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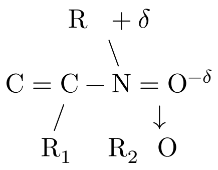
STUDY OF THE STRUCTURE OF UNSATURATED NITRO COMPOUNDS BY THE METHOD OF RAMAN LIGHT SCATTERING

(Presented by Academician A. N. Terenin, 14 IV 1958)

Numerous studies have shown that, for the successful interaction of unsaturated nitro compounds with nucleophilic reagents—in particular with compounds containing mobile hydrogen atoms in methyl and methylene groups—the presence of an electron deficiency ($+\delta$) at the α-carbon atom of the ethylene residue of the nitroolefin is of decisive importance. The magnitude of the electron deficiency, caused by conjugation of the nitro group with the double bond, depends substantially on the chemical structure of the unsaturated nitro compounds (the nature of the radicals bonded to the ethylene residue).



$$\begin{array}{ccccccc} & & R & & +\delta & & \\ & & & & \backslash & & \\ C & = & C & - & N & = & O^{-\delta} \\ & & / & & & & \downarrow \\ & & R_1 & & R_2 & & O \end{array}$$

where $R = H$, alkyl, aryl, heterocycle; $R_1, R_2 = H$, alkyl, aryl.

To solve a number of synthetic problems, sufficiently objective information was needed on the nature of conjugation in nitroolefins. For this purpose, the intensities of the Raman scattering bands of a series (XXII) of unsaturated nitro compounds, nitromethane, and several aromatic nitro derivatives were investigated. The spectra of most of these compounds were obtained for the first time.

As is known (^{1}), the intensities of Raman scattering lines, changing sharply depending on conjugation, can be used for its evaluation. In addition, Raman scattering lines, being characteristic—in contrast to ultraviolet absorption bands—make it possible to judge local changes in the electron cloud, rather than the behavior of the molecule as a whole.

The studies were carried out using a photoelectric apparatus. Acetone served as the solvent in all cases. The concentrations of the substances were varied within the range from 10^{-1} to 10^{-3} mol/l, which practically excluded the possibility of interaction between molecules of the substances studied. The reproducibility of the results lay, for intensities, within ±3–4%, and for frequencies, ±5 cm^{-1}. The intensities and frequencies of the lines of the totally symmetric and antisymmetric vibrations of the nitro group, the antisymmetric vibration of the benzene ring, and the vibrations of the double bond were measured. In this case, the measure of the line intensity was its ratio to the intensity of the 1707 cm^{-1} line of acetone. For nine compounds, quantitative polarization measurements were also made. All data on frequencies, intensities reduced to the same concentration of substances and to the same number of nitro groups and double bonds, and on the polarization state of the lines are collected in Table 1.

The investigation carried out showed that the intensities of the lines vary within very wide limits (Table 2). For the same molecules, especially strong changes are undergone by the intensities of the antisymmetric vibration of the benzene ring.

Table 1

Frequencies (in cm^{-1}), intensities (on an arbitrary scale), and degrees of depolarization of some Raman lines in the spectra of styrene and nitro compounds

Formula	Symmetric vibration of the NO_2 group	Antisymmetric vibration of the NO_2 group	Antisymmetric ring vibration	Vibration of the C=C double bond
(I) CH_3NO_2	1380-1400(0.02;$\rho = 0.32$)	1555(0.005$\rho = 0.74$)	–	–
(II) $CH_3CH_2CH_2CH=CH-NO_2$	1340 (0.36)	1510(0.054)	–	1650(0.187)
(III) $CH_3CHCH=CH$ –	1340 (0.38)	1510 (0.042)	–	1650(0.183)
NO_2	$\vert$ CH_3			
(IV) benzene–NO_2	1345 (0.75;$\rho = 0.22$)	1510 (0.04;$\rho = 0.72$)	1600 (0.16;$\rho = 0.55$)	–
(V) benzene–$CH=CH_2$	–	–	1610(0.3, $\rho = 0.55$)	1640 (0.42;$\rho = 0.28$)
(VI) benzene–$CH=CH-NO_2$	1320 (9;$\rho = 0.32$)	?	1600 (2.4$\rho = 0.43$)	1630 (4.3,$\rho = 0.35$)

