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Yu. P. EGOROV and E. D. LUBUZH

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Abstract

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ON THE APPLICATION OF IR SPECTRA IN THE REGION OF CH VALENCE VIBRATIONS TO DETERMINING THE STRUCTURE OF ALKANES, AROMATIC HYDROCARBONS, AND COMPOUNDS CONTAINING HETEROATOMS

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In a number of studies it has been shown ($^{1-6}$) that, by measuring the intensity of IR absorption spectra in the region of the stretching vibrations of C –H (2800–3000 cm^{-1}), it is possible successfully to determine the number of methyl and methylene groups in molecules of paraffin hydrocarbons, thereby forming a judgment about the structure of these compounds. However, for hydrocarbons containing an aromatic ring or heteroatoms (oxygen, sulfur, silicon, halogen), the solution of such a problem was complicated by the influence of these atoms (groups) on the intensity and position of the bands characteristic of CH_2 and CH_3 groups situated in their immediate vicinity ($^{7-10}$). Having at our disposal a large number of individual compounds, we attempted to determine the limits and possibilities of this method as applied both to alkanes of various degrees of branching and to mono- and diphenylalkanes, certain alkyl tetralins, alkyl naphthalenes, alcohols of normal structure, *n*-alkyl bromides, ketones, and organosilicon hydrocarbons*.

As is known (^{11}), in the region under consideration of the IR spectrum of hydrocarbons four bands are observed: 2875, 2960, 2856, and 2930 cm^{-1}, of which the first two correspond, respectively, to the symmetric and degenerate vibrations in CH_3 groups, and the second two to the symmetric and antisymmetric vibrations in CH_2 groups. The band corresponding to methyl groups is of low intensity. In practice it has been established that the intensities of the bands of antisymmetric vibrations (2930 and 2960 cm^{-1}) are most amenable to accurate measurement; these have high intensity and, in comparison with the symmetric bands, a sharper contour.

Experimental Part

For all compounds, solutions in CCl_4 were prepared at concentrations not exceeding 1-3 g/l, and then IR spectra were recorded in the region 2800-3060 cm^{-1} on an IKS-12 spectrometer with a LiF prism in a cuvette with a constant layer thickness of 1 mm. In addition to the general recording of the spectrum, the intensities at the maxima of the bands 2930 and 2960 cm^{-1} were measured by the "point-by-point" method, with the width of the entrance and exit slits of the spectrometer in this region about 6 cm^{-1} according to the spectrum. Since the bands under consideration overlapped one another, this complex contour was resolved into components. In the resolution it was assumed that the contour of both bands is symmetric and can be described by the Lorentz formula $\left(y = \frac{A}{x^2+B}\right)$, where $4B = (\Delta\nu_{1/2})^2$, and $\Delta\nu_{1/2}$ is the half-width of the band, $A = BD_{\max}$. Such an approximation was successfully used— was also used previously (18,19). As it turned out (see below), the half-width of the 2960 cm^{-1} band for most alkanes was 20 cm^{-1}, and for the 2930 cm^{-1} band, 26 cm^{-1}. The same half-width of the bands was observed for derivatives of benzene, naphthalene, and naphthenes. For alcohols, tetralins, and alkyl halides it increased somewhat. The constancy of the half-widths of the bands and of the distance between these bands in the spectra of compounds with $n_{CH2} > 5$, generally speaking, makes it possible to obtain a calculation formula determining the fraction of overlap of one band by the other. Subsequently the absorption coefficient (ε) was calculated by the usual relation: $\varepsilon = \dfrac{DM}{Cd}$ (M is the molecular weight, C is the concentration in g/l, d is the layer thickness in cm). The correction to the intensity, taking into account the finite slit width of the instrument under the conditions of our experiment, amounted to no more than 5% and was not taken into account (20). By our estimate the total relative error in determining ε did not exceed 6%. The results are presented in Table 1, where for all the classes of compounds studied the following are given: n^0, the number of compounds of the given class investigated; $\varepsilon_{\text{av}}^{(1)}$ and $\varepsilon_{\text{av}}^{(2)}$, coefficients characterizing the absorption of one CH_2 and CH_3 group, respectively ($\varepsilon_{\text{av}} = \varepsilon/n$, where n is the number of the corresponding groups); $\Delta\nu_{1/2}$, the half-width of the corresponding band; A, the influence coefficient (see below).

