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MOLECULAR SPECTRA OF NITROISOXAZOLINONES

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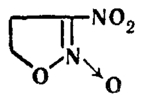
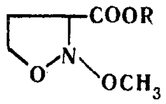
A study is made of IR and UV spectra of N-oxides of nitroisoxazolinones, and of derivatives of isoxazolidine and isoxazolizidine. Absorption bands are related to valence vibrations of N-O in the NO_2 group; in conjugated systems (in N-oxides of nitroisoxazolines) ν_s and γ_{as} are equal to ~1310 and ~1510 cm^{-1}, in non-conjugated systems (in nitroisoxazolidines) ~1360 and ~1560 cm^{-1}, respectively. Frequencies of N-O bond vibrations in N-oxides appear in the region 830-870 cm^{-1}, of the O-N-O fragment in isoxazolidines and isoxazolizidines in the 1010-1060 cm^{-1} region. Measurements are made of total intensities of N-O valence vibrations in the NO_2 group in N-oxides of nitroisoxazolines and nitroisoxazolizidines, as well as of C=N valence vibrations in N-oxides of nitroisoxazolines.

We recently showed [1] that γ-halogenodinitro compounds containing a terminal gem-dinitro group, readily undergo intramolecular cyclization in alkaline media to give the corresponding 3-nitroisoxazoline N-oxides. These compounds can be regarded as cyclic ethers of the azi-forms of the gem-dinitro compounds, where there are nitro groups differing in structure at individual carbon atoms (I).

Furthermore it was found that the ethers of the azi forms of the nitro compounds undergo 1, 3 dipolar cycloaddition, to give N-hydroxyisoxazolidine derivatives [2]. Thus in particular, the O-ethers of nitroacetic ester, phenylnitromethane, trinitromethane, and N-oxides of nitroisoxazolines gave compounds of type II-V.



I



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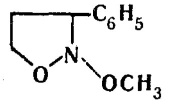

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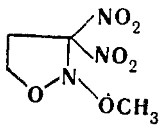
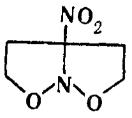


IV

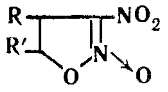


V

All these compounds contain the hitherto unknown structural element, a nitrogen atom covalently bonded to two oxygen atoms; in compounds IV and V that element occurs in combination with mono- or dinitro groups.

Table 1*

Intensities of N-O and C=N Valence Vibrations in 3-Nitroisoxazoline N-oxides



R	R'	NO_2								C=N			
		ν_s	$A \cdot 10^{-3}$	ε_s	l_s	ν_{as}	$A_{as} \cdot 10^{-3}$	ε_{as}	l_{as}	ν	$A_s \cdot 10^{-3}$	ε	l
H	H	1310	11.7	431	20	1510	4.5	174	18	1640	13.3	491	18
H	CH_3	1315	12.6	506	19	1510	4.8	211	17.5	1645	13.7	545	18
C_6H_5	H	1316	9.1	288	20	1515	4.1	160	18	1640	14.1	611	18
H	C_6H_5	1360	10.2	337	18	1540	5.4	246	18	1610	3.2	99	18

Within the ambit of our researches on the structures of nitro-compounds, it was undoubtedly of interest to investigate the molecular spectra of the compounds obtained, to determine the mutual interaction of the nitro groups in I, as well as of the interaction between the nitro groups and the structural element O-N-O in IV-V. Further, there was an analytical purpose behind the work: the occurrence of spectral characteristics necessary for identification of the newly prepared compounds I-V.

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