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

II.* INTERPRETATION OF THE VIBRATIONAL SPECTRA OF 3-NITRO- AND 1-METHYL-3-NITRO-1,2,4-TRIAZOLE DERIVATIVES

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The frequencies and forms of the normal vibrations of 3-nitro-1,2,4-triazole, its 1-deutero- and 1-methyl derivatives, and 1-methyl-3-nitro-5-chloro(bromo)-1,2,4-triazole, which are classified as having C_s group symmetry, were calculated. The potential energy constants were refined by solution of the reciprocal spectral problem, and the frequencies in the experimental spectra were assigned to the principal types of vibrations.

We have previously shown [2] that the IR and Raman spectra of all – without exception – nitro derivatives of 1,2,4-triazole derivatives contain bands at ~ 1555 cm^{-1}, which characterize the antiphase vibration of the nitro groups, in connection with which it was assumed that the nitro group in the 3 position should be situated in the plane of the triazole ring.

For the calculations of the vibrational spectra of derivatives of 3-nitro- and 1-methyl-3-nitro-1,2,4-triazole, we therefore selected models pertaining to the C_s symmetry group, i.e., the nitro group in the 3 position is situated in the plane of the triazole ring. In conformity with the symmetry of the investigated compounds, the normal vibrations are broken down in the following manner with respect to symmetry: for 3-nitro-1,2,4-triazole

$$\Gamma_v = 17A' + 7A'',$$

for 1-methyl-3-nitro-1,2,4-triazole and its 5-halo derivatives

$$\Gamma_v = 22A' + 11A''.$$

Rotation of the nitro and methyl groups about the corresponding bonds was disregarded in the calculations. The natural vibrational coordinates of 3-nitro-1,2,4-triazole and 1-methyl-3-nitro-1,2,4-triazole are presented in Fig. 1.

The geometrical parameters of the triazole ring were in conformity with the data from x-ray diffraction analysis [3], the N–O and C–N bond lengths were taken as 1.22 and 1.40 Å, the ONO valence angle was assumed to be 126°, and the methyl group was assumed to have the standard geometry. The geometrical parameters of the $C-NO_2$ group were estimated from the "bond order–bond length" correlation curves [4] in conformity with the data calculated by the MO LCAO method [5]. The constants presented in [1, 6] were used for the zero approximation of the force constants of the triazole ring, the nitro group, and the methyl group. The force constants selected in this manner were refined by calculation of the partial derivatives from the frequencies with respect to the force constants and by solution of the reciprocal spectral problem for all of the investigated compounds.

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*See [1] for communication I.

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

K_{q_1}	K_{q_2}	K_{q_4}	K_{q_5}	K_{Q_1}	K_{Q_2}	K_{Q_3}	K_{Q_4}	K_{Q_5}	K_{α_1}	K_{α_4}	$K_{\beta_{1;2}}$	$K_{\beta_{3;4}}$	K_{ρ_1}	K_{ρ_2}	K_{ρ_3}	K_{ρ_4}	$H_{q_1Q_1}$
8,55	14,0	8,65	9,15	12,9	10,60	11,20	13,40	11,7	3,0	2,80	1,54	1,20	0,70	0,65	0,46	0,54	1,20
$H_{q_1q_2}$	$H_{q_2q_3}$	$H_{q_2Q_1}$	$A_{\beta_1}^{q_1}$	$A_{\beta_3}^{q_1}$	$A_{\alpha_1}^{q_1}$	$A_{\beta_1}^{q_2}$	$A_{\beta_2}^{q_2}$	$A_{\beta_3}^{q_2}$	$l_{\beta_2}^{\beta_1}$	$l_{\beta_4}^{\beta_3}$	$l_{\beta_3}^{\alpha_1}$	$l_{\alpha_2}^{\alpha_1}$	$l_{\beta_8}^{\beta_7}$	$l_{\rho_2}^{\rho_1}$	$l_{\rho_4}^{\rho_3}$		
0,937	1,65	0,65	0,645	0,6	−0,78	0,76	−0,20	0,35	−0,06	0,3	−0,2	0,38	0,35	0,25	0,20		

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*The force constants were designated in accordance with [6]; ρ_1, ρ_2, ρ_3, and ρ_4 are the out-of-plane vibrations of the N−O, C−N, N−H, and C−H bonds; χ are the out-of-plane ring vibrations.