Table 1

Characteristics of the infrared bands of antisymmetric CH vibrations in CH_2 and CH_3 groups

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* The compounds were synthesized at the Institute of Organic Chemistry of the Academy of Sciences of the USSR; their synthesis is described in papers (12–17).

Types of compounds	n^0	CH$_2$: $\varepsilon_{\text{av}}^{(1)}$	CH$_2$: $\Delta\nu_{1/2}$	CH$_2$: A	CH$_2$: Δn	CH$_3$: $\varepsilon_{\text{av}}^{(2)}$	CH$_3$: $\Delta\nu_{1/2}$
n-Alkanes	7	75	26	0	0	113	20
Methyl-substituted alkanes	13	75	26	0	0	97	24
"T-shaped" alkanes	10	55	26	100	1.33	132	20
[benzene derivative with R substituent]	10	83	26	−40	−0.53	97	21
[naphthalene derivative with R substituent], [biphenyl derivative with R substituent]	17	63	26	60	0.8	100	20
R–[p-phenylene]–R	7	51	26	120	1.6	100	20
[tetralin derivative with R substituent]	5	51	32	120	1.6	98	20

Types of compounds	n^0	CH_2: $\varepsilon_{av}^{(1)}$	CH_2: $\Delta\nu_{1/2}$	CH_2: A	CH_2: Δn	CH_3: $\varepsilon_{av}^{(2)}$	CH_3: $\Delta\nu_{1/2}$
R_3Si—R	10	53	28	110	1.46	120	19
α-$C_{10}H_7$—R	6	43	26	160	2.13	100	20
HO—R	13	43	30	160	2.13	110	20
CH_3—C(= O)—R	9	35	32	200	2.67	120	20
Br—R	11	31	32	220	2.94	110	20
Cl—R	3	21	30	270	3.6	110	20

Discussion of the results

Analysis of the experimental material makes it possible to establish that, both for alkanes of normal structure (6) and for other types of compounds, there is a dependence between the number of CH_2 groups (n) and $\varepsilon_{av}^{(1)}$, which becomes linear beginning with a certain n (see Fig. 1). (For convenience of representation, only some of the curves are shown in Fig. 1.) The rectilinear portion of each curve can be described by the formula $\varepsilon = 75n - A$, where A is a quantity characterizing the influence of groups X ($X = C_6H_5, OH, R_3Si, Hal$, etc.) on neighboring methylene groups of the aliphatic chain R (see Table 1). This influence of substituent X on the CH_2 groups, as is seen from Fig. 1, is manifested in a lowering of the intensity of the bands of the CH_2 groups, and the number of CH_2 groups to which the influence of X extends depends on the nature of X.

The greatest influence, in comparison with alkanes ($X = CH_3$, for which $A = 0$), is exerted by a halide (A for Br 200, Cl 270). Since $\varepsilon_{av}^{(1)}$ depends on n ($\varepsilon_{av}^{(1)} = 75 - A/n$) for all classes of compounds where $A \neq 0$, the number of CH_2 groups in the molecule should be determined from the formula $n = \varepsilon/75 + \Delta n$, where $\Delta n = A/75$, or graphically. (In Table 1 $\varepsilon_{av}^{(1)}$ was calculated for $n = 5$.) Δn is numerically equal to the number of CH_2 groups that "disappears" owing to the influence of substituent X on the intensity of the CH_2 groups nearest to it. The influence of X is also reflected in the intensities of the bands of CH_3 groups. For example, the band of a CH_3 group at an aromatic ring (in toluene) has an intensity of 30 units, in ethylbenzene (β-position to C_6H_5) 65 units, and farther on has the value indicated in Table 1. Almost analogously, the intensity of the CH_3 band changes in organosilicon compounds; for example, in $Si(CH_3)_4$ $\varepsilon = 175$ units, i.e. $\varepsilon_{av}^{(2)}$ per CH_3 group is about 44 units; for a CH_3 group in the β-position to Si, $\varepsilon_{av}^{(2)} = 70$ units, in the γ-position—110 units, etc. In haloalkanes the change in the intensities of the bands of the α-, β-, and γ-CH_3 groups is still sharper. However, in all cases $\varepsilon_{av}^{(2)}$ for a CH_3 group located in the δ-position and beyond already has the constant value given in Table 1; therefore, for $n_{CH_2} > 3$, the number of methyl groups can be determined from the additive scheme.

