Reports of the Academy of Sciences of the USSR

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1961

SovietRxiv

Abstract

Full Text

Reports of the Academy of Sciences of the USSR

1961. Vol. 139, No. 6

PHYSICAL CHEMISTRY

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INVESTIGATION OF THE STRUCTURE OF NITROAMINOBUTADIENE DERIVATIVES BY THE RAMAN-SCATTERING METHOD

(Presented by Academician A. N. Terenin, 23 III 1961)

It may be considered that the nitroaminobutadienes, the general method for preparing which was first developed by two of us (^{1}), are an equilibrium mixture of ketimine-enamine tautomers

$$\mathrm{RNH{-}CH{=}C(NO_2){-}CH{=}C(R')(R'')} \rightleftarrows \mathrm{RN{=}CH{-}CH(NO_2){-}CH{=}C(R')(R'')} \qquad (1)$$

or have the structure

[[structural formula: cyclic form with intramolecular hydrogen bond]]
$(R = \mathrm{CH_3}, \mathrm{C_6H_5};\ R', R'' = \mathrm{NO_2}, \mathrm{CN}, \mathrm{H})$

characterized by a ring with an intramolecular hydrogen bond. The data of the chemical experiment are more readily compatible with the latter structural formula. For an unambiguous and reliable choice between these two possibilities, and for establishing the features of conjugation and the distribution of electron densities in the molecules under consideration, we employed the Raman-spectra method.

As in previous works (^{2,3}), the substances were dissolved in acetone, and the measure of intensity was the ratio of the intensity of the line being measured to the acetone line ($\sim 1710\ \mathrm{cm}^{-1}$). Many of the substances containing phenyl nuclei had a strong yellow coloration. They were studied in highly dilute solutions ($10^{-4} \div 10^{-3}$ mole/l). The very obtaining of spectra at such low concentrations became possible owing to the phenomenon of optical resonance (the proximity of the exciting line to the absorption bands of the molecules). In other cases more concentrated solutions were prepared ($10^{-3} \div 10^{-2}$ mole/l). The experimental setup was the same as in works (2,3). The results of the investigation carried out are collected in Table 1.

One characteristic feature of the spectra of nitroaminobutadienes (I–IX) is that in the region ~ 1310—1390 cm^{-1} two lines are observed instead of one, which undoubtedly belong to the split totally symmetric stretching vibration of the nitro group. The substances (VI and VIII) are probably not an exception: judging from the appearance of the spectra, it must be assumed that the corresponding components, being located close to one another, are not resolved by the instrument. In total intensity, the two lines under consideration, as a rule, considerably exceed all the others in the spectrum.

Furthermore, the low intensity of the vibrations of the double bond C=C in all molecules is noteworthy, with the exception of (VII) and (IX), as a result of which

Table 1

Frequencies and intensity coefficients of the lines

	Compound	$-NO_2$ symmetric vibrations	$-NO_2$ antisymmetric vibrations	$-C_6H_5$ antisymmetric vibrations	>C=C<
I *	$H_3C–NH–CH=C(NO_2)–C(=O)H$	1325+1350(1.3+1.2)	1500(0.25)	–	1610(0.1)
II *	$H_3C–NH–CH=C(NO_2)–CH=C(COOC_2H_5)(CN)$	1315+1340(10+6.2)	1490(0.2)	–	1655(0.1–0.2)
III *	$H_3C–NH–CH=C(NO_2)–CH=C(CN)(CN)$	1315+1325(12)	1490(0.2)	–	?
IV **	$H_5C_6–NH–CH=C(NO_2)–C(=O)H$	1320+1390(4.0+4.8)	1500(6)	1585(11)	1640(1.6)

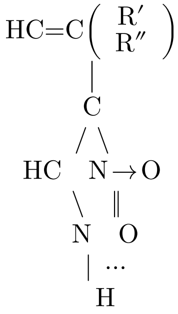
	Compound	$-NO_2$ symmetric vibrations	$-NO_2$ anti-symmetric vibrations	$-C_6H_5$ antisym-metric vibrations	>C=C<
V	$H_5C_6-NH-CH=C(NO_2)-CH=C(COOC_2H_5)(CN)$	1310+1340(50+50)	1490(17)	1550+1595(16+17)	?
VI	$H_5C_6-NH-CH=C(NO_2)-CH=C(CN)(CN)$	1320(95)	1480(6)	1520+1580(12+12.5)	?
VII	$H_5C_6-NH-CH=C(NO_2)-CH=CH-NO_2$	1315+1350(60+90)	?	1590(80)	1615(90)
VIII	$H_5C_6-NH-CH=C(NO_2)-CH=N-C_6H_5$	1345(140)	1500(46)	1555+1580(60+65)	?
IX	$H_5C_6-NH-CH=CH-CH=N-C_6H_5$	–	–	1555+1590(75+45)	1655(20)
X	$H_5C_6-CH_3$	–	–	1585+1605(0.02–0.03)	–
XI	$H_5C_6-NH-C_6H_5$	–	–	1600(0.36)	–
XII	$H_5C_6-NH-C(=O)CH_3$	–	–	1530+1590(0.08+0.25)	–
XIII	$H_5C_6-CH=N-C_6H_5$	–	–	1595(3.6)	–
XIV	$H_5C_6-C\ C-C_6H_5$	–	–	1590(2.8)	–

