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1,2,3,4-Tetrazine 1,3-Di-*N*-oxides – Novel High Nitrogen Compounds: Vibrational Spectra and Structure

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In a spectroscopic study of furazano- and benzo-1,2,3,4-tetrazine 1,3-di-*N*-oxides, characteristic frequencies of vibration of the tetrazine dioxide fragment have been revealed, the dependence of the change in frequency on the substituent in the benzene ring has been studied and some specific properties of the electronic structure have been determined (calculations of the electronic parameters of the molecules have been performed by the MNDO method).

It was found previously[1] by studing the vibrational spectra of 1-aryl-2-nitrodiazene 1-oxides that vibrational interaction between diazene oxide groups is absent in molecules with more than one diazene oxide fragment. In addition, a noticeable influence of the subtituents in an aromatic ring on the frequency $\nu_{N=N}$ was discovered. In the molecules of condensed 1,2,3,4-tetrazine 1,3-di-*N*-oxides (TDO),[2] two diazene oxide groups are bound to each other directly. The question of the interaction of the above groups in a new combination and of the influence of substituents in the benzene ring on

characteristic frequencies is interesting, and a solution to the problem is given in this paper.

In order to assign vibrations of directly interlinked diazene oxide groups in the tetrazine dioxide fragment we carried out a strict interpretation of the vibrational spectra[†] of the furazano-1,2,3,4-tetrazine 1,3-di-*N*-oxide **1**. During the interpretation we used isotopic substitution, comparison of the IR and Raman spectra with a recording of the degree of depolarization of the bands in the Raman spectra, and a calculation[‡] of the frequencies and forms of the normal vibrations of **1** and its isotopically-substituted derivative **1a**, including isotope ^{15}N at the 3 position of the molecule.

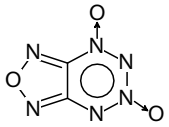
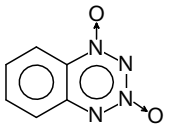
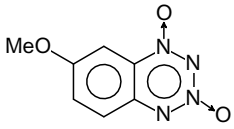
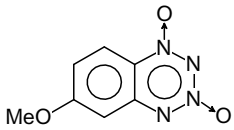
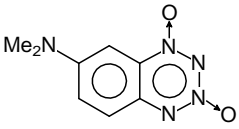
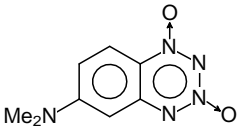
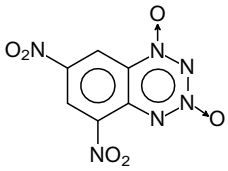
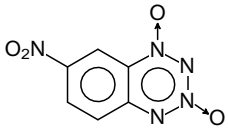
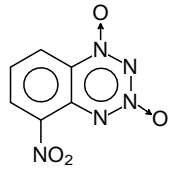
During the experimental and theoretical study of the vibrational spectra of **1**, characteristic vibrations of the whole TDO fragment, not individual diazene oxide groups, were picked out. Vibrational interaction between diazene oxide groups exists. These vibrations were interpreted as $\nu^{syn}_{N=N}$ (ν_{calc} 1555 cm^{-1}) and $\nu^{asyn}_{N=N}$ (ν_{calc} 1410 cm^{-1}) because in the first one the N=N bonds of both diazene oxide groups are vibrating in the same phase, and in the second one in antiphase. These vibrations give an intense absorption in the IR spectrum, but in the Raman spectrum their bands are weak, polarized and depolarized, respectively.

Results of the interpretation of the vibrational spectra of **1** were used for the assigment of the frequencies of the TDO fragment stretching vibrations in the spectra of benzo-1,2,3,4-tetrazine 1,3-di-*N*-oxide (BTDO) with different substituents in the benzene ring (see Table 1). For a more accurate assigment of the above frequencies in the spectra of the nitro derivatives **2f**–**h**, isotopic substitution was used, because the overlapping of the bands $\nu^{as}_{NO_2}$ and $\nu^{syn}_{N=N}$ cannot be excluded. The ^{15}N label was introduced in the 3 position of the TDO fragment in molecule **2g**.

