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Abstract

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ON SOME FEATURES OF THE VIBRATIONAL SPECTRA OF CONJUGATED DIENES AND ON THE INFLUENCE OF THE DIENE CONFIGURATION ON THE INTERACTION OF DOUBLE BONDS

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As is known, the values of the vibration frequencies of double bonds $\nu_{\mathrm{C=C}}$ in the spectra of olefins lie in the region 1625–1680 cm^{-1}, varying regularly depending on the type of substitution of the double bond (see, for example, (^{1})). In cycloolefins the values of $\nu_{\mathrm{C=C}}$ depend not only on the type of substitution, but also on the size of the ring and on the character of the cyclic system as a whole (^{2}). Regularities in the behavior of $\nu_{\mathrm{C=C}}$ have found wide application in solving structural-analytical problems. Very little is known about the factors influencing the behavior of $\nu_{\mathrm{C=C}}$ in the spectra of conjugated diene systems, both aliphatic and cyclic (see, for example, (^{3})).

In the spectra of diene systems* two types of coupled vibrations of double bonds appear: symmetric ($\nu^{\mathrm{sym}}_{\mathrm{C=C}}$) and antisymmetric ($\nu^{\mathrm{ac}}_{\mathrm{C=C}}$)**. In identifying $\nu^{\mathrm{sym}}_{\mathrm{C=C}}$ and $\nu^{\mathrm{ac}}_{\mathrm{C=C}}$, one usually uses the values of the degree of depolarization of the line in Raman spectra (Raman), as well as the ratio of band intensities in Raman and infrared absorption (IR) spectra.

Apparently the most reliable criterion is the ratio of line intensities in Raman spectra, whereas the use of other criteria in a number of cases leads to contradictions. For conjugated systems the intensity of the lines of symmetric vibrations of double bonds in Raman spectra is always considerably higher than that of the lines of antisymmetric vibrations. This regularity apparently has a general character and may be associated with the considerable magnitude of the derivative $\partial\nu_e/\partial Q$ for symmetric vibrations, which are accompanied by a change in the overall length of the conjugated system. At the same time, the values of ρ of the lines in Raman spectra and of band intensities in IR spectra are very sensitive to substituents and to changes in the overall symmetry of the molecule, and may be useful mainly in identifying $\nu^{\mathrm{sym}}_{\mathrm{C=C}}$ and $\nu^{\mathrm{ac}}_{\mathrm{C=C}}$ only in the spectra of symmetric dienes.

The assignment of $\nu^{\mathrm{sym}}_{\mathrm{C=C}}$ and $\nu^{\mathrm{ac}}_{\mathrm{C=C}}$ given in Table 1 is based on all the criteria indicated above; in the case of unsymmetrical dienes, it is based chiefly on the ratio of line intensities in Raman spectra.

Consideration of the data in Table 1 permits the following observations:

1. In aliphatic dienes, $\nu^{\text{sym}}_{\text{C=C}}$, as a rule, is substantially greater than $\nu^{\text{ac}}_{\text{C=C}}$ (the exceptions will be considered separately). The considerable separation of the frequencies is connected with the strong interaction of vibrations of the individual $\text{C} = \text{C}$ bonds. There is no clear connection between the frequencies of the diene system and the values of $\nu_{\text{C=C}}$ of the types of monoolefinic bonds composing it; however, a tendency toward an increase in $\nu^{\text{sym}}_{\text{C=C}}$ and $\nu^{\text{ac}}_{\text{C=C}}$ with methyl substitution of the system is observed (as also in the spectra of monoolefins). The question of the relationship between the frequencies $\nu^{\text{sym}}_{\text{C=C}}$ and $\nu^{\text{ac}}_{\text{C=C}}$ of die-

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* Here and below, conjugated dienes are meant.

** Strictly speaking, for symmetric dienes. In the remaining cases these vibrations should properly be called, respectively, in-phase and anti-phase.

