations of the isomers, the system proton—aromatic anion of cyclopentadienyl was considered. It may be assumed that the comparative ease of migration of the system of conjugated double bonds in the ring is due to the existence, already in the ground state of the molecule, of prerequisites for transformations of this kind (some equalization of bonds, etc.). In this case the cyclopentadiene molecule should be somewhat anomalous in its properties directly connected with the structure of its electron cloud, i.e., different from other diene systems.

Valuable information on the character of the bonds and the structure of the electron cloud of cyclopentadiene can be obtained by studying vibrational spectra. The data available in the literature on the spectra of cyclopentadiene itself are incomplete and at times contradictory ([2–6])*. There are very few reliable data on the spectra of its derivatives.

The present communication is devoted to the spectra of cyclopentadiene and isomeric monodeuterocyclopentadienes. We obtained the IR absorption spectra of cyclopentadiene in the liquid and gas phases, and also measured the frequencies and intensities of lines in the Raman spectrum. For individual lines the degrees of depolarization and integral intensities were also measured. In addition, IR absorption and Raman spectra were obtained for 5-monodeuterocyclopentadiene (I) and mixtures of 5—1 (II)—2(III)-monodeuterocyclopentadienes with different contents of the components. The method of synthesis and determination of the percentage content of the isomers in the mixtures, as well as the procedure for obtaining and measuring the spectra, have been described earlier ([1,7,8]).

Cyclopentadiene (constants, see ([1a]))

Raman spectrum, $\Delta\nu$ (cm^{-1})**: 210 (2), 260 (3), 349 (10), 508 (8?), 675 (3), 708 (4), 806 (6), 896 (8), 916 (108), 930 (20, b), 963 (14), 996 (44), 1093 (82),

1108 (330), (1366) (145, s), 1380 (85), 1485 (20, b), 1500 (820, s), 1545 (4), 2885 (440), 2904 (175, b), 2988 (25), 3075 (175, b), 3092 (300), 3154 (40, s).

IR spectrum, ν (cm^{-1})***: 463 (5), 664 (10), 806 (8), 890 (9–10), 916 (9), 960 (9), 992 (1), 1089 (4), 1106 (1), 1176 (0), 1238 (7), 1292 (4), 1366 (9), 1500 (0–1), 1590 (3), 1623 (5), 1715 (0), 1813 (1), 1845 (1–2), 2025 (0), 2195 (0–1), 2723 (1), 2838 (sh.), 2887 (6), 2903 (sh.), 3042 (5), 3076 (6), 3105 (6), 3150 (1), 3225 (0), 3850 (1).

5-Monodeuterocyclopentadiene

Raman spectrum, see ([1a]).

IR spectrum, ν (cm^{-1}): 450 (4), 485 (1), 590 (5?), 650 (10), 791 (8), 847 (9), 912 (7), 1020 (4?), 1153 (1), 1226 (7–8), 1292 (2), 1373 (7–8), 1545 (0–1), 1572 (1), 1613 (2), 1769 (0), 1843 (0–1), 2160 (1–2), 2860 (sh.), 2889 (5), 3043 (3), 3077 (6), 3104 (5).

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* Thus, the IR spectrum of cyclopentadiene reported by Lecomte ([3]) is, for the most part, the spectrum of the dimer.

** s –sharp, b –background, sh. –shoulder.

*** The numbers in parentheses are proportional to absorption in percent; frequency values in the region 2700–3200 cm^{-1} were obtained with a LiF prism.

1- and 2-monodeuterocyclopentadienes (II and III)

Raman spectrum, cm. ([1a]).

IR spectra ν (cm^{-1})*: 453 (4), 466 (4), 541 (8), 625 (10), 680 (9)[a], 756(3)[a], 756(3)[a], 834 (3sh), 877 (2sh), 895 (10), 928 (4sh), 928 (4sh), 950 (3)[a], 965 (3), 981 (2)[a], 1091(1sh), 1120 (4), 1271 (2)[a], 1351 (8), 1370 (?),, 1490 (0–1), 1590–1610 (3), 1718 (0–1), 1795 (0), 1818 (0), 2300 (2), 2340 (0), 2732 (2), 2850 (2sh), 2886 (6), 2900 (4sh), 3044 (4), 3077 (6), 3095 (5–6).

