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

IV.* NITROTRIAZOLE ANIONS

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UDC 547.79+543.422.4

The frequencies and forms of the normal vibrations of the anions of 1,2,4-triazole and 3-nitro-, 3-nitro-5-methyl-, and 3,5-dinitro-1,2,4-triazoles were calculated. The potential energy constants were calculated by solution of the reciprocal spectral problem, and the frequencies in the experimental spectra were assigned to the fundamental types of normal vibrations. It is shown that the nitro groups in the 3 and 5 positions in the anions of the triazoles are located in the plane of the triazole ring. The coordination of the metal in crystalline salts of nitrotriazoles was studied by the methods of vibrational spectroscopy, and an assumption is stated that the most probable position of the metal is near the oxygen atoms of the nitro group along the Me−O−N line. As a result of a theoretical analysis of the vibrational spectra of the anions it was ascertained that equalization of the lengths of the ring CN bonds does not occur during ionization of the covalent triazoles. Calculations by the MO LCAO SCF method are in agreement with the data from vibrational spectroscopy.

As in the case of 1,2,4-triazole derivatives, it seemed expedient to commence the investigation of the structure and interpretation of the vibrational spectra of the anions with the simplest compound – the anion of 1,2,4-triazole. The problem of the three-dimensional and electronic structure of the 1,2,4-triazole anion is currently under discussion, and some authors feel that equalization of the lengths of the ring CN bonds and equalization of the charges of the symmetrical nitrogen and carbon atoms should occur during the ionization of covalent 1,2,4-triazole, i.e., the symmetry should be raised from C_s for covalent 1,2,4-triazole to C_{2v} in the anion [2].

To solve this problem, we used the methods of vibrational spectroscopy to calculate the frequencies and forms of the normal vibrations of two models of the 1,2,4-triazole anion for the C_{2v} and C_s symmetry groups. The normal vibrations of the anion with C_{2v} symmetry are represented with respect to symmetry types as follows:

$$\Gamma_v = 6A_1 + 5B_2 + 2A_2 + 2B_1,$$

while in the case of a model with C_s symmetry, we have

$$\Gamma_v = 11A' + 4A''.$$

In the calculation of the model with C_{2v} symmetry, the 1,2,4-triazole anion was considered to be a regular pentagon with bond lengths 1.34 Å and internal angles of 108°, while angles HCN were assumed to be 126° [3]. The geometrical equivalence of coordinates Q_1 and Q_3 and Q_4 and Q_5 (Fig. 1) required the introduction into the vibrational problem of identical values of the force constants for equivalent coordinates of the ring. However, we were unable to select a set of potential energy constants that would satisfactorily

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*See [1] for communication III.

Lensovet Leningrad Technological Institute. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 10, pp. 1423-1431, October, 1973. Original article submitted December 12, 1972.

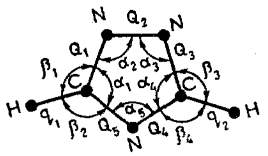

Fig. 1. Structure and natural coordinates of the 1,2,4-triazole anion.

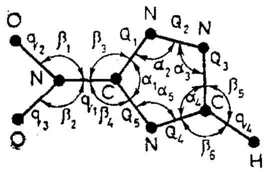

Fig. 2. Structure and natural coordinates of the 3-nitro-1,2,4-triazole anion.

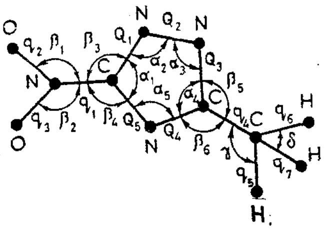

Fig. 3. Structure and natural coordinates of the 3-nitro-5-methyl-1,2,4-triazole anion.

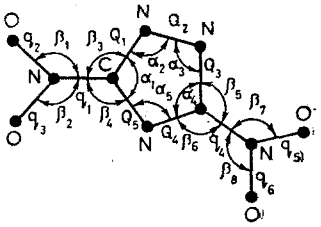

Fig. 4. Structure and natural coordinates of the 3,5-dinitro-1,2,4-triazole anion.