Table 1

Parameters of the C=C lines in the Raman spectra of dienes

Substance*	$\nu^{\text{sym}}_{C=C}$ (I^M_∞; ρ)	$\nu^{\text{as}}_{C=C}$ (I^M_∞; ρ)	Note
Butadiene	1637(3200; 0.21)	1592(i.-k.)**(4)	$I_{ac} \gg I_{\text{sym}}$(i.-k.)
Isoprene	1638(3400; 0.24; i.-k.)	1595(i.-k.)(4)	$I_{ac} \gg I_{\text{sym}}$(i.-k.)
2-Ethylbutadiene	1633(k.r.; i.-k.)(5)	1590(i.-k.)(5)	$I_{ac} \ll I_{\text{sym}}$(k.r.)
2-tert-Butylbutadiene (cis-conf.)	1610(k.r.; i.-k.)(5)	1645(i.-k.)(5)	$I_{ac} < I_{\text{sym}}$(i.-k.), $I_{ac} \ll I_{\text{sym}}$(k.r.)
cis-Piperylene	1645}(4800; 0.33; i.-k.)	1594}(240;0.45,i.-k.)	$I_{ac} \simeq I_{\text{sym}}$(i.-k.)
trans-Piperylene	1654}(4800; 0.33; i.-k.)	1604}(240;0.45,i.-k.)	
2,3-Dimethylbutadiene	1630(860***)(6)	1603(i.-k.)(4)	
4-Methylpentadiene-1,3	1650(150***; i.-k.)(4,6)	1604(120***; i.-k.)(4,6)	$I_{ac} < I_{\text{sym}}$(i.-k.)
trans-trans-Hexadiene-2,4	1655(6000; 0.37)	1628(i.-k.)	

Substance*	$\nu^{\text{sym}}_{C=C}$ (I^M_∞; ρ)	$\nu^{\text{as}}_{C=C}$ (I^M_∞; ρ)	Note
3-Methylpentadiene-1,3	1645(4300; 0.28; i.-k.)	1609(400;0.35; i.-k.)	$I_{ac} \simeq I_{\text{sym}}$(i.-k.)
trans-2-Methylhexadiene-2,4	1622}(9500; 0.41; i.-k.)	1623(i.-k.)	$I_{ac} \simeq I_{\text{sym}}$(i.-k.)
cis-2-Methylhexadiene-2,4	1650}(9500; 0.41; i.-k.)	1610(i.-k.)	$I_{ac} \simeq I_{\text{sym}}$(i.-k.)
2,4-Dimethylpentadiene-1,3 (trans-conf.)	1647(k.r.; i.-k.)(13)	1604(k.r.; i.-k.)(13)	$I_{ac} \ll I_{\text{sym}}$(k.r.), $I_{ac} \simeq I_{\text{sym}}$(i.-k.)
2,4-Dimethylpentadiene-1,3 (cis-conf.)	1628(k.r.; i.-k.)(13)	1659(k.r.; i.-k.)(13)	$I_{ac} < I_{\text{sym}}$(k.r.), $I_{ac} < I_{\text{sym}}$(i.-k.)
Dicyclopentenyl (1,1′)	1633(8100; 0.34)	1592(i.-k.)	
Dicyclohexenyl (1,1′)	1635(7500; 0.32)	1618(i.-k.)	
2,5-Dimethylhexadiene-2,4	1668(13000; 0.45)	1622(i.-k.)	
Cyclopentadiene	1500(1200; 0.07)	1623(i.-k.)	
Cyclohexadiene	1578(2600;0.15; .-.)(6)	1604(i.-k.)(4)	$I_{ac} \gg I_{\text{sym}}$(i.-k.)
Cycloheptadiene	1613(4000; 0.21; i.-k.)	1646(200; dp; i.-k.)	$I_{ac} < I_{\text{sym}}$(i.-k.)

* The designations "cis" and "trans" before the name of the diene characterize the type of substitution of the double bonds; in parentheses after the hydrocarbon name the configuration of the double bonds is indicated.
** Observed in the i.-k. (infrared) spectrum.
*** Intensity at the maximum.

