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VIBRATIONAL SPECTRA OF THE HYDRAZIDES OF (TETRAZOL-1-YL)-AND (TETRAZOL-2-YL)ACETIC ACIDS AND THEIR DEUTERATED ANALOGS

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The hydrazides of (tetrazol-1-yl)- and (tetrazol-2-yl)acetic acids and their deuterated analogs are investigated by means of IR spectroscopy. On the basis of the data obtained, assignments in the vibrational spectra of the isomers are made.

Establishing the mode of coordination of potentially polydentate, organic ligands, among which are the isomers of the hydrazides of tetrazolylacetic acids, is one of the major problems in coordination chemistry. The basic method for solving this problem is usually IR spectroscopy, but its application requires accurate knowledge of the positions of the vibrational bands of the fragments taking part in coordination.

Since calculations of the frequency and shape of the normal vibrations of various tetrazole derivatives [1-3], as well as of compounds containing the hydrazide fragment [4-6], have been described, the problem of assigning the bands in the IR spectra of the isomers of the hydrazides of tetrazolylacetic acids reduces to subtracting from the spectra the bands due to vibrations of the heterocyclic, hydrazide, and methylene groups. To help in this, it is necessary to investigate the vibrational spectra of deuterated analogs of the compounds to be studied.

The isomeric hydrazides of (tetrazol-1-yl)- and (tetrazol-2-yl)acetic acids (I and II) were obtained by the hydrazinolysis of the corresponding ethyl esters III and IV. In the PMR spectra, the proton signal from the tetrazole ring of isomer I was shifted to a weaker field compared to the signal in the spectrum of compound II. This is analogous to what was observed with the initial esters III and IV [7].

In the high-frequency region of the IR spectra of isomers I and II, three groups of bands are observed that arise from the stretching vibrations of the N–H bonds in the hydrazide group (3327-3223 cm^{-1}), the C–H bond in the tetrazole ring (3170 cm^{-1}), and the CH_2 group (3067-3037 cm^{-1}) (Fig. 1). On deuteration, the first group of bands is shifted in the spectra of compounds I-d_3 and I-d_4 to the 2530-2400 cm^{-1} region.

Deuteration of the hydrazide group makes it easy to subtract the eight vibrational bands of the tetrazole ring (R_1-R_8) from the spectrum of compound I. Their positions in the spectra of compounds I, I-d_3, and I-d_4 are virtually unchanged. Inasmuch as these vibrations preserve their relative identity with respect to frequency [1], the assignment of these bands is done. The assignment of the stretching vibrations of the ring are: two at 1483 and 1437 cm^{-1} (R_1 and R_2) arising basically from the stretching vibrations of the C=N and N=N bonds, and a band at 1257 cm^{-1} (R_3) arising from the vibrations of the C–N and N–N bonds. The ring breathing vibrations appear at 1176 cm^{-1} (R_4), then come three strong bands, 1108, 1032, and 972 cm^{-1}

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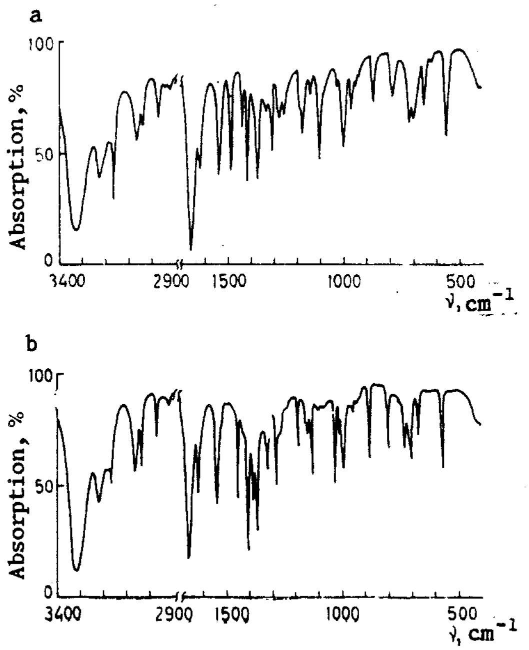

Fig. 1. IR absorption spectra: a) hydrazide of (tetrazol-1-yl)acetic acid; b) hydrazide of (tetrazol-2-yl)acetic acid.