TABLE 1. Vibrational Spectrum of the 1,2,4-Triazole Anion

Symmetry	Ag salt	K salt		ν_{calc}, cm^{-1}	Assignment*
	IRspectrum, ν, cm^{-1}[14]	IR spectrum, ν,cm^{-1} [14]	Raman spect. ν,cm^{-1} [5]		
A'	3140 sh	—	—	3159	$\nu_{(CH)}$
A'	3130 w	—	—	3132	$\nu_{(CH)}$
A'	1507 s	1490 vs	1482 (2,2)	1488	$\nu_{(Q_1, Q_4)}$
A'	1410 sh	1460 sh	—	1436	$\nu_{(Q_3, Q_4, Q_5)}$, $\delta_{(CH)}$
A'	—	1385	1381 (3,1)	1380	$\nu_{(Q_2)}$, $\delta_{(CH)}$
A'	1340 vs	—	1339 (2,4)	1347	$\nu_{(Q_1, Q_3, Q_5)}$
A'	1290 vs	1256 vs	1259 (10)	1261	$\delta_{(\beta_1 \beta_2)}$
A'	1230 sh	1250 sh	—	1252	$\delta_{(\beta_1-\beta_4)}$, ν_r
A''	1205 w	1200 m	1191 (1,6)	1206	$\rho_{(CH)}$, χ
A''	1170 vs	1158 vs	1158 (2,9)	1150	$\rho_{(CH)}$, χ
A'	1086 m	1070 vw	1069 (1,4)	1093	$\delta_{(CH)}$, ν_r, δ_r
A'	960 sh	980 m	984 (1,0)	970	δ_r, $\delta_{(CH)}$
A'	890 m	882 s	—	882	δ_r
A''	—	—	—	552	χ
A''	—	—	—	550	χ

*Symbols: ν_r are the ring stretching vibrations, δ_r are the ring deformation vibrations, ρ are the out-of-plane vibrations, and χ are the ring bending vibrations.

describe the experimental spectra of 1,2,4-triazole salts in crystalline form and aqueous solutions for the investigated model by methods of calculation of the partial derivatives of the frequencies with respect to the force constants and solution of the reciprocal spectral problem. The calculation of the model with C_s symmetry was carried out with the use of data from x-ray diffraction analysis for covalent 1,2,4-triazole. The potential energy constants of 1,2,4-triazole [4] were used as the zero approximation of the force field, and they were then refined by calculation of the partial derivatives of the frequencies with respect to the force constants and solution of the reciprocal spectral problem.

$$K_{q_1}=K_{q_2}=9{,}0;\ K_{Q_1}=K_{Q_4}=13{,}3;\ K_{Q_2}=12{,}4;\ K_{Q_3}=K_{Q_5}=12{,}1;\ K_{\beta_i}=0{,}9;\ K_{\alpha_{1,5}}=3{,}55;$$

$$K_{\alpha_2}=2{,}9;\ K_{\alpha_3}=2{,}8;\ K_{\alpha_4}=3{,}4;\ K_{\rho_{1,2}}=0{,}6;\ K_{\chi}=0{,}3;\ H_{q_1Q_1}=H_{q_1Q_5}=H_{q_2Q_3}=H_{q_2Q_4}=0{,}3;$$

$$H_{Q_1Q_2}=H_{Q_2Q_3}=2{,}0;\ H_{Q_1Q_3}=H_{Q_1Q_4}=H_{Q_2Q_4}=H_{Q_2Q_5}=H_{Q_3Q_5}=0{,}8;\ H_{Q_1Q_5}=H_{Q_3Q_4}=H_{Q_4Q_5}=2{,}1;$$

$$A_{\beta_i}^{q_1}=A_{\beta_i}^{q_2}=0{,}2;\ A_{\alpha_1}^{q_1}=A_{\alpha_4}^{q_2}=-0{,}16;$$

$$A_{\beta_1}^{Q_1}=A_{\beta_3}^{Q_3}=A_{\beta_4}^{Q_4}=A_{\beta_2}^{Q_5}=0{,}96;\ A_{\beta_2}^{Q_1}=A_{\beta_4}^{Q_3}=A_{\beta_3}^{Q_4}=A_{\beta_1}^{Q_5}=0{,}58;$$

$$A_{\alpha_{1,2}}^{Q_1}=A_{\alpha_{2;3}}^{Q_2}=A_{\alpha_{3;4}}^{Q_3}=A_{\alpha_{4;5}}^{Q_4}=A_{\alpha_{1;5}}^{Q_5}=2{,}1;\ l_{\beta_{i+1}}^{\beta_i}=0{,}35;$$

$$l_{\alpha_1}^{\beta_1}=l_{\alpha_1}^{\beta_2}=l_{\alpha_4}^{\beta_3}=l_{\alpha_4}^{\beta_4}=-0{,}28;\ l_{\alpha_{i+1}}^{\alpha_i}=0{,}32;$$

$$l_{\alpha_3}^{\alpha_1}=l_{\alpha_4}^{\alpha_1}=\ldots=-0{,}8;\ l_{\chi_{i+1}}^{\chi_i}=0{,}05;\ l_{\chi_{i+2}}^{\chi_i}=0{,}02.$$

