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

I. INTERPRETATION OF THE VIBRATIONAL SPECTRA OF 1,2,4-TRIAZOLE AND 3-CHLORO- AND 3-BROMO-1,2,4-TRIAZOLES

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The vibrational spectra of 1,2,4-triazole and its 3-chloro and 3-bromo derivatives were calculated for the C_s point symmetry group. The potential energy constants were computed, and it is shown that the force field of the triazole ring has the additivity property; i.e., it remains practically constant when electron-acceptor groups such as chlorine and bromine are introduced into the 3 position. The force constants of interaction of the valence and angular coordinates of the ring have high values; this is a characteristic of the considerable rigidity of the triazole ring. The fundamental frequencies in the experimental spectra were assigned on the basis of an analysis of the calculated forms of the normal vibrations.

The literature contains numerous publications relative to the IR and Raman spectra of 1,2,4-triazole derivatives [1-11], but at the present time there are no sufficiently convincing data to make it possible to assign the frequencies in the experimental spectra and to investigate the effect of substitution in the ring on the characteristic nature of the vibrations; this is of great importance in carrying out structural-group analysis. An intimate combination of experimental and theoretical methods with the application of model calculations of the frequencies and forms of the normal vibrations is necessary for the complete solutions of these problems.

It seemed expedient to begin the systematic investigation of the structures and interpretation of the spectra of 1,2,4-triazole derivatives with the simplest compound of this series – 1,2,4-triazole.

The calculation of the matrices of the kinematic coefficient, the ordering of the matrices with respect to symmetry, the allowance for additional expressions, and the comparison and solution of the secular equations were carried out with a Minsk-22 computer from programs developed by L. A. Gribov and coworkers [12]. The anharmonicity of the vibrations was taken into account by introduction of the "spectroscopic" masses of the atoms.

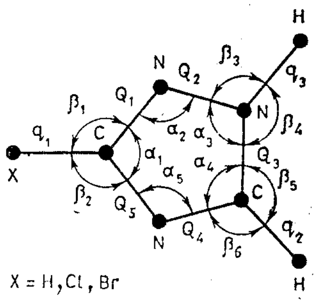

Fig. 1. Structure and vibrational coordinates of 1,2,4-triazole derivatives.

The geometrical parameters of the triazole ring used for the calculations corresponded to the data from the x-ray diffraction analysis of 1,2,4-triazole [13], and the lengths of the CCl and CBr bonds for 3-Cl- and 3-Br-1,2,4-triazoles were taken as 1.70 and 1.84 Å, respectively [14].

In accordance with the symmetry of 1,2,4-triazole and its halo derivatives (C_s symmetry group), the normal vibrations were reduced in the following way with respect to symmetry:

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$$\Gamma_v = 13A' + 5A''.$$

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

Since up to now there have been no data whatsoever with respect to the potential energy constants of 1,2,4-triazole and its derivatives in the literature, the force constants roughly estimated on the basis of the calculated bond orders [15] from "bond order-force constant" correlation tables [16] were used as a zero approximation. In the calculations, the force field of 1,2,4-triazole was corrected in conformity with the values of the derivatives of the frequencies with respect to the force constants. A similar variation of the potential energy constants was accomplished until there was satisfactory agreement between the calculated and experimental frequencies.

The force constants of 1,2,4-triazole were then used to calculate the frequencies and forms of the normal vibrations of 3-Cl- and 3-Br-1,2,4-triazoles, during which satisfactory agreement between the calculated and experimental spectra confirmed the reliability of the set of force constants of the triazole ring that we obtained.

$K_{CH} = 9{,}0$
$K_{NH} = 5{,}45$
$K_{Q_1} = 13{,}3$
$K_{Q_2} = 9{,}8$
$K_{Q_3} = 11{,}3$
$K_{Q_4} = 12{,}8$
$K_{Q_5} = 11{,}4$
$H_{CHQ_1} = 0{,}3$
$H_{CHQ_5} = 0{,}3$
$H_{Q_1Q_2} = 1{,}6$
$H_{Q_1Q_3} = 0{,}8$
$H_{Q_1Q_4} = 0{,}8$
$H_{Q_1Q_5} = 2{,}2$
$H_{Q_2q_2} = 0{,}35$
$H_{Q_2Q_3} = 1{,}5$
$H_{Q_2Q_4} = 0{,}8$
$H_{Q_2Q_5} = 0{,}8$
$H_{q_2Q_3} = 0{,}35$
$H_{Q_3q_3} = 0{,}3$
$H_{Q_3Q_4} = 2{,}0$
$H_{Q_3Q_5} = 0{,}8$
$H_{Q_4q_3} = 0{,}3$

