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Abstract

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The Conjugation Effect in the Infrared Spectra of Nitro Compounds

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The nitro group C—N(= O)O possesses, among others, two characteristic valence vibrations: ν_c, symmetric (1300-1400 cm^{-1}), and ν_{ac}, antisymmetric (1500-1600 cm^{-1}), with respect to the symmetry axis of the group.

We have measured the comparatively little-studied (^{1}) integrated intensities of both vibrations for a broad series of nitro compounds of different structures —more than 50 substances—and found the regularities discussed below. The intensities were measured with an accuracy of 5-10% on an H-800 instrument with a CaF_2 prism, in chloroform solutions; the solvents have almost no effect on the intensity of the bands considered.* When bands were split—rather often for ν_c—the total intensity was taken. For substances measured previously, our data are close to those obtained in (^{1}), but disagree with the results of measurements in KBr pellets (^{2}).

Table 1

Integrated intensities $A\left(\mathrm{cm}^2 \cdot \mathrm{molec}^{-1} \cdot \mathrm{sec}^{-1}\right)$ of the ν_c and ν_{ac} vibrations for a series of nitro compounds

No.	$O_2N—X$	$A_c \cdot 10^7$	$A_{ac} \cdot 10^7$	No.	$O_2N—X$	$A_c \cdot 10^7$	$A_{ac} \cdot 10$
1	Cyclohexyl radical	3.4	15.2	8	*p*-tolyl radical	14.7	16.9
2	CH_3	4.6	15.3	9	*p*-iodophenyl radical	16.5	13.7

No.	$O_2N{-}X$	$A_c \cdot 10^7$	$A_{ac} \cdot 10^7$	No.	$O_2N{-}X$	$A_c \cdot 10^7$	$A_{ac} \cdot 10$
3	Phenyl radical with NO_2 substituent shown on the ring	6.3	15.9	10	*p*-hydroxyphenyl radical	25.5	18.0
4	Naphthyl radical	9.0 × 2	18.0 × 2	11	*p*-aminophenyl radical	36.5	18.0
5	Naphthyl radical	10.1	13.8	12	$O_2N{-}C_6H_4{-}NH{-}C_6H_4{-}NO_2$	57 × 2	20 × 2
6	Chlorophenyl radical	13.0	10.5	13	*p*-$N(CH_3)_2$-phenyl radical	75	17.5
7	Naphthyl radical	13.4	15.4	14	*p*-$N(C_2H_5)_2$-phenyl radical	95	23.5

From Table 1, where a representative part of the results has been selected, it is seen that on going from saturated nitro compounds to conjugated ones, A_c—the intensity of the ν_c vibration, polarized along the C—N direction—increases substantially, by about a factor of ~ 30, whereas A_{ac}—the intensity perpendicularly polarized vibration ν_{as}—remains approximately constant*.

The vibrations of the nitro group under consideration are among the strongest in infrared absorption, and it should be emphasized that the increase in A_c in absolute magnitude is exceptionally large. The ν_c band of compounds Nos. 11–14 is stronger than the most intense vibrations of unconjugated groups (the C—F, C = O bands, etc.) and, apparently, is in general the strongest of the known infrared bands of molecules. These facts do not fit within the framework of

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* This question is considered in greater detail in a paper submitted to the journal *Optics and Spectroscopy.*

Fig. 1

Figure 1: Fig. 1

the valence-optical (additive) scheme. Possible contributions from other (non-nitro-group) bonds are negligible in comparison with the increase in A_c. (For example, the intensity of the "strong" bands of vibrations of the benzene ring amounts to 0.5% of this increase.) A change in the values $d\mu/dr$ for the bonds of the nitro group itself is excluded by the constancy of A_{as} and is not consistent with other properties.

Fig. 1. Relation between the intensities of the vibration ν_c in combination scattering (I_c) and infrared absorption (A_c). The numbering of the compounds is according to Table 1.

Obviously, what is observed here is a conjugation effect analogous to that investigated by G. P. Shorygin (^{3}) in the combination scattering of the same compounds. Indeed, as Fig. 1 shows, there is a relation between A_c—the intensity of the vibration ν_c in absorption—and I_c—the intensity of the same vibration in scattering. For all 13 compounds for which I_c has been measured (measurements from work (^{3}); for nitrocyclohexane (No. 1), I_c on the scale of (^{3}) was measured by us) and A_c, spanning a very wide range of intensity variation (5 orders for I_c), the relation $I_c \sim A_c^3$ is satisfied within the errors of measurement (for dinitro compounds Nos. 4 and 12, calculated per one nitro group). This dependence holds too well to be accidental, but apparently is not explained by existing theoretical concepts.

It makes it possible, in practice, to pass from I_c to A_c and conversely, in particular to obtain from the known I_c (^{3}) the values of A_c needed by us (for Fig. 2) for several other conjugated nitro compounds.

The increase in A_c can be explained by assuming that, when the vibration ν_c is polarized along the conjugated system, the redistribution of electron density is not localized in the NO_2 group but propagates along the chain of conjugated bonds. The greater length of the π-electron chain in comparison with the nitro group will lead to a corresponding increase in the vibrational moment, and the intensity increases, as is known, in proportion to the square of the latter**. Then $\sqrt{A_c}$ should increase linearly with the length of the system of conjugated bonds. That this is close to reality is confirmed by Fig. 2, which gives the relation between $\sqrt{A_c}$ and h for a series of nitro hydrocarbons R—NO_2, where h is the projection onto the C–N axis of the skeleton conjugated with the nitro group, at standard bond lengths and angles of 120°.

[*] A noticeable increase in A_{as} in n-nitroamino compounds, where ν_{as} decreases to 1500-1520 cm^{-1}, is possibly caused by overlap with bands of vibrations of aromatic rings having close frequencies. In alkylbenzenes their intensity is relatively small, but in derivatives it changes sharply and may become comparable with A_{as}.

Fig. 2. Increase in absorption intensity as a function of the size of the chain of conjugated π-bonds. For compounds with the indicated structural formula, A_c was calculated from I_c. Numbering of compounds according to Table 1.

Figure 2: Fig. 2. Increase in absorption intensity as a function of the size of the chain of conjugated π-bonds. For compounds with the indicated structural formula, A_c was calculated from I_c. Numbering of compounds according to Table 1.

** N. D. Sokolov kindly informed us that a similar mechanism, called the antenna effect, had been proposed to explain the increase in intensity upon formation of a hydrogen bond (see ([4])).

From the slope of the line in Fig. 2, one can give an estimate: the constant effective charge (corresponding to A_c of an isolated nitro group when its length is 2Å) must be transferred over half the length of the conjugated chain.

An increase in A_c with increasing size of the conjugated system is also observed in n-nitroamino compounds; however, in them A_c also depends strongly on the type of substituents in the benzene ring (Table 1).

Fig. 2. Increase in absorption intensity as a function of the size of the chain of conjugated π-bonds. For compounds with the indicated structural formula, A_c was calculated from I_c. Numbering of the compounds according to Table 1.

It should be noted that the regularities found in the intensities make it possible reliably to distinguish conjugated nitro groups in molecules of unknown structure, which cannot be done from the frequencies. In the substances studied, the latter vary by several tens of reciprocal centimeters and only on average, but irregularly, decrease in conjugated compounds. Thus, in infrared spectra only the intensity of certain vibrations is substantially connected with conjugation of multiple bonds.

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