HETEROCYCLIC NITRO COMPOUNDS

XI.* IR AND RAMAN SPECTRA OF NITRO DERIVATIVES OF 1,2,4-TRIAZOLE

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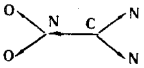
An intense band, which is shifted to lower frequencies (to 1350 cm^{-1}) on introduction of a nitro group into the 5-position, is observed in the Raman spectra of nitro derivatives of 1,2,4-triazole which contain a nitro group in the 3-position. Bands with frequencies of 1540-1560 cm^{-1}, which are practically insensitive to the introduction of various substituents into the ring, are observed in the IR and Raman spectra. The frequencies and forms of the normal vibrations of 3-nitro-1,2,4-triazole (symmetry group C_s) were calculated. The characteristic (with respect to frequency) vibration with $\nu_{exp} = 1550$ cm^{-1} is related to the symmetrical antiphase vibration of the nitro group, while the bands at 1400-1430 cm^{-1} are the complex planar vibration of the fragment of the molecule which includes the nitro group and three ring atoms, i.e.,



, with a substantial contribution of the deformation vibrations.

The IR and Raman spectra of 1,2,4-triazole derivatives have been investigated by a number of researchers [2-10]. It has been shown that at 700-1600 cm^{-1} the experimental spectra of triazoles contain several groups of vibrations which can be related to the valence vibrations of the C−N and N−N bonds and also to the valence and deformation vibrations of the C−H bonds. However, the assignment of the frequencies in the spectra of triazoles to one or another type of vibrations has been carried out only on the basis of analogies with other five-membered rings [11] without a detailed calculation and analysis of the vibrational forms.

The IR and Raman spectra of 3(5)-nitro-1,2,4-triazoles have not been reported. This complicates the selection of three-dimensional models of 1,2,4-triazoles in solutions, which play an important role in estimating the reactivities of these compounds.

In this connection we undertook a study of the IR and Raman spectra of a number of nitro derivatives of 1,2,4-triazole.

The IR spectra obtained are presented in Fig. 1.

Comparative data on the intensities of the bands in the IR and Raman spectra of the investigated compounds are presented in Fig. 2.

In addition to the experimental investigations of the spectra, we also calculated the frequencies and forms of the normal vibrations of 3-nitro-1,2,4-triazole with a "BÉSM-3M" computer with the programs of Gribov and co-workers [12].

X-ray diffraction data from an investigation of 1,2,4-triazole [13, 14]† were used as the geometrical configuration of the triazole ring. Since the geometrical orientation of the nitro group in the 3-position relative to the plane of the ring is currently unknown, a planar model of 3-nitro-1,2,4-triazole (symmetry

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*See [1] for communication X.

† The data of [14] were put into the calculation.

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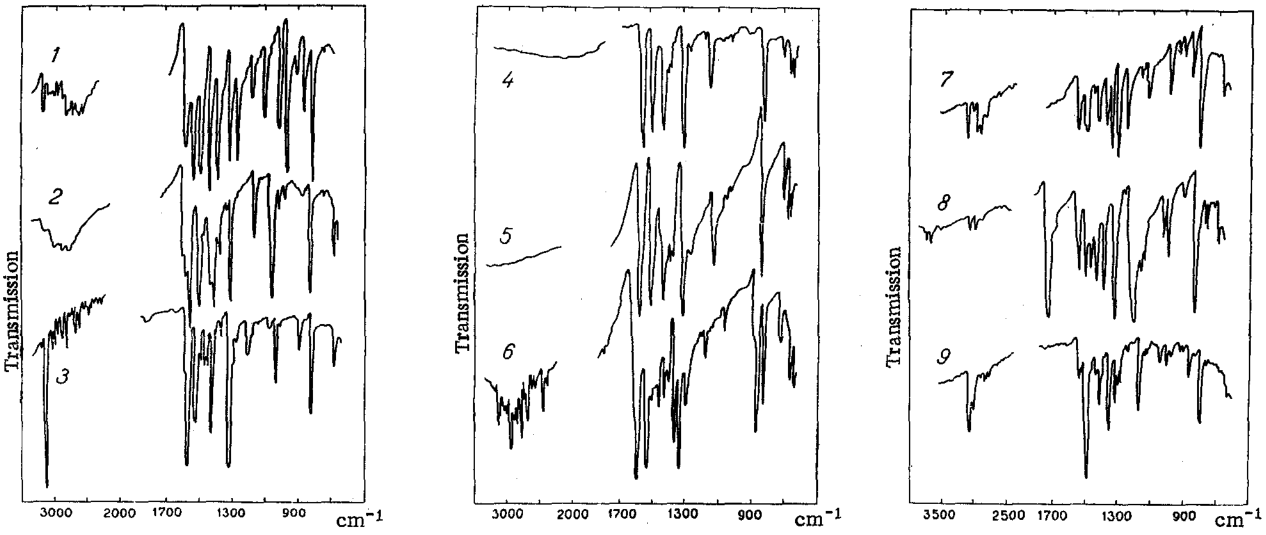


Fig. 1. IR spectra of nitro derivatives of 1,2,4-triazole (IKS-14 spectrophotometer, NaCl and LiF prisms): 1) 3-nitro-1,2,4-triazole; 2) 3-nitro-5-methyl-1,2,4-triazole; 3) 1-methyl-3-nitro-1,2,4-triazole; 4) 1-methyl-3-nitro-5-chloro-1,2,4-triazole; 5) 1-methyl-3-nitro-5-bromo-1,2,4-triazole; 6) 1-methyl-3,5-dinitro-1,2,4-triazole; 7) 1-methyl-5-nitro-1,2,4-triazole; 8) 1-methyl-3-carbomethoxy-5-nitro-1,2,4-triazole; 9) 3-nitro-4-methyl-1,2,4-triazole.