Formula	Symmetric vibration of the NO_2 group	Antisymmetric vibration of the NO_2 group	Antisymmetric ring vibration	Vibration of the C=C double bond
(VII) benzene–CH=C(NO_2)–CH_3	1325 (4.3)	?	1600 (1.3)	1660 (2.3)
(VIII) H_3C–benzene–NO_2	1340 (1.5;$\rho = 0.32$)	?	1600 (0.41)	–
(IX) H_3C–benzene–CH=CH–NO_2	1335 (10.6)	1510 (0.9)	1620 (4.1)	1640 (4.2)
(X) H_3C–benzene–CH=C(NO_2)–CH_3	1320 (7.3)	?	1615 (2.6)	1660 (3.7)
(XI) C_2H_5O–benzene–NO_2	1340 (5;$\rho = 0.42$)	1500 (0.2,$\rho = 0.50$)	1600 (1;$\rho = 0.50$)	–
(XII) H_3CO–benzene–CH=CH–NO	1325 (40;$\rho = 0.39$)	1500 (3.7)	1600 (19;$\rho = 0.38$)	1625 (10;$\rho = 0.30$)
(XIII) H_3CO–benzene–CH=C(NO_2)–CH_3	1305 (26)	?	1590 (10)	1640 (10)
(XIV) O_2N–benzene–CH=CH–NO_2	1335 (3.4)	1510 (0.45)	1590 (4.1)	1630 (4.8)
(XV) O_2N–benzene–CH=C(NO_2)–CH_3	1345 (2.8)	?	1600 (3)	1665 (3)

Formula	Symmetric vibration of the NO_2 group	Antisymmetric vibration of the NO_2 group	Antisymmetric ring vibration	Vibration of the C=C double bond
(XVI) O_2N–benzene–CH=CH–CH=CH–NO_2	1340 (30)	?	1590 (39)	1630 (27)
(XVII) furan–CH=CH–CH=CH–NO_2	1335 (255)	?	–	1620 (95)
(XVIII) O_2N–HC=CH–benzene–CH=CH–NO_2	1335 (16;$\rho = 0.36$)	1510 (2.8)	1610 (50;$\rho = 0.41$)	1625 (18;$\rho = 0.39$)
(XIX) O_2N–$C(CH_3)$=CH–benzene–CH=$C(NO_2)$–CH_3	1325 (14;$\rho = 0.43$)	1515 (0.7)	1610 (25;$\rho = 0.49$)	1660 (11;$\rho = 0.43$)
(XX) benzene–NO_2, NO_2	1340 (0.4)	1520 (0.13)	1595 (0.14)	–
(XXI) O_2N–HC=CH–benzene–CH=CH–NO_2	1340 (8)	1510 (1.0)	1595 (3.56)	1630 (5.4)
(XXII) O_2N–$C(CH_3)$=CH–benzene–CH=$C(NO_2)$–CH_3	1325 (3.5)	1510 (0.20)	1610 (1.3)	1665 (2.8)

Changes in the intensities of the lines of the Raman spectra of the nitro group, the double bond, and the aromatic nucleus directly

Table 2

Nature of vibration	Substances compared	Change in intensity (number of times)
Totally symmetric vibration of the nitro group	(I) and (XII)	2000
Antisymmetric vibration of the benzene ring	(IV) and (XVIII)	~ 312
Vibration of the double bond	(II) and (XVIII)	~ 98

reflect their participation in π-electron interaction, creating a clear picture of the dependence of conjugation in nitroolefins on their structure, and make it possible to draw the following conclusions.

1. Unsaturated olefins constitute a single conjugated system: in aliphatic nitroolefins the nitro group is conjugated with the double bond, while in aromatic ones the nitro group, the double bond, and the benzene nucleus participate in conjugation; this is manifested in an even sharper increase in the intensity of the spectral lines compared with compounds that do not simultaneously contain these three residues. Nucleophilic substituents located in the para position of the benzene ring (methyl and methoxy groups) favor conjugation in exactly the same way as in the case of aromatic nitro compounds, according to the data of P. P. Shorygin (^{1}).

2. In para-dinitroolefins (XVIII) and (XIX), conjugation increases sharply in comparison with the corresponding meta isomers (XXI) and (XXII) and mononitroolefins (VI) and (VII), although in (XVIII) and (XIX) one would have expected weakening of the lines owing to the presence in the molecules of oppositely directed conjugated systems.

3. Methyl groups at the ethylenic carbon bonded to the nitro group weaken conjugation, apparently as a result of disruption of the coplanarity of the molecule (compare the intensities of the bands of the nitro group, the benzene ring, and the double bond in compounds (VI), (IX), (XII), (XIV) and, respectively, in (VII), (X), (XIII), and (XV)).

4. The degree of depolarization of the totally symmetric vibration of the nitro group, in agreement with earlier observations by one of us (^{2}), for most of the compounds lies within the range 0.22–0.43. A comparison of compounds XII and XI, for which $I_1 = 40$, $\rho_1 = 0.39$ and $I_2 = 5$, $\rho_2 = 0.42$, respectively, indicates that introduction of a carbon-carbon double bond

into the chain leads not to a simple elongation of one of the axes of the ellipsoid $\frac{d\alpha}{dq}$ of the nitro group, but to a simultaneous elongation of all its axes, i.e., to a substantial change in the shape of the ellipsoid. In molecules distinguished by favorable conditions for conjugation, the vibration line of the benzene ring becomes distinctly polarized (in the case of compound (XII) the degree of depolarization of this line is 0.38). The latter fact would appear to indicate a change in the form of the "antisymmetric" vibration of the ring as a result of bond conjugation.

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

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