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schematic formulas and vibrational modes: (I), (II), (Ic) 1659 (Raman, IR), (Ia) 1643 (Raman, IR), (IIc) 1638 (Raman), (IIa) 1603 (IR)

Figure 1: schematic formulas and vibrational modes: (I), (II), (Ic) 1659 (Raman, IR), (Ia) 1643 (Raman, IR), (IIc) 1638 (Raman), (IIa) 1603 (IR)

Abstract

Full Text

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OPTICAL STUDY OF THE GEOMETRICAL AND ROTATIONAL ISOMERISM OF CERTAIN DIENES

(Presented by Academician B. A. Arbuzov, December 2, 1959)

Butadiene-1,3 exists, as is known, in the form of two planar conformations—cisoid (I) and transoid (II) ([1]). In these conformations the vibrations of the double bonds are not independent; they are coupled through one single C—C bond, which gives rise to two forms of these vibrations—symmetric (s) and antisymmetric (a). The frequencies of all these vibrations are different. The transoid conformation (II) possesses a center of symmetry, and consequently in the Raman spectrum (k. r. s.) only one higher frequency of the symmetric vibration should be observed (1638 cm^{-1}); in the infrared absorption spectra (i. k. p.), on the contrary, only one lower frequency of the antisymmetric vibration should be observed (1603 cm^{-1}). This was in fact established experimentally in spectra of butadiene-1,3 recorded at room temperature ([2-4]):

The data presented indicate the unconditional predominance in butadiene-1,3 at room temperature of the transoid planar conformation (II) (according to the combined data of physicochemical studies—up to 96%). The cisoid conformation of butadiene-1,3 (I) has no center of symmetry; consequently, both in the Raman spectrum and in the IR absorption spectrum of this conformation, the frequencies of both forms of vibration of the double bonds, (Ic) and (Ia), should be observed, with the more intense frequency being (Ia) in the former and (Ic) in the latter. In the Raman spectrum ([4]) they were indeed observed in the gas phase of butadiene-1,3 at 55°: 1643 and 1659 cm^{-1}, the first being considerably more intense than the second; both lie in a higher region of the spectrum than for (II), owing to the greater energetic strain of (I).* In the IR absorption spectrum, of these frequencies the more intense should be ~1659 cm^{-1}; it was observed in ([3]) at room temperature in the form of a weak band, since under these conditions the cisoid form of butadiene-1,3 exists only as an admixture

structural scheme of isomers III, IV, V, VI, showing non-equivalence/equilibrium between conformations

Figure 2: structural scheme of isomers III, IV, V, VI, showing non-equivalence/equilibrium between conformations

to the transoid form; the frequency ~1643 cm^{-1}, being very weak under these conditions, naturally was not detected.

What has been said is confirmed chemically: at room temperature, butadiene-1,3 enters only slowly into the Diels–Alder reaction because of the unconditional predominance under these conditions of the transoid conformation (II). This reaction proceeds more readily when the temperature is raised, which promotes —

* The considerably higher frequencies of the vibrations of the double bonds in the cisoid conformation (I) of butadiene-1,3 than in ethylene (1621 cm^{-1}) indicate a substantial shortening of the double-bond lengths in (I) compared with the double bond of ethylene as a standard ([2]).

corresponding to the transition of the transoid conformation (II) into the cisoid conformation (I), which is precisely the basis of the Diels—Alder reaction.

In the mono- and disubstituted butadienes-1,3 studied by us below, rotational isomerism is possible, as in butadiene-1,3, but in some cases it is superimposed on geometrical isomerism, as, for example, in 1-chlorobutadiene-1,3 and piperylene (pentadiene-1,3).* As a consequence of such superposition, the following four isomers may be assumed possible for these latter compounds (X = Cl, CH_3):

Naturally, in these substituted butadienes-1,3, as in butadiene-1,3 itself, at room temperature in the liquid phase the transoid conformations (III) and (V) predominate. They have no center of symmetry; therefore in their Raman spectra (as well as in the IR spectra) the frequencies of both

Table 1

Cis (III)	Mixture cis + transtrans (V)	Mixture cis + transcis (III)	Cis (III)	Mixture cis + transtrans (V)	Mixture cis + transcis (III)	Cis (III)	Mixture cis + transtrans (V)	Mixture cis + transcis (III)
Combination-scattering spectrum of cis-1-chlorobutadiene-1,3 and a mixture of cis- and trans-1-chlorobutadiene-1,3, transoid conformations								
175 (5)*184* (4)366 (8)— *628* (3)643 (3*) — 752 (5)—	—— 398 (3sh, dv)466 (5)— 663 (1)745 (3*)– 810 (4)839 (4)	174 (4)*185* (3)366 (6)— 628 (2)*642* (2)— 754 (4*) —	–929 (6sh) –1226 (10sh)1276 (5)*1291* (5)1302 (5)*1325* (4r)*1360* (0sh, dv)– *1421* (6)*1625* (10)	912 (4)– *1157* (6)– *1282* (6) ——— 1408 (2*) —	–929 (5*sh)* *–1226* *(8sh)Coincides* (3)1304 (3)*1325* (2r)*1360* (0sh, dv)– *1421* (4)1625 (9**)	1640 (10*)* — *2846* (1)*2917* (1)– *2954* (3)2973 (3*)– 3014 (10)3091 (6)–	–1649 (3)**1669** (**3**)— *2846 is 1292* 2945 (0)— 3000 (3*)– 3101 (2**) –	1640 (9**) — 2846 (0)2919 (0)– 2956 (1)*2972* (1)– 3014 (7*)3090 (4**) –