The final set of potential energy constants that satisfactorily describes the experimental spectra of the 1,2,4-triazole anion is presented above (in units of 10^6 cm^{-2}).

As a result of a theoretical analysis of the vibrational spectra it was ascertained that the 1,2,4-triazole anion has C_s symmetry, i.e., equalization of the ring CN bonds does not occur when a proton is split off from the nitrogen atom. The results of the assignment of the frequencies in the experimental spectrum of the 1,2,4-triazole anion to the fundamental types of normal vibrations are presented in Table 1.

Several characteristic peculiarities were exposed on comparison of the positions of the absorption bands in the spectra of the salts of mononitrotriazoles [5]: the frequency of the synphase vibration of the nitro group is found in a narrow spectral region (ν 1300-1315 cm^{-1}), and this makes it possible to assume, in analogy with the covalent nitrotriazoles [1], that the nitro group and ring are coplanar; the frequency of the antiphase vibration is shifted by 15-20 cm^{-1} to lower frequencies as compared with covalent nitrotriazoles [6]. This sort of lowering of the vibrational frequency may be evidence for an increase in the participation of the nitro group in delocalization of the negative charge and a decrease in the multiplicity of the NO bonds. Insofar as the spectra of dinitrotriazoles are concerned, the splittings of the absorption bands that characterize the antiphase and synphase vibrations of the nitro groups are not observed in the IR spectrum of the sodium salt of 3,5-dinitro-1,2,4-triazole or in the spectra of aqueous solutions of alkali salts. The splitting of these bands is less in the spectra of the crystalline potassium, cesium, and ammonium salts than in the spectra of the covalent compound. On the basis of these experimental data, it can be assumed that the nitro groups are spatially and electronically equivalent in the 3,5-dinitro-1,2,4-triazole anion in aqueous solutions and in the crystalline sodium salt. The splitting of the bands in the spectra of other crystalline salts, in analogy with the salts of dinitromethyl compounds [7], may be explained by the effect of the bulky cations in the crystal lattice on the vibrations of the nitro groups.

To confirm the above assumptions regarding the structure of the anions and the detailed interpretation of the vibrational spectra of the salts of nitrotriazoles, we calculated the frequencies and forms of the normal vibrations of the anions of 3-nitro-, 3-nitro-5-methyl-, and 3,5-dinitro-1,2,4-triazole. All of the calculated models have C_s point group symmetry. The geometrical parameters of the triazole ring were used just as in the case of the 1,2,4-triazole anion; the NO bond lengths for the nitro groups were assumed to be 1.24 Å, and the ONO angle was assumed to be 120° [7-9]. The rotation of the NO_2 and CH_3 groups about the CN and CC bonds was disregarded. Since increases in the symmetry of the ring under the influence of two electronegative nitro groups might have been expected for the 3,5-dinitro-1,2,4-triazole anion, appropriate calculations were made for a model with C_{2v} symmetry; the geometrical parameters of the ring were assumed to be the same as for the 1,2,4-triazole anion with C_{2v} symmetry. The potential energy constants of the 1,2,4-triazole anion were used as a zero approximation of the force field of the ring (C_s symmetry), identical values of the force constants for equivalent coordinates were selected for 3,5-dinitro-1,2,4-triazole with C_{2v} symmetry, and the force constants of the NO_2 and CH_3 groups were used from data resulting from calculations of nitrotriazoles [10].

The normal vibrations of the anions are represented as follows with respect to symmetry: 3-nitro-1,2,4-triazole – $\Gamma_V = 15A' + 6A''$; 3-nitro-5-methyl-1,2,4-triazole – $\Gamma_V = 20A' + 10A''$; 3,5-dinitro-1,2,4-triazole – $(C_{2v})\ \Gamma_V = 10A_1 + 9B_2 + 4A_2 + 4B_1$, $(C_s)\ \Gamma_V = 19A' + 8A''$.

