Spectroscopic investigation of 2-nitrodiazenoxides

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2-Nitrodiazenoxides have been studied by vibrational spectroscopy methods. The main regularities of the changes in the stretching vibration frequencies of the nitro and diazenoxide groups were studied as functions of different factors.

Key words: 2-nitrodiazenoxides, vibrational spectra, characteristic frequencies, band intensity.

Nitrodiazenoxides (NDO) are nitroderivatives of a new type containing well known nitro and diazenoxide groups that are connected in a previously unknown way. It is not yet clear which interactions occur between these groups in this new combination, and how these interactions effect the structure and physicochemical properties of NDO. The purpose of the present work is to investigate this problem by vibrational spectroscopy methods.

There is no data on the analysis of the diazenoxide group vibrations for known types of diazenoxides[1–4] in the literature, and there are contradictions in the assignment of the $\nu(N\rightarrow O)$ vibration frequencies, which was not interpreted at all in the spectra of fluorodiazenoxide.[3] In view of this and taking into account the fact that NDO contain a new combination of the nitro and diazenoxide groups, the correct interpretation of the vibrational spectra of 1-phenyl-2-nitrodiazenoxide (**1**) as a reference compound appeared to be an urgent task. The assignment of the frequencies in the spectra of compound **1** was performed by using isotopic substitution (the introduction of the ^{15}N isotope into the diazenoxide group of the molecule), by comparison between the IR and Raman spectra of compound **1** and its isotope-substituted derivative $Ph^{15}N{=}NNO$ (**1a**) (by

measuring the degree of depolarization of the bands in the Raman spectra), and by calculation of the frequencies and forms of the normal vibrations of **1** and **1a**.

In our calculations, we used the averaged geometrical parameters obtained from the X-ray analysis (XRA) data for 1-(2,6-dichlorophenyl)-2-nitrodiazenoxide (**2**)* and 1-(4-bromophenyl)-2-nitrodiazenoxide (**3**)*: l_{CC} 1.397 Å, l_{CH} 1.08 Å, l_{CN} 1.46 Å, $l_{N=N}$ 1.28 Å, $l_{N\rightarrow O}$ 1.25 Å, l_{NN} 1.48 Å, l_{NO} 1.21 Å; the angles: O—N—O 129°, N—N—N 111°, N—N—O 129°, C—C—C 120°.

As an initial approximation for the force field of compound **1**, the force constants of the nitrobenzene molecule[5] and the force constants of the molecule $HN{=}NNO_2$ were used, which were calculated by the *ab*

initio method in the 4—31 G basis set. The diagonal and non-diagonal force constants were calculated as the second derivatives of energy with respect to the intrinsic coordinates analogously to the procedure reported earlier.[6] The initial force field of compound **1** was refined by varying the force constants in the course of solution of the direct vibrational problem simultaneously for compounds **1** and **1a** under the condition of minimal deviations of the calculated frequencies from the experimental frequencies. To evaluate the intristic character of the vibrations, the distributions of the potential energy (DPE) with respect to the internal coordinates for every normal vibration were calculated.

The assignment of the frequencies in the spectrum of **1** shows that the stretching vibrations of the CH-bonds and the stretching and bending vibrations of the benzene ring manifest themselves in the regions that are characteristic of aromatic nitro derivatives.[7] Therefore, we considered only the vibrations involving nitro and diazenoxide groups.

The characteristic vibration of the nitro group with respect to frequency and form is the anti-symmetrical $\nu^{as}(NO_2)$ stretching vibration at 1612 cm^{-1}, which is observed in the IR spectrum as an intense narrow band (ε = 719 L mol^{-1} cm^{-1}, A^* = 8500 L mol^{-1} cm^{-2}) and in the Raman spectrum as a weak depolarized line. According to the DPE, this vibration is only caused by the NO bond vibrations (Table 1). The symmetrical stretching vibration of the nitro group $\nu^{s}(NO_2)$ at 1270 cm^{-1} is not characteristic with respect to the form. Table 1 shows that the contribution of the other coordi-

* X-ray data for compounds **2** and **3** will be reported later.

* A is the integral intensity of the band.