The cyclopentadiene molecule has 27 normal vibrations, which, by symmetry (C_{2v}), fall into 4 classes. Vibrations A (totally symmetric) appear in the Raman spectrum as polarized lines (with the exception of purely deformation vibrations). Assignment of lines to B_1 vibrations (planar asymmetric) can also be made from the degree of depolarization (the corresponding lines in the Raman spectrum are depolarized) and from the rotational contour in the IR absorption spectrum of the gas phase. The bands of these vibrations should have a rotational contour of type A and B (change of the dipole moment along the axes of smaller moments of inertia of an almost symmetric top), i.e., two well-pronounced outer maxima with a weakly pronounced central one, with the distance between the outer maxima $\sim$ 20—25 cm^{-1} ([9,10]).

Table 1

Interpretation of the vibrational spectra of cyclopentadiene

No.	ν, cm^{-1}	Polarization	Contour type of IR gas phase	Assignment	Note
1	3105	–	–	A_1 = C—H	–
2	3092	p	–	A_1 = C—H syn-phase	= C—D 2302
3	2885	p	–	A_1 CH_2	C—D 2156
4	1500	0.07 I_ρ = 1200 (Raman)	–	A_1 C = C	C = C—D 1485
5	1380	0.85*	–	A_1 CH_2	HCD 1228
6	1366	p	$A + B$	A_1	–
7	1108	p	–	A_1 ring pulsation	–
8	996	p	$A + B$	A_1	–
9	930	p	–	A_1(?)	–
10	916	p	$A + B$	A_1	–
11	3075	dp	–	B_1 = C—H	–
12	3042	–	–	B_1 = C—H	–
13	?	–	C?	B_1 CH_2	–
14	1623	–	$A + B$	B_1 C = C	resonates with 1590 (according to Fermi)
15	1292	–	$A + B$	B_1	–
16	1238	–	$A + B$	B_1	–
17	1093	dp	$A + B$	B_1	A_1 = C—H def.?*
18	963	dp	$A + B$	B_1	–
19	2904	–	C	B_2 CH_2	–
20	890	–	C	B_2CH_2	HCD 847

No.	ν, cm^{-1}	Polarization	Contour type of IR gas phase	Assignment	Note
21	806	–	C?	B_2 = C—H	B_1?
22	664	–	C	B_2 = C—H syn-phase	= C—D 541
23	463	–	–	B_2 ring	–

* A high degree of depolarization indicates the deformation character of the vibrations ([11]).

The nonplanar vibrations B_2 should have a rotational contour of type C (a sharply pronounced central maximum with a distance between the two outer ones ~ 35 cm^{-1}). Assignment of lines to the nonplanar vibrations A_2, inactive in the IR spectrum and, apparently, weakly active in Raman, has not yet been carried out. The results are given in Table 1.

Of interest is the behavior of the frequencies of the double-bond vibrations $\nu^{\text{sym}}_{\text{C=C}}(A_1)$ and $\nu^{\text{asym}}_{\text{C=C}}(B_1)$. The vibration ν^{sym} in the Raman spectrum corresponds to the intense polarized line 1500 cm^{-1}; its frequency in the spectrum of I is practically–

* a and are bands of 1- and 2-monodeuterocyclopentadienes, are the combined bands of both isomers; the assignment of unmarked bands is uncertain; bands of isomer I are excluded. For the spectra figures see ([1a,b]).

tically the same, whereas in spectra II and III it is lowered by 15 cm^{-1}. In the IR spectrum the band ν^{sym} is of low intensity; much more clearly expressed here is the vibration ν^{as}, appearing as a double band with components at 1590 and 1623 cm^{-1}. The double character of the band is also retained in the IR spectrum I; however, the components here are considerably shifted and more widely separated; at the same time the ratio of their intensities also changes. All this makes it possible to suppose that the splitting of the ν^{as} band is caused by Fermi resonance with one of the combination tones.

The order of the frequencies of the stretching vibrations C=C in cyclopentadiene, as in the spectra of other cyclic conjugated dienes [12], is reversed in comparison with open-chain dienes having the trans conformation; however, here this effect is expressed most strongly: the magnitude of the frequency separation ($\nu^{\text{as}} - \nu^{\text{sym}} \simeq 120$ cm^{-1}) stands out sharply in the series of cyclic dienes. It may therefore be assumed that, in addition to the dynamic effect leading in cyclic dienes to inversion of ν^{sym} and ν^{as} in comparison with aliphatic dienes [12,13], other factors also play an essential role in cyclopentadiene.

Fig. 1. IR spectrum of cyclopentadiene: "Leitz" instruments (NaCl prism) and IKS-15 (KBr); l (mm). The dimer bands are marked with crosses. A typical contour of a type "C" absorption band of the gas phase (1664 cm^{-1}) is shown.