Figure 1

Figure 1: Figure 1

Fig. 1. Dependence of the intensity of the band ~ 2930 cm^{-1} on the number of CH_2 groups:
1—*n*-alkanes, 2—C_6H_5—R, 3—$(CH_3)_3Si$—R, 4—HO—R, 5—Br—R.

As is seen from Table 1, the half-widths of the 2930 and 2960 cm^{-1} bands ($\Delta\nu_{1/2}$) for the investigated types of compounds vary little; and since there is a linear dependence between the intensity at the band maximum and the number of CH_2 and CH_3 groups, it may be assumed that their integrated intensity is also a linear function of the number of groups.

Let us dwell on certain details revealed in the study of the spectra of particular compounds. In a repeated and careful study of alkanes (cf. $^{(4)}$) it was found that methyl-substituted alkanes (2-methyl-, 3,5-dimethyl-, 2,4,6-trimethylalkanes and similar compounds), in the intensity characteristics of the i.r. bands, differ very little from *n*-alkanes (Table 1), but alkanes of "T-shaped" structure (for example, 4-propylheptane, 5-butylnonane) have a coefficient *A* equal to 100, which leads to a "loss" of 1.33 CH_2 groups for each branching. In alkanes with two adjacent quaternary carbon atoms, splitting of the CH_3-group band at 2960 cm^{-1} is observed, not always resolved by the instrument. Owing to this the visible contour of the band attains a half-width of the order of 45 cm^{-1}. This effect sometimes also appears in hydrocarbons with one quaternary carbon atom, which leads to some lowering of the mean absorption coefficient for CH_3 groups, but without a noticeable change in $\varepsilon_{av}^{(1)}$ for CH_2 groups. In monosubstituted cyclohexane the opposite effect is observed—a certain increase in $\varepsilon_{av}^{(1)} CH_2$; this effect is additively extended to compounds with two or more cyclohexyl radicals (with four rings *A* is equal to 160). In determining the structure of compounds containing several radicals at an aromatic ring (but not in ortho positions, where steric factors are substantial), it is necessary to take into account the influence of the ring on each of the radicals R. Thus, from a comparison of the data in Table 1 it is seen that *A* in disubstituted alkylbenzenes (the same in diphenyl) is twice as high as in monosubstituted ones.

The change in the intensity of the CH-vibration bands under the influence of the substituent X occurs simultaneously with a shift of the bands (toward longer wavelengths for X = Hal, OH, and toward shorter wavelengths for X of the type C_6H_5, R_3Si—). Therefore, in a short carbon chain (ethyl, propyl) it is not always possible to assign the observed bands unambiguously to the CH_2 and CH_3 groups. When, however, the chain contains more than four adjacent methylene groups, the bands at 2960 and 2930 cm^{-1} already appear distinctly, and their intensity is determined reliably. This supports the applicability of this method to the determination of the structure of hydrocarbons with long aliphatic chains.

In conclusion, it is of interest to note that the value of the influence coefficient A (Table 1) is qualitatively related to the electronegativities of the groups X. Thus, arranging the coefficient A in decreasing order of its magnitude, we obtain:

$$\mathrm{Cl} > \mathrm{Br} > \mathrm{H_3C{-}C(=O){-}} > \mathrm{OH} > \alpha\text{-}\mathrm{C_{10}H_7} > \mathrm{R_3Si} > \mathrm{C_6H_5} > \mathrm{CH_3} > \mathrm{C_6H_{11}},$$

which is in general agreement with the electronegativity of the groups, according to the work of a number of investigators ([21,22]) and others.

It is interesting that the group R_3Si is more electronegative than phenyl, which agrees with the opinion of some authors ([23,24]).

A detailed discussion of this question is not part of the aim of the present work, but the character of the gradual attenuation of the influence of X along the chain and its relation, through A, to the electronegativity of the radical X speak in favor of the predominance of the induction effect in the mutual influence of the radical X and the adjacent methylene and methyl groups.

Institute of Organic Chemistry
named after N. D. Zelinsky
Academy of Sciences of the USSR

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