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

## V.* 3-AZIDO-1,2,4-TRIAZOLE DERIVATIVES

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The frequencies and forms of the normal vibrations of 3-azido- and 3-azido-5-methyl-1,2,4-triazoles and their 1-deutero-substituted derivatives were calculated, the effect of the geometrical parameters of 3-azido-1,2,4-triazole on the vibrational spectra was investigated, and the most probable three-dimensional model of the molecule was selected. The solution of the inverse spectral problem was effected by the method of least squares, and the potential energy constants of the azidotriazoles were calculated. It is shown that the force constants of the azido group increase and the elastic constants of the ring decrease when an azido group is introduced into the 1,2,4-triazole molecule. The frequencies in the experimental spectra were assigned to the principal types of normal vibrations.

The vibrational spectra and electronic structures of aliphatic azido compounds were investigated in [2-4], and it was shown that the introduction of electron-acceptor groups into the $\beta$ and, particularly, the $\alpha$ positions leads to a decrease in the negative charge on the $N^3$ atom of the azido group (Fig. 1) and, correspondingly, to an increase in the reactivities of the alkyl azides in 1,3-dipolar cycloaddition reactions. Data on the electronic and three-dimensional structures of heterocyclic azides are lacking, in connection with which we also undertook a study of the vibrational spectra of 3-azido-, 1-deutero-3-azido-, 3-azido-5-methyl-, and 1-deutero-3-azido-5-methyl-1,2,4-triazoles.

The natural vibrational coordinates of the investigated compounds are presented in Fig. 1. The geometrical parameters of the triazole ring presented in [5] were used for the calculations of the vibrational spectra; parameters determined by microwave spectroscopy [6, 7] were selected for the azido group: bond lengths $N^1H = 1.03$, $N^1N^2 = 1.359$, $N^2C^3 = 1.323$, $C^3N^4 = 1.359$, $N^4C^5 = 1.324$, $C^5H = 0.93$, $C^5C = 1.54$, $CH = 1.09$,

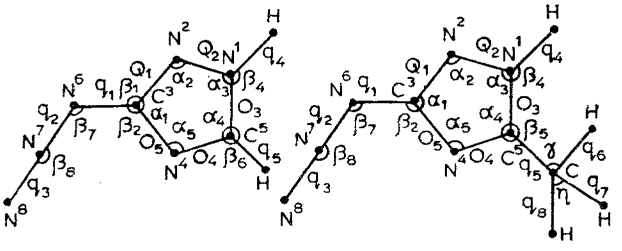

Fig. 1. Structures and natural coordinates of 3-azido-5-methyl-1,2,4-triazole.

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* See [1] for communication IV.
† Deceased.

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TABLE 1. Frequencies and Forms of the Normal Vibrations of 3-Azido-1,2,4-triazole

