Available online at www.sciencedirect.com
ScienceDirect
Mendeleev Commun., 1991, **1**(**3**), 106–108

Mendeleev Communications

Vibrational Spectra and Structure of Sulphonium Nitroimides

Klavdiya I. Rezchikova, Natal'ya V. Grigor'eva, Oleg P. Shitov and Vladimir A. Shlyapochnikov

N. D. Zelinsky Institute of Organic Chemistry, Academy of Sciences of the USSR, 117913 Moscow, USSR

During a physico-chemical study of three new types of sulphonium nitroimides by vibrational spectroscopy and X-ray analysis the structural parameters of Me_2SNNO_2, $Me_2S(O)NNO_2$ and $Me_2S(NNO_2)_2$ molecules were determined; variations in the stretching vibrations of the nitro group in the spectra of sulphonic nitroimides, nitroamines and their salts were found to result from large differences in the force constants, especially the nondiagonal, of these molecules.

We have previously studied the vibrational spectra of sulphonium nitroylides[1] and ammonium nitroimides.[2] It was found that the spectra of these compounds differ considerably from those of nitro compounds and their salts. These differences are greatest in the stretching region of the nitro group. A physico-chemical study of *N*-nitrosulphimides,† *N*-nitrosulphoximides† and *N,N*-dinitrosulphodiimides† was undertaken to find out if the above properties were characteristic of the spectra of sulphonium nitroimides and if they were general for all nitro-substituted onium compounds. The results of this study are given in the present paper.

In order to assign frequencies to the spectra of *N*-nitrosulphimides ($R^1R^2\overset{+}{S}\overset{-}{N}NO_2$), *N*-nitrosulphoximides [$R^1R^2\overset{+}{S}(O)\overset{-}{N}$-$NO_2$] and *N,N*-dinitrosulphodiimides [$R^1R^2\overset{+}{S}(\overset{-}{N}NO_2)_2$] we carried out isotopic substitution (introduction of deuterium into the methyl groups of the molecules), comparison of the IR and Raman spectra with a measurement of the degree of depolarization of the bands in the Raman spectra,‡ calculations of the frequencies and forms of the normal vibrations in molecules of elementary representatives of the above compounds and their isotopically substituted analogues.§

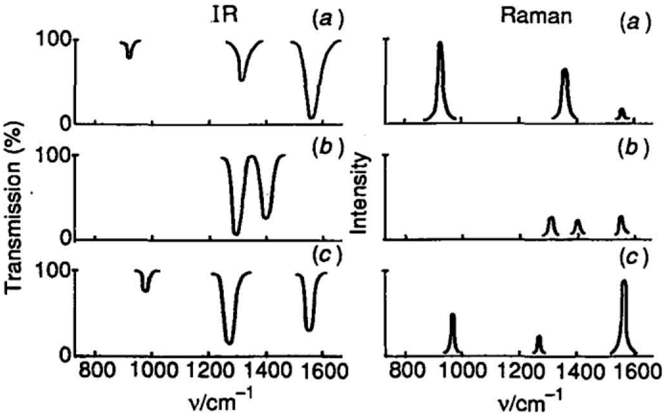

Fig. 1 Position and relative intensity of stretching bands of nitro groups in the vibrational spectra of (*a*) *N*-nitro compounds, (*c*) their salts and (*b*) *N*-nitrosulphimides

Comparison of the frequencies of the stretching vibrations of the sulphonium nitroimide nitro group with the corresponding frequencies of the *N*-nitro compounds and their salts revealed considerable differences. The band intensities in the IR and Raman spectra, and the band polarization in the latter were also different. Fig. 1 gives a schematic comparison of the frequencies of the stretching vibrations of the nitro group in $R^1R^2\overset{+}{S}\overset{-}{N}NO_2$, the *N*-nitro compounds and their salts. The stretching vibrations of the nitroimide groups are characterized

---

† The sulphonium nitroimides were obtained according to the procedures described in ref. 3.