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Table 1. Observed and calculated frequencies (ν/cm^{-1}) of the vibrations of the nitro and diazenoxide groups in the spectra of 1-phenyl-2-nitrodiazenoxide and distribution of the potential energy (DPE)

ν/cm^{-1}					DPE[a] (%)
IR		Raman		Calcu-	
KBr in tablet	CCl_4[b]	solid	CCl_4[c]	lation	
1612 s	1620 s	1612 v.w	1616 v.w	1612	NO (100)
1491 m	1494 m	1492 w	1491 w	1491	N=N (40), CC (30)
1315 w	1317 w	1319 m	1320 m	1327	N=N (27), NO (17), N→O (13), CC (41)
1270 s	1270 s	1271 v.s	1272 s	1264	NO (32), N=N (20), N→O (15), CC (20)
—	—	836 v.w	—	825	N=N (14), N—N (54)
775 w	—	—	—	777	ω NO_2 (57)
617 w	—	614 w	—	634	NNO (58), ω CN (25), ω CH (19)
557 v.w	—	560 v.w	—	557	NO (11), NNO (89), ω CN (24), CCC (21)

[a] Contributions less than 10 % are not given. [b] C = 0.07 mol L^{-1}. [c] C = 1.81 mol L^{-1}.

nates of molecule **1**, in particular, the diazenoxide group, to this vibration is relatively high. Therefore, the introduction of the ^{15}N isotope into the diazenoxide group results in a 12 cm^{-1} shift of the band corresponding to the above-mentioned vibration to the low frequencies region. The $\nu^s(NO_2)$ vibration manifests itself as an intense narrow band (ε = 600 L mol^{-1} cm^{-1}, A = 7500 L mol^{-1} cm^{-2}) in the IR spectrum, and as a strongly polarized line in the Raman spectrum.

The bending vibrations of the nitro group and the ν(N—N) vibration are relatively characteristic (see Table 1). In the IR and Raman spectra, the bands corresponding to these vibrations are weak.

Now we shall consider the vibrations involving the participation of the diazenoxide group. Of these vibrations, the ν(N=N) vibration, caused mainly by the contribution of the N=N bond, is relatively characteristic. The contribution of the N→O bond to this vibration is 1 %. In the IR spectrum ν(N=N) is observed as a narrow band of medium intensity (ε = 390 L mol^{-1} cm^{-1}, A = 4200 L mol^{-1} cm^{-2}), and in the Raman spectrum it is a weak depolarized line. In the spectra of compound **1**, the ν(N=N) vibration is shifted to the high frequency region (1491 cm^{-1}) relative to that of azoxybenxene[4] (ν(N=N) 1440 cm^{-1}). This is associated with the differences between the force constants, mainly, those of the N=N bonds ($K_{N=N}$ of compound **1** is $16.67 \cdot 10^6$ cm^{-2}, $K_{N=N}$ of azoxybenxene is $12.75 \cdot 10^6$ cm^{-2}).

The second stretching vibration of the diazenoxide group, ν(N=N)(O), to which the 1327 cm^{-1} frequency band was conditionally assigned, is not characteristic (see Table 1). The contribution of the other coordinates of molecule **1** to this vibration is greater than that of the coordinates of the diazenoxide group. The analogous vibration of azoxybenxene[4] at 1330 cm^{-1} is, according to DPE, mainly due to the CN bonds (40 %). Therefore, authors[4] interpreted this vibration as ν(CN). In the IR spectrum of **1**, the ν(N=N)(O) vibration manifests itself as a weak band, and in the Raman spectrum it is a polarized line of medium intensity.

It should be noted that the coordinates of the diazenoxide group contribute to a series of vibrations. The N=N bond, for example, participates in the benzene ring vibration at 1446 cm^{-1}. Therefore this band is shifted 14 cm^{-1} to the low frequency region when the ^{15}N isotope is introduced to the diazenoxide group. This is probably the reason why the bands located in the 1430—1450 cm^{-1} interval in the spectra of alkyldiazenoxides were earlier[8] assigned to the ν(N→O) vibrations.