Cis (III)	Mixture cis + transtrans (V)	Mixture cis + transcis (III)	Cis (III)	Mixture cis + transtrans (V)	Mixture cis + transcis (III)	Cis (III)	Mixture cis + transtrans (V)	Mixture cis + transcis (III)
Combination-scattering spectrum of cis-piperylene and a mixture of cis- and trans-piperylene, transoid conformations								
–206 (2)*214* *(2)*228 (2)363 (4dv)392 (8)– 615 (4)*626* *(2)*– 886 (4)**– 902** **(4)**914 (2**) –958 (5)–	191 (2)208 (2) ——— 458 (1)481 (8r)– 815 (4sh) –889 (5*)902 (5)– 952 (0)**– 965** **(0)**	——— 390 (3)– 613 (0) ———	–1035 (3sh) —— 1166 (6)– 1252 ~~(9sh)~~ –1297 (8sh)1325 (0)– 1361 (2)– 1387 (4)*1397* *(0)*–	1015 (0)1035 (3dv)1080 (3dv)1110 (3)*1127* *(3)*– 1175 (8)**1190** **(8)**– 1292 (9sh*) –1352 (0)– 1378 (5)—— 1416 (5)	——— 1165 (2**) —— 1253 (4sh)1297 (3*) ———	–1439 (5)**1454** **(5)**– 1638 (10)*1656* *(10)* —— 2857 (3)**– 2918** **(6)**2961 (0)**– 2991** **(2)**– 3014 (8**)3085 (3)	1434 (0)– 1452 (6)*1462* *(4)*– 1645 (10)**– 1670** **(7)**2854 (4)– *2885* *(4)*2917 (8)– *2968* *(2)*– 2996 (9)*3012* *(4)*3089 (5)	——— 1637 (2)**1656** **(2)** ———

Note. Asterisks denote lines situated against a background common with adjacent lines denoted by the same number of asterisks.

forms of vibrations of the double bonds—symmetric and antisymmetric—must be observed; moreover in (V) (as the trans configuration of a disubstituted ethylene) these frequencies must be higher than in (III) (as in the cis configuration of a disubstituted ethylene). All this we did observe. The spectra were investigated

* The data available in the literature on the Raman spectra of some of the compounds studied by us are very unsatisfactory; some of them ([5,6]) contain gross errors, while other spectra ([7]) were obtained almost 30 years ago on instruments of low resolving power, with substantial omissions and the resulting inaccuracies in the region of double-bond vibration frequencies important for our investigation.

cross sections (III): cis-1-chlorobutadiene-1,3 (for the synthesis see (8)) and cis-piperylene. In the spectra there are frequencies of both forms of vibrations of the double bonds—symmetric and antisymmetric: at $X = \mathrm{Cl}$, 1625, 1640 cm^{-1}; at $X = \mathrm{CH_3}$, 1638 and 1656 cm^{-1}. The Raman spectra of trans-1-chlorobutadiene and trans-piperylene were then investigated; these were obtained not in pure form, but as mixtures with the cis configurations (8). In the spectra of the trans configurations, frequencies were also found for both the symmetric and the antisymmetric vibration of the double bonds: at $X = \mathrm{Cl}$, 1649, 1669 cm^{-1}; at $X = \mathrm{CH_3}$, 1645, 1670 cm^{-1}. As the optical study showed, the fraction of the trans configuration in the mixture of cis- and trans-1-chlorobutadiene-1,3 is $\sim 20\%$, and in the mixture of cis- and trans-piperylene $\sim 80\%$ (see Table 1*). In agreement with the above, the frequencies of the double-bond vibrations of the trans configurations in both compounds are higher than those of the cis configurations.

The chemical data are in agreement with what has been set forth above: the cis configurations of the transoid conformation (III), at $X = \mathrm{Cl}, \mathrm{CH_3}$, do not enter into the Diels–Alder reaction even when the temperature is raised, since in this case (III) can pass only into the cis configuration of the cisoid conformation (IV), which is not realized or is realized only with difficulty because of steric hindrance. By contrast, the trans configurations of the transoid conformation (V) enter into the Diels–Alder reaction when the temperature is raised, since under these conditions they pass into the trans configuration of the planar cisoid conformation (VI), which favors the occurrence of this reaction.