(R$_5$-R$_7$) arising from deformational vibrations, and a band at 658 cm^{-1} (R$_8$), arising from torsional vibrations of the ring (Table 1).

In [2, 3], calculations were made of the frequencies and shapes of the normal vibrations of 1-H- and 2-H-5-(trifluoromethyl)tetrazoles, from which it follows that the IR spectra of tetrazole derivatives are very sensitive to isomerism. Thus, vibrational bands of the 2-isomer are shifted, according to the calculations, by 100-200 cm^{-1} with respect to the bands of the 1-isomer. However, the authors of [2] had only the 1-isomer, so that they could not verify experimentally the correctness of the calculations. It follows from the results of the present work (Table 1) that the IR spectrum of isomer II is very similar to the spectrum of compound I; the vibrational bands of the ring are located in the same regions, differing from the bands in the spectrum of isomer I by no more than 10-30 cm^{-1}.

On deuteration the bands arising from the deformational vibrations of the methylene groups were not shifted. Despite the fact that they are located in the same regions as the ring vibrations, their rather pronounced distinctive nature allows a reliable assignment to be made. Additional aid is afforded here by a comparison of the spectra of isomers I and II, in which these bands differ insignificantly. Thus, the scissoring (δ_{CH_2}), wagging (ω_{CH_2}), twisting (τ_{CH_2}), and rocking (ρ_{CH_2}) vibrations of the methylene group in the spectrum of isomer I are located at 1414, 1370, 1144, and 790 cm^{-1}, and at 1409, 1370, 1151, and 805 cm^{-1}, respectively, in the spectrum of isomer II. Bands at 1396, 1347, and 1205 cm^{-1} are assigned to the first three vibrations in the spectrum of cyanoacethydrazide, which has a similar structure [4].

The deformational vibrations of the C–H bond makes a contribution to almost all of the ring vibrations [1]. This is reflected in the shifting somewhat of the bands on deuteration, but basically these vibrations appear in three bands, the shifting of which is maximal: 1437, 1187, and 883 cm^{-1}. The first band, containing the δ_{CH_2} vibration, is covered by the band from ring stretching vibrations R$_2$. There are two bands in the IR spectrum of tetrazole located in this region at 1450 and 1440 cm^{-1} [1]. On deuteration the first of these is shifted to 1360 cm^{-1}, and the second is shifted only very slightly. In the spectrum of the I-d$_4$ deuteroderivative, the band arising from the ring vibrations is found at 1431 cm^{-1}, while a band appears at 1350 cm^{-1} that is absent from the spectrum of compound I.

The shoulder at 1187 cm^{-1} on the band from the R$_4$ ring vibrations is assigned to the ρ_{C-H} vibrations on the grounds that, besides the 1173 cm^{-1} band, there is a new band at 1056 cm^{-1} compared to the spectra of compounds I and I-d$_3$ ($\nu_{H/D}$ 1.111). The band at 1165 cm^{-1} in the spectrum of 1-methyltetrazole also contains ring and ρ_{C-H} vibrations [1]. Isomerism has a weak effect on the position of the bands of the deformational vibrations of the C–H group. Because the ring vibrational bands in the spectrum of compound II are shifted in comparison to the spectrum of isomer I, the C–H group vibrations appear in the form of separate bands (1390, 1193, and 885 cm^{-1}). It should be noted that for sym-triazine, which has an analogous N=CH–N fragment, bands at 1410, 1174, and 830 cm^{-1} were assigned to the deformational vibrations of the C–H group on the basis of a calculation of the normal vibrations [8].