TABLE 2. Force Constants of 1-Methyl-3-nitro-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_6}	K_{Q_4}	K_{Q_5}	K_{α_1}	K_{α_2}	K_{α_3}	K_{α_4}	K_{α_5}	K_{β_1}	K_{β_5}	K_{γ_1}
8,3	12,6	10,1	7,2	12,0	8,85	8,3	13,2	11,6	3,3	3,1	3,1	3,2	3,3	1,4	1,1	1,1
K_{γ_4}	K_{ρ_2}	$K_{\rho_3}^{*}$	$H_{q_4Q_2}$	$H_{Q_3Q_2}$	$H_{q_4Q_3}$	$H_{q_6q_7}$	$A_{\alpha_1}^{q_1}$	$A_{\beta_3}^{q_2}$	$A_{\beta_5}^{q_4}$	$A_{\alpha_3}^{q_4}$	$A_{\gamma_1}^{q_6}$	$A_{\gamma_4}^{q_6}$	$l_{\beta_5}^{\alpha_3}$	$l_{\beta_5}^{\beta_6}$	$l_{\gamma_1}^{\gamma_2}$	$l_{\gamma_5}^{\gamma_4}$
0,7	0,71	0,61	1,2	2,0	1,2	0,05	−0,74	0,32	0,6	−0,7	0,6	0,35	−0,2	0,3	−0,03	−0,03

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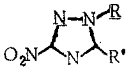
*The symbol δ_3 is the out-of-plane vibration of the C−N bond (q_4).

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

K_{q_1}	K_{CCl}	K_{CBr}	K_{Q_1}	K_{Q_2}	K_{Q_3}	K_{Q_4}	K_{Q_5}	K_{NCCl}	K_{NCBr}	K_{α_4}
8,2	8,5	7,1	12,2	10,3	12,6	11,9	11,9	1,3	1,2	3,2
$K_{\rho_{\mathrm{CCl}}}$	$K_{\rho_{\mathrm{CBr}}}$	$H_{Q_3(\mathrm{CCl})}$	$H_{Q_3(\mathrm{CBr})}$	$H_{Q_4(\mathrm{CCl})}$	$H_{Q_4(\mathrm{CBr})}$	$l_{\beta_7}^{\alpha_4}$	$l_{\beta_7}^{\beta_8}$	$l_{\alpha_4}^{\beta_8}$	$A_{\beta_7}^{\mathrm{CCl(Br)}}$	$A_{\alpha_4}^{\mathrm{CCl(Br)}}$
0,25	0,20	1,9	1,8	1,8	1,7	−0,2	0,3	−0,2	0,6	−0,7