* In the spectra, weak lines with frequencies 1540–1590 cm^{-1} appear.
** In the spectra, ring vibrations with frequency 1500 cm^{-1} are strongly activated.

The corresponding band could be recorded only in the case of the least-colored solutions (molecules I, II, and IV). The same is observed also for vibrations of the C N bond in (II, III, V, and VI).

Also deserving special attention is the fact that in the spectra of aliphatic molecules (I–III) lines are found with frequencies falling in a region unusual for such molecules (1540 and 1590 cm^{-1}). Although the intensity of these lines is comparatively small, they certainly cannot be assigned to overtones or combination vibrations. It is quite possible that analogous lines also appear in the spectra of the aromatic derivatives, being superposed on the considerably more intense antisymmetric vibration of the benzene ring.

The entire set of observations made is in satisfactory agreement with structural formula (2) of the nitroaminobutadienes. Indeed, an intramolecular hydrogen bond may be the cause of the splitting of the totally symmetric vibration of the nitro group. It is natural to assign to the vibrations of a six-membered ring with a hydrogen bond the weak lines with frequencies 1540 and 1590 cm^{-1}, mentioned above*. One may also suppose that, in such a ring, the double bond $C = C$ loses much of its characteristic nature, which explains the low value of the coefficient $I_{C=C}$ for this vibration in most spectra. The sharp increase of the same coefficient in (IX) is evidently caused by the absence of the possibility of forming a hydrogen bond of the type under consideration, and in (VII) by the strong influence of the side chain of conjugation. Finally, the general sharp strengthening of all vibrations, and in particular those belonging to the nitro group, in the aromatic derivatives, as compared with the aliphatic ones, signifies the inclusion of the benzene ring through the imino group into the conjugated ring according to the scheme



In this connection the question arises: to what extent is the imino group in general capable of being a "conductor" in a chain of conjugated bonds? In a recently published work by Shorygin and Alaune (4) it was shown that the NH bridge does not completely separate phenyl nuclei and certain groups in the para position. At the same time, other groups and atoms, for example CH_2, O, S, serve as a barrier hindering conjugation. In the opinion of the authors cited above, the NH bridge plays an essential role in the excited state of the molecules.

We, in turn, carried out measurements in the spectra of comparatively simple molecules with imino groups (Table 1, XI and XII). Included there as well are results relating to an isolated phenyl nucleus (X) and to phenyl nuclei known to be conjugated by means of $C = N$ (XIII) and $C = C$ (XIV) bonds. Our data agree practically exactly, for the same molecules, with those published in (1). Indeed, it turns out that the imino group partially favors conjugation. It is hardly necessary, however, to regard only the excited states of the molecules as responsible for this. As can be seen from Table 1, in practically all cases the frequencies of the totally symmetric vibration of the nitro group have low values. This proves the influence of conjugation also on the normal states of the molecules; therefore the conclusions of the authors (4) are not universal in character.

Let us note, in conclusion, that the cause of the splitting of the nitro-group vibration, besides internal hydrogen bonding, may also be external hydrogen bonding, as well as Fermi resonance. It is known that precisely the latter circumstance explains an analogous phenomenon in the spectra of nitroparaffins (5). However, the experiments we carried out make it possible to reject external hydrogen bonding as a possible cause of the splitting under consideration. The experiments consisted in studying the concentration dependence of the relative intensity of the splitting components. For the study, a saturated solution of molecule I in acetone was taken, which was successively diluted with a neutral solvent—carbon tetrachloride. No redistribution of intensities in the spectrum was observed in this process.

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[*] It is not excluded, however, that these lines belong to the split components of the antisymmetric vibration of the nitro group, but then the interpretation of the line with frequency ~ 1500 cm^{-1} is unclear.

Thus, no external hydrogen bond is formed either between molecules I themselves or between them and acetone molecules.

A completely unambiguous solution to the question of whether the splitting of the vibration under consideration is caused by the formation of an internal hydrogen bond or by Fermi resonance can be obtained by studying the valence vibration of the NH group by means of infrared spectra.

Received
23 II 1961

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