VIBRATIONAL SPECTRA AND STRUCTURE OF 1,2,4-TRIAZOLE DERIVATIVES

III.* THE QUESTION OF THE STRUCTURE OF THE DINITROTRIAZOLES

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From an analysis of the IR and Raman spectra and a calculation of the frequencies and forms of the normal vibrations of the nitrotriazoles, conclusions have been drawn on the structure of 3,5-dinitro-1,2,4-triazole and 1-methyl-3,5-dinitro-1,2,4-triazole. The nitro group in position 3 of the triazole ring is located in the plane of the molecule, and that in position 5 is rotated about the CN bond. The spatial nonequivalence of the nitro groups leads to the splitting of the absorption bands in the IR spectra that are characteristic for the anti- and synphase vibrations of the nitro groups.

In the IR spectra of nitrotriazoles investigated previously, absorption bands were found in the ~1555 and 1310 cm^{-1} regions which were assigned to the antiphase and synphase vibrations of the nitro group. The calculations of the frequencies and shapes of the normal vibrations of a series of 3-nitro-1,2,4-triazole and 1-methyl-3-nitro-1,2,4-triazole derivatives that were performed [1] confirmed the hypothesis of the coplanar arrangement of the nitro group in position 3 and the triazole ring. It was established that the conjugation of the nitro group and the ring leads to lowering the frequency of the synphase vibration of the nitro group, as compared with aliphatic nitro compounds [3], to 1300-1315 cm^{-1}.

In the IR spectra of the dinitrotriazoles, splitting of the absorption bands characterizing the vibrations of the nitro groups is observed, and this has served as a basis for a hypothesis of their spatial and electronic nonequivalence [2]. An indirect confirmation of this is the capacity of a nitro group in position 5 of the ring for taking part fairly readily in nucleophilic exchange reactions [4]. In view of this, the task of studying the influence of kinematic factors characterizing the change in the geometry of the molecule on the frequency shift in the vibrational spectrum, which will apparently permit the question of the spatial structure of the dinitrotriazoles to be answered, has become an urgent one.

In order to investigate the influence of kinematic factors, we calculated the frequencies and shapes of the normal vibrations of a plane model of 3,5-dinitro-1,2,4-triazole and of two models of 3,5-dinitro-1,2,4-triazole and 1-methyl-3,5-dinitro-1,2,4-triazole with rotation of the nitro group in position 5 about the CN bond by 90°. The geometric parameters of the ring used in the calculations corresponded to the results of an x-ray structural analysis of 1,2,4-triazole [5]. The parameters of the nitro group were calculated from information on bond orders [6]; the length of the CN bond for a nitro group rotated by 90° was taken as 1.46 Å.

All the models calculated belong to symmetry group C_s. The normal vibrations are given according to the types of symmetry in the following way:

3,5-Dinitro-1,2,4-triazole (plane model) – $\Gamma_V = 21A' + 9A''$;

3,5-Dinitro-1,2,4-triazole (model with rotated nitro group) – $\Gamma_V = 20A' + 10A''$;

1-Methyl-3,5-dinitro-1,2,4-triazole – $\Gamma_V = 25A' + 14A''$.

*For Communication (II), see [1].

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TABLE 1. Force Constants of 3,5-Dinitro-1,2,4-triazole (in units of 10^6 cm^{-2})

K_{q_1}	K_{Q_1}	K_{Q_2}	K_{q_4}	K_{Q_3}	K_{q_5}	K_{Q_4}	K_{Q_5}	K_{q_6}	K_{β_1}	K_{α_1}	K_{α_2}	K_{α_3}	K_{α_4}	K_{α_5}
8,3	12,4	10,8	8,6	11,9	7,5	12,8	11,4	14,0	1,7	3,3	3,1	3,0	3,2	3,3
K_{β_7}	K_{β_9}	$H_{q_3Q_3}$	$H_{q_5Q_4}$	$H_{q_5q_6}$	$H_{q_6q_7}$	$H_{q_2Q_3}$	$A^{q_1}_{\alpha_1}$	$A^{q_2}_{\beta_1}$	$A^{q_2}_{\beta_2}$	$l^{\beta_{10}}_{\beta_9}$	$l^{\alpha_2}_{\alpha_1}$	$A^{q_5}_{\beta_9}$	$A^{q_6}_{\beta_9}$	$A^{q_6}_{\beta_{10}}$
1,3	1,3	1,2	1,4	0,45	1,62	0,65	−0,74	0,78	−0,2	−0,06	0,36	0,5	0,5	−0,1