TABLE 4. Frequencies and Forms of the Normal Vibrations of Nitrotriazoles



Symmetry	R=CH₃, R′=H			R=CH₃, R′=Cl			R=CH₃, R′=Br			Form of vibrations
	ν(IR), cm^{-1}	ν(Raman), cm^{-1}	νcalc cm^{-1}	ν(IR), cm^{-1}	ν(Raman), cm^{-1}	νcalc, cm^{-1}	ν(IR), cm^{-1}	ν(Raman), cm^{-1}	νcalc, cm^{-1}	
A′	3105 s	—	3106	—	—	—	—	—	—	$-q_5$ (ν_{CH})
A′	3010	—	3010	3048 w	—	3010	3035 w	—	3009	q_6, $-q_7$, $-q_8$
A″	3010 s, b	—	3009	2950 w	—	3009	2950 w	—	3009	q_7, $-q_8$
A′	2900		2943	2900	—	2943	—		2943	q_7, q_8, q_6
A′	1555 vs	1549 (1,2)	1558	1555 vs	1557 (1,8)	1556	1555 vs	1555 (1,3)	1555	q_2, $-q_3$
A′	1510 vs	1498 (4,7)	1524	1495 vs	1486 (2,8)	1512	1490 vs	1482 (3,1)	1520	$-q_1$, Q_1, Q_4
A′	1483 m	—	1483	—	—	1476	—	—	1475	$-\gamma_1$, $-\gamma_2$, $-\gamma_3$, γ_4, γ_5
A′	1470 m	—	1473	1472 sh, b	—	1472	1480 sh, b	—	1473	γ_1, $-\gamma_2$, $-\gamma_3$, $-\gamma_4$, $-\gamma_5$, γ_6
A″	1457 s	—	1466	—	—	1466	—	—	1466	$-\gamma_2$, γ_3, γ_4, $-\gamma_5$
A′	1445 s	1439 (4,9)	1442	—	—	—	—	—	—	$-Q_1$, Q_4, β_7, β_8
A′	1420 vs	1400 (10)	1416	1425 s	1421 (10)	1409	1420 s	1412 (10)	1417	$-Q_5$, γ
A′	—	—	—	1400 m		1384	1398 m	—	1395	Q_1, $-Q_4$
A′	1390 m 1368 m	1360 (0,5)	1379	1385 m 1369 w	1380 (3,9)	1364	1380 m 1367 m	1368 (1,8)	1363	$-Q_3$, γ
A′	1313 vs	1302 (0,5)	1316	1312 s	1308 (1,0)	1307	1313 vs	1304 (1,0)	1307	q_2, q_3
A′	1280 1271 m	1278 (4,0)	1295	1272 m	1273 (3,4)	1273	1269 m	1266 (3,8)	1272	Q_2, γ
A′	1207 s	—	1197	—	—	—	—	—	—	$-\beta_7$, β_8
A″	1130 w	—	1110	1120 w	—	1108	1120 w	—	1108	γ_2, $-\gamma_3$, γ_4, $-\gamma_5$
A′	1073 w	1051 (2,1)	1075	1147 s	—	1135	1130 s	—	1139	γ_1, $-\gamma_2$, $-\gamma_3$, γ_4, γ_5, $-\gamma_6$
A′	1039 s	1022 (0,5)	1031	1045 w	1042 (1,2)	1033	1046 w	1039 (1,4)	1032	α_1, $-\alpha_2$, α_3, $-\alpha_5$
A′	1019 w	1009 (1,0)	991	1021 w	1022 (0,6)	1010	1023 w	1021 (0,8)	1009	Q_2, α_2, α_3, $-\alpha_4$, α_5
A″	902 m	—	916	—	—	—	—	—	—	ρ_2, $-\rho_4$, χ
A″	837 vs	832 (0,6)	818	843 s	835 (0,4)	877	841 vs	—	878	$-\rho_2$, ρ_4, χ
A′						821			806	$-q_1$, q_4, q_5
A′	775 w 740 w 723 w		767							q_4, α_2, $-\alpha_3$, α_4, $-\alpha_5$
A″	—	—	—	723 m	723 (0,8)	714	713 m	—	705	ρ_3, $-\rho_4$, χ
A″	700 s	702 (0,4)	693	685 m	—	679	680 m	—	678	ρ_1, χ
A″	663 vs	—	654	—	—	—	—	—	—	ρ_1, $-\rho_3$, χ
A′	~650 w	—	608	644 m	—	640	645 w	—	619	$-\beta_1$, $-\beta_2$, $-\alpha_1$, α_2
A′	—	—	537	590 w	—	580	—	—	573	β_1, $-\beta_2$, $-\beta_3$, β_4
A′	—	—	—	536 m	—	520	420 w	—	428	q_5
A′	—	—	352	—	371 (0,3)	393	—	384 (0,2)	360	β_1, β_2, β_5, β_6
A″	—	—	238	—		374			362	ρ_2, $-\rho_3$, ρ_4, χ
A′	—	—	287	—	243 (0,2)	282		299 (0,1)	266	β_1, β_2
A′	—	—				206		209 (0,3)	186	β_7, $-\beta_8$
A′	—	—	173	—		153	—	136 (1,2)	132	$-\beta_1$, β_2, $-\beta_3$, β_4
A″	—	—	125	—		123	—	—	122	χ
A″						84	—	—	66	ρ_{C-Hal}, χ