The natural vibrational coordinates of the anions are presented in Figs. 2-4.

As in the case of the 1,2,4-triazole anion, we were unable to select potential energy constants for the 3,5-dinitro-1,2,4-triazole anion that would satisfactorily describe the experimental spectra of the salts, i.e., equalization of the CN bond lengths does not occur in a triazole ring containing symmetrically arranged nitro groups.

The force constants of the investigated anions were calculated by solution of the reciprocal spectral problem. The force constants (in 10^6 cm^{-2}), which underwent changes as compared with the constants for the 1,2,4-triazole anion, are presented below:

3-nitro-1,2,4-triazole anion:

$$K_{q_1}=8{,}3;\ K_{q_{2,3}}=13{,}7;\ K_{q_4}=9{,}7;\ K_{Q_1}=11{,}8;\ K_{Q_2}=12{,}4;\ K_{Q_3}=12{,}2;\ K_{Q_4}=12{,}0;\ K_{Q_5}=11{,}3;$$

$$K_{\beta_{1,2}}=1{,}5;\ K_{\beta_{3,4}}=1{,}2;\ K_{\alpha_1}=3{,}1;\ K_{\alpha_2}=3{,}0;\ K_{\alpha_{3,4}}=3{,}1;\ K_{\alpha_5}=3{,}0;\ K_{\rho_1}=0{,}86;\ K_{\rho_2}=0{,}64;$$

$$K_{\rho_3}=0{,}48;\ H_{q_1,q_2}=0{,}94;\ H_{q_1Q_1}=H_{q_1Q_5}=1{,}2;;\ H_{q_2q_3}=1{,}7;\ H_{q_2Q_1}=H_{q_3Q_5}=1{,}3;\ H_{Q_1Q_5}=2{,}0;$$

TABLE 2. Vibrational Spectrum of the 3-Nitro-1,2,4-triazole Anion

Symmetry	Na salt			ν_{calc}, cm^{-1}	ν_{calc} for N–K, cm^{-1}	ν_{cal} for $\genfrac{}{}{0pt}{}{O}{O}\rangle K$, cm^{-1}	ν_{calc} for O–K, cm^{-1}	Assignment
	IR spec. ν, cm^{-1}	IR spec. ν, cm^{-1}	Raman spec. ν, cm^{-1}					
	cryst.*	H_2O	H_2O					
A'	3260 m	—	—	3251	3251	3251	3251	$\nu_{(q_4)}$
A'	1543 s	1538 s	1533 (1,4)	1539	1539	1538	1544	$\nu_{(q_2, -q_3)}$
A'	1502 s	1496 vs	1482 (0,9)	1500	1502	1499	1502	$\nu_{(Q_1, q_1)}$
A'	1410 vs	1412 vs	1401 (10)	1425	1425	1425	1426	$\nu_{(Q_3, Q_5)}, \delta_{(CH)}$
A'	1372 s	1378 s	1367 (10)	1364	1365	1364	1364	$\nu_{(Q_1, Q_3)}, \delta_{(CH)}$
A'	—	—	1336 (7)	1359	1361	1359	1359	$\nu_{(Q_2)}, \delta_{(CH)}$
A'	1310 m	1308 m	1300 (0,9)	1300	1301	1300	1311	$\nu_{(q_2, q_3)}$
A'	1182 w	1172 w	1170 (8,0)	1179	1182	1179	1180	$\delta_{(CH)}, \nu_\Gamma$
A''	1081 s	1078 m	1074 (7)	1069	1069	1069	1069	$\rho_{(CH)}, \chi$
A'	994 m	996 m	993 (0,4)	994	994	994	997	$\delta_{\Gamma(\alpha_1, \alpha_4, \alpha_5)}$
A'	905 w	—	—	905	928	905	906	$\delta_{\Gamma(\alpha_2, \alpha_3)}$
A''	840 s	—	838 (1,3)	841	841	841	841	$\rho_{(q_1, q_2, q_3)}, \chi$
A''	688 m	—	—	681	681	681	681	$\rho_{(q_2, q_3)}$
A'	660 s	—	—	621	630	621	664	$\nu_{(q_1)}, \delta_{(\beta_1, \beta_2)}$
A'	—	—	538 (0,4)	538	541	583	594	$\delta_{(\beta_1, \beta_2)}, \delta_{(\beta_3, \beta_4)}$
A''	—	—	—	524	524	524	524	χ
A'	—	—	—	297	314	526	306	$\delta_{(\beta_1, \beta_2)}$
A'	—	—	—	213	213	358	289	$\delta_{(\beta_3, \beta_4)}$
A''	—	—	—	184	184	184	184	χ
A'	—	—	—	—	239	—	—	$\nu_{(N---K)}$
A'	—	—	—	—	—	201	229	$\nu_{(O---K)}$
A'	—	—	—	—	—	134	210	$\nu_{(O---K)}$

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*Aggregate state of the substance: cryst. indicates crystals; H_2O indicates aqueous solutions.

