HETEROCYCLIC NITRO COMPOUNDS

XIII.* IR AND RAMAN SPECTRA OF THE ANIONS OF NITRO DERIVATIVES OF 1,2,4-TRIAZOLE

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The IR and Raman spectra of a number of anions of the nitro derivatives of 1,2,4-triazole were investigated. On the basis of the position of the absorption maxima of the asymmetric and symmetric† vibrations of the nitro group, it is assumed that the nitro groups in the 3 and 5 positions of the triazole ring are coplanar, which should lead to an increase in the participation of the nitro group in the delocalization of the negative charge of the anion. Shifts of the frequencies as a function of the nature of the cation (NH_4, Na, K, Cs) were not detected in the IR spectra of the crystalline salts. In addition, the IR spectra of the crystalline salts are similar (with respect to the frequencies) to the spectra of aqueous solutions of the salts, which may serve as proof of the identical structure of the anions in crystals and aqueous solutions.

To accomplish our research relative to the elucidation of the character of the interaction of the nitro group and the triazole ring and of the steric and electronic structures of the anions of nitro derivatives of 1,2,4-triazole, it was necessary to have the experimental IR and Raman spectra of these anions. The IR spectra of the alkali salts of anions of nitro derivatives of 1,2,4-triazole, recorded in a solid film, are presented in Fig. 1, the IR spectra of aqueous solutions of the salts are presented in Fig. 2, and the Raman spectra are presented in Fig. 3. If the positions of the bands in the spectra of the salts at 1500 and 1300 cm^{-1} that are ascribed to the asymmetric and symmetric vibrations of the nitro groups [2] are compared, several characteristic features are revealed.

Two intense bands with maxima at 1542 and 1310 cm^{-1} are observed in the spectra of the potassium salt of 3-nitro-1,2,4-triazole (Fig. 1); the introduction of a methyl group into the 5 position of the triazole ring does not lead to a shift in the frequency of the asymmetric vibration of the nitro group, and the symmetric vibration is shifted to 1338 cm^{-1}. The appearance of these bands in the IR spectra and the Raman spectra (Fig. 3) of the anions of nitro derivatives of 1,2,4-triazole, in analogy with the salts of dinitromethyl compounds [3], leads one to the opinion of an increase in the participation of the nitro group in delocalization of the negative charge in the anion, which should lead to a decrease in the multiplicity in the NO bond, a decrease in the force constant of the NO bond, and correspondingly, to a decrease in the frequency of the asymmetric vibration of the nitro group, as compared with the covalent nitro derivatives of 1,2,4-triazole.

On the basis of the experimental and calculated spectra of nitro derivatives of 1,2,4-triazole, we previously made an assumption regarding the coplanar orientation of the nitro group in the 3 position and regarding rotation of the nitro group in the 5 position by a certain angle relative to the CN bond [4, 5]. It

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*See [1] for communication XII.

†The vibrations relative to the elements of symmetry of the NO_2 group are considered.

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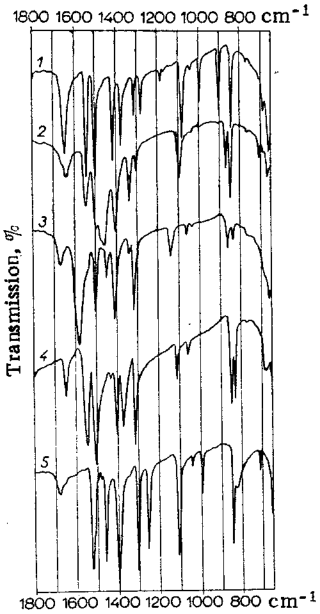

