Spectroscopic study of fused 1,2,3,4-tetrazine 1,3-dioxides

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Vibrational spectra of furazano- and benzo-1,2,3,4-tetrazine 1,3-dioxides were studied, and the main regularities of the changes in frequencies of stretching vibrations of the tetrazine dioxide fragment with respect to the nature of the substituent in the benzene ring were established.

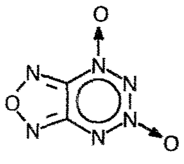
Key words: furazano- and benzo-1,2,3,4-tetrazine 1,3-dioxides, IR and Raman spectra.

In order to continue studying vibrational spectra of compounds containing diazenoxide groups,[1] spectra of fused 1,2,3,4-tetrazine 1,3-dioxides[2] (TDO) have been studied. TDO are a new type of stable high-nitrogen compound containing a unique combination of two diazene oxide groups directly bound to one another.

Experimental

IR and Raman spectra of TDO were obtained by standard procedures on UR-20 and Ramanor U 1000 spectrometers, respectively, with krypton laser as the excitation source (λ_{exc} = 647.1 nm).

In order to assign vibrations of diazene oxide groups bound to one another in the tetrazine dioxide fragment (TDOF), the vibrational spectra of furazano-1,2,3,4-tetrazine 1,3-dioxide (**1**) were interpreted, using isotope substitution, comparison of IR and Raman spectra with account for depolarization of lines in Raman spectra, and calculations of frequencies and forms of normal vibrations of **1** and its 3-[^{15}N]-isotope-substituted derivative **1a**.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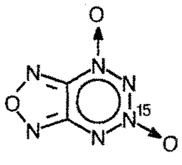
1a

Calculations were performed by the program described in Ref. 3, using averaged geometrical parameters from the X-ray diffraction analysis (XDA) data for 5,7-nitrobenzo-1,2,3,4-tetrazine 1,3-dioxide (the XDA data will be published elsewhere) and furazane[4]: l_{CN} = 1.41, 1.32 Å; $l_{N=N}$ = 1.31 Å; $l_{N\to O}$ = 1.24 Å, l_{N-N} = 1.39 Å, ∠ONN = 117°, ∠NNN = 114°, 129°; ∠CNN = 123°, 115°.

Force constants for 1-phenyl-2-nitrodiazene oxide[1] and azoxybenzene[5] molecules were used as an initial approximation for the force field of compound **1**. The initial force field was refined in the process of solution of the direct vibrational problem for compounds **1** and **1a** under the condition of minimum deviations between calculated and experimental frequencies. In order to estimate the characteristics of vibrations, the potential energy distribution over internal coordinates was calculated for each normal vibration.

The results of the experimental and theoretical studies of the vibrational spectra of TDO are presented in Tables 1—3.

Results and Discussion

Since a molecule of **1** is related to point symmetry group C_1, all of its 27 vibrations are active in both IR and Raman spectra. The intensities of bands in the both spectra are comparable, excluding the 1400 to 1600 cm^{-1} range, in which intense bands of the IR spectra correspond to weak lines of the Raman spectra. When the ^{14}N atom is substituted for ^{15}N at position 3 of a molecule of **1**, several lines (see Table 1) are shifted to the low-frequency range. This allows one to assert that they are assigned to vibrations involving the coordinates of TDOF.

According to the potential energy distribution over the maximum contribution of the corresponding coordinates, only four bands with ν_{calc} 1555, 1410, 1147, and 669 cm^{-1} can be assigned to stretching vibrations of

Table 1. Vibrational frequencies in the IR and Raman spectra of furazano-1,2,3,4-tetrazine 1,3-dioxide (**1**) and its isotope-substituted derivative (**1a**) (ν/cm^{-1})

IR		Raman	IR		Raman
pellets KBr	CH_2Cl_2*	solid	pellets KBr	CH_2Cl_2*	solid
1548 s	1547 s	1544 w	1538 s	1537 s	1538 w
1537 w	1537 v w	1540 v w	1530 w	1530 w	1532 v w
1517 s	1516 s	1508 v w	1507 s	1505 s	1500 v w
1420 s	1420 s	1412 w	1415 s	1415 s	1406 w
1148 s	1137 s	1151 s	1141 s	1131 s	1142 s
676 w	—	676 v w	662 w	—	664 v w

* c = 0.05 mol/L. ** c = 0.14 mol/L.