TABLE 3. Vibrational Spectrum of the 3-Nitro-5-methyl-1,2,4-triazole Anion

Symmetry	Na salt			ν_{calc}, cm^{-1}	Assignment
	IR spectrum, ν, cm^{-1}	IR spectrum, ν, cm^{-1}	Raman spec. ν, cm^{-1}		
	cryst.	H_2O	H_2O		
A'	3150 s	—	—	3154	$\nu_{(q_5, q_6, q_7)}$
A''		—	—	3154	$\nu_{(q_6, q_7)}$
A'	—	—	—	3080	$\nu_{(q_5, q_6, q_7)}$
A'	1542 s	1536 m	1529 (0,8)	1539	$\nu_{(q_2, -q_3)}$
A'	1492 s	1490 s	—	1511	$\nu_{(Q_1, Q_3, Q_4, q_1)}$
A'	1470 w	1470 w	1465 (2,1)	1474	$\delta_{(CH_3)}$
A''	1450 s		1434 (1,0)	1460	$\delta_{(CH_3)}$
A'				1451	$\delta_{(CH_3)}, \nu_{(Q_5)}$
A'	1402 s	1402 s	1388c	1407	$\nu_{(Q_1, Q_5)}, \delta_{(CH_3)}$
A'				1391	$\nu_{(Q_2, Q_4)}, \delta_{(CH_3)}$
A'	1338 s	1339 s	1328 (7,2)	1348	$\nu_{(Q_3)}, \delta_{(CH_3)}$
A'	—	—	—	1341	$\nu_{(Q_2)}, \delta_{(CH_3)}$
A'	1302 m	1307 m	1293 (2,0)	1298	$\nu_{(q_2, q_3)}, \nu_\Gamma$
A''	1097 m	1092 m	1084 (9,8)	1094	$\delta_{(CH_3)}$
A'	1062 w	—	—	1055	$\delta_{(\alpha_1, \alpha_4, \alpha_5)}$
A'	1039 w	—	1036 (0,7)	1014	$\delta_{(CH_3)}$
A'	998 w	—	992 (1,0)	1002	$\delta_{(\alpha_2, \alpha_3)}$
A''	845 s	—	840 (1,4)	838	$\rho_{(q_1, q_2, q_3)}, \chi$
A'	770 w	—	—	760	$\nu_{(q_4)}, \delta_\Gamma$
A''	708 s	—	706 (0,3)	722	$\rho_{(q_1, q_2, q_3)}, \chi$
A''	667 s	—	—	670	$\rho_{(q_2, q_3)}, \chi$
A'	—	—	—	602	$\nu_{(q_1)}, \delta_{(\beta_1, \beta_2)}$
A'	—	—	551 (0,5)	550	$\delta_{(\beta_1, \beta_2, \beta_3, \beta_4)}$
A'	—	—	368 (0)	373	$\delta_{\beta_5 \beta_6}$
A'	—	—	—	292	$\delta_{(\beta_1, \beta_2)}$
A''	—	—	—	254	χ, ρ
A'	—	—	—	172	$\delta_{(\beta_3, \beta_4)}$
A''	—	—	—	123	χ

$$H_{Q_2Q_3}=2{,}2;\ H_{Q_3Q_4}=2{,}1;\ H_{Q_4Q_5}=2{,}0;\ A_{\beta_1}^{q_1}=0{,}65;\ A_{\beta_3}^{q}=0{,}6;\ A_{\alpha_1}^{q_1}=-0{,}74.$$

$$A_{\beta_1}^{q_2}=0{,}76;\ A_{\beta_2}^{q_2}=-0{,}2;\ A_{\beta_3}^{q_2}=0{,}6;\ A_{\alpha_1}^{Q_1}=A_{\alpha_2}^{Q_1}=A_{\alpha_1}^{Q_5}=A_{\alpha_5}^{Q_5}=1{,}92;\ l_{\beta_2}^{\beta_1}=-0{,}06;$$

$$l_{\beta_4}^{\beta_3}=0{,}3;\ l_{\alpha_1}^{\beta_3}=-0{,}2;\ l_{\alpha_2}^{\alpha_1}=\ldots=l_{\alpha_1}^{\alpha_5}=0{,}38;\ l_{\rho_2}^{\rho_1}=0{,}25;$$