The connection between the frequencies of the new system and the frequencies $\nu_{C=C}$ is rather complex. A diene, in comparison with isolated double bonds, constitutes a new system in mechanical and dynamical respects. In a diene a new type of ordinary bond (the central bond) appears between two sp^2-hybridized carbon atoms, absent in olefins. Therefore it is natural to expect some change in the force constants of coordinates that include this bond and the adjacent angles. Finally, one may also assume a change in the force field of the diene caused by the conjugation of the double bonds.

An unambiguous determination of the distinctive features of the force field of dienes by solving the inverse vibrational problem without invoking additional data is hardly possible, even when there is a redundant system of equations for calculating the elements of the matrix $\|K_{ij}\|$. In view of the approximate character of the calculation, it is difficult to detect small, apparently, changes in the coefficients K_{ii}. It is still more difficult to determine the true values of the off-diagonal coefficients K_{ij}, on which the frequencies usually depend little (see, for example, (7)). Sverdlov and Tarasova (8), in calculating the frequencies of butadiene, succeeded in obtaining, on the whole, satisfactory agreement with the experimental frequency values by using a somewhat modified system of force constants of monoolefins. However, the calculation procedure adopted by them in general excluded the possibility of objectively revealing the features of the force field of butadiene: the calculation consisted in varying certain force constants in order to bring the calculated frequencies into agreement with the experimental ones. Such a procedure already contains elements of arbitrariness, if only because

the number of determinable K_{ij} is substantially greater than the number of frequencies. For this reason, the system of force constants for butadiene found by Sverdlov and Tarasova cannot be regarded as objective, which was also confirmed in the present work (see below).

The observed order of the frequencies $\nu_{C=C}^{\text{sym}}$ and $\nu_{C=C}^{\text{as}}$ in aliphatic dienes can be obtained from general considerations, when analyzing the matrices that include the corresponding vibrations*. Thus, the matrix of symmetric vibrations includes the coordinate of the central bond, and the interaction coefficients $D_{C=C,=C-C=}$ (D_{ij} and D_{ji}) are considerable in magnitude and have the same sign. Since $D_{ii}(C=C) > D_{jj}(=C-C=)$, this interaction should lead to an increase in $\nu_{C=C}^{\text{sym}}$. In the matrix that includes the asymmetric vibration of the double bonds, there is no such interaction; therefore $\nu_{C=C}^{\text{as}}$, other things being equal, should be lower than $\nu_{C=C}^{\text{sym}}$. We have considered here the case of symmetric dienes, but it is easy to see that these arguments are, in general, also valid for unsymmetric dienes to the extent that the pseudosymmetry of the vibration is preserved.

2. In analyzing the data of Table 1, it may be noted that in all cyclic dienes without exception the order of the double-bond frequencies is reversed: $\nu_{C=C}^{\text{sym}} < \nu_{C=C}^{\text{as}}$. As possible causes of such an inversion, the following were considered: a) a difference in the mechanical interaction for the cis and trans configurations of the double bonds; b) the specificity of coordinate interaction in cyclic dienes, associated with closure of the diene system into a ring.

The role of the first of these factors is small, as follows from calculation of the spectra of cis- and trans-butadiene with the same system of force constants ([8]). For the frequencies of the trans form, values of 1640 ($\nu_{C=C}^{\text{sym}}$) and 1580 ($\nu_{C=C}^{\text{as}}$) were obtained; for the cis form, 1652 ($\nu_{C=C}^{\text{sym}}$) and 1568 cm^{-1} ($\nu_{C=C}^{\text{as}}$), i.e., in both cases $\nu_{C=C}^{\text{sym}}$ is substantially greater than $\nu_{C=C}^{\text{as}}$.

To assess the role of the second factor, which might prove significant in small rings, a calculation was made of $\nu^{\text{sym}}_{C=C}$ and $\nu^{\text{as}}_{C=C}$ for cyclopentadiene with the same system of force constants as for butadiene**. In doing so, some variation was made in the values, known from the literature (^{9}), of the angles and bond lengths. In all cases the calculated values of $\nu^{\text{sym}}_{C=C}$ proved to be substantially greater than $\nu^{\text{as}}_{C=C}$, in sharp contradiction to experiment. Analogous results are obtained also in the calculation of other cyclic dienes.