TABLE 1. IR Absorption Spectra of Tetrazolylacethydrazide Isomers

Compound	Band assignment, cm^{-1}*								
	ν_{N-H}	ν_{C-X}	ν_{CH_2}	Amide I	δ_{NX_2}	Amide II	R_1	R_2, δ_{C-X}	δ_{CH_2}
I	3327 s. 3228 m.	3168 s.	3066 m. 3040 m.	1668 v.s	1626 s.	1541 s.	1483 s.	1437 m.	1414 s.
I**	3359 s.	3150 s.		1708 s.	1630 m.				
I-D_3	2531 s. 2505 s. 2484 s.	3168 s.	3069 m. 3030 m.	1665 s.	1212 m. 1202 m.	1456 s.	1486 s.	1433 m.	1419 m.
I-D_4	2528 s. 2491 s. 2478 s.	2342 m.	3063 m. 3032 m.	1663 s.	1209 m. 1201 m.	1456 s.	1483 s.	1431 s. 1350 sh	1405 s.
II	3319 v.s 3223 m.	3170 m.	3062 m. 3024 s.	1665 m.	1629 s.	1546 s.	1456 s.	1390 s.	1409 s.

Compound	Band assignment, cm^{-1}*								
	ω_{CH_2}	δ_{NX}	Amide III	R_3	δ_{CX}	R_4	τ_{CH_2}	R_5	τ_{NX_2}
I	1370 s.	1311 m.	1280 m.	1257 m.	1085 sh	1176 s.	1144 w.	1108 v.s	1102 sh
II**			1270 m.	1242 m.		1170 s.	1114 w.	1097 s.	
I-D_3	1352 s.	1058 m.	964 s.	1253 s.	1187 s.	1174 s.	1156 m.	1108 s.	869
I-D_4	1338 s.	1066 m.	961 s.	1254 m.	1056 m.	1173 m.	1156 w.	1106 s.	869 s.
II	1370 s.	1327 m.	1287 m.	1270 m.	1193 m.	1164 m.	1151 w.	1139 s.	1104 w.

Compound	Band assignment, cm^{-1}*								
	R_6	ω_{NH_2}	R_7	ν_{C-C}	γ_{C-X}	ρ_{CH_2}	δ_{N-CH_2}	R_8	δ_{NCC}
I	1032 w.	1002 v.s	972 s.	964 w. 953 m. 938 w.	873 m.	790 m.	701 s.	658 m.	562 s.
II**		981 s.	968 s.	943 m.	872 m.	785 m.	709 m.	656 m.	533 m.
I-D_3	1027 m.	822 s.	970 m.	941 w. 919 w.	885 m.	780 m.	702 m.	663 m.	553 m.
I-D_4	1024 w.	820 m.	968 m.	941 w. 919 w.	661 m.	779 m.	702 m.	661 m.	548 m.
II	1034 s.	1011 m.	994 s.	957 w. 951 w. 930 w.	885 m.	805 m.	706 s.	672 m.	573 s.

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*ν) stretching; deformational: δ) scissoring; ω) wagging; τ) twisting; ρ) rocking; γ) in-plane vibrations; v.s) very strong; s) strong; m) medium; w) weak; sh) shoulder.

**In CH_3CN.

The amide fragment –CONH– usually has three characteristic vibrational bands in the IR which are easily recognized in the spectrum of compound I (1668, 1541, and 1280 cm^{-1}) as well as in the spectrum of isomer II (1665, 1546, and 1287 cm^{-1}). On deuteration the first band, "amide-I," containing predominantly C=O group stretching vibrations, is virtually unshifted, and the "amide-II" band, arising from basically C–N group vibrations, is shifted only slightly ($\nu_{H/D}$ 1059). However, the "amide-III" band, containing NH group deformational vibrations along with C=O and C–N group vibrations, is strongly shifted ($\nu_{H/D}$ 1.320). Vibrations of the NH group also are responsible for the band at 1300 cm^{-1} in the spectra of isomers I and II ($\nu_{H/D}$ 1.257). A similar strong shift on deuteration occurs with the NH_2 group deformational vibrational bands: the scissoring vibrational band (δ_{NH_2}) at 1628 cm^{-1} in the spectrum of compound I-d_3 appears as bands at 1212 and 1202 cm^{-1}, the twisting vibrational band (τ_{NH_2}) at 1102 cm^{-1} is shifted to 869 cm^{-1}, and the wagging vibrational band (ω_{NH_2}) at 1002 cm^{-1} to 822 cm^{-1}.

