VIBRATIONAL SPECTRA AND STRUCTURES OF 1,2,4-TRIAZOLE DERIVATIVES.
VI.* THE PROBLEM OF THE ELECTRONIC STRUCTURE OF AZIDOTRIAZOLES

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The frequencies and forms of the normal vibrations of a number of azido derivatives of 1,2,4-triazole [3-bromo-5-azido- (I), 1-methyl-3-azido- (II), and 3-azido-5-nitro-1,2,4-triazole (III)] were calculated. The inverse spectral problem for the parameters of the azido group was solved by the method of least squares. A similar method was used to calculate the potential energy constants of the triazole ring with the aid of data on the force fields of the previously investigated nitrotriazoles. It is shown that the introduction of electron-donor or electron-acceptor substituents in the triazole ring does not affect the force constants of the CN and NN bonds of the azido group. Transmission of the electronic effects in the ring as a function of the nature and position of the substituent was investigated.

The change in the potential energy constants of conjugated heterocyclic compounds such as azido derivatives of 1,2,4-triazole that contain various electron-donor and electron-acceptor substituents in the ring may offer valuable information regarding both the interaction of the azido group with the triazole ring and transmission of the electronic effects within the triazole ring under the influence of substituents that differ in nature. Attempts to establish definite principles relating the properties of substituents with the force constants evidently make sense for the diagonal and nondiagonal elements of the

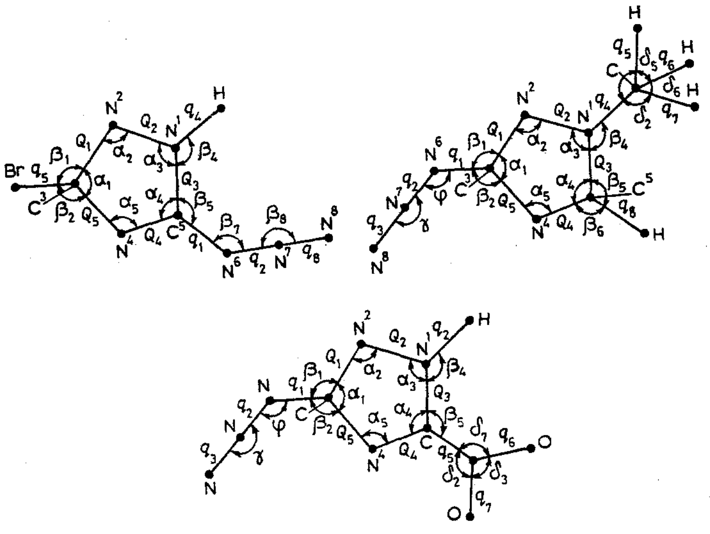

Fig. 1. Structure and natural vibrational coordinates of azido derivatives of 1,2,4-triazole.

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*See [1] for communication V.

†Deceased.

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TABLE 1. Potential Energy Constants of the Azido Group of Azidotriazole Derivatives (in 10^6 cm^{-2} units)

Compound	$K^*_{q_1}$	K_{q_2}	K_{q_3}	K_{φ}	K_{γ}	$K_{\rho N_3}$	$H_{q_2}^{q_1}$	$H_{q_3}^{q_2}$	$A_{\varphi}^{q_1}$	$A_{\varphi}^{q_2}$
3-Azido-1,2,4-triazole	7,70	13,28	24,35	3,30	1,38	2,92	0,2	−0,2	1,21	0,29
3-Bromo-5-azido-1,2,4-triazole	7,70	13,28	24,35	3,30	1,38	2,92	0,2	−0,2	1,21	0,29
1-Methyl-3-azido-1,2,4-triazole	7,70	13,28	24,35	3,30	1,57	2,82	0,2	−0,2	1,21	0,29
3-Azido-5-methyl-1,2,4-triazole	7,70	13,28	24,35	3,30	1,57	2,92	0,2	−0,2	1,21	0,29
3-Azido-5-nitro-1,2,4-triazole	7,70	13,28	24,35	2,27	1,38	2,92	0,2	−0,2	0,49	0,29

*The force constants are symbolized in accordance with [9].

matrices of the potential energy constants that have maximum values and take into account the specific character of the interaction of the chemically bonded atoms. However, the remaining constants, because of the error in their determination, cannot be used for the solution of such problems.