‡ IR spectra were recorded by means of UR-20 and Perkin Elmer 577 spectrometers, Raman spectra using a RAMANOR HG-2S spectrometer (argon laser as excitation source) according to standard procedures.

§ The calculation of the frequencies and forms of normal vibrations was carried out on an ES-1022 computer using the program of ref. 4 and experimental geometries.

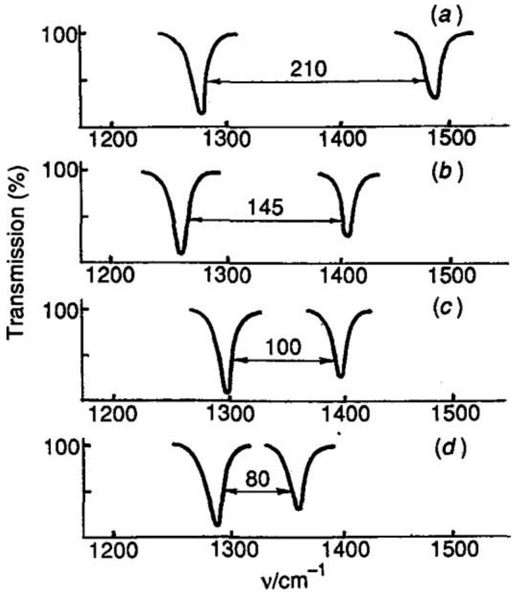

Fig. 2 Position and relative intensity of stretching bands of nitro groups in the vibrational spectra of (*a*) *N*-nitrosulphoximides, (*b*) *N*-nitrosulphimides, (*c*) sulphonium nitroylides and (*d*) ammonium nitroimides

by intensive absorption in the IR spectra and by weak absorption in the case of the Raman spectra. Two and three bands due to stretching vibrations of the nitro group are observed in the IR and Raman spectra of $R^1R^2\overset{+}{S}\overset{-}{N}NO_2$, respectively. The order of the bands ($\nu_{NN} > \nu^{as}_{NO_2} > \nu^{s}_{NO_2}$) in the $R^1R^2\overset{+}{S}\overset{-}{N}NO_2$ spectra differs from that of those of the non-ionized *N*-nitro compounds ($\nu^{as}_{NO_2} > \nu^{s}_{NO_2} > \nu_{NN}$) and the salts of the nitro-derivatives, where $\nu^{s}_{NO_2} > \nu^{as}_{NO_2} > \nu_{NN}$. The $\nu^{as}_{NO_2}$ and $\nu^{s}_{NO_2}$ are much closer together in the spectra of $R^1R^2\overset{+}{S}\overset{-}{N}NO_2$ than those in the spectra of the *N*-nitro compounds and their salts (Fig. 1). Similar features are also characteristic of the spectra of $R^1R^2\overset{+}{S}(O)\overset{-}{N}NO_2$ and $R^1R^2\overset{+}{S}(\overset{-}{N}NO_2)_2$. However in contrast with the spectra of $R^1R^2\overset{+}{S}\overset{-}{N}NO_2$ in which the gap between the $\nu^{as}_{NO_2}$ and $\nu^{s}_{NO_2}$ is 150 cm^{-1}, in the spectra of $R^1R^2\overset{+}{S}(O)\overset{-}{N}NO_2$ it is 210 cm^{-1} and in those of $R^1R^2\overset{+}{S}(\overset{-}{N}NO_2)$ it is 230 cm^{-1} (Fig. 2). In the spectra of the sulphonium nitroylides[1] and the ammonium nitroimides[2] the $\nu^{as}_{NO_2}$ and $\nu^{s}_{NO_2}$ bands are closer to each other (Fig. 2). At the same time $\Delta\nu = \nu^{as} - \nu^{s}$ for nitro compounds of various types and their salts is considerably greater [300 cm^{-1} (ref. 5)].