3-nitro-5-methyl-1,2,4-triazole anion

$$K_{q_1}=8{,}1;\ K_{\mathrm{NO}}=13{,}7;\ K_{q_4}=7{,}3;\ K_{\mathrm{CH}}=9{,}1;\ K_{Q_1}=11{,}8;\ K_{Q_2}=12{,}4;\ K_{Q_3}=11{,}3;\ K_{Q_4}=12{,}0;$$

$$K_{Q_5}=11{,}7;\ K_{\beta_{3,4}}=K_{\beta_{5,6}}=1{,}2;\ K_{\alpha_{1,3}}=K_{\alpha_{4,5}}=3{,}3;\ K_{\alpha_2}=3{,}2;\ K_{\gamma}=1{,}03;\ K_{\delta}=0{,}7;\ K_{\rho_1}=0{,}84;$$

$$K_{\rho_2}=0{,}65;\ K_{\rho_3}=0{,}5;\ K_{\chi}=0{,}27;\ H_{q_1q_2}=1{,}0;\ H_{q_1Q_1}=H_{q_1Q_5}=1{,}5;\ h_{q_2Q_1}=H_{q_3Q_5}=1{,}1;$$

$$H_{Q_1Q_5}=2{,}0;\ H_{Q_3Q_4}=2{,}0;\ H_{q_4Q_4}=1{,}3;\ H_{q_4q_5}=0{,}3;\ H_{Q_4Q_5}=2{,}0;\ h_{q_5q_6}=0{,}05;\ A_{\beta_3}^{q_1}=0{,}6;$$

$$A_{\alpha_1}^{q_1}=-0{,}74;\ A_{\alpha_1}^{Q_1}=\ldots=A_{\alpha_5}^{Q_5}=1{,}92;\ A_{\beta_5}^{q_4}=0{,}6;\ A_{\alpha_4}^{q_4}=-0{,}72;\ A_{\gamma}^{q_4}=0{,}5;\ A_{\gamma}^{q_5}=0{,}6;$$

$$A_{\delta}^{q_5}=0{,}35;\ l_{\beta_4}^{\beta_3}=0{,}3;\ l_{\alpha_1}^{\beta_3}=-0{,}2;\ l_{\alpha_2}^{\alpha_1}=\ldots=l_{\alpha_1}^{\alpha_5}=0{,}36;\ l_{\gamma}^{\gamma}=l_{\delta}^{\gamma}=l_{\delta}^{\delta}=-0{,}03;$$

3,5-dinitro-1,2,4-triazole anion

$$K_{q_1}=K_{q_4}=8{,}0;\ K_{\mathrm{NO}}=13{,}8;\ K_{Q_1}=11{,}7;\ K_{Q_2}=12{,}8;\ K_{Q_3}=11{,}8;\ K_{Q_4}=11{,}7;\ K_{Q_5}=11{,}4;$$

$$K_{\mathrm{ONC}}=1{,}6;\ K_{\beta_3,\ldots,\beta_6}=1{,}2;\ K_{\alpha_{1,4}}=3{,}7;\ K_{\alpha_{2,3}}=3{,}6;\ K_{\alpha_5}=3{,}9;\ K_{\rho_{1,4}}=0{,}84;\ K_{\rho_{2,3}}=0{,}6;$$

$$K_{\chi}=0{,}3;\ H_{q_1q_2}=1{,}3;\ H_{q_1Q_1}=H_{q_1Q_5}=1{,}5;\ H_{q_2Q_1}=1{,}15;\ H_{Q_1Q_2}=2{,}2;\ H_{Q_2Q_3}=2{,}2;\ H_{Q_3q_4}=1{,}5;$$

$$H_{Q_3q_5}=1{,}15;\ H_{Q_4q_6}=1{,}15;\ A_{\beta_3}^{q_2}=0{,}55;\ l_{\beta_4}^{\beta_3}=0{,}3;\ l_{\alpha_1}^{\beta_3}=l_{\alpha_4}^{\beta_6}=-0{,}2;\ l_{\rho_2}^{\rho_1}=l_{\rho_4}^{\rho_3}=0{,}25.$$

As compared with the covalent derivatives of 1,2,4-triazole, the elastic characteristics of the ring bonds have changed in the anions: they have increased for the 1,2,4-triazole anion but have decreased for the nitrotriazole anions (the greatest changes are observed for the NN bond).