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Table 2. Experimental (ν_{exp}/cm^{-1}) and calculated (ν_{calc}/cm^{-1}) frequencies of normal vibrations of the furazano-1,2,3,4-tetrazine 1,3-dioxide fragment, potential energy distribution (%)

ν_{exp}	ν_{calc}	Potential energy distribution
1589	1589	C—N (12); C—C (26); C=N′ (16); CNN (19)
1548	1555	N—N (10); N=N (64); NNO (13)
1537	1541	C—N″ (46); C=N′ (36); CCN′ (17)
1517	1516	C—N (22); C=N′ (43); CCN′ (12)
1460	1461	N=N (12); N→O (12); C—N (12); C=N′ (51)
1420	1410	N=N (74); N→O (12); NNO (16)
1316	1310	C=N′ (15); N′—O′ (77); CN′O′ (25)
1208	1217	N=N (16) N→O(31); C—C(12); N′—O′(18); CN′→O′(18)
1178	1181	C=N′ (14); N′—O′ (65)
1148	1147	N=N (47); N→O (36); C—N′(23); N′—O′(25)
1016	1015	N—N (11); N=N (12); N→O(28); NNO (19)
941	934	C—C (33); N′—O′(37); N′O′N′(49)
871	878	ω N=N (16); ω N→O (75); ω C—N (10)
855	867	N→O (43); NNO (39)
843	846	ω N=N (18); ω N→O (50); ω C—N (31)
722	709	ω N=N (25); ω N→O (32); ω C—N (37)
676	669	N—N (32); N=N (22); C—N″ (12); C—N (10)
585	567	N=N (20); N′—O′(25);NNN (34); CNN (20)
548	529	N=N (19); N→O (24); NNO (20); CNN (42)
479	482	ω N=N (23); ω N←O (11); ω C—N (52)
418	413	N—N (37); N←O (22); C—N (13); NNO (12); CN″N (15)
375	341	ω C—N1 (41); ω N=N (33); ω C—N (18)
329	317	N—N (20); N=N (11); C—N″ (19); NNO (36); CN″N (13)
234	248	C—N″ (10); C—N (12); N″NN (14); NNN (10); CCN (41); CCN′ (11)
226	217	ω CN″ (29); ω N=N (51); ω C—N (19)
146	151	ω C—C (77); ω C—N (14)
74	48	ω C—C (16); ω C—N″ (15); ω N=N (32); ω N→O (13); ω C—N (24)

* Contributions that amount to less than 10 % are not presented.

** The N′ and O′ atoms belong to the furazane cycle; the N″ atom is bound to the oxygen atom in TDOF.

Table 3. Frequencies of stretching vibrations of the 1,2,3,4-tetrazine 1,3-dioxide fragment in the IR spectra of compounds **1** and **2** (ν/cm^{-1})

Compound	ν^{syn}(N=N)	ν^{ansyn}(N=N)	$\nu^{as}NO_2$	$\nu^{s}NO_2$
1	1548 s	1420 s	—	—
2a	1497 s	1402 s	—	—
2b	1486 s	1404 m	—	—
2c	1496 s	1424 s	—	—
2d	1468 s	1404 m	—	—
2e	1474 s	1408 s	—	—
2f	1520 s	1432 s	1548	1342
2g	1517 s	1431 s	1540	1345
2h	1507 s	1428 s	1552	1350

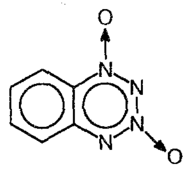
TDOF, and the other are assigned to stretching vibrations of the furazane cycle (see Table 1). The first two vibrations occur with predominant participation of N=N bonds. Since in the first of them N=N bonds vibrate in phase and in the second N=N bonds vibrate in antiphase, these vibrations can approximately be considered as synphase (ν^{syn}(N=N)) and antiphase (ν^{ansyn}(N=N)) vibrations, respectively. The participation of the N→O bonds in the ν^{syn}(N=N) vibration and the N—N bond in the ν^{ansyn}(N=N) vibration is weak. Almost all bonds of TDOF are involved in its third (ν_{calc} 1147 cм$^{-1}$) and fourth (ν_{calc} 669 cm^{-1}) vibrations, and the participation of the coordinates of the furazane cycle is great in the third vibration. In the IR spectrum the ν^{syn}(N=N) and ν^{ansyn}(N=N) vibrations appear as intense bands, and in the Raman spectra they appear as weak polarized and depolarized lines, respectively. The band with ν_{calc} 1147 cm^{-1} is intense in the IR spectrum and intense polarized in the Raman spectrum. The band with ν_{calc} 669 cm^{-1} is weak both in the IR and Raman spectra.

All other vibrations of a molecule of **1**, except the vibrations with ν_{calc} 1589, 1460, 1316, and 1178 cm^{-1} related to the furazane cycle, are mixed vibrations, and the contributions of natural coordinates related to the change in bonds into the most of them are approximately equal to the contribution of coordinates related to the change in planar and nonplanar angles. Therefore, the assignment of such vibrations is rather arbitrary.

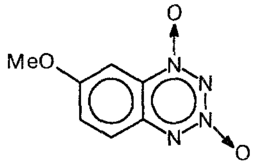
Thus, based on the experimental and theoretical studies of the vibrational spectra of **1**, one can draw the conclusion that the ν^{syn}(N=N), ν^{ansyn}(N=N), and ν_{calc} 669 cm^{-1} are characteristic vibrations of TDOF. However, since the latter appears in IR and Raman spectra as a weak band and can be overlapped by other bands, it is not always possible to assign this vibration in spectra of TDO only on the basis of experiments.

