

Vibrational Spectra and Structure of 2-Nitrodiazene 1-Oxides

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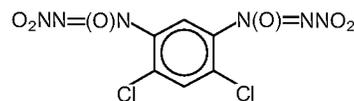
The vibrational spectra of a new type of nitro compounds, the 2-nitrodiazene 1-oxides, have been interpreted and the main trends in the change of frequency of the stretching vibrations of the nitro and diazene oxide groups have been revealed and some specific properties of the nitrodiazene oxide structure determined.

The results of a systematic study of the vibrational spectra of 2-nitrodiazene 1-oxides \dagger $A-N(O)=NNO_2$ (NDO; A = aromatic ring with different substituents) are presented. The aim of this study was to reveal the main trends in the change of stretching vibration frequencies of the nitro and diazene oxide groups and to determine some specific properties of the NDO structure.

In order to assign frequencies to the spectra \ddagger of NDO we carried out isotopic substitution (introduction of ^{15}N into the diazene oxide group of the 1-phenyl-2-nitrodiazene oxide **1** molecule). We then compared the IR and Raman spectra of **1** and its isotopically-substituted analogue $Ph^{15}N(O)=NNO_2$ **1a**, measured the degree of depolarization of the bands in the Raman spectra and performed calculations \S of the frequen-

cies and forms of the normal vibrations of **1** and **1a**.

As we see in Fig. 1, the stretching vibrations of the NDO nitro group give intense absorptions in the IR spectra, but in the Raman spectra the $\nu_{NO_2}^{as}$ band is strong and depolarized whereas $\nu_{NO_2}^s$ is weak and polarized. The above bands are located in the ranges 1600–1640 cm^{-1} and 1255–1310 cm^{-1} , respectively. The introduction of electronegative substituents in the aromatic ring, for example, the NO_2 -group, increases the frequency $\nu_{NO_2}^{as}$ by 20–30 cm^{-1} , but an electropositive substituent (*e.g.* Me) decreases it by 5 cm^{-1} . An analysis of the spectra of an NDO with two diazene oxide groups testifies to a vibrational interaction between nitro groups



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being absent because of the long distance between them. For example, in the spectra of **4** the gap between the $\nu_{NO_2}^{as}$ bands is only 25 cm^{-1} ($\nu_{NO_2}^{as}$ 1616–1641 cm^{-1}).

A comparison of the frequencies of the NDO nitro group

\dagger NDOs were synthesized *via* substituted nitration of the corresponding acetyldiazene oxides (the procedures will be published in this journal later). Some NDOs studied were obtained by S. E. Semenov.

\ddagger IR spectra were recorded using a UR-20 instrument and Raman spectra using a RAMANOR U 1000 spectrometer (krypton laser as an excitation source), according to standard procedures.

\S The calculations of the frequencies and forms of the normal vibrations were carried out using the program in ref. 1 and X-ray structural parameters for 1-(2,6-dichlorophenyl)-2-nitrodiazene oxide **2** and 1-(4-bromophenyl)-2-nitrodiazene oxide **3**. Complete details of the X-ray crystallographic data will be published later.

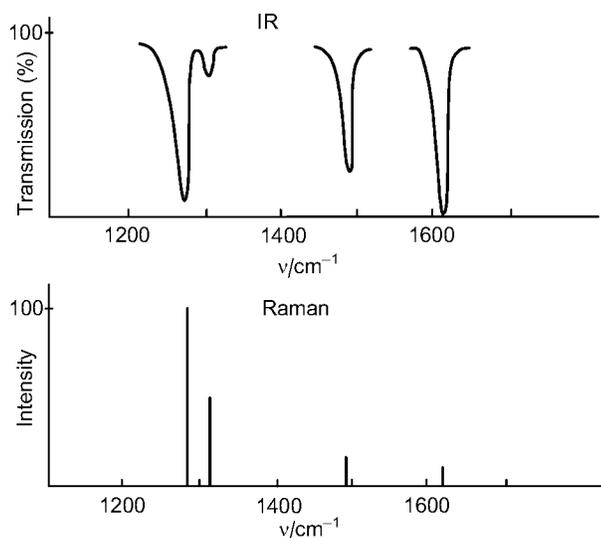


Fig. 1 Position and relative intensity of the stretching bands of nitro- and diazene oxide groups in the vibrational spectra of nitrodiazeno oxides.