The specific properties of the stretching vibration bands of the nitro groups in the spectra of sulphonium nitroimides, according to the calculations of the normal vibration frequencies and forms for $Me_2\overset{+}{S}\overset{-}{N}NO_2$, $Me_2\overset{+}{S}(O)\overset{-}{N}NO_2$ and $Me_2\overset{+}{S}(\overset{-}{N}NO_2)_2$ result from the specificity of their force fields.¶ In particular, the differences between the frequencies of the stretching vibrations of the nitro group in the spectra of sulphonium nitroimides, nitro compounds and their salts exist mainly due to a considerable change in the nondiagonal force constants $f_{NN,NO}$ and $f_{NO,NO}$. For the sulphonium nitroylides their values are similar, and they are high (~ 2 mdyn Å^{-1}) (in nonionized nitro groups $f_{XN,NO} < f_{NO,NO}$, where X = C, N) for salts, $f_{XN,NO} > f_{NO,NO}$.[6] A high-frequency ν_{XN} absorption and a smaller gap between $\nu^{as}_{NO_2}$and $\nu^{s}_{NO_2}$ are direct consequences of this.

In order to determine the structural characteristics of the

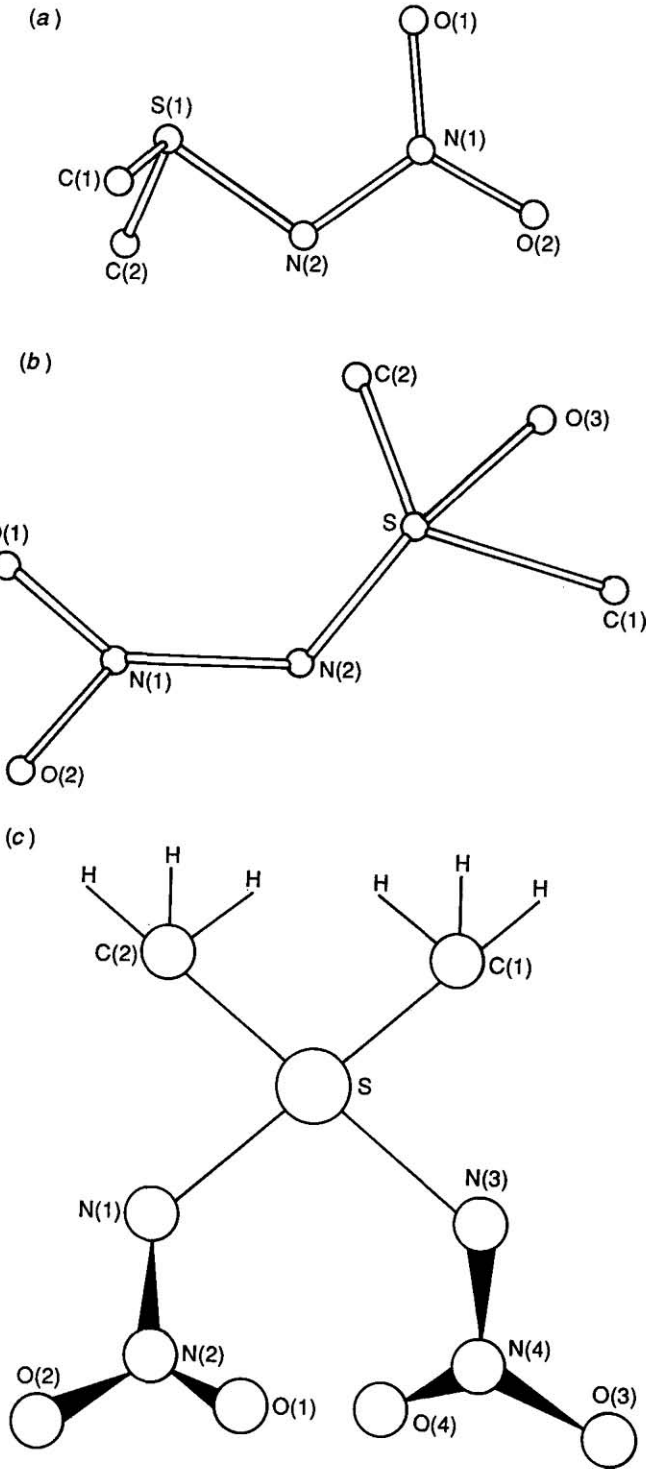

Fig. 3 X-Ray crystal structures, with selected bond lengths (Å) and angles (°). (*a*) One of the two independent molecules of **1** [values for the other molecule in square brackets]: C(1)–S(1) 1.77 [1.74]; C(2)–S(1) 1.80 [1.79]; S(1)–N(2) 1.67 [1.70]; N(1)–N(2) 1.35 [1.30]; N(1)–O(1) 1.23 [1.27]; N(1)–O(2) 1.26 [1.22]; angles at S(1) 102°; S(1)–N(2)–N(1) 109 [110]; N(2)–N(1)–O(1) 123 [122]; N(2)–N(1)–O(2) 114 [116]; O(1)–N(1)–O(2) 123 [122]. (*b*) Compound **2**: S–C(1) 1.74; S–C(2) 1.77; S–O(3) 1.43; S–N(2) 1.60; N(1)–N(2) 1.37; N(1)–O(1) 1.21; N(1)–O(2) 1.26; S–N(2)–N(1) 112; O(1)–N(1)–N(2) 122; O(2)–N(1)–N(2) 115; O(1)–N(1)–O(2) 123. (*c*) Compound **3**: C(1)–S 1.76; C(2)–S 1.75; S–N(1) 1.60; S–N(3) 1.61; N(1)–N(2) = N(3)–N(4) = 1.38; N(2)–O(1) = N(2)–O(2) = N(4)–O(3) = 1.22; N(4)–O(4) 1.23; C(1)–S–C(2) 105.7; C(1)–S–N(3) 99.1; C(2)–S–N(1) 99.6; N(1)–S–N(3) 121.4; N(1)–N(2)–O(1) 119.4; N(1)–N(2)–O(2) 115.2; O(1)–N(2)–O(2) 125.4; N(3)–N(4)–O(3) 114.0; N(3)–N(4)–O(4) 122.2; O(3)–N(4)–O(4) 123.8.

¶ The magnitudes of the force fields were obtained in the process of solving a direct vibrational calculation by varying the force constants calculated [*ab initio* (STO-3G)] to give a minimal deviation of the experimental and calculated frequencies.

Mendeleev Commun., 1991, 1(3), 106–108

sulphonium nitroimides X-ray structural studies[‖] were performed, providing a complete set of structural parameters for the molecules. The parameters of nitroimide fragments of $Me\overset{+}{S}\overset{-}{N}NO_2$ **1**, $Me\overset{+}{S}(O)\overset{-}{N}NO_2$ **2** and $Me_2\overset{+}{S}(\overset{-}{N}NO_2)_2$ **3** are shown in Fig. 3.

$R^1R^2\overset{+}{S}\overset{-}{N}NO_2$
1 ($R^1 = R^2 = Me$)

$R^1R^2\overset{+}{S}(O)\overset{-}{N}NO_2$
2 ($R^1 = R^2 = Me$)

$R^1R^2\overset{+}{S}(\overset{-}{N}NO_2)_2$
3 ($R^1 = R^2 = Me$)