TABLE 2. Force Constants of 1-Methyl-3,5-dinitro-1,2,4-triazole (in units of 10^6 cm^{-2})

K_{Q_1}	K_{Q_2}	K_{q_4}	K_{Q_3}	K_{Q_5}	K_{α_1}	K_{α_2}	K_{α_4}	K_{α_5}	$K_{\gamma_1-\gamma_3}$	$K_{\gamma_4-\gamma_6}$	K_{ρ_3}	K_{ρ_4}	K_{ρ_5}
12,6	10,2	7,6	12,2	11,6	3,4	3,1	3,4	3,5	1,16	0,7	0,61	0,53	0,70

TABLE 3. Vibrational Spectra of the Dinitrotriazoles

Type of symmetry	3,5-Dinitro-1,2,4-triazole				1-Methyl-3,5-dinitro-1,2,4-triazole			Assignment*
	IR spectrum, ν, cm^{-1}	Raman spec., ν, cm^{-1}	ν_{calc}, cm^{-1}		IR spectrum, ν, cm^{-1}	Raman spec., ν, cm^{-1}	ν_{calc}, cm^{-1}	
			nonplanar model	planar model				
A'	3080 w.br.		3037	3037				ν_{NH}
A'					3045 w.br		3010	ν_{CH_3}
A''							3009	ν_{CH_3}
A'					2950 s.br		2944	ν_{CH_3}
A'	1577 v.s	1566 (1,7)	1572	1570	1568 v.s.br	1566 (1,6)	1569	$\nu_{antiph\ NO_2}$ (q_2q_3)
A''	1549 s		1548	1580	1543 v.s.sh		1547	$\nu_{antiph\ NO_2}$ (q_6q_7)
A'	1515 s		1527	1540	1512 v.s		1528	ν_{ring}, δ_{CH_3}
A'					1503 v.s.sh		1497	δ_{CH_3}
A'					1475 v.s	1467 (2,9)	1481	δ_{CH_3}
A''					1462 v.s		1473	δ_{CH_3}
A'	1442 m	1408 (10)	1444	1459	1440 s	1430 (10)	1434	ν_{ring}
A'	1405 m		1412	1414	1410 s		1413	ν_{ring}
	1392 m							
A'	1373 s	1367 (3,1)	1377	1389	1386 s	1378 (3,6)	1379	ν_{ring}, δ_{CH_3}
A'	1330 s	1310 (0,9)	1338	1316	1347 v.s	1334 (2,1)	1342	$\nu_{synph\ NO_2}$ (q_6q_7)
A'	1316 s		1308	1308	1327 v.s	1308 (2,4)	1318	$\nu_{synph\ NO_2}$ (q_2q_3)
A'	1277 m		1278	1274	1284 s	1280 (1,6)	1283	ν_{ring}
A'					1169 m	1151 (0,5)	1152	δ_{CH_3}, δring
A''					1131 m		1132	δ_{CH_3}
A'	1058 s		1055	1058				δ_{NH}
A'	1047 m	1020 (0,5)	1048	1046	1053 m	1046 (1,4)	1053	δ_{ring}
A'	980 m		981	983	1027 v.w.	1026 (0,7)	1020	δ_{ring}, δ_{CH_3}, δ_{NH}
A'',	849 s		885	879	867 s.sh		872	ρ_{CN}, ρ_{NH}, χ
A''	834 s		841	787	857 v.s		816	ρ_{CN}, ρ_{NH}, χ
A'					829 s	828 (0,7)	827	ν_{CN}
A''	775 v.w	760 (0,4)	779	411	715 m		725	ρ_{NO}, δ_{CN}
A''			725	698				ρ_{NH}, ρ_{CN}, χ
A'	670 v.w.sh		695	734				ν_{CN}, δ_{NO_2}, δ_{ring}
A''	655 m		647	625	635 m		627	ρ_{NO}, χ
					625 m			
A'					650 m		652	δ_{NO_2}, δ_{CN}
A'				610				ν_{CN}, δ_{NO_2}
A'			599	584			590	δ_{NO_2}, δ_{CN}
A'			541	525			553	δ_{CN}, δ_{NO_2}
A''			418		510 w.sh		517	ρ_{CN}, δ_{NO_2}
A'							390	δ_{CN}, δ_{NO_2}
A'			332	343			325	δ_{NO_2}
A''			304				307	δ_{NO_2}, ρ_{CN}, δ_{CN}
A'				280				δ_{NO_2}, δ_{CN}
A'			261	261			262	δ_{NO_2}, δ_{CN}
A'							191	δ_{CN}
A'			143	130			138	δ_{CN}
A''			194	203				ρ_{CN}, χ
A''							125	ρ_{CN}, χ
A''			86	93			88	χ, ρ_{CN}

*ν, stretching; δ, deformation; ρ, nonpolar vibrations; χ, vibrations of the triazole ring.