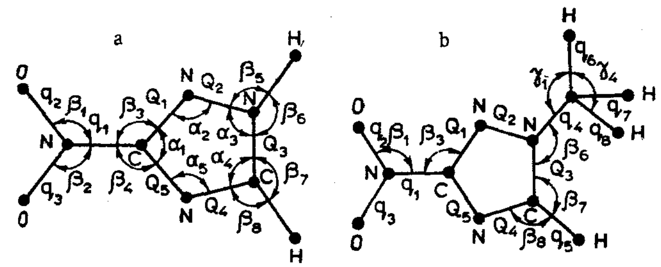


Fig. 1. Structure and natural vibrational coordinates of 3-nitro-1,2,4-triazole (a) and 1-methyl-3-nitro-1,2,4-triazole (b).

The final values of the potential energy constants for 3-nitro- and 1-methyl-3-nitro-1,2,4-triazole and its 5-halo derivatives are presented in Tables 1-3, in which the force constants, altered as compared with the data in [1], are presented for the triazole ring.

When an electron-acceptor nitro group is introduced into the 3 position of the ring, one observes, as expected, a change in the potential energy constants of the valence and angular coordinates of the triazole ring, which interact directly with the coordinates of the nitro group, and the force constants of the N−N and C−N (Q_4) bonds increase; this increase should lead to an increase in the degree of double-bond character of the latter. The results are in good agreement with the results in [5], in which it was shown that the orders of the N−N and C−N (Q_4) bonds for 3-nitro-1,2,4-triazole increase as compared with 1,2,4-triazole.

Replacement of the proton in the 1 position by a methyl group leads to an increase in the force constants of the C−N (Q_3) bond and the angular coordinates of the ring and to a slight decrease in the force constants of the remaining valence bonds of the ring, and there is a still more significant increase in the constant of the C−N (Q_3) bond and a decrease in the elastic constant of the C−N (Q_4) bond when the proton in the 5 position is replaced by halogen (chlorine or bromine) (Tables 1-3), i.e., the force field of the triazole ring, which characterizes the electronic interaction of the atoms, is sensitive to the introduction of both electron-acceptor (NO_2, Cl, and Br) and electron-donor (CH_3) substituents into the ring.

For a more reliable interpretation of the vibrational spectra of the nitrotriazoles, the frequencies and forms of the normal vibrations of the N-deuterated derivative of 3-nitro-1,2,4-triazole,* 1-methyl-3-nitro-

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*This compound was obtained after repeated recrystallization from D_2O. The IR spectra of mineral oil suspensions of the compounds were recorded by the usual method with IKS-14 and IKS-22 spectrometers.

TABLE 5. Frequencies and Forms of Normal Vibrations of Isotopically Substituted 3-Nitro-1,2,4-triazoles