It was found that the nitroimide fragment in molecules **1** and **2** had a flat structure whereas in molecule **3** the NO_2 groups deviated from the SNN plane by 66°. The bonds between the imide and onium atoms (S–N) are shorter than single bonds but longer than double bonds. Such S–N bond lengths are characteristic of sulphimides of various types.[7] The sulphur atom in **1** has a pyramidal configuration, but in **2** and **3** it is tetrahedral. The bonds between the imide and nitrogen atoms of the nitro groups in **1** and **2** are shorter, the NO bonds are longer and the ONO angle is smaller than the corresponding parameters in nitroamines.[8] The geometric parameters of the nitro group in **3** are similar to those of the nitroamines. The above differences in the geometry of the nitro groups in **1** and **2** and the nitro groups in covalent nitro compounds are also apparent for sulphonium nitroylides[9] and ammonium nitroimides.[10]

Thus the present study allows us to conclude that sulphonium nitroimides, in their spectroscopic characteristics, differ considerably from *N*-nitro compounds and their salts, this being a general characteristic of α-nitro derivatives of onium compounds.

Received in USSR, 5th March 1991
Received in UK, 26th April 1991; *Com. 1/01045J*

[‖] *Crystal data* for **1**: $C_2H_6N_2O_2S$, orthorhombic, space group $Pn2_1a$, $a = 20.00(2)$, $b = 7.58(1)$, $c = 6.93(1)$ Å, $Z = 8$, $D_c = 1.55\ g\ cm^{-3}$. The intensities of 872 reflections (Weissenberg camera, *hk*0–*hk*6) were measured using a microphotometer (MP-4). The structure was solved by direct methods using the X-ray 75 program on a BESM-6 computer and refined by least squares techniques isotropically. H atoms were not located. Final $R = 0.094$ for 872 reflections.

Crystal data for **2**: $C_2H_6N_2O_3S$, monoclinic, space group $P2_1/c$, $a = 9.22(1)$, $b = 7.55(1)$, $c = 8.30(1)$ Å, $\beta = 90.0(2)°$, $Z = 4$, $D_c = 1.60\ g\ cm^{-3}$. The intensities of 713 reflections (Weissenberg camera, *hk*0–*hk*6) were measured and the structure solved and refined as for **1** to a final *R* value of 0.082 for 671 reflections.

Crystal data for **3**: $C_2H_6N_2O_4S$, monoclinic, space group $P2_1/c$, $a = 12.14(3)$, $b = 7.66(2)$, $c = 7.52(2)$ Å, $\beta = 91.0(5)°$, $Z = 4$, $D_c = 1.74\ g\ cm^{-3}$. The intensities of 770 reflections (Weissenberg camera, *hk*0–*hk*6) were measured and the structure solved and refined as for **1** and **2**. Five H atoms were located in an electronic density difference synthesis. Final *R* factor 0.079.

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, *J. Chem. Soc., Chem. Commun.*, 1991, Issue 1.

References

1 K. I. Rezchikova, O. P. Shitov, V. A. Tartakovsky and V. A. Shlyapochnikov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1981, 1403.

2. K. I. Rezchikova, V. A. Shlyapochnikov, O. P. Shitov and V. A. Tartakovsky, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1986, 2810.

3 O. P. Shitov, A. P. Seleznev and V. A. Tartakovsky, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1991, in the press.

4 V. P. Novikov and A. I. Malyshev, *Zh. Prikl. Spektrosk.*, 1980, **33**, 545.

5 V. A. Shlyapochnikov, *Vibration Spectra of Aliphatic Nitro compounds*, Nauka, Moscow, 1989.

6 K. I. Rezchikova and V. A. Shlyapochnikov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1985, 947.

7 T. L. Gilchrist and C. J. Moody, *Chem. Rev.*, 1977, **77**, 409.

8 L. V. Vilkov, D. S. Mastryukov and N. I. Sadova, *The Determination of Geometrical Structure of Free Molecules*, Khimia, Leningrad, 1978.

9 V. V. Semenov, L. O. Atovmyan, N. I. Golovina, G. A. Mukhina, K. J. Burstein and S. A. Shevelev, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1981, 801.

10 A. F. Cameron, N. J. Hairrand and D. G. Morris, *J. Chem. Soc., Perkin Trans. 2.*, 1972, 1071.