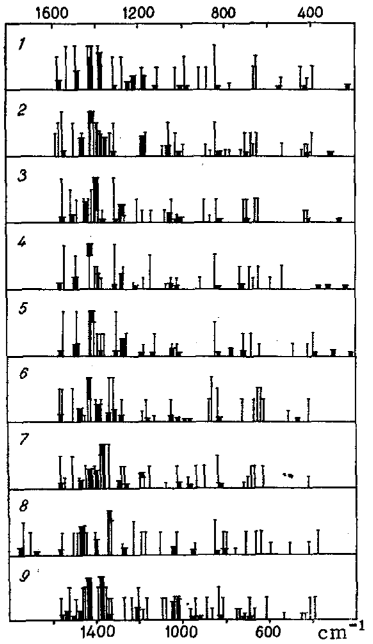
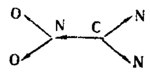


Fig. 2. Relative intensities of the maxima of the bands in the IR (narrow lines) and Raman spectra (broad lines) of nitro derivatives of 1,2,4-triazole. (The numbers of the compounds are the same as in Fig. 1.)

group C_s) was selected for the calculations. The CN and NO bond lengths were calculated on the basis of data obtained via the MO LCAO method [1] and were 1.40 and 1.22 Å, respectively. The force constants were taken from [15].

Satisfactory agreement between the calculated and experimental frequencies was obtained as a result of our calculation.*

As seen from Fig. 2, the most intense line in the Raman spectra of 1-H- and 1-methyl derivatives of 1,2,4-triazole which contain a nitro group in the 3-position of the ring is situated at 1400-1430 cm^{-1}. When a nitro group is introduced into the 5-position, one observes its shift to lower frequencies (to 1370 cm^{-1} for 1-methyl-5-nitro-1,2,4-triazole and to 1340 cm^{-1} for 1-methyl 3-carbomethoxy-5-nitro-1,2,4-triazole). On the basis of an analysis of the forms of the normal vibrations these bands in the experimental spectra should be assigned to the planar valence vibrations of the nitro group and of the fragment of the thiazole ring with a substantial contribution of the deformation vibrations of the $(O\widehat{N}C)$ and $(N\widehat{C}N)$ valence angles.



A more detailed examination of the band at about 1555 cm^{-1} (Figs. 1 and 2), which is intense in the IR spectra and relatively weak in the Raman spectra, is deserving of attention.

This band in the experimental spectra of the investigated compounds relates to the antiphase symmetrical vibration of the

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*The results of an analysis of the vibrational spectra of nitro derivatives of 1,2,4-triazole will be published later.

nitro group. The characteristic nature of this vibration with respect to frequency and the satisfactory agreement between the calculated and experimental frequency constitute, in our opinion, a sufficiently convincing substantiation of the planar model which we selected for the calculation, i.e., the nitro groups in the 3- and 5-positions are apparently situated in the plane of the ring.

An exception to this is 1-methyl-3,5-dinitro-1,2,4-triazole; in the IR spectra of solutions and crystals of this compound one observes splitting of this band into two, which may attest to not only the electronic [1] but also the steric nonequivalence of the nitro groups. This position finds its confirmation in the chemical behavior of 1-methyl-3,5-dinitro-1,2,4-triazole [16].

Vibrations with frequencies below 1400 cm^{-1} are uncharacteristic in form and frequency and are the result of superimposition of valence and deformation vibrations of the ring.

EXPERIMENTAL

The Raman spectra of solutions were obtained with a DFS-12 spectrometer, and the rate of scanning of the spectrum with respect to the slit was 6.1 Å/min. The mercury line with wavelength 435 Å was used as the exciting source. A filter (saturated aqueous sodium nitrite [17]) was used for the absorption of the short-wave portion of the radiation of a DRS-600 mercury lamp.

The Raman spectra of nitro derivatives of 1,2,4-triazole were obtained in the following spectrally pure solvents: chloroform, dichloroethane, dibromoethane, tetrabromoethane, acetone, dioxane, dimethylformamide, and dimethyl sulfoxide.

The values of the frequencies in the Raman spectra were preserved within the limits of experimental error regardless of the polarity of the solvent. The IR spectra were obtained with an IKS-14 double-beam IR spectrometer using KBr, NaCl, and LiF prisms. To obtain solid films, several drops of an organic solvent were poured onto a small amount of crystalline substance applied to the surface of the cuvette window (made of KBr, NaCl, LiF, and CaF_2), and the solvent-moistened crystals were ground for several minutes while covering the second window of the same sort. The solid film thus obtained was used to obtain the spectra.

The spectra of solutions of nitro derivatives of 1,2,4-triazole were obtained with compensation for the solvent band.

All of the nitrotriazoles for the investigation were obtained via the methods described in [16, 18-20].

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