Symmetry	1-H-3-Nitro-1,2,4-triazole			1-D-3-Nitro-1,2,-4-triazole		Form of vibrations
	ν (IR), cm^{-1}	ν(Raman) cm^{-1}	ν calc cm^{-1}	ν (IR), cm^{-1}	νcalc, cm^{-1}	
A′	3155 s	—	3156	3155 m	3156	q_5
A′	3058 s	—	3045	2230 vs	2267	q_4
A′	1566 vs	1558(2,3)	1566	1558 vs		$q_2, -q_3, -\beta_1, \beta_2, \beta_3, -\beta_4$
				1568 vs	1566	
A′	1524 vs	—	1525	1505 vs	1524	$q_1, -Q_1, -Q_4, -\beta_7, \beta_8$
A′	1484 vs	1480(4,7)	1467	1447 s	1462	$-q_1, Q_1, -Q_4, -\beta_7, \beta_8$
A′	1430 vs	1417(10)	1427	1435 m	1426	$-q_1, Q_5$
A′	1383 vs	1385(8,6)	1376	1366 vs	1368	$Q_3, -\beta_7, \beta_8$
A′	1314 vs	1304(1,0)	1314	1315 vs	1314	q_2, q_3
A′	1272 s	1245(2,0)		1276 m		$Q_2, -Q_3$
		1218(3,5)	1281	1238 s	1276	
A′	1186 m	1179(3,0)	1186	1187 sh, m	1174	$-\beta_7, \beta_8$
A″	1111 s	1110(0,5)	1109	1104 s	1085	ρ_4
A′	1018 s	1001(1,0)	1032	—	—	$-\beta_5, \beta_6$
A′	981 vs	973(0,5)	983	972 vs	998	$-\alpha_1, \alpha_2, -\alpha_4, \alpha_5$
A′	918 m	—	917	900 m	912	$\alpha_2, -\alpha_3, \alpha_4, -\alpha_5$
A″	879 s	—	902	—	—	ρ_3
A″	837 vs	835(0,8)	814	842 vs	855	$-\rho_2, \rho_3$
A″	—	—	—	778 w	771	$-\rho_2, \rho_3$
A′	—	—	—	725 w	757	$-\beta_5, \beta_6$
A″	655 s	—	668	665 s	667	ρ_1
A′	645 s	—	643	650 m	641	$-\beta_1, -\beta_2, q_1$
A′	540 vw	542(0,5)	543	527 vw	539	$-\beta_1, \beta_2, \beta_3, -\beta_4$
A″	447 m	435(0,5)	429	—	373	$\chi, -\rho_3$
A′	—	—	307	—	306	β_1, β_2
A′	—	225(1,0)	215	—	212	$\beta_3, -\beta_4$
A″	—	—	182	—	176	χ, ρ_2

1,2,4-triazole and its 5-chloro(bromo) derivatives with the force constants obtained from solution of the reciprocal spectral problem.

The results of the assignment of the frequencies in the experimental spectra for the investigated nitrotriazoles are presented in Tables 4 and 5.

Despite the uncharacteristic nature of the form of the vibrations (Tables 4 and 5), narrow regions of frequencies that describe the vibrations of definite structural fragments of the molecules can be isolated for the investigated nitrotriazoles.

The vibrations of the nitro group, which are localized over quite narrow spectral intervals, are the most characteristic with respect to frequency: the symmetrical stretching antiphase vibration of the nitro group is ~ 1555 cm^{-1}, the synphase vibration is 1302-1315 cm^{-1}, the out-of-plane vibration is 680-700 cm^{-1}, and the deformation vibration is ~ 645 cm^{-1}.

Insofar as the deformations of the triazole ring are concerned, the stretching vibrations of the ring C—N bonds (Q_3 and Q_5) appear at ~ 1385 and 1420 cm^{-1}, respectively, while the vibrations of the remaining C—N (Q_1 and Q_4) bonds appear together at 1400-1480 cm^{-1}. The vibration of the N—N bond at ~ 1275 cm^{-1} is also relatively characteristic with respect to frequency. Because of the quite considerable magnitude of the kinematic and dynamic coefficients of interaction between the vibrational coordinates of the triazole ring, it is practically impossible to isolate the narrow spectral regions of the frequencies for the deformation and out-of-plane vibrations, i.e., the vibrations are also uncharacteristic with respect to frequency.

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