$K_{\alpha_1} = 3{,}5$
$K_{\alpha_2} = 2{,}9$
$K_{\alpha_3} = 2{,}7$
$K_{\alpha_4} = 3{,}3$
$K_{\alpha_5} = 3{,}0$
$K_{\beta_{1,2}} = 0{,}9$
$K_{\beta_{3,4}} = 0{,}8$
$H_{Q_4Q_5} = 2{,}0$
$H_{C\text{-}ClQ_1} = 1{,}0$
$H_{C\text{-}ClQ_5} = 1{,}0$
$H_{C\text{-}BrQ_1} = 0{,}8$
$H_{C\text{-}BrQ_5} = 0{,}8$
$A^{CH}_{\beta_{1,2}} = 0{,}2$
$A^{q_2}_{\beta_{3,4}} = 0{,}2$
$A^{CH}_{\alpha_1} = -0{,}16$
$A^{Q_1}_{\beta_1} = 0{,}96$
$A^{Q_1}_{\beta_2} = 0{,}58$
$A^{Q_1}_{\alpha_{1,2}} = 2{,}1$
$A^{Q_2}_{\alpha_{2,3}} = 2{,}1$
$A^{Q_2}_{\beta_3} = 0{,}96$
$A^{Q_2}_{\beta_4} = 0{,}58$

$K_{\beta_{5,6}} = 0{,}9$
$K_{\rho\,CH} = 0{,}6$
$K_{\rho\,NH} = 0{,}45$
$K_{\rho\,\mathrm{ring}} = 0{,}27$
$K_{\rho\,C-Cl} = 0{,}3$
$K_{\rho\,C-Br} = 0{,}2$
$A^{q_2}_{\alpha_3} = -0{,}15$
$A^{q_3}_{\beta_{5,6}} = 0{,}2$
$A^{q_3}_{\alpha_4} = -0{,}16$
$A^{C-Cl}_{\beta_{1,2}} = 0{,}6$
$A^{C-Cl}_{\alpha_1} = -0{,}7$
$A^{C-Br}_{\beta_{1,2}} = 0{,}6$
$A^{C-Br}_{\alpha_1} = -0{,}7$
$l^{\beta_1}_{\beta_2} = 0{,}33$
$l^{\alpha_1}_{\alpha_{2,5}} = 0{,}32$
$l^{\alpha_1}_{\alpha_{3,4}} = -0{,}8$
$l^{\alpha_1}_{\beta_{1,2}} = -0{,}28$
$l^{\beta_3}_{\beta_4} = 0{,}35$
$l^{\alpha_3}_{\alpha_5} = -0{,}8$
$l^{\rho_2}_{\rho_3} = 0{,}1$
$l^{\rho_4}_{\rho_5} = -0{,}02$

The final set of force constants for the 1,2,4-triazole and 3-chloro- and 3-bromo-1,2,4-triazole molecules is presented above (in units of 10^6 cm^{-2}). K_i is the force constant of the i bond or angle, H_{ij} is the force constant of interaction of the coordinates of the i and j bonds, A_i^{mn} is the force constant of interaction of the coordinate of the i bond and the change in the valence angle formed by the n and m bonds, and $l\,^i_j$ is the force constant of interaction of the angular or nonpolar coordinates.

Thus the potential energy constants of the bonds and the valence angle constants and the force constants that characterize the interaction of the ring coordinates have high values; this is surely a characteristic of the considerable rigidity of the triazole ring.

As expected, replacement of a hydrogen atom in the 1,2,4-triazole molecule by chlorine and bromine atoms leads to an increase in the force constants of interaction of the coordinates of the C−Hal bond and of the adjacent angles with the CN bonds of the five-membered ring.

The calculations of the frequencies and forms of the normal vibrations demonstrated that almost all of the vibrations of 1,2,4-triazole and of the halo derivatives, except for the stretching vibrations of the C−H and N−H bonds, encompass rather large groups of atoms, i.e., they are noncharacteristic in form. However, on the basis of an analysis of the calculated forms of the normal vibrations and comparison of the frequencies in the experimental (IR and Raman) and calculated spectra, we realized an approximate assignment of the frequencies to definite types of vibrations of the valence bonds, angles, and other molecular fragments.

TABLE 1. Assignment of the Fundamental Frequencies in the Vibrational Spectra of 1,2,4-Triazole Derivatives