During the interpretation of the spectra of compounds **2a**–**h**, it was found that the $\nu^{syn}_{N=N}$ and $\nu^{asyn}_{N=N}$ are located in the ranges 1460–1550 and 1400–1440 cm^{-1}, respectively. The bands corresponding to these vibrations are intense in the IR spectra. The introduction of a nitro group in the benzene ring increases the frequencies of both TDO fragment vibrations (see Table 1). The introduction of the MeO group in the 6 position of the BTDO molecule increases the frequency $\nu^{asyn}_{N=N}$, but the same group in the 7 position decreases $\nu^{syn}_{N=N}$. The introduction of a Me_2N group in the 7 position of the BTDO molecule decreases the frequency $\nu^{syn}_{N=N}$ to a greater extent than in the 6 position.

The different influence of the same substituents in different positions of the benzene ring on the TDO fragment frequencies is caused by the difference in the donor-acceptor effect of these groups on the TDO fragment, *i.e.* by the difference in the electronic structure of the isomeric compounds. The calculations of molecular electronic parameters of the methoxy- and dimethylamino derivatives **2b**–**e** by the MNDO method,[5] including geometry optimization, confirmed the above assumption. The charges at the nitrogen and oxygen atoms of the TDO fragment are higher in the 6-substituted derivatives. Besides, the 6-substituted derivatives are characterized by the alternation of charges both in the TDO fragment and in the benzene ring. In molecules of 7-substituted derivatives if the charges alternate in the TDO fragment, the charges at the carbon atoms of the benzene ring are near to zero except for the atoms bound to the TDO fragment.

Table 1 Stretching vibration frequencies of the 1,2,3,4-tetrazine 1,3-di-*N*-oxide fragments in the spectra of compounds **1** and **2** (ν/cm^{-1}).

Compound	Structural formula	$\nu^{syn}_{N=N}$	$\nu^{asyn}_{N=N}$
1		1548s	1420s
2a		1497s	1402s
2b		1486s	1404m
2c		1496s	1424s
2d		1468s	1404m
2e		1474s	1408s
2f[a]		1520s	1432s
2g[b]		1517s	1431s
2h[c]		1507s	1428s

[a] $\nu^{as}_{NO_2}$ 1548 cm^{-1}, $\nu^{s}_{NO_2}$ 1342 cm^{-1}. [b] $\nu^{as}_{NO_2}$ 1540 cm^{-1}, $\nu^{s}_{NO_2}$ 1345 cm^{-1}. [c] $\nu^{as}_{NO_2}$ 1552 cm^{-1}, $\nu^{s}_{NO_2}$ 1350 cm^{-1}.

Thus, during our study of the vibrational spectra of TDO, the characteristic frequencies of the TDO fragment stretching vibrations representing two directly interlinked diazene oxide groups were revealed. The influence of substituents in the benzene ring on these frequencies was studied. It was shown that the differences in the absorption frequencies $\nu^{syn}_{N=N}$ and $\nu^{asyn}_{N=N}$ of the isomeric compounds were found to result from differences in their electronic structure.

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[†] IR spectra were recorded using a UR-20 spectrometer in KBr tablets or in CH_2Cl_2 solutions at room temperature, and Raman spectra using a RAMANOR U 1000 spectrometer (krypton laser as an excitation source, samples in the solid state).

[‡] The calculations of the frequencies and forms of normal vibrations were carried out using the program in ref. 3 (the calculation procedure is similar to that given in ref. 4) and using X-ray structural parameters for 5,7-dinitrobenzo-1,2,3,4-tetrazine 1,3-di-*N*-oxide **2f**. Complete details of the X-ray crystallographic data will be published later.

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