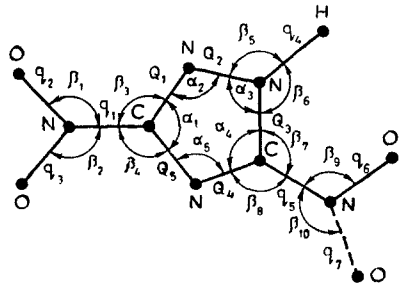

Fig. 1. Structure and natural coordinates of 3,5-dinitro-1,2,4-triazole.

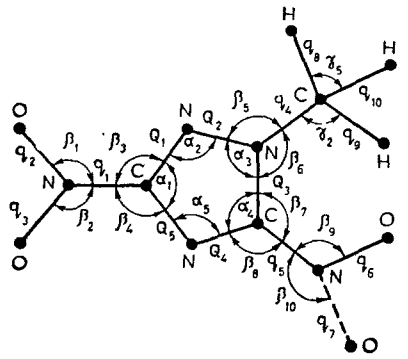

Fig. 2. Structure and natural coordinates of 1-methyl-3,5-dinitro-1,2,4-triazole.

In the calculations, the rotation of the CH_3 and NO_2 groups about the CN double bonds was not taken into account. The natural vibrational coordinates of the compounds investigated are given in Figs. 1 and 2.

To calculate the spectra of the dinitrotriazoles in the zero approximation, we used the set of potential-energy constants for 3-nitro-1,2,4-triazole, assuming that the force constants of the two nitro groups of the plane model of 3,5-dinitro-1,2,4-triazole were identical. With the rotation of a nitro group by 90° about the CN bond, the π orbitals of the triazole ring and of the nitro group become orthogonal. As a result of this, the potential-energy constants characterizing the interaction of the coordinates of the nitro group and of the ring fall. Tables 1 and 2 give the values of the force constants for 3,5-dinitro-1,2,4-triazole and 1-methyl-3,5-dinitro-1,2,4-triazole; for the triazole ring, the constants that have been changed since the previous paper [1] are given.

As was to be expected, the best agreement of the calculated and experimental frequencies is observed for models of the dinitrotriazoles with a rotated nitro group in position 5 of the ring (Table 3). The frequency of the stretching vibrations of the nitro group and the frequencies of the stretching vibrations of the ring (coordinates Q_3 and Q_4) proved to be the most sensitive to the rotation of the nitro group. Thus, on the basis of an analysis of the vibrational spectra of different spatial models of the dinitrotriazoles it may be assumed that the nitro group in position 5 of the ring has departed from conjugation with the triazole ring, i.e., has been turned by some angle about the CN bond not only for 1-methyl-3,5-dinitro-1,2,4-triazole, where rotation may be due to the steric repulsion of the fairly voluminous methyl group, but also for 3,5-dinitro-1,2,4-triazole.

Table 3 gives the results of the assignment of frequencies made in the experimental spectra to the main types of normal vibrations.

LITERATURE CITED

1. V. V. Mel'nikov, V. V. Stolpakova, M. S. Pevzner, and B. V. Gidaspov, Khim. Geterotsikl. Soedin., 707 (1973).
2. V. V. Mel'nikov, V. V. Stolpakova, and M. S. Pevzner, Khim. Geterotsikl. Soedin., 414 (1971).
3. L. Bellamy, Infrared Spectra of Complex Molecules, 1st ed., Methuen (1954).
4. L. I. Bagal, M. S. Pevzner, and V. Ya. Samarenko, Khim. Geterotsikl. Soedin., 269 (1970).
5. P. Goldstein, I. Ladell, and G. Abowitz, Acta Cryst., B25, 135 (1969).
6. V. V. Mel'nikov, M. S. Pevzner, V. V. Stolpakova, and L. F. Khor'kova, Khim. Geterotsikl. Soedin., 409 (1971).