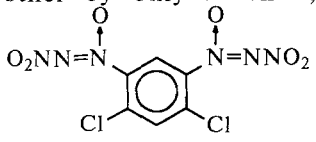
The results of the interpretation of the vibrational spectra of **1** were used for the assignment of the frequencies to the stretching vibrations of the nitro and diazenoxide group in the spectra of a large series of NDO of the general formula A—N=NNO_2(O), where A is an aromatic or heteroaromatic ring with various substituents. The results are given in Tables 1 and 2, which show that the bands of the nitro group stretching vibrations are localized in a narrow range : 40 cm^{-1} for $\nu^{as}(NO_2)$ and 55 cm^{-1} for $\nu^s(NO_2)$. In the IR spectra $\nu^{as}(NO_2)$ and $\nu^s(NO_2)$ bands are intense, while in the Raman spectra the former are weak depolarized lines and the latter are intense polarized lines. The introduction of the nitro group into the benzene ring results in an increase in $\nu^{as}(NO_2)$ by 20—30 cm^{-1} . For example, the $\nu^{as}(NO_2)$ vibrations in the IR spectra of PhN=NO_2(O) and *m*-NO_2—C_6H_4N=NNO_2(O) manifest themselves at 1612 cm^{-1} and 1638 cm^{-1}, respectively (see Table 3).

The analysis of the spectra of NDO that contain two nitrodiazenoxide groups in a molecule revealed the absence of vibrational interaction between the nitro groups. The $\nu^{as}(NO_2)$ bands are either overlapped, as in the

Table 2. Frequencies of the valence vibrations of the nitro group (ν/cm^{-1}) in the IR spectra of nitramines and nitrodiazenoxides

Compound	$\nu^{as}(NO_2)$	$\nu^{s}(NO_2)$
A–N(→O)=NNO$_2$	1600—1640	1250—1310
R, Alk, N–NO$_2$ (R = COOR′, CONH$_2$)	1580—1620	1260—1315
Alk, H, N–NO$_2$	1510—1560	1260—1315
Alk, Hal, N–NO$_2$	1620—1650	1260—1315

spectrum of $O_2NN{=}N(\rightarrow O)FzN{=}N(\rightarrow O)FzN{=}NNO_2$, where Fz is a furazane moiety, or separated from each other by only 25 cm^{-1}, as in the spectrum of

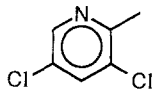
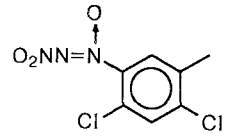
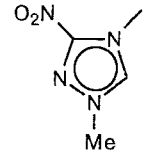
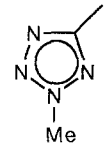


($\nu^{as}(NO_2)$ 1616 and 1641 cm^{-1}).

A comparison between the stretching vibration frequencies of the nitro group bound to the diazenoxide group and the corresponding frequencies of nitramines allows one to draw the following conclusions. In the spectra of NDO, the stretching vibrations of the nitro group are observed in ranges that are characteristic of nitramines containing electron-withdrawing groups at the nitrogen atom[9] and of halogen nitroamine[9] (see Table 2). Therefore, the electronic structures of the nitro groups in NDO and of the above-mentioned nitramines appear to be similar. However, the stretching vibrations of the nitro group of the nitrodiazenoxide fragment differ from the corresponding vibrations of nitramines by the highly characteristic of $\nu^{as}(NO_2)$. In addition, in the spectra of NDO, the absorption of $\nu^{as}(NO_2)$ in the region characteristic of the above-mentioned nitramines indicates that the only interaction between the nitro and diazenoxide groups is inductive.

In the IR spectra of NDO (see Table 3), the stretching vibrations of the diazenoxide groups occur in the 1475—1515 cm^{-1} and 1290—1330 cm^{-1} regions for

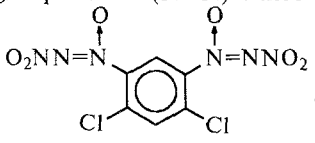
Table 3. Frequencies of the stretching vibrations of the nitro and diazenoxide groups (ν/cm^{-1}) in the IR spectra of A–N(→O)=NNO$_2$*

