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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

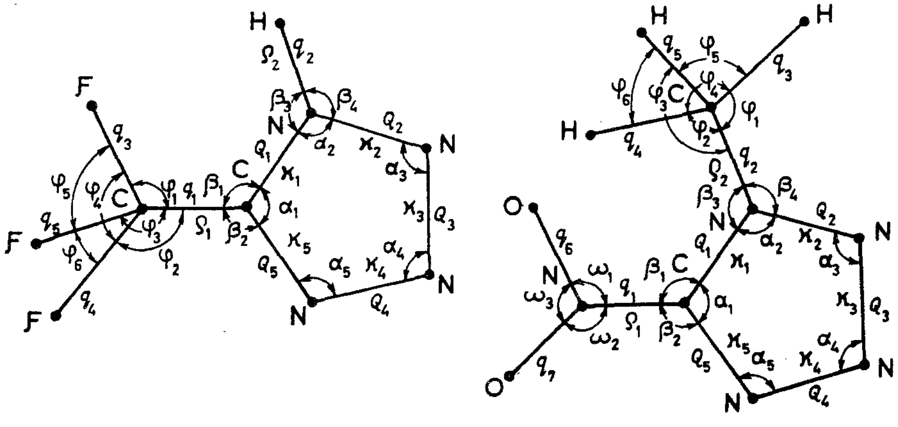

Fig. 1. Structure and natural vibrational coordinates of 5-trifluoromethyltetrazole and 1-methyl-5-nitrotetrazole.

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zero approximation of the potential energy constants in the calculations of 5-trifluoromethyl- and 1-methyl-5-nitrotetrazoles. The calculations of the spectra were made for models with c_s symmetry.

During the calculations we refined the force constants in conformity with the calculated values of the partial derivatives of the frequencies with respect to the force constants until the calculated frequencies were in satisfactory agreement with the experimental values. It was found that the frequencies of the vibrations of the tetrazole ring with electron-acceptor substituents supplement the arbitrary classification of vibrations presented in [1]. The conclusions drawn in this research relative to the characteristic nature of the ring vibrations and the aromatic character of the tetrazole ring also remain valid in this case. The force constants of 5-trifluoromethyl- and 1-methyl-5-nitro-tetrazole, which differ from the force constants of 5-methyl- and 1-methyltetrazole, respectively, are presented below in 10^6 cm^{-2} units. The symbolization of the force constants is in accordance with [9].

5-Trifluoromethyltetrazole:

$$K_{q_1}=7.0;\ K_{Q_3}=12.9;\ K_{q_3}=K_{q_4}=K_{q_5}=9.5;\ K_{\beta_3}=0.83;$$

$$K_{\alpha_2}=2.8;\ K_{\alpha_5}=2.5;\ K_{\varphi_1}=0.9;\ K_{\varphi_4}=K_{\varphi_5}=1.0;$$

$$K_{\varkappa_2}=0.8;\ K_{\rho_2}=0.7;\ H_{q_1}^{q_3}=0.05;\ H_{q_1}^{q_4}=H_{q_1}^{q_5}=0.01;\ H_{\varkappa_2}^{\varkappa_3}=-0.1;$$

$$H_{\varkappa_2}^{\varkappa_5}=-0.05;\ H_{q_3}^{q_4}=H_{q_3}^{q_5}=0.5;$$

$$A_{q_1}^{\alpha_1}=-0.5;\ A_{q_1}^{\varphi_2}=A_{q_1}^{\varphi_3}=0.8;\ A_{q_3}^{\varphi_1}=0.8;\ A_{q_3}^{\varphi_4}=A_{q_3}^{\varphi_5}=0.9;$$

$$A_{q_4}^{\varphi_2}=A_{q_5}^{\varphi_3}=1.0;\ A_{q_4}^{\varphi_4}=A_{q_5}^{\varphi_5}=0.7;$$

$$l_{\beta_1}^{\beta_2}=0.2;\ l_{\beta_4}^{\alpha_2}=-0.5;\ l_{\varphi_2}^{\varphi_3}=-0.05.$$