For chloroprene and isoprene one may assume two possible planar conformations—transoid (VII) and cisoid (VIII) ($X = \mathrm{Cl}, \mathrm{CH_3}$), as also for 2,3-dimethylbutadiene (IX) and (X), of which at room temperature (VII) and (IX) are predominant:

$$\text{(VII)} \rightleftarrows \text{(VIII)} \qquad \text{(IX)} \rightleftarrows \text{(X)}$$

Conformation (VII), since it has no center of symmetry, should be characterized

in the Raman spectrum (as also in the infrared spectrum) by frequencies of both forms of vibrations of the double bonds—symmetric and antisymmetric, as are the cisoid conformations (VIII) and (X). Conformation (IX), because of the presence in it

Table 2

Combination-scattering spectra of chloroprene, isoprene, and 2,3-dimethylbutadiene

Compound	$\Delta\nu$, cm^{-1}
Chloroprene	236 (1*), 247 (3*), 259 (1*), 378 (1**), 388 (4**), 397 (1**), 511 (0*), 518 (5*), 535 (1*), 631 (7), 881 (3*), 891 (1*), 919 (3**), 931 (3**), 1010 (1*), 1021 (4*), 1032 (1*), 1217 (3), 1289 (8), 1354 (0), 1379 (1*), 1391 (1*), 1421 (8), 1588 (4), 1614 (1*), 1629 (10*), 1658 (1*), 2998 (1**), 3021 (7**), 3051 (1**), 3098 (2*), 3113 (4*), 3128 (2*).
Isoprene	272 (1*), 285 (2*), 291 (1*), 413 (1**), 421 (3**), 431 (4**), 521 (1*), 529 (6*), 537 (1*), 779 (3 sh), 878 (0*), 891 (4* sh), 903 (4* sh), 913 (2*), 955 (5), 996 (3), 1066 (7*), 1072 (2*), 1293 (8* sh, dv), 1304 (3*), 1382 (2), 1416 (2*), 1426 (8*), 1437 (2*), 1598 (1), 1623 (0), 1639 (10 sh), 1658 (0), 2865 (0), 2908 (3), 2931 (3), 2982 (2), 3011 (8), 3088 (3).
2,3-Dimethylbutadiene	383–435 (3, band), 495 (5), 552 (2), 729 (7), 895 (6 sh), 967 (5), 1025 (10), 1341 (3), 1381 (5), 1411 (10), 1443 (3), 1470 (3), 1628 (10* sh), 1652 (4*), 1693 (2), 2706 (2), 2736 (2), 2895 (5*), 2917 (10*), 2947 (4*), 2975 (5*), 3007 (7*), 3092 (7).

a center of symmetry, should be characterized in the Raman spectra by one frequency of the symmetric vibration of the double bonds (in the infrared spectra —by one frequency of their antisymmetric vibration). In the Raman spectra in the liquid phase at room temperature, we found intense

* All the Raman spectra in this article were recorded on a domestic ISP-51 spectrograph and on a Hilger E-612 spectrograph.

frequencies in chloroprene at 1588, 1629 cm^{-1}, and in isoprene at 1598, 1639 cm^{-1}, which belong to the predominant transoid conformations (VII). The weak frequencies 1614(1), 1658(1) in chloroprene and 1623(0), 1658(0) in isoprene owe their origin to insignificant admixtures of cisoid conformations (VIII) (see Table 2). The unquestionable predominance under the indicated conditions of the transoid conformations (VII) is confirmed chemically: under these conditions the Diels–Alder reaction is more readily carried out with increasing temperature, when the transoid conformations (VII) pass into the cisoid ones (VIII). In the Raman spectrum of 2,3-dimethylbutadiene in the liquid phase at room temperature, three frequencies of double-bond vibrations were observed: a very intense 1628 cm^{-1} frequency of their symmetric vibration in (IX), and two weaker frequencies, 1652(4), 1693(2), of the antisymmetric and symmetric vibrations of the double bonds in (X) (see Table 2). According to the optical data, the fraction of the cisoid conformation in the mixture reaches 20–25%. It is known that in the liquid phase at room temperature, 2,3-dimethylbutadiene, unlike all the butadienes discussed above, enters comparatively readily into the Diels–Alder reaction; this is apparently due to the presence under these conditions of a fairly considerable amount of the cisoid conformation (X), which ensures this reaction.

We give the physical properties of the compounds investigated:

Compound	b.p., °C/mm	d_4^{20}	n_D^{20}
cis-1-Chlorobutadiene-1,3 (III)	66.8–67°	0.9553	1.4703
Mixture of cis- and trans-1-chlorobutadiene-1,3 (III) + (V)	67.2–67.5°	0.9537	1.4712
cis-Piperylene	43.2°/747	0.6923	1.4363
Mixture of cis- and trans-piperylene (III) + (V)	41.6°/741	0.6772	1.4304
Chloroprene	58.7°/745	0.9585	1.4883
Isoprene	33.4–33.5°/753	0.6760	1.4212
2,3-Dimethylbutadiene-1,3	67.3°/731	0.7269	1.4385

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