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A. V. BOBROV, Kh. E. STERIN, and E. V. SOBOLEV

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Abstract

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ON THE DEGREE OF DEPOLARIZATION OF LINES IN THE RAMAN SPECTRA OF HYDROCARBONS WITH CONJUGATED DOUBLE BONDS

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The question of the influence of conjugation on the degree of depolarization of lines in Raman scattering of light has been discussed more than once in the literature. Thus, T. V. Yakovleva (^{1}), M. M. Sushchinskii and V. I. Tolin (^{2}) showed that, in the case of two conjugated C=C bonds, the degree of depolarization ρ of the lines $\Delta\nu_s(\mathrm{C=C})$* is significantly greater than that of the lines $\Delta\nu(\mathrm{C=C})$ of isolated bonds. On passing to three conjugated bonds there is a further increase of ρ for these lines (^{3}). The effect of an increase of ρ for some lines upon conjugation was also observed by P. P. Shorygin (^{4}) and by Ya. S. Bobovich with coauthors (^{5}, ^{6}) in examples of more complex systems. The increase of ρ was explained by the appearance of a "distinguished direction of greatest polarizability of the system, passing through the conjugating elements" (^{6}), in other words, by an elongation of the ellipsoid of the derivative polarizability with respect to the normal coordinate $d\alpha/dQ$ in one direction (^{1}, ^{2}).

However, in the case where conjugated C=C bonds are in a ring, the degree of depolarization ρ of the lines $\Delta\nu_s(\mathrm{C=C})$ turns out to be rather low (^{2}). It is of interest to determine what accounts for such different behavior of ρ in open chains and in rings.

In small rings with the number of carbon atoms $n = 5, 6, 7$, the conjugated bonds are coplanar and are in the cis position (I) relative to one another. In open chains both the cis (I) and trans (II)

$$\mathrm{C{=}C-C{=}C} \quad (I) \qquad \mathrm{C{=}C-C{=}C} \quad (II)$$

positions of the conjugated bonds are possible.** The results of studies of the simplest open system—butadiene-1,3—by various methods, including spectral methods (^{7}, ^{8}), show that in the liquid at room temperature the trans form predominates (~97%). As for various substituted butadienes, in the opinion of many authors, for example (^{9}, ^{10}), at least the simplest of them are found predominantly in the trans form.***

We associate the difference in the values of ρ of the lines $\Delta\nu_s(\mathrm{C}=\mathrm{C})$ of rings and open chains precisely with the difference in the mutual arrangement of the bonds.

The degree of depolarization ρ is related to the invariants of the tensor $\partial\alpha/\partial Q = \alpha'$–the trace $b = \alpha'_1 + \alpha'_2 + \alpha'_3$ and the anisotropy

$$g = \left\{ \frac{1}{2} \left[(\alpha'_1 - \alpha'_2)^2 + (\alpha'_2 - \alpha'_3)^2 + (\alpha'_3 - \alpha'_1)^2 \right] \right\}^{1/2}$$

by the known relation

$$\rho = \frac{6g^2}{5b^2 + 7g^2}. \qquad (1)$$

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* $\Delta\nu_s(\mathrm{C}=\mathrm{C})$ –symmetric valence vibration of double bonds.
** In the absence of steric hindrance the bonds are coplanar.
*** In the absence of significant steric hindrance.

Table 1

No.	Substance	Structural formula	$\Delta\nu$, cm^{-1}	ρ measured	ρ calculated
1	Butadiene-1,3	C=C–C=C	1637	0.21	
2	2-Methylbutadiene-1,3	C=C–C=C | C	1638	0.24	
3	3-Methylpentadiene-1,3	C=C–C=C–C | C	1645	0.28	
4	Pentadiene-1,3	C=C–C=C–C	1656	0.33	
5	Hexadiene-2,4	C–C=C–C=C–C	16551668	0.37	
6	2-Methylhexadiene-2,4	C–C=C–C=C–C | C	16501662	0.41	
7	2,5-Dimethylhexadiene-2,4	C–C=C–C=C–C | | C C	16501667	0.46	

No.	Substance	Structural formula	$\Delta\nu$, cm^{-1}	ρ measured	ρ calculated
8	1-Methylene-4-methylcyclopentene-2	cyclopentene ring with exocyclic =C and methyl substituent	1635	0.32	
9	Cyclopentadiene-1,3	cyclopentadiene ring	1500	0.07	0.06
10	Cyclohexadiene-1,3	cyclohexadiene ring	1579	0.15*	
11	Cycloheptadiene-1,3	cycloheptadiene ring	1610	0.21	0.21
12	Cycloheptatriene	cycloheptatriene ring	1534	0.09	

* Taken from (2).

In the approximation of the valence-optical scheme (11), the components of the tensor α'_{ik} of the whole molecule (its valence part) are expressed in terms of the components of the tensors of the individual bonds $\alpha^{*'}_{mn}$ as follows:

$$\frac{\partial\alpha_{ii}}{\partial Q_l} = \sum_{m,n} \frac{\partial\alpha^*_{mn}}{\partial g_n}\cos^2(mni)\frac{\partial q_n}{\partial Q_l}; \qquad \frac{\partial\alpha_{ik}}{\partial Q_l} = 0 \quad (i \neq k) \tag{2}$$

(Q_l is a normal coordinate; q is a natural coordinate; mni is the angle between the n-th component of the m-th bond and the axis i fixed in the molecule.)