Fig. 1

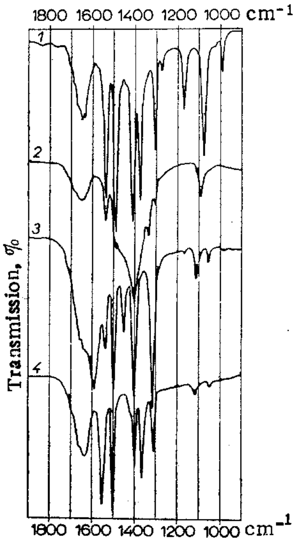

Fig. 2

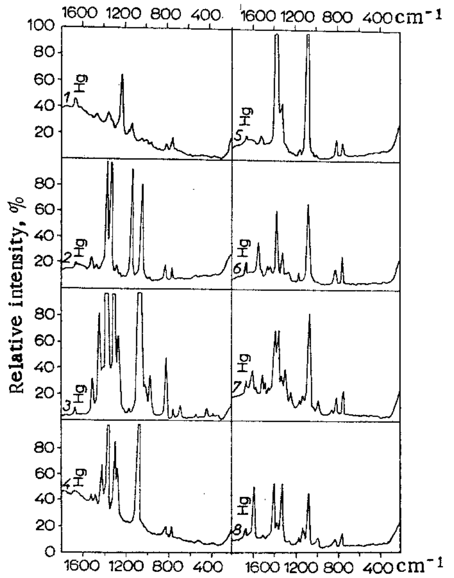

Fig. 3

Fig. 1. IR spectra of alkali salts of nitrotriazoles: 1) potassium salt of 3-nitro-1,2,4-triazole; 2) potassium salt of 3-nitro-5-methyl-1,2,4-triazole; 3) dipotassium salt of 3-nitro-5-carboxy-1,2,4-triazole; 4) sodium salt of 3,5-dinitro-1,2,4-triazole; 5) disodium salt of 3,3'-dinitrobis-1,2,4-triazol-5-yl.

Fig. 2. IR spectra of aqueous solutions of alkali salts of nitrotriazoles: 1) 3-nitro-1,2,4-triazole; 2) 3-nitro-5-methyl-1,2,4-triazole; 3) 3-nitro-5-carboxy-1,2,4-triazole; 4) 3,5-dinitro-1,2,4-triazole.

Fig. 3. Raman spectra of nitrotriazole anions: 1) 1,2,4-triazole; 2) 3-nitro-5-methyl-1,2,4-triazole; 3) 3-nitro-5-methyl-1,2,4-triazole; 4) 3-nitro-5-carboxy-1,2,4-triazole; 5) 3,5-dinitro-1,2,4-triazole; 6) 3,3'-dinitrobis-1,2,4-triazol-5-yl; 7) 3-nitro-5-(m-nitrophenyl)-1,2,4-triazole; 8) 3-nitro-5-(p-nitrophenyl)-1,2,4-triazole.

follows from the experimental spectra presented in Figs. 1-3 that, from the position of the absorption maxima (ν_{as} 1540 cm^{-1}) that are characteristic for the vibration of the nitro group, one can conclude that the nitro group in the 3 position is coplanar relative to the plane of the triazole ring. If the nitro group in the 5 position in the 3,5-dinitro-1,2,4-triazole anion were removed from the plane, which would lead to nonequivalency of the two nitro groups, splitting of the frequencies of the asymmetric and symmetric vibrations of the nitro group would be observed in the experimental spectra. In fact, splitting of the frequencies could not be detected (Figs. 1-3) in either the IR spectra of the crystalline salts in aqueous solutions of them or in the Raman spectra, which apparently may serve as proof of the planar orientation of the nitro groups. Thus both nitro groups should participate to an equal degree in delocalization of the negative charge in the 3,5-dinitro-1,2,4-triazole anion, which should lead to an increase in the symmetry of the anion within limits up to C_{2v}.

The IR spectra of the dipotassium salt of 3-nitro-5-carboxy-1,2,4-triazole contain a broad intense band with a maximum at 1580 cm^{-1} that is characteristic for carboxylic acid salts [6] and partially overlaps the nitro group band (Figs. 1 and 2). Data on the Raman spectra [7] of carboxylic acids indicate that the salt formation leads to disappearance of the C = O absorption band. In fact, the band at 1580 cm^{-1} in the Raman spectrum vanishes, whereas the band characteristic for the vibration of the nitro group at 1530 cm^{-1} remains.