With this in mind, as a supplement to the available data [1] we calculated the vibrational spectra of the 3-bromo-5-azido-, 1-methyl-3-azido-, and 3-azido-5-nitro-1,2,4-triazole molecules. The natural vibrational coordinates of the investigated compounds are presented in Fig. 1. We used the geometrical parameters of the triazole ring presented in [2] for the calculations of the vibrational spectra and selected the parameters determined by electron diffraction and microwave spectroscopy [3-5] for the azido and nitro groups. Rotation of the various functional groups about the corresponding bonds was not taken into account in the calculations. We selected the force constants of the triazole ring and of the azido and nitro groups presented in [1, 6] as a zero approximation of the potential energy constants of the investigated 1,2,4-triazoles.

We first established the three-dimensional structure of the azido group in 3-azido-1,2,4-triazole derivatives with the aid of vibrational spectroscopy and the dipole moments [1, 7]. Data of this sort are presently unavailable for the 3-azido-5-nitro-1,2,4-triazole structure. With this in mind, we investigated the effect of the kinematic coefficients in the case of rotation of the nitro group relative to the CN bond from 0 to 90° on the shift of the frequencies in the vibrational spectrum. The calculations of the vibrational spectrum showed that, in contrast to the spectra of 3,5-dinitro-1,2,4-triazoles [6], the frequencies are relatively insensitive to rotation of the nitro group, in conformity with which for the subsequent calculations we assumed the three-dimensional model of the 3-azido-5-nitro-1,2,4-triazole molecule with orientation of the nitro group in the same plane as the triazole ring (Fig. 1).

The force constants for the geometrical models of azidotriazoles selected in this way were refined by solution of the inverse spectral problem by the method of least squares for the parameters of the azido group. The force constants of the triazole ring were similarly calculated for the azido derivative and a number of nitro derivatives of 1,2,4-triazole [6].

The calculations showed that the introduction of electron-donor or electron acceptor substituents in the triazole ring does not lead to a change in the force constants of the CN and NN bonds of the $C-N_3$ fragment; the potential energy constants of the angular coordinates and the interaction coefficients change somewhat in the investigated compounds but to a lesser degree than in alkyl azides [8] (Table 1). The interaction of the σ and π electrons in conjugated system of azidotriazoles is rather complex, and in conformity with this attempts to establish the dependence of the change in the force constants on the empirical parameters that characterize the electronic properties of the substituents of the R—azidotriazole system were unsuccessful. Thus, the potential energy constants of the azido group for azidotriazoles have transferability and can be used for calculations of various azido derivatives of 1,2,4-triazole.

Insofar as the potential energy constants of the triazole ring are concerned, the introduction of substituents with different electronic properties in the 1,2,4-triazole molecule leads to a change in a number of the force constants (Table 2).

TABLE 2. Force Constants of the Triazole Ring (in 10^6 cm^{-2} units)

Compound	K_{Q_1}	K_{Q_2}	K_{Q_3}	K_{Q_4}	K_{Q_5}	K_{α_1}	K_{α_2}	K_{α_3}	K_{α_4}	K_{α_5}
1,2,4-Triazole	13.3	9,8	11,3	12,8	11,4	3,5	2,9	2.7	3,3	3,0
3-Azido-1,2,4-triazole	13,3	9,8	10,65	12,9	12,0	3,0	2,36	2,2	3,3	2,8
3-Bromo-5-azido-1,2,4-triazole	13.3	9,8	11,1	11,7	11,9	3.3	2,75	2,7	3,0	2,8
1-Methyl-3-azido-1,2,4-triazole	13,3	10,0	10,75	12,9	12,0	3,0	2,50	2,42	3,3	3,30
3-Azido-5-methyl-1,2,4-triazole	13,2	9,8	10,64	11,2	12,0	3,0	2,36	2,2	2,9	2,8
3-Azido-5-nitro-1,2,4-triazole	11.2	8,4	10,88	11,7	10,45	2,65	2,36	2,2	3,5	3,3

Thus the π bonds of the triazole ring are polarized and the electron density is shifted from the C_5 atom to the C_3 atom along the system of ring $C_5 \rightarrow N_4 \rightarrow C_3$ bonds under the influence of such a weak acceptor as the azido group. When an electron-donor methyl group is introduced in the 1 position, in addition to the above-described shift of the electrons, one observes a secondary opposite direction of electrons along the $N_1 \rightarrow N_2 \rightarrow C_3$ bonds; this is retained regardless of the position of the methyl group in the ring, i.e., it is also retained for the 3-azido-5-methyl-1,2,4-triazole molecule.