The results obtained by the methods of vibrational spectroscopy are in agreement with the values calculated by the MO LCAO SCF method within the approximation of complete neglect of differential overlap (CNDO/2)* for the covalent 3-nitro-1,2,4-triazole molecule and its anion and the 3,5-dinitro-1,2,4-triazole anion (Fig. 5). An increase in the population and, consequently, in the electron density on the NN bond is observed in the formation of the anion; this leads to an increase in its force constant. As compared with covalent compounds, redistribution of the electron density during the formation of the anion led to a change in the interaction of the nitro group and the ring bonds. On the whole, conjugation increased, and the coefficients of interaction of the nitro group and the ring bonds increased by a factor greater than two. At the same time, the force constants of the NO bonds of the nitro groups and the force constant of the CN bond of the CNO_2 group decreased somewhat. The character of the interaction of the ring coordinates remained the same as before, and the potential energy constants of interaction of the bonds and angles have approximately the same values as for covalent molecules.

It seemed of interest to investigate the effect of the coordination of the metal in salts on the position of the bands in the vibrational spectra. With this end in mind, we calculated the frequencies and forms of the normal vibrations of three models of the 3-nitro-1,2,4-triazole anion with the introduction of new nitrogen–potassium and oxygen–potassium vibrational coordinates. The N–K and O–K bond lengths were assumed to be equal to the sums of the atomic radii of the nitrogen and potassium, and oxygen and potassium atoms, and were, respectively, 2.89 and 2.72 Å. Calculations of two variants were made in the case of coordination of the metal around the oxygen atoms of the nitro group: in the first, the metal is situated at a certain distance from the oxygen atoms of the nitro group at an angle to the N–O bonds;

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*The semiempirical CNDO/2 method takes into account the interaction of all of the valence electrons without a priori separation into σ and π electron shells and makes it possible to obtain accurate representations regarding the charge distribution in organic compounds [11]. Slater 1s orbitals for the H atoms and Slater 2s and 2p orbitals for the C, N, and O atoms were used as the basis in the calculations. The semiempirical values of the computational parameters were taken from [12, 13].

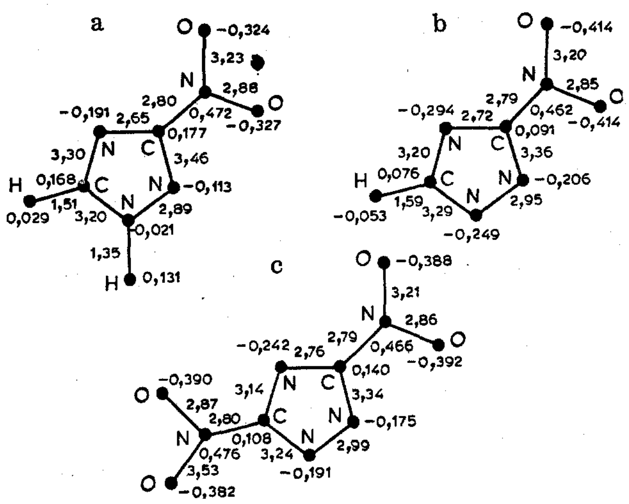

Fig. 5. Electronic structure of nitrotriazoles: a) 3-nitro-1,2,4-triazole; b) 3-nitro-1,2,4-triazole anion; c) 3,5-dinitro-1,2,4-triazole anion.