| Symmetry | 3-Amzido-1,2,4-triazole | | | 1-D-3-Azido-1,2,4-triazole | | Vibrational forms* |
|---|---|---|---|---|---|---|
| | IR spectrum, $\nu$, $cm^{-1}$ | Raman spectrum, $\nu$, $cm^{-1}$ | calc. $\nu$, $cm^{-1}$ | IR spectrum, $\nu$, $cm^{-1}$ | calc., $\nu$, $cm^{-1}$ | |
| A′ | 3110s | — | 3109 | 3110s | 3109 | $q_5$ |
| A′ | 3065 | — | 3061 | 2285s | 2274 | $q_4$ |
| A′ | 2160vs | 2137(0,6) | 2160 | 2155vs | 2160 | $q_2, -q_3$ |
| A′ | 1514s | 1522(1,1) | 1507 | 1518vs | 1506 | $-q_1, Q_4, Q_5, -\beta_5, -\beta_6$ |
| A′ | 1486o.s | 1493(2,6) | 1493 | 1470vs | 1493 | $Q_1, Q_4, -Q_5, -\beta_1, \beta_2$ |
| A′ | 1455o.s | 1444(3,9) | 1422 | 1400w | 1418 | $-q_1, Q_1, -Q_4, \beta_5, \beta_6$ |
| A′ | 1338o.s | 1321(4,3) | 1322 | 1336s | 1321 | $-Q_1, Q_3, Q_4, -\beta_5, \beta_6$ |
| A′ | 1286s | 1281(0,9) | 1269 | 1260m | 1268 | $-q_2, Q_2, -\beta_3, \beta_4$ |
| A′ | 1220m | 1229(1,3) | 1214 | 1197m | 1209 | $-q_2, -q_3, -\beta_3, \beta_4$ |
| A′ | 1173vs | 1187(3,5) | 1164 | 1163w | 1148 | $Q_2, Q_3, \beta_5, -\beta_6$ |
| A″ | 1086s | — | 1087 | 1086s | 1087 | $\rho_4, \chi$ |
| A′ | 1010m | 1047(4,0) | 1026 | 780w | 754 | $-\beta_3, \beta_4$ |
| A′ | 976vs | — | 954 | 970s | 953 | $-q_1, -\alpha_1, \alpha_5$ |
| A″ | 956w | 958(1,5) | 945 | 730 | 749 | $\rho_3, \chi$ |
| A′ | 854s,br | — | 891 | 902w | 890 | $-Q_2, \alpha_2, \alpha_3, -\alpha_4, -\alpha_5$ |
| A′ | | 838(3,3) | 835 | 854s,br | 843 | $-\beta_1, \beta_2, -\beta_7, \beta_8$ |
| A″ | 790w | 775(10,0) | 789 | | 851 | $-\rho_2, \chi$ |
| A″ | 631m | 622(3,5) | 624 | — | 623 | $\rho_2, \chi$ |
| A′ | 524m | 496(0,4) | 504 | — | 500 | $q_1, \beta_7, \beta_8$ |
| A″ | 415m | 423(0,6) | 407 | — | 363 | $-\rho_3, \rho_4, \chi$ |
| A′ | 340w | — | 325 | — | 324 | $\beta_8$ |
| A′ | — | 233(0,2) | 239 | — | 238 | $\beta_1, -\beta_2$ |
| A″ | — | 207(0,6) | 194 | — | 190 | $\rho_2, \chi$ |

* Out-of-plane vibrations: $\rho_1$ for the $N^6H^7$ bond, $\rho_2$ for the $C^3N^7$ bond, $\rho_3$ for the NH bond, $\rho_4$ for the CH bond, and $\chi$ for the ring vibrations.

$C^3N^6 = 1.47$, $N^6N^7 = 1.24$, and $N^7N^8 = 1.12$ Å; valence angles $HN^1N^2 = 124°$, $\angle N^1N^2C^3 = 102°$, $\angle N^2C^3N^4 = 115°$, $\angle C^3N^4O^5 = 103°$, $\angle N^4C^5N^1 = 110°$, $\angle N^4C^5H = 127°$, $\angle HN_1C_5 = 126°$, $\angle N^2C^3N^6 = 122°30'$, $\angle HCH = 109°28'$, $\angle C_3N_6N_7 = 120°$, and $\angle N^6N^7N^8 = 180°$. Rotation of the azide and methyl groups about the C − N and C=C bonds was disregarded. The force constants of the triazole ring and the azido group, which are presented in [2, 8], were selected as the zero approximation of the potential energy constants.

Inasmuch as the three-dimensional structure of 3-azido-1,2,4-triazole is unknown, we calculated the frequencies and forms of the normal vibrations of three geometrical models – the planar model presented in Fig. 1 and models with 90 and 180° rotation of the azido group relative to the C−N bond.

The potential energy constants, which take into account the interaction of the azide group with the ring, were assumed to be zero for the model with 90° rotation of the azide group, inasmuch as in this case the $\pi$-electron orbitals of the $N_3$ group and the triazole ring are orthogonal. The best agreement between the calculated spectra and the experimental spectra was obtained for planar configurations of 3-azido-1,2,4-triazole, although it should be noted that the rather close frequencies in the calculated spectra of the planar structures do not make it possible to unambiguously select a certain geometrical model. In this connection, the geometrical configuration of 3-azido-1,2,4-triazole depicted in Fig. 1 was selected for the calculations of the vibrational spectra. The force field of 3-azido-1,2,4-triazole was refined during the calculations in conformity with the derivatives of the frequencies with respect to the force constants up to the point where the calculated frequencies coincided with the experimental values.