In our opinion, the comparatively simple spectrum and the absence of splitting of the frequencies in the IR and Raman spectra of the disodium salt of 3,3'-dinitrobis-1,2,4-triazol-5-yl that is characteristic for vibrations of the nitro group and the triazole ring can be due to only one reason — the planar orientation of the two triazole rings and the nitro groups.

It seemed of interest to ascertain how the effect of the crystal lattice is manifested in the IR spectra of anions of nitro derivatives of 1,2,4-triazole. For this, we recorded the spectra of solutions of the alkali salts in water. In comparing the spectra, it was observed that the spectra of aqueous solutions do not differ from the spectra of crystalline substances with respect to the position of the absorption bands, which may serve as proof of the identical structures of the anions in the crystals and aqueous solutions. The IR spectra of all of the salts that we investigated contain a band at ~1650 cm^{-1}, which was assigned to the vibrations of the water of hydration. The hydration of the cation apparently weakens the electrostatic interaction between the nitrotriazole anion and the metal cation, thereby making the spectra of the crystalline salts similar to the spectra of aqueous solutions. In addition, shifts of the bands as a function of the nature of the cation (NH_4, Na, K, Cs) are not observed in any of the investigated IR spectra of salts of nitro derivatives of 1,2,4-triazole.

While the assignment of the absorption bands in the experimental spectra of the anions of nitro derivatives of 1,2,4-triazole to vibrations of the nitro group does not present great difficulties, the situation is not as satisfactory in the assignment of frequencies to vibrations of the triazole ring. A sufficiently complete solution of this problem can be realized only by using calculations of the vibration spectra,* and a partial solution without detailed assignment of the frequencies to the vibrations of definite structural fragments of the ring can be accomplished by means of an analysis of the Raman spectra. The assignment of the absorption band in the IR spectrum of the potassium salt of 1,2,4-triazole to vibrations of the triazole ring that is presented in [8] confirms our data on the Raman spectra. The IR and Raman spectra of the 1,2,4-triazole anion contains a band at 1381 cm^{-1}, which was assigned to the ring vibration by Grinshtein and co-workers [8]. The absorption band at 1380-1420 cm^{-1} in the IR spectra of the anions of nitro derivatives of 1,2,4-triazoles should be assigned to this vibration, during which it should be noted that the introduction of a nitro group into the triazole ring leads to a sharp increase in the intensity of this vibration in the Raman spectra (Fig. 3). An increase in the intensity of the bands at 1070-1100 cm^{-1}, which characterize the pulsation ring vibrations, is similarly observed in the Raman spectra, and an increase in the frequency to ~1130 cm^{-1} is observed when both electron-donor and electron-acceptor substituents are introduced into the triazole ring. Thus the ring vibrations at 1400 and 1100 cm^{-1} can be considered to be relatively characteristic with respect to frequency. The remaining bands in the experimental spectra of the anions of nitro derivatives of 1,2,4-triazole, which characterize the deformation and out-of-plane ring vibrations, can be reliably interpreted only as a result of a theoretical analysis of the vibrational spectra.

EXPERIMENTAL

The IR spectra of salts of alkali metals and aqueous solutions of the salts were recorded with an IKS-22 double-beam IR spectrophotometer by known methods [9]. The Raman spectra of saturated aqueous solutions were recorded with a DFS-12 spectrometer at a scanning rate of 6.1 Å/min with respect to the slit. A mercury lamp with a wavelength of 4358 Å was used as the source of excitation. A saturated aqueous sodium nitrite solution was used as a filter for the absorption of the short-wave radiation of a DRS-600 mercury lamp.

The mononitrotriazole salts were obtained by mixing alcohol solutions of the nitrotriazole and alkali metal hydroxides. The resulting precipitates were removed by filtration and crystallized from alcohol. The dinitrotriazole salts were obtained by the methods in [10, 11]. Despite drying in a vacuum desiccator, all of the salts contained water of hydration.

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*For this purpose, we present calculations of the frequencies and forms of the normal vibrations of the anions of nitro derivatives of 1,2,4-triazole at the present time.

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