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In order to obtain the inversion of the frequencies ν^{sym} and ν^{as} observed experimentally and to achieve such a considerable separation between them, it is necessary to introduce into the matrix of dynamic coefficients substantial changes, much larger than for other cyclic dienes; namely, to increase the coefficient of interaction of the double bonds with the central single bond (up to 1.0)*, and to introduce a considerable negative interaction constant between the double bonds (down to −0.5). It is characteristic that similar changes also have to be introduced into the systems of force constants of furan, pyrrole, thiophene, and other five-membered unsaturated heteroaromatic rings, which indicates a considerable similarity of cyclopentadiene to these heterocycles. The appearance of strong interactions of this kind is very characteristic of truly aromatic systems with a closed cloud of π-electrons (benzene, $K_{Q_1Q_2} = 1.04$, $K_{Q_1Q_3} = -0.87$ [14]; ferrocene $K_{Q_1Q_2} = 1.00$, $K_{Q_1Q_3} = -0.85$ [15]). The data obtained may be interpreted as evidence of a partial closed character of the π-electron cloud of cyclopentadiene (quasiaromaticity). This conclusion agrees with the low value of the intensity of the ν^{sym} C=C line in the Raman spectrum in comparison with other dienes [16]. Let us note several important features of the vibrations of the CH_2 group.

The frequency of the scissoring vibration (1380 cm^{-1}) is much lower than its usual value, 1410–1468 cm^{-1} [17]; in spectrum I the line is shifted to 1228 cm^{-1}. We note that in partially deuterated polyethylene an analogous vibration has a frequency of 1300 cm^{-1} [17]. In spectra II and III the frequency of this vibration of CH_2 is slightly lower than in cyclopentadiene (1372 cm^{-1}). The intensity of the band in the IR absorption spectrum of cyclopentadiene is low (apparently it is masked by the intense band at 1366 cm^{-1}).

* In units of 10^6 cm^{-2}.

The intense band at 890 cm^{-1}, shifted in spectrum I (847 cm^{-1}) and changing its position only slightly in spectra II and III (895 cm^{-1}), has been assigned to the pendular vibration of $CH_2(B_2)$. The frequency of this vibration is also clearly anomalous (in paraffin spectra, 720 cm^{-1} [17]).

The totality of these facts can be explained on the assumption that the HCH

angle in cyclopentadiene is smaller than the usual value, although another interpretation of them is also not excluded. In any case, the distinctly anomalous character of the CH_2 group in cyclopentadiene, in comparison with methylene groups in other systems, is quite obvious. This is apparently caused by the fact that the methylene group participates in the general conjugation chain, partially closing it with the formation of a quasi-aromatic system.

Let us dwell in somewhat greater detail on the determination of the percentage content of isomers in the equilibrium mixture of monodeuterocyclopentadienes, carried out in [1a]. As already indicated, the concentration ratio $1 : (II + III)$ in the mixture was determined by comparing the integral intensities of the C=C lines in the Raman spectrum: 1499 (I) and 1485 cm^{-1} (II, III). Assuming that the molar integral intensity of the C=C lines is retained for the various deuterium-substituted compounds, the measured ratio of their intensities ($I_{1499}/I_{1485} = 1 : 2$) should reflect the concentration ratio of the isomers in the mixture. To determine the concentrations of II and III we made use of the ability of cyclopentadienes to dimerize. In this case, the structure of the initial dienes can be determined from the structure of the dimers formed from them. In particular, the dimer of cyclopentadiene itself contains double bonds in the bicyclo-(2,2,1)-heptene (1574 cm^{-1}) and cyclopentene (1614 cm^{-1}) rings. In the spectrum of the mixture of dimers formed from the equilibrium mixture of monodeuterocyclopentadienes, along with these lines, weaker satellite lines appear, shifted in frequency by 15 cm^{-1} and corresponding to deuterated C=C bonds (1559 and 1600 cm^{-1}). The intensity ratio of the lines in each pair proves to be 2:1, which, as a simple statistical analysis* shows, is possible only when the ratio of the initial deuterocyclopentadienes in the mixture is $1 : 1 : 1$. Here again it is assumed that the molar intensities of the C=C-bond lines (in Raman spectra) are retained when hydrogen is replaced by deuterium.

The results of the present work clearly show significant anomalies in the electronic structure of the cyclopentadiene molecule in comparison with other dienes, and a far-reaching similarity to five-membered heteroaromatic rings. We relate all these facts to the special quasi-aromatic character of the cyclopentadiene ring.

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* It is difficult to doubt that the activities of the isomeric monodeuterocyclopentadienes in the diene-synthesis reaction (both as dienes and as dienophiles) will be practically identical.

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