We assign to each conjugated C=C bond its own ellipsoid α^* and assume that the ratio between its components $\alpha^{*'}_1 : \alpha^{*'}_2 : \alpha^{*'}_3$ does not change on passing from a trans to a cis arrangement of the bonds. Such a decomposition of the tensor into individual bonds is, of course, a rather rough approximation, especially for conjugated systems. Nevertheless, the results given below show that even in this approximation the experimental material can be explained satisfactorily.

Then from formulas (2) and (1) it follows that ρ will be smaller for arrangement (I) than for (II). One may also set the goal of determining the ratio $\alpha^{*'}_1 : \alpha^{*'}_2 : \alpha^{*'}_3$ for the cis and trans forms of one compound or of similar systems. By similar systems we mean systems having substitution of the conjugated bonds that is close in character. As measurements show, the value of ρ increases strongly with an increase in the number of substituents at the ends of the conjugated chain (Table 1, Nos. 1, 4–7). At the same time, substitution in a lateral position deschematic diagrams of tensor axes for cis- and trans-forms, with axes labeled α_1', α_1'', α_3', α_3'', α_1^*, α_3^*, and angles 120°

Figure 1: schematic diagrams of tensor axes for cis- and trans-forms, with axes labeled α_1', α_1'', α_3', α_3'', α_1^*, α_3^*, and angles 120°

is less significant (Nos. 2, 3). Differences associated with the cis- or trans-position of substituents relative to the double bonds apparently play a secondary role and may be disregarded in the rough approximation considered here.

In practice, we compare open chains and rings and assume that the ring-closing atom in the latter should be excluded from consideration. Thus, the following pairs of compounds are compared: butadiene-1,3 with cyclopentadiene, pentadiene-1,3 with cyclohexadiene-1,3, and hexadiene-2,4 with cycloheptadiene-1,3.

For measuring ρ, a photographic setup (^{12}) with an inclined illuminator (^{13}) was used. The aperture of the exciting light in the plane lamp—vessel and in the plane perpendicular to the axis of the vessel was limited to 6°. An Osipov prism (^{13}) served to separate the polarized components. The reduction of the observed values of ρ to the true values was carried out graphically. The graph was constructed from known lines of benzene, cyclohexane, and CCl_4.

Using formulas (1) and (2), taking into account the positions of the principal axes of the cis- and trans-forms (the axes α_2^* and α_2' are perpendicular to the plane of the drawing), we found

from the measured values of ρ for the lines $\Delta\nu_s(\mathrm{C=C})$ of cyclohexadiene-1,3 and pentadiene-1,3 (Table 1, Nos. 10 and 4), that the ratio of the tensor axes α^* of one conjugated bond $\alpha_1^* : \alpha_2^* : \alpha_3^*$ is equal to $1.0 : 1.1 : 7.0$. This shows that, in calculations of this kind, the ellipsoid may be considered axially symmetric. Further, taking into account the axial symmetry of the tensor α^* ($\alpha_1^* = \alpha_2^*$), we calculated from the value of ρ for the trans-form the ratio

$$\alpha_1^*/\alpha_3^* = \left(1 - \sqrt{\frac{5\rho}{6-7\rho}}\right) / \left(2\sqrt{\frac{5\rho}{6-7\rho}} + 1\right)$$

for one conjugated $\mathrm{C=C}$ bond, and then ρ for the cis-form as well. It is evident from Table 1 that the values of ρ, recalculated in this way from the trans-forms of butadiene-1,3 and hexadiene-2,4 to the cis-forms, agree well with those measured for cyclopentadiene and, respectively, cycloheptadiene-1,3.

Extending these assumptions to systems of three conjugated double bonds shows that the degree of depolarization of the $\Delta\nu_s(\mathrm{C=C})$ lines of the cis-form should be much lower than that of the corresponding lines of the trans-form. This is well confirmed by the result of studies of cycloheptatriene. The value of ρ for its line $\Delta\nu_s(\mathrm{C=C})$ is 0.09, whereas for trienes with a trans-arrangement of bonds, for example in allo-ocimene (3), $\rho = 0.44$. Such a low value of ρ in cycloheptatriene is connected, in our opinion, chiefly with the cis-arrangement of the double bonds, although in this system, as in some others (cyclopentadiene), the features of the structure of the electron cloud associated with the cyclic nature of the system may also partly manifest themselves.

Thus, the degree of depolarization ρ of the line $\Delta\nu_s(\mathrm{C=C})$ can serve as a means of establishing the mutual arrangement (cis or trans) of conjugated double bonds. For example, in 1-methylene-4-methylcyclopentene-2, which represents a system with a fixed trans position of the double bonds, the value of ρ for the line $\Delta\nu_s(\mathrm{C=C})$ (Table 1, No. 8) is equal to 0.32, i.e., the same as in trans forms of open chains, for example in compounds Nos. 3–5 of Table 1.

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

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