TABLE 4. Vibrational Spectrum of the 3,5-Dinitro-1,2,4-triazole Anion

Symmetry	Na salt			K salt		ν_{calc}, cm^{-1}	Assignment
	IR spectr. ν, cm^{-1}	IR spectr. ν, cm^{-1}	Raman ν, cm^{-1}	IR spectr. ν, cm^{-1}	IR spectr. ν, cm^{-1}		
	cryst.	H_2O	H_2O	cryst.	H_2O		
A'	1545 s	1550 s	1543 (0,6)	1558 s	1558 s	1545	$\nu_{(q_2, -q_3)}$
A'				1540 s	—	1545	$\nu_{(q_5, -q_6)}$
A'	1507 vs	1505 s	—	1507 vs	1505 vs	1519	$\nu_{(Q_1, Q_3, Q_4), q_1 q_4}$
A'	1430 w	—	—	1424 m	1422 w	1420	$\nu_{(Q_2, Q_3, Q_4)}$
A'	1402 m	1400 m	1403 (10)	1400 vs	1402 s	1411	$\nu_{(Q_5)}$
A'	1372 m	1367 m	1361 (1,8)	1370 vs	1370 s	1377	$\nu_{(Q_1, Q_5)}$
A'	—	—	—	1350 s	—	1352	$\nu_{(Q_2, Q_3, Q_4)}$
A'	1315 s	1315 m	1312 (0,4)	1318 m	1312 m	1314	$\nu_{(q_5, q_6)}$
A'	—	—	—	1308 s	—	1301	$\nu_{(q_2, q_3)}$
A'	1115 w	1116 w	1117 (5,5)	1112 m	1120 w	1105	$\delta_{(\alpha_1, \alpha_4, \alpha_6)}$
A'	1060 w	1053 w	1032 (0)	1057 w	1055 w	1039	$\delta_{(\alpha_2, \alpha_3)}$
A''	855 m	—	—	852 s	—	859	$\nu_{(q_1)}, \chi$
A'	—	—	—	775 w	—	787	$\rho_{(q_2, q_3)}, \rho_{(q_1)}$
A'	—	—	—	721 w	—	718	$\nu_{(q_1, q_4)}$
A''	670 m	—	—	672 m	—	676	$\rho_{(q_2, q_3)}$
A''	650 s	—	—	652 s	—	669	$\rho_{(NO)}$
A'	—	—	—	—	—	597	$\nu_{(CN)}, \delta_{(NO_2)}$
A'	—	—	—	—	—	581	$\delta_{(NO_2)}, \delta_{(CN)}$
A'	520 s	—	—	—	—	510	$\delta_{(NO_2)}$
A'	—	—	—	—	—	326	$\delta_{(NO_2)}$
A'	—	—	—	—	—	273	$\delta_{(NO_2)}$
A'	—	—	—	—	—	261	$\delta_{(CN)}$
A''	—	—	—	—	—	248	χ, ρ
A'	—	—	—	—	—	126	$\delta_{(CN)}$
A''	—	—	—	—	—	107	χ, ρ

in the second, coordination is realized by two atoms of the metal along the K–O–N line. In both cases, two O–K vibrational coordinates were introduced, and it was assumed that the metal atom lies in the plane of the anion. The potential energy coordinates for the new vibrational coordinates were selected in the interval 0.2-2.2 · 10^6 cm^{-2} until there was satisfactory coincidence of the calculated frequencies with the experimental values in the IR spectrum of the crystalline salt; the force constants of interaction of the O–K and N–K coordinates with the coordinates of the nitro group and the ring were disregarded, since their effect on the vibrational spectrum is unimportant.

When the metal was coordinates only with the ring N_1 atom, the three frequencies associated with the deformation vibrations of the ring and nitro group changed only slightly (Table 2). In this case, the force constant of the N–K bond was –1.8 · 10^6 cm^{-2}. When the metal was situated near the oxygen atom of the nitro group, the greatest changes were obtained for coordination of the metal along the K–O–N line, in which case there is a small increase in the frequencies of not only the deformation vibrations but also of the symmetrical antiphase and synphase vibrations of the nitro group in the calculated spectrum (the force constant of the O–K bond is $2.0 \cdot 10^6$ cm^{-2}).

A comparison of the experimental spectra of crystals of alkali salts of 3-nitro-1,2,4-triazole with the calculated spectra shows that the best coincidence of the frequencies is observed for the second variant of coordination of the metal with the oxygen atoms. It should be noted that a similar type of coordination of the metal near the oxygen atoms of the nitro group was proved for the alkali salts of polynitro compounds by the methods of x-ray diffraction analysis [8, 9]. The coincidence of the frequencies in the IR and Raman spectra of the crystalline salts of nitrotriazoles and their aqueous solutions may serve as proof of the approximately identical structures of the investigated anions in different aggregate states. The results of assignment of the frequencies in the spectra of nitrotriazoles to the principal types of normal vibrations are presented in Tables 2-4.

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