1-Methyl-5-nitrotetrazole:

$$K_{q_1}=6.5;\ K_{q_2}=6.9;\ K_{Q_4}=9.5;\ K_{q_4}=K_{q_5}=8.0;$$

$$K_{q_6}=K_{q_7}=14.0;\ K_{\beta_1}=K_{\beta_2}=0.8;\ K_{\beta_3}=K_{\beta_4}=0.9;$$

$$K_{\varphi_1}=1.3;\ K_{\varphi_6}=0.65;\ K_{\omega_1}=K_{\omega_2}=1.54;\ K_{\omega_3}=3.3;$$

$$K_{\varkappa_1}=0.3;\ K_{\rho_3}=0.76;\ H_{\varkappa_1}^{\varkappa_5}=-0.04;\ H_{q_2}^{q_4}=H_{q_2}^{q_5}=0.5;$$

$$H_{q_3}^{q_4}=H_{q_3}^{q_5}=0.01;\ H_{Q_1}^{q_2}=0.1;\ H_{q_4}^{q_5}=0.02;\ H_{q_6}^{q_7}=1.3;$$

$$H_{Q_2}^{Q_4}=0.6;\ A_{q_4}^{\varphi_2}=A_{q_5}^{\varphi_3}=0.8;\ A_{q_2}^{\varphi_2}=A_{q_2}^{\varphi_3}=0.2;$$

$$A_{q_6}^{\omega_3}=A_{q_7}^{\omega_3}=0.4;\ A_{q_1}^{\beta_2}=0.3;\ A_{q_1}^{\alpha_1}=-0.7;\ A_{Q_2}^{\beta_3}=0.15;$$

$$A_{Q_2}^{\beta_4}=0.6;\ l_{\alpha_3}^{\alpha_5}=-0.9;\ l_{\beta_3}^{\beta_4}=0.01;$$

$$l_{\varphi_1}^{\varphi_2}=l_{\varphi_1}^{\varphi_3}=-0.05.$$

It is apparent that the trifluoromethyl group has a substantial effect on the ring force constants. Thus, in comparison with 5-methyltetrazole, the force constant of the C=C bond decreases from 8.1 to 7.0, and the force constant of the N=N bond (K_{Q_3}) decreases from 13.5 to 12.9, during which these changes in the force constants and, consequently, the transmission of the electronic effects in the tetrazole ring under the influence of the trifluoromethyl group are also realized via two chains from the N_2 and N_3 atoms to the C_5 atom, as in the case of electron-donor substituents in the 5 position [1].

The effect of an electron-acceptor nitro group in the 5 position on the force field of 1-methyltetrazole is manifested primarily in the substantial change in the force constants of the methyl group through the C_5-N_1 bond (Q_1). Thus, the potential energy constant of the

$C-N_1$ bond (K_{q_2}) is reduced from 8.3 to 6.9, and the constants of the C-H bonds (K_{q_4} and K_{q_5}) and the interaction constants of the O-H bonds change from 8.4 to 8.0 and from 0.05 to 0.01, respectively; in addition, the interaction of the C_5-N_1 and $N^1=C$ bonds ($H_{Q_1}^{q_2}$) decreases to 0.1 as compared with 0.35 for 1-methyltetrazole.

The strong interaction of the nitro and methyl groups with one another does not exclude the effect of the nitro group on the ring force field (K_{Q_4}, $H_{Q_2}^{Q_4}$, and $l_{\alpha_3}^{\alpha_5}$) with retention of all of the principles of transmission of electronic effects in the ring that are valid for tetrazole derivatives with donor substituents.

Since no data whatsoever on the spatial orientation of the nitro group relative to the plane of the tetrazole ring are presently available, we investigated the effect of a change in the kinematic coefficients on the shifts of the frequencies in the vibrational spectrum of 1-methyl-5-nitrotetrazole. For this we calculated the spectra for a molecular configuration with 90° rotation of the nitro group relative to the C-N bond. The potential energy constants for the structure with a 90°-rotated nitro group were assumed to be the same as those for the planar model.

The calculations showed that 90° rotation of the nitro group with respect to the plane of the molecule does not lead to a change in the frequencies of the vibrations within the limits of the computational accuracy and that in this case one observes a certain change in the forms of the normal vibrations, which is particularly significant for ν_7 and ν_8 (Table 1); this is in conformity with the results in [10].

Thus, the vibrational spectrum of 1-methyl-5-nitrotetrazole was found to be insensitive to a change in the angle of rotation of the nitro group in the 5 position, and the methods of vibrational spectroscopy do not make it possible to make a choice in favor of one or another molecular conformation.