The set of force constants obtained in this way was used for calculations of 1-deutero-3-azido-, 3-azido-5-methyl-, and 1-deutero-3-azido-5-methyl-1,2,4-triazoles. The satisfactory agreement between the calculated frequencies and the experimental values may serve as a confirmation of the reliability of the set of force constants obtained above. The potential energy constants of the azido group and the triazole ring were subsequently refined for the investigated compounds by solution of the inverse spectral problem by the method of least squares (MLS).

The final set of force constants for 3-azido-1,2,4-triazole is presented below (in units of $10^6$ $cm^{-2}$):*

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*The force constants are designated in accordance with [9].

$K_{q_1}=7.70,$ $K_{q_2}=13.28,$ $K_{q_3}=24.36,$ $K_{q_4}=8.75,$ $K_{q_5}=8.88,$

$K_{Q_1}=13.30,$ $K_{Q_2}=9.8,$ $K_{Q_3}=10.65,$ $K_{Q_4}=12.80,$ $K_{Q_5}=12.0,$

$K_{\alpha_1}=3.0,$ $K_{\alpha_2}=2.36,$ $K_{\alpha_3}=2.20,$ $K_{\alpha_4}=3.30,$ $K_{\alpha_5}=2.80,$

$K_{\beta_1}=1.40,$ $K_{\beta_2}=0.96,$ $K_{\beta_{3,4}}=0.80,$ $K_{\beta_{5,6}}=0.90,$ $K_{\beta_7}=3.30,$

$K_{\beta_8}=1.38,$ $K_{\rho_1}=2.92,$ $K_{\rho_2}=0.58,$ $K_{\rho_3}=0.49,$ $K_{\rho_4}=0.54,$

$K_{\chi}=0.25,$ $H_{q_2}^{q_1}=0.20,$ $H_{q_3}^{q_2}=1.15,$ $H_{Q_{3,4}}^{q_5}=0.30,$ $H_{Q_{1,2}}^{Q_4}=0.80,$

$H_{Q_4}^{Q_3}=1.85,$ $H_{Q_5}^{q_1}=0.15,$ $H_{Q_5}^{Q_1}=1.80,$ $H_{Q_5}^{Q_3}=0.60,$ $H_{Q_5}^{Q_4}=2.0,$

$A_{\beta_1}^{q_1}=0.05,$ $A_{\beta_1}^{Q_1}=0.80,$ $A_{\beta_2}^{q_1}=0.78,$ $A_{\beta_2}^{q_2}=0.55,$ $A_{\beta_2}^{q_3}=-0.34,$

$A_{\beta_2}^{Q_1}=0.38,$ $A_{\alpha_1}^{q_1}=-0.78,$ $A_{\alpha_{1,2}}^{Q_1}=A_{\alpha_3}^{Q_2}=A_{\alpha_4}^{Q_4}=A_{\alpha_5}^{Q_5}=2.10,$

$A_{\beta_{3,4}}^{Q_{2,3}}=0.96,$ $A_{\beta_{3-6}}^{q_{4,5}}=0.20,$ $A_{\beta_3}^{Q_3}=A_{\beta_4}^{Q_2}=A_{\beta_5}^{Q_4}=0.58,$

$A_{\alpha_3}^{q_4}=-0.15,$ $A_{\alpha_{3,4}}^{Q_3}=2.30,$ $A_{\beta_5}^{Q_3}=1.0,$ $A_{\beta_6}^{Q_3}=0.50,$

$l_{\alpha_2}^{\alpha_1}=0.35,$ $l_{\beta_4}^{\beta_3}=0.35$ $l_{\alpha_{3-5}}^{\alpha_1}=-0.8,$ $l_{\alpha_3}^{\alpha_2}=0.43,$ $l_{\alpha_{4,5}}^{\alpha_2}=-0.6,$