stretching vibrations with the corresponding frequencies of nitroamines revealed that the above vibrations in the NDO spectra are located in the range characteristic of nitroamines with electronegative groups at the N atom: 2 RNHNO₂, R = CONH₂ and COOR (1580–1620 cm⁻¹, 1260–1315 cm⁻¹) and halogenonitroamines: 2 RHalNNO₂ (1620–1650 cm⁻¹, 1260–1315 cm⁻¹). Therefore, it can be suggested that the electronic structure of the nitro group of NDO is similar to that of nitroamines. The stretching vibrations of the nitro group of NDO differ from those of nitroamines since the $\nu_{\text{NO}_2}^{\text{as}}$ vibrations of the former are more characteristic. According to calculations of the frequencies and forms of the normal vibrations of **1**, only NO bonds contribute to this vibration, their contribution being 100%.

The stretching vibrations of diazene oxide groups are observed in the IR spectra of NDO in the range 1475–1515 cm⁻¹ and 1290–1330 cm⁻¹ (modes $\nu_{\text{N}=\text{N}}$ and $\nu_{\text{N}=\text{N}-\text{O}}$, respectively). The $\nu_{\text{N}=\text{N}}$ bands are strong in the IR spectra, but weak and depolarized in the Raman ones. The bands assigned to the mode $\nu_{\text{N}=\text{N}-\text{O}}$ have different intensities depending on the compound structure, but are basically weak. According to calculations of the frequencies and forms of the normal vibrations of **1**, the above mode is not characteristic of any form. In this vibration not only do the coordinates of the diazene oxide group contribute but also those of the phenyl ring (C–C) and nitro group (N–O). The intensity of the $\nu_{\text{N}=\text{N}-\text{O}}$ band results not only from changes of the dipole moment in the diazene oxide group, but also from the other structural fragments contributing to this vibration. Therefore, it is useless to trace trends in the change of frequency of the $\nu_{\text{N}=\text{N}-\text{O}}$ mode. We now turn to the $\nu_{\text{N}=\text{N}}$ mode frequencies. The substituents in the aromatic ring exhibiting coplanary of ring and diazene oxide group render a noticeable influence. For example, the frequency of the $\nu_{\text{N}=\text{N}}$ mode decreases in the following order: *p*-MeOC₆H₄.N(O)=NNO₂ ($\nu_{\text{N}=\text{N}}$ 1501 cm⁻¹), PhN(O)=NNO₂ ($\nu_{\text{N}=\text{N}}$ 1491 cm⁻¹) and *p*-BrC₆H₄N(O)=NNO₂ ($\nu_{\text{N}=\text{N}}$ 1480 cm⁻¹). The π -accepting ability of the aromatic ring increases in the same series as a consequence of differences in the donor acceptor activity of the substituents.³ An increase in the number of diazene oxide groups in the NDO molecule leads to a decrease in the $\nu_{\text{N}=\text{N}}$ mode frequency. The $\nu_{\text{N}=\text{N}}$ bands do not split because vibrational interaction between these groups is absent.

From a comparison of the frequencies of the stretching vibrations of the diazene oxide group of NDO with the

Table 1 Frequencies of the stretching vibrations of the azoxy group in the spectra of diazene oxides.

Compound	$\nu_{\text{N}=\text{N}}$	$\nu_{\text{N}-\text{O}}$
RN(O)=NR ¹	1470–1510	1270–1330
RN(O)=NF	1480–1540	—
RC ₆ H ₄ N=N(O)C ₆ H ₄ R ¹	1410–1505	1330–1350
R ¹ R ² CHCOC(R ¹ R ²)N(O)=NOR ³	1485–1500	1275–1300
A–N(O)=NNO ₂	1475–1515	1290–1330

corresponding frequencies (see Table 1) of the alkyl,⁴ alkoxy,⁵ fluorodiazeno oxides⁶ and azoxybenzenes⁷ we can conclude that vibrations of the diazene oxide group of NDO are observed in the ranges characteristic of alkyldiazeno oxides. The bands of these vibrations are shifted to the high frequency range in comparison with those of azoxybenzenes, but when compared with fluorodiazeno oxides they are shifted to the low frequency range. This indicates that conjugation between diazene oxide and nitro groups is absent. According to the X-ray data for **2** and **3** the diazene oxide and nitro groups are in fact perpendicular.

Thus, the present study has allowed us to reveal the main trends in the change of frequency of the nitro and diazene oxide group stretching vibrations, to pick out the intervals of these frequencies and to determine some specific properties of NDO, clearly reflected in their vibrational spectra.

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