The presence of the strong electron-acceptor nitro group in the 5 position leads to an opposite shift of electrons. In this case, as demonstrated by the calculations (Table 2), one observes a rather sizeable decrease in the potential energy constants of the ring bonds and some of the angular coordinates and their interaction coefficients.

A comparison of the force constants of the valence and angular coordinates of the rings of methyl derivatives of 3-azido-1,2,4-triazole shows that shifting the methyl group from the 1 position to the 5 position leads to a decrease in their absolute values, except for the $Q_5(C^3N^4)$ and $\alpha_1(\angle N^2C^3N^4)$ coordinates, i.e., the force field and, consequently, the electronic structure of the triazole ring are rather sensitive to a change in the position of the electron-donor substituent. If it is assumed that the degree of equilization of the ring force constants, which characterizes the delocalization of the electron density, is a measure of the aromatic character of the heteroring, on the basis of the data obtained in this research the N-methyl derivative of 3-azido-1,2,4-triazole has greater character than the C-methyl derivative. This is evidently explained by the greater participation of the unshared electron pair of the N atom in the creation of a unified delocalized electronic system under the influence of the electron-donor methyl group.

EXPERIMENTAL

All of the azidotriazoles for the study were obtained by the methods described in [10]. The IR spectra of the compounds were recorded by standard methods with Perkin–Elmer 457 and IKS-22 spectrometers. The Raman spectra of solutions of the compounds in organic solvents were recorded with a DFS-12 spectrometer. The calculation of the frequencies and forms of the normal vibrations and the solution of the inverse spectral problem were accomplished with a Minsk-22 computer with the programs presented in [9]. The anharmonicity of the vibrations was taken into account by the introduction of the spectroscopic masses of the atoms.

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VIBRATIONAL SPECTRA OF STRUCTURES OF 5-TRIFLUOROMETHYL-AND 1-METHYL-5-NITROTETRAZOLE

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The frequencies and forms of the normal vibrations of 5-trifluoromethyl- and 1-methyl-5-nitrotetrazole and the potential energy constants were calculated, and the effect of electron-acceptor substituents on the electronic structure of the tetrazole ring was investigated. The position of the hydrogen atom for 5-trifluoromethyltetrazole was established by the methods of vibrational spectroscopy. The frequencies in the experimental spectra were assigned to the principal types of normal vibrations.

It has been previously shown [1] that electron-donor substituents have a specific effect on the electronic structure of the tetrazole ring that depends on both the character of the substituent and on its position in the ring. The observed mechanism for transmission of the electronic effects by substituents is apparently characteristic only for tetrazole derivatives: we did not observe it previously for 1,2,4-triazole derivatives [2-6]. In this connection, we studied the vibrational spectra of tetrazole derivatives with electron-acceptor substituents.

The natural vibrational coordinates of the investigated compounds are presented in Fig. 1.

The geometrical parameters and the zero approximation of the force constants of the CF_3 and NO_2 groups necessary for the calculations of the frequencies and forms of the normal vibrations were taken from [7, 8] (a coplanar orientation of the NO_2 group was assumed). The force fields of the 5-methyl- and 1-methyltetrazole molecules, respectively, were used as a

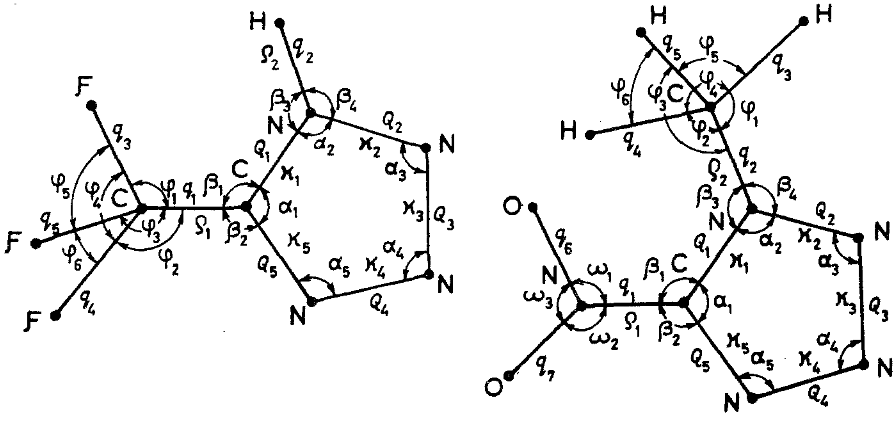

Fig. 1. Structure and natural vibrational coordinates of 5-trifluoromethyltetrazole and 1-methyl-5-nitrotetrazole.

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