$l_{\beta_{3,4}}^{\alpha_3}=0.28,$ $l_{\beta_{5,6}}^{\alpha_4}=-0.28,$ $l_{\alpha_4}^{\alpha_3}=l_{\alpha_5}^{\alpha_4}=0.38,$ $l_{\alpha_5}^{\alpha_3}=-0.6,$

$l_{\beta_6}^{\beta_5}=0.33,$ $l_{\chi_{i+1}}^{\chi_i}=-0.03.$

The introduction of a methyl group into the 5-position of the ring led to a slight change in the following force constants of the coordinates of the triazole ring adjacent to the methyl group, during which, as one should have expected, the force constants of the azido group did not change:

$K_{q_5}=6.91,$ $K_{q_{6-8}}=8.34,$ $K_{Q_4}=11.2,$ $K_{\beta_5}=1.39,$

$K_{\alpha_4}=2.9,$ $K_{\gamma}=0.88,$ $K_{\delta}=0.71,$ $K_{\beta_8}=1.57,$

$K_{\rho_3}=0.43,$ $K_{\rho_4}=0.51,$ $H_{q_6}^{Q_3}=0.02,$ $H_{q_7}^{q_6}=0.05,$

$H_{Q_4}^{Q_1}=0.56,$ $H_{Q_3}^{Q_4}=1.50,$ $H_{Q_6}^{Q_4}=0.60,$ $A_{\beta_4}^{Q_2}=0.42,$

$A_{\beta_4}^{Q_3}=1.02,$ $A_{\beta_5}^{Q_3}=0.40,$ $A_{\beta_5}^{q_5}=l_{\beta_4}^{\beta_3}=0.33.$ $A_{\gamma}^{q_{5,6}}=0.43,$

$A_{\beta_5}^{q_6}=A_{\delta}^{q_6}=0.35,$ $A_{\beta_5}^{Q_4}=0.28,$ $A_{\alpha_4}^{Q_4}=2.7,$ $A_{\alpha_5}^{Q_5}=1.63,$

$l_{\alpha_5}^{\alpha_1}=0.17,$ $l_{\gamma}^{\gamma}=0.02,$ $l_{\delta}^{\gamma}=l_{\delta}^{\delta}=-0.03.$

A comparison of the potential energy constants obtained for 3-azido-1,2,4-triazole derivatives with the force constants of alkyl azides and 1,2,4-triazole showed that a decrease in the force constants of the triazole ring and, correspondingly, an increase in the elastic constants of the N=N valence bonds of the azido group are observed for the azidotriazoles; this should lead to an increase in the electron density of the azido group as compared with aliphatic azido compounds.

The results of the assignment of the principal frequencies in the experimental IR and Raman spectra are presented in Tables 1 and 2.

## EXPERIMENTAL

The IR spectra were recorded by standard methods with Perkin-Elmer 457 and IKS-22 spectrometers. The Raman spectra of aqueous solutions were recorded with a DFS-12 spectrometer; the spectral scanning rate with respect to the slit was 6.1 Å/min, $\lambda_{\text{excit}}$ was 4358 Å, and the relative intensities of the Raman

TABLE 2. Frequencies and Forms of the Normal Vibrations of 3-Azido-5-methyl-1,2,4-triazole