Analysis of the $A_g(A_1)$ and $B_u(B_1)$ matrices of butadiene and the corresponding cyclic dienes shows:

1. With one and the same system of force constants, the difference between the matrices of the kinematic coefficients of dienes with a cis configuration and the corresponding matrices of trans dienes leads not to an inversion of the frequencies but, on the contrary, to an increase in the difference $\Delta\nu = \nu^{\text{sym}}_{C=C} - \nu^{\text{as}}_{C=C}$, i.e., to an even greater contradiction with experiment.
2. Generally speaking, it is possible to select a common system of force constants that would correspond to the experimental data on the order of frequencies in both aliphatic and cyclic dienes. However, to do this it is necessary to introduce into the force field of monoolefins such large and unjustified changes that it casts doubt on the objectivity of such a common system of force constants.
3. On the other hand, the order of $\nu^{\text{sym}}_{C=C}$ and $\nu^{\text{as}}_{C=C}$ in cyclic dienes can be explained, without resorting to a substantial restructuring of the entire system of force constants, if one starts from the assumption of a difference between the force field of aliphatic and cyclic dienes. In this case, in order to reconcile the calculations with experiment, it is formally necessary to introduce into the system of force

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* Using, in a first approximation, the force field of monoolefins.

** We take this opportunity to express our sincere gratitude to L. M. Sverdlov and N. V. Tarasova for kindly communicating the complete system of force constants for the planar vibrations of butadiene.

of constant cyclic dienes, a coefficient $H^{*}_{C=C,C=C}$ that is appreciable in magnitude and negative in sign ($-(0.1\text{-}0.2)$) and, in addition, to increase somewhat the coefficient $H_{C=C,=C-C=}$.

The assumption that there is a difference between the force fields of aliphatic and cyclic dienes appears reasonable if one also takes into account other differences between these systems, for example the different absorption spectra in the UV region $^{(10)}$: the absorption band of the N—V transition of cyclic dienes is shifted to the long-wavelength side and is less intense than the corresponding band of aliphatic dienes. The conclusion suggests itself that the peculiarities of the force field of cyclic dienes are due to the cis configuration of the double bonds. This point of view proves very fruitful in considering examples of anomalous behavior of the frequencies of multiple bonds in the vibrational spectra of certain conjugated systems.

Thus, elementary calculations show that the cis configuration of the double bonds (possibly somewhat twisted) in 2-tert.-butylbutadiene is sterically more favorable than the trans configuration. Experimentally, an inversion of $\nu^{\mathrm{sim}}_{C=C}$ and $\nu^{\mathrm{ac}}_{C=C}$ is observed. Another example is the molecule 2,4-dimethylpentadiene-1,3, which exists in the liquid phase as a mixture of rotational isomers. In the cis isomer the order of the frequencies is inverted in comparison with the trans isomer (13). In the same way, i.e., by the different order of the frequencies ν^{sim} and ν^{ac} of multiple bonds in cis and trans configurations, one can explain irregularities in the ratio of the intensities of the $C = C$ and $C = O$ bands in the spectra of certain α, β-unsaturated ketones (14).

An additional check of the correctness of the conclusion concerning the influence of the diene configuration on the order of $\nu^{\mathrm{sim}}_{C=C}$ and $\nu^{\mathrm{ac}}_{C=C}$ can be carried out using 1,2-dimethylenecyclanes as an example.

The results of the present work clearly emphasize the difference between the force field of conjugated dienes and that of olefins with isolated double bonds, which points to the significance of the effects of interaction between double bonds (conjugation) in vibrational spectra. Although these effects are revealed by the example of cis dienes, there is, of course, no reason to believe that they are unimportant in dienes with a trans configuration.

At the same time, the conjugation effect apparently is not the same for cis and trans arrangements of double bonds. This observation, in our view, is essential for characterizing the nature of conjugation as a phenomenon.

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* We note that the formal introduction of a significant nondiagonal coefficient of interaction of multiple bonds proved necessary for explaining the splitting of $\nu_{C=O}^{\text{sim}}$ and $\nu_{C=O}^{\text{ac}}$ in maleic anhydride, succinimide, and other similar systems (11,12).