It is known that nitrous acid and organic azides react with compounds that contain multiple bonds, including nitriles, to give the corresponding tetrazole derivatives [11, 12]. The mechanism of the reaction of azides with dipolarophiles is a one-step many-center mecha-

TABLE 1. Vibrational Spectra of Tetrazole Derivatives

No.	Symmetry	1-Methyl-5-nitrotetrazole		5-Trifluoromethyltetrazole		Assignment
		IR spectrum, cm^{-1}	calc.	IR spectrum, cm^{-1}	calc.	
1	A′	3040 (w)	3020	1180 (vs)	1189	q_3; $-(q_4+q_5)$
2	A′	2860 (w)	2884	—	—	q_4+q_5; q_3
3	A′	1550 (vs)	1549	—	—	q_6; $-q_7$
4	A′	—	1470	1500, 1528 (m)	1516	ν_{ring}
5	A′	1480 (s)	1486	1410 (m)	1426	ν_{ring}
6	A′	1467 (m)	1481	1370 (step)	1379	δ_{CH_3}; ν_{ring}
7	A′	1411 (s)	1393	—	—	ν_{ring}; δ_{CH_3}
8	A′	1365 (s)	1362	—	—	δ'_{CH_3}; ν_{ring}
9	A′	1330 (vs)	1340	—	—	q_6; q_7
10	A′	1283 (w)	1286	1310 (step)	1286	ν_{ring}
11	A′	—	—	1235 (s)	1225	ν_{ring}; q_3
12	A′	1209 (m)	1184	—	—	ν_{ring}
13	A′	—	—	1160 (vs)	1133	q_1; ν_{ring}; q_3
14	A′	1073 (m)	1083	1045 (s)	1062	ν, δ_{ring}
15	A′	1025 (m)	1008	1020 (m)	997	ν, δ_{ring}
16	A′	—	931	870 (vw)	877	δ_{ring}
17	A′	846 (vs)	830	—	—	q_1; ω_3
18	A′	720 (vs)	717	2920—3180 (w)	3057	q_2
19	A′	535 (w)	553	—	—	ω_2; $-\omega_1$
20	A′	430 (m)	456	570 (w)	589	q_1; δ_{CF_3}
21	A′	—	128	410 (m)	431	β_1; $-\beta_2$; δ_{CF_3}
22	A′	370 (m)	343	—	—	β_3; $-\beta_4$
23	A′	—	—	—	318	δ_{CF_3}
24	A′	—	—	—	291	δ_{CF_3}
25	A′	—	—	—	168	δ_{CF_3}
1	A″	2960 (vw)	2955	1190 (vs)	1210	$-(q_4-q_5)$
2	A″	1445 (m)	1424	375 (w)	400	$\varphi_4-\varphi_5$
3	A″	1040 (m)	1068	—	311	$\varphi_2-\varphi_3$
4	A″	—	897	780 (w)	786	ρ, $\varkappa$, φ
5	A″	698 (w)	681	755 (s)	732	$\varkappa$, ρ
6	A″	660 (m)	637	—	—	ρ_3
7	A″	300 (m)	266	—	136	ρ_2, ρ_1
8	A″	—	147	—	—	$\varkappa$, ρ_3
9	A″	—	—	—	1177	$\varkappa$, ρ

nism and consists in the addition of the primary and tertiary atoms of the azido group to the atoms of the group containing multiple bonds [13-16].

The establishment of the structures of the reaction products is of great value for the investigation of the mechanism of 1,3-dipolar cycloaddition. Thus it was established by PMR spectroscopy that only one isomer is formed in the reaction of trifluoroacetonitrile with nitrous acid; however, this method did not enable us to unambiguously establish the position of the hydrogen atom in the ring. The most probable structures are those with fixation of the hydrogen atom in the 1 or 2 position. In order to solve this problem we calculated the vibrational spectra for 2-H-5-trifluoromethyltetrazole with the force field that was obtained for the 1-H derivatives. The calculations showed that the vibrational spectrum of the 2-H derivative differs from both the experimental spectrum and the spectrum calculated for 1-H tetrazole.

The frequencies that undergo the most significant changes are presented below:

	Exptl.	1-H-	2-H-
ν_4	1500, 1528	1516	1695
ν_5	1410	1426	1619
ν_6	1370	1379	1491
ν_{10}	1310	1286	1008
ν_{11}	1235	1225	991
ν_{13}	1160	1133	1376

The considerable difference in the calculated and experimental spectra in the case of the model with a hydrogen atom in the 2 position leads to the conclusion that the formation of the 5-trifluoromethyltetrazole isomer with a hydrogen atom in the 1 position is most likely.

The results of the assignment of the frequencies in the experimental spectra to definite types of normal vibrations are presented in Table 1.

EXPERIMENTAL

The IR spectra of films of liquid 5-trifluoromethyltetrazole and of mineral oil and perfluorinated mineral oil suspensions of crystalline samples of 1-methyl-5-nitrotetrazole were recorded with a Perkin—Elmer 457 spectrometer. The frequencies and forms of the normal vibrations were calculated with a Minsk-22 computer from previously published programs [9]. The anharmonicity of the vibrations was taken into account by introduction of the reciprocal spectroscopic masses of the atoms.

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