| Symmetry | 3-Azido-5-methyl-1,2,4-triazole |  |  | 1-D-3-Azido-5-methyl-1,2,4-triazole |  | Vibrational forms |
|---|---|---|---|---|---|---|
|  | IR spectrum $\nu$, cm$^{-1}$ | Raman spec. $\nu$, cm$^{-1}$ | calc. $\nu$, cm$^{-1}$ | IR spectrum, $\nu$, cm$^{-1}$ | calc. $\nu$, cm$^{-1}$ |  |
| A′ | 3035 m |  | 3061 |  | 2274 | $q_4$ |
| A′ |  |  | 3015 |  | 3015 | $q_6, q_7$ |
| A′ |  |  | 3028 |  | 3029 | $q_6, -q_7, -q_8$ |
| A′ | 2942 vs |  | 2944 |  | 2944 | $q_6, q_7, q_8$ |
| A′ | 2160 vs | 2154 (1,1) | 2157 | 2160 vs | 2157 | $q_2, -q_3$ |
| A′ | 1500 s | 1516 (4,2) | 1520 | 1510 s | 1519 | $-q_1, Q_4, Q_5, \beta_5, -\beta_6$ |
| A′ |  | — | 1504 |  | 1499 | $-q_1, Q_1, Q_3, \gamma, \alpha_5, \eta$ |
| A′ | 1465 vs | — | 1469 | 1470 vs | 1469 | $-Q_1, -Q_4, Q_5, \gamma, -\eta$ |
| A′ | 1441 sh | — | 1454 | 1430 vs | 1454 | $\eta$ |
| A′ | 1425 vs | — | 1418 |  | 1417 | $-\gamma, -\eta$ |
| A′ | 1402 vs | 1393 (3,7) | 1410 | 1415 vs | 1409 | $-\gamma, \eta$ |
| A′ | 1378 vs | 1346 (10,0) | 1364 | 1382 m | 1360 | $-Q_1, q_5, Q_4, \beta_3, -\beta_4, \alpha_4$ |
| A′ | 1225 m | 1245 (5,5) | 1244 | 1220 m, br | 1239 | $-q_2, -Q_2, -\alpha_1, \alpha_3$ |
| A′ | 1200 sh | 1198 (9,1) | 1190 | 1200 sh | 1180 | $-q_2, -q_3$ |
| A″ | 1150 w | — | 1158 | 1156 w | 1158 | $\gamma, \chi$ |
| A′ | 1063 vs | — | 1064 | 780 m | 782 | $-\beta_3, \beta_4$ |
| A′ | 1039 m | 1032 (6,0) | 1015 | 1040 m | 1020 | $-q_1, \beta_3, -\beta_4, \gamma$ |
| A′ | 1017 w | 1018 (0,1) | 983 | 1000 sh | 982 | $Q_2, -Q_4, -\alpha_1, -\alpha_3, \alpha_5$ |
| A′ | 984 vw | 980 (5,7) | 957 | 988 w | 959 | $-q_1, \alpha_2, -\alpha_3$ |
| A″ | 900 m, br. | 909 (6,7) | 907 | 780 m | 781 | $\rho_3, \chi$ |
| A′ | 850 sh | 846 (2,0) | 834 | 850 vw | 841 | $-q_1, \beta_7, \beta_8$ |
| A″ | 800 m | — | 808 | 840 sh | 838 | $\rho_2, \chi$ |
| A′ | 660 vw | — | 641 | — | 635 | $q_5, -\alpha_2, \alpha_3, -\alpha_4$ |
| A″ |  | — | 633 | — | 543 | $\rho_4, \chi$ |
| A″ | 600 w | — | 601 | — | 628 | $\rho_1, \chi$ |
| A′ | 525 m | — | 508 | — | 504 | $q_1, \beta_1, -\beta_2, \beta_7, -\beta_8$ |
| A′ | 452 m | 469 (0,8) | 443 | — | 435 | $-\beta_5, \beta_6$ |
| A′ | 350 w | — | 336 | — | 336 | $-\beta_8$ |
| A″ | 280 m | — | 254 | — | 236 | $\rho_3, \chi$ |
| A′ | — | 213 (2,7) | 207 | — | 206 | $-\beta_1, \beta_2$ |
| A″ | — | — | 152 | — | 152 | $\rho_2, \chi$ |

lines are presented on a ten-point scale. The calculation of the frequencies and forms of the normal vibrations and the solution of the inverse spectral problem by the method of least squares were accomplished with a Minsk-22 computer from programs developed in [9]. The anharmonicity of the vibrations was taken into account by introduction of the spectroscopic masses of the H and D atoms.

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