Type of symmetry	1,2,4-Triazole			3-Cl-1,2,4-Tri.		3-Br-1,2,4-Tri.		Assignment‡
	ν_{IR}, cm^{-1}	ν_R, * cm^{-1}	ν_{calc}, cm^{-1}	ν_{IR},† cm^{-1}	ν_{calc} cm^{-1}	ν_{IR},† cm^{-1}	ν_{calc}, cm^{-1}	
A'	3138	—	3136	3139	3130	3130	3131	$\nu(\mathrm{CH}-q_1, q_2)$
A'	3128	—	3127	—	—	—	—	$\nu(\mathrm{CH}-q_1, q_2)$
A'	2400	—	2414	2400	2414	2700	2414	$\nu(\mathrm{NH})$
A'	1486		1488	1520	1525	1520	1512	$\nu(Q_1, Q_4), \delta(\mathrm{CH})$
A'	1479	1482 (3,3)	1484	1485	1473	1478	1467	$\nu(Q_1, Q_4), \delta(\mathrm{CH})$
A'	1385	1374 (8,0)	1395	1385	1401	1365	1397	$\nu(Q_3, Q_5), \delta(\mathrm{CH})$
A'	1368	—	1363	1350	1365	1340	1358	$\nu(Q_3, Q_5), \delta(\mathrm{CH})$
A'	1277	1281 (5,5)	1283	1270	1264	1266	1263	$\nu(Q_2), \delta(\mathrm{CH, NH})$
A'	1260	1256 (10,0)	1252	—	—	—	—	$\delta(\mathrm{CH}-q_1)$
A''	1182	1183 (3,3)	1181	—	—	—	—	$\rho(\mathrm{CH}-q_1)$
A'	1147	1158 (7,5)	1131	1190	1178	1180	1171	$\nu(Q_2), \delta(\mathrm{CH}-q_2)$
A''	1130	—	1122	1150	1138	1150	1136	$\rho(\mathrm{CH}-q_2)$
A'	1057	1069 (3,2) 1010 (1,8)	1024	1088 1065	1042	1080 1040	1035	$\delta(\mathrm{NH})$
A'	978	978 (2,0)	959	1003	1009	1000	995	$\delta(\alpha_{1-5})$
A'	953 928	939 (1,0)	915	980 900	929	975 910	928	$\delta(\alpha_{2-5})$
A''	882	—	895	878	901	872	900	$\rho(\mathrm{NH})$
A''	—	—	—	640	645	638	605	ρ(C—Hal), ρ ring
A'	—	—	—	500 515	576	—	441	ν(C—Hal)
A''	430	—	442	—	396	—	396	ρ ring ($\rho_{4,5}$)
A''	400	—	396	—	143	—	115	ρring ($\rho_{4,5}$)
A''	—	—	—		325	—	277	ρ(C—Hal) δ(C—Hal)

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*The Raman spectrum of a saturated aqueous solution of 1,2,4-triazole was recorded with a DFS-12 spectrometer (λ_{ex} = 4358 Å). The spectral scanning rate with respect to the slit was 6.1 Å/min, and the filter was $NaNO_2$ solution; the relative intensities on a scale of ten are given in parentheses.

† The IR spectra of 3-chloro- and 3-bromo-1,2,4-triazoles were borrowed from [10].

‡ The following symbols were used: ν are the stretching vibrations, δ are the deformation vibrations, ρ are the out-of-plane vibrations, and ring ρ are the out-of-plane ring vibrations.

The results of the assignment of the fundamental frequencies are presented in Table 1.

A broad band with an absorption maximum at ~2400 cm^{-1}, which characterizes the stretching vibration of the associated N−H bond, is observed in the IR spectrum of 1,2,4-triazole. The change in the force constants of the N−H bond from $5 \cdot 10^6$ to $9 \cdot 10^6$ cm^{-2} made it possible to obtain the frequency of this stretching vibration within the limits of the experimental band (~2200-3000 cm^{-1}) and, without exception, no shift in the frequencies at 600-1500 cm^{-1}, which characterize the ring vibrations, was observed in any case. Thus the disturbing effect of the hydrogen bond apparently does not change the electron and three-dimensional structures of the triazole ring.

LITERATURE CITED

1. W. Otting, Angew. Chem., 68, 417 (1956).
2. W. Otting, Chem. Ber., 89, 2887 (1956).
3. W. Otting, Chem. Ber., 89, 1940 (1956).
4. W. Zimmermann, Z. Elektrochem., 63, 601 (1959).
5. W. Zimmermann, Z. Elektrochem., 63, 608 (1959).
6. E. Lieber, D. Levering, and L. Patterson, Ind. Eng. Chem., Anal. Ed., 23, 1594 (1951).
7. H. G. O. Becker, H. Moll, and H. Haufe, Wiss. Z. Techn. Hochschule Chem. Leuna-Merseburg, 8, 120 (1966).
8. M. Dziewonska, Spectrochim. Acta, 23A, 1195 (1967).
9. G. I. Chipen, Ya. A. Éidus, Ya. S. Bobovich, and V. Ya. Grinshtein, Zh. Strukt. Khim., 6, 53 (1965).
10. V. Ya. Grinshtein, A. A. Strazdin', and A. K. Grinvalde, Khim. Geterotsikl. Soedin., 248 (1970).

11. V. V. Mel'nikov, V. V. Stolpakova, and M. S. Pevzner, Khim. Geterotsikl. Soedin., 414 (1971).
12. L. A. Gribov, Introduction to the Theory and Calculation of the Vibrational Spectra of Polyatomic Molecules [in Russian], Izd. LGU (1965).
13. P. Goldstein, I. Ladell, and G. Abowitz, Acta Cryst., B25, 135 (1969).
14. D. Wheland, Resonance Theory [Russian translation], IL, Moscow (1948).
15. V. V. Mel'nikov, M. S. Pevzner, V. V. Stolpakova, and L. F. Khor'kova, Khim. Geterotsikl. Soedin., 409 (1971).
16. E. Wilson, D. Deshuis, and P. Cross, Theory of the Vibrational Spectra of Molecules [Russian translation], IL, Moscow (1960).