A	$\nu^{as}(NO_2)$	$\nu^{s}(NO_2)$	ν(N=N)	ν(N(→O)=N)
Ph	1612	1270	1491	1315
p-MeO–C$_6$H$_4$	1600	1256	1501	1316
p-Br–C$_6$H$_4$	1607	1280	1480	1307
p-NO$_2$–C$_6$H$_4$	1636	1276	1480	1318
o-NO$_2$–C$_6$H$_4$	1610	1286	1496	1318
m-NO$_2$–C$_6$H$_4$	1638	1283	1498	1320
2,6-Cl$_2$–C$_6$H$_3$	1630	1275	1492	1300
2,4,6-Cl$_3$–C$_6$H$_2$	1627	1284	1496	1330
2-N$_3$-5-NO$_2$–C$_6$H$_3$	1606	1309	1496	—
	1620	1280	1495	1330
	1641	1276	1494	1320
	1616			
	1626	1266	1478	1306
	1630	1267	1515	1297
Me–Fz–**	1636	1280	1500	1318
NH$_2$–Fz–	1632	1280	1509	1315
Fz–N=N–Fz–N(→O)=NNO$_2$	1629	1280	1502	1310

* Solid compounds in tablets with KBr, Me–Fz–N(→O)=NNO$_2$ between KBr glass. ** Fz is a furazane moiety.

ν(N=N) and ν(N(→O)=N), respectively. The ν(N=N) bands are intense in the IR spectra, while in the Raman spectra they are weak and depolarized. The bands conditionally assigned to ν(N(→O)=N) have different intensities depending on the compound structure, but in general

they are weak. This is because of the fact that, according to the calculations of the frequencies and forms of the normal vibrations of **1**, the vibration in question is not characteristic, and, therefore, the intensity of this band depends on changes not only in the dipole moment of the diazenoxide group, but also in the other structural fragments that participate in this vibration. The ν(N=N) frequency is notably affected by the substituents in the *para*-position of the aromatic ring. This frequency, for example, decreases as follows: *p*-MeO–C_6H_4N(→O)=NNO_2 (1501 cm^{-1}), PhN(→O)=NNO_2 (1491 cm^{-1}), *p*-Br–C_6H_4N(→O)=NNO (1480 cm^{-1}). This sequence also corresponds to the increase in the π-acceptor ability of the aromatic ring due to the different donor-acceptor activities of the substituents.[10] The tendency observed is exactly the opposite of the tendency typical of the double bonds,[11] for example, in the spectra of aromatic nitro derivatives.[12] This phenomenon is difficult to explain without quantum-chemical calculations. In the spectra of *p*-NO_2–C_6H_4N(→O)=NNO and *p*-Br–C_6H_4N(→O)=NNO, the ν(N=N) frequency is 1480 cm^{-1}, which is probably caused by the fact that analogously to the *para*-substituted dinitrobenzenes, in which the nitro groups are bent 19° relative to the benzene ring plane (see Ref. 13), the diazenoxide group and the ring are not coplanar.

Analisis of the spectra of NDO* containing more than one nitrodiazenoxide fragment in a molecule shows that there is no vibrational interaction between the diazenoxide groups. The ν(N=N) bands overlap. In the spectrum of  , for example, this frequency is 1494 cm^{-1}, while in the spectrum of O_2NN=NFzN=NFzN=NNO_2 (→O) it is 1502 cm^{-1} (see Table 3).

Thus, based on the analysis of the vibrational spectra of NDO the observed frequencies have been assigned to the stretching vibrations of the nitro and diazenoxide groups, the main regularities of the changes of these frequencies within the intervals under consideration were elucidated, and it was found that the only interaction between the nitro and diazenoxide groups is inductive, and results in a high-frequency $\nu^{as}(NO_2)$ absorption and a longer N—N bond.[14]

* NDO for the spectral studies were given by Dr. A. M. Churakov and S. E. Semenov (Inst. Organic Chem. of the RAS).

Experimental

The IR and Raman spectra were obtained on UR-20 and Ramanor U-1000 spectrometers (with a krypton laser as the exitation source) using the standard procedures. The calculations of the frequencies and forms of the normal vibrations were performed by a program reported earlier,[15] and the non-empirical force constants were calculated by the GAUSSIAN 76 program (see Ref. 16).

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