The results of the interpretation of the vibrational spectra of compound **1** were used for assigning the frequencies of stretching vibrations of TDOF in the spectra of benzo-1,2,3,4-tetrazine 1,3-dioxide (BTDO) (**2a**) and its derivatives with various substituents (MeO, Me_2N, and NO_2) in the benzene ring (**2b—h**).

The IR and Raman spectra of the 3-[^{15}N]-isotope-substituted derivative of compound **2g** (3-[^{15}N]-**2g**) were used for a more strict assignment of these frequencies in spectra of nitro-substituted derivatives of BDTO in which the possibility of overlapping the $\nu^{as}NO_2$ and ν^{syn}(N=N) bands cannot be excluded. In the spectra of compound 3-[^{15}N]-**2g** the ν^{syn}(N=N) and ν^{ansyn}(N=N) bands are shifted to the low-frequency range by 19 and 13 cm^{-1}, respectively, compared to the spectra of **2g**.



2a



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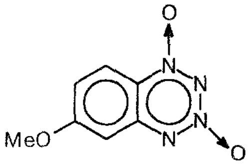
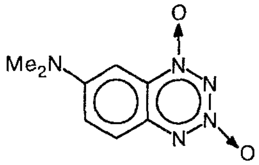
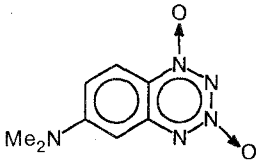


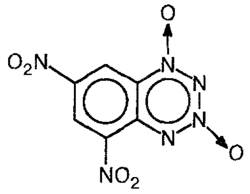
2c



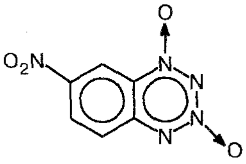
2d



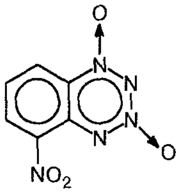
2e



2f



2g



2h

It can be seen from Table 3 that $\nu^{syn}(N{=}N)$ and $\nu^{ansyn}(N{=}N)$ in the spectra of BDTO are localized in the 1460—1550 and 1400—1440 cm^{-1} ranges, respectively. The bands corresponding to these vibrations are intense mainly in IR spectra. The introduction of the nitro group into the benzene ring increases the frequencies of the both vibrations of TDOF. The introduction of the methoxy group in position 6 exerts almost no effect on $\nu^{syn}(N{=}N)$ and increases $\nu^{ansyn}(N{=}N)$, and the introduction of this group in position 7 does not change $\nu^{ansyn}(N{=}N)$ and decreases $\nu^{syn}(N{=}N)$. The dimethylamino group decreases $\nu^{syn}(N{=}N)$, and this effect for 7-substituted BDTO is larger than for 6-substituted BDTO. It is noteworthy that the $\nu^{syn}(N{=}N)$ bands are not overlapped with the $\nu^{as}NO_2$ bands in the spectra of nitro-substituted derivatives of BDTO (see Table 3). The frequencies of stretching vibrations of nitro groups of the latter were assigned on the basis of the literature data on aromatic nitro compounds[6] (according to which these compounds exhibit $\nu^{as}NO_2$ ~1540 cm^{-1} and $\nu^{s}NO_2$ ~1350 cm^{-1}) and by the splitting of the corresponding bands in the spectrum of the isotope-substituted derivative **2f** due to the fact that the introduction of the ^{15}N label in position 3 of a molecule of **2f** results in the 100 % substitution of the nitrogen atom of the nitro group in position 5 and the 25 % substitution in position 7.

Compound	$\nu^{as}NO_2/cm^{-1}$	$\nu^{s}NO_2/cm^{-1}$
2f	1548	1342
3-[^{15}N]-**2f**	1548, 1515	1343, 1312

The $\nu^{as}NO_2$ and $\nu^{s}NO_2$ bands in the spectra of compounds **2g** and **2h** were assigned similarly to those of **2f**.

Thus, the study of vibrational spectra of TDO revealed the characteristic frequencies of stretching vibrations of TDOF ($\nu^{syn}(N{=}N)$ and $\nu^{ansyn}(N{=}N)$), which is two directly bound diazene oxide groups. These vibrations are the result of the strong vibrational interaction between diazene oxide groups in TDOF, and, hence, their bands in IR spectra are removed from one another by 70—150 cm^{-1}. Compared to azoxybenzenes,[5] in the spectra of which $\nu(N{=}N)$ is localized within the 1410 to 1505 cm^{-1} range, in the spectra of TDO $\nu^{syn}(N{=}N)$ is localized in a higher-frequency range and $\nu^{ansyn}(N{=}N)$ is in a shorter-frequency range. Compared to nitrodiazene oxides[1] containing more than one nitrodiazene oxide group, $\nu^{syn}(N{=}N)$ of TDO appears in the absorption range of $\nu(N{=}N)$ of nitrodiazene oxide groups.

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