The N–N stretching vibrational band of the hydrazide fragment is usually located in the 1000-1100 cm^{-1} region and is, to all appearances, covered by one of the strong, ring vibrational bands.

In the spectra of compound II, the vibrational bands of the hydrazide fragment and the amino group occupy virtually the same positions as in the spectrum of isomer I. In the spectrum of cyanoacethydrazide the bands of the corresponding vibrations are located at 1698, 1534, 1258, and 1313, and at 1625, 1105, and 1009 cm^{-1} [4]. In a solution of acetonitrile, the vibrational "amide-I" bands in the isomer are shifted to higher frequencies (1703 cm^{-1}), which indicates the presence of association in the solid state.

In the 560-580 cm^{-1} region of the spectra of the isomers and their deutero analogs, there is a band that is also found in the IR spectrum of compound III. This gives grounds for considering this band to arise from skeletal vibrations.

EXPERIMENTAL

The PMR spectra of solutions in DMSO-d_6 were recorded on a Tesla BS-467 (60 MHz) instrument. The ^1H chemical shifts are given relative to external HMDS.* The IR spectra were obtained on IKS-24 and IR-75 spectrophotometers for suspensions in mineral oil (1800-1500, 1300-400 cm^{-1}) and hexachlorobutadiene (4000-1800, 1500-1300 cm^{-1}).

Elemental analyses of compounds I and II for C and H correspond to the calculated values.

In the work we used the ethyl esters of (tetrazol-1-yl)- and (tetrazol-2-yl)acetic acid (III and IV), prepared by the method in [7].

Ester III was further purified by recrystallization from hexane (by cooling a hexane solution saturated at room temperature to −10°C, mp 46-47°C (according to [9], mp 32-34°C). PMR spectrum, δ, ppm: 9.47 (1H, s, CH); 5.6 (2H, s, CH_2), 4.22 (2H, qt, $J_{HH} = 3.5$ Hz, CH_2), 1.25 (3H, t, $J_{HH} = 3.5$ Hz, CH_3).

Ester IV, mp 51-52°C (according to [7], mp 49-52°C). PMR spectrum: 9.10 (1H, s, CH), 5.90 (2H, s, CH_2), 4.25 (2H, qt, $J_{HH} = 3.5$ Hz, CH_2), 1.25 (3H, t, $J_{HH} = 3.5$ Hz, CH_3).

(Tetrazol-1-yl)acethydrazide (I). We dissolved 6.24 g (40 mmoles) of compound III in 25 ml of isopropyl alcohol, added 2.1 ml (44 mmoles) of hydrazine hydrate, heated the solution to boiling, and held it overnight at room temperature. We filtered off the precipitate that had formed, recrystallized it from 69 ml of 93% aqueous isopropyl alcohol, and obtained 4.6 g (81%) of colorless crystals, mp 118.0-118.5°C. PMR spectrum, δ, ppm: 9.30 (1H, s, CH), 9.23 (1H, t, J = 10 Hz, NH), 5.13 (2H, s, CH_2), 4.40 (2H, d, J = 10 Hz, NH_2).

We prepared the deuterated sample I-d_4 by the repeated exchange reaction of I with D_2O at 90°C followed by vacuum distillation at 40°C. The analogous operation, but without the preliminary heating, leads to compound I-d_3.

Tetrazol-2-yl)acethydrazide (II) was synthesized from compound IV in a manner analogous to that of compound I in a 76% yield, mp 118-119°C. PMR spectrum, δ, ppm: 9.20 (1H, m, NH), 8.86 (1H, s, CH), 5.31 (2H, s, CH_2), 3.86 (2H, m, NH_2).

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*The spectral plots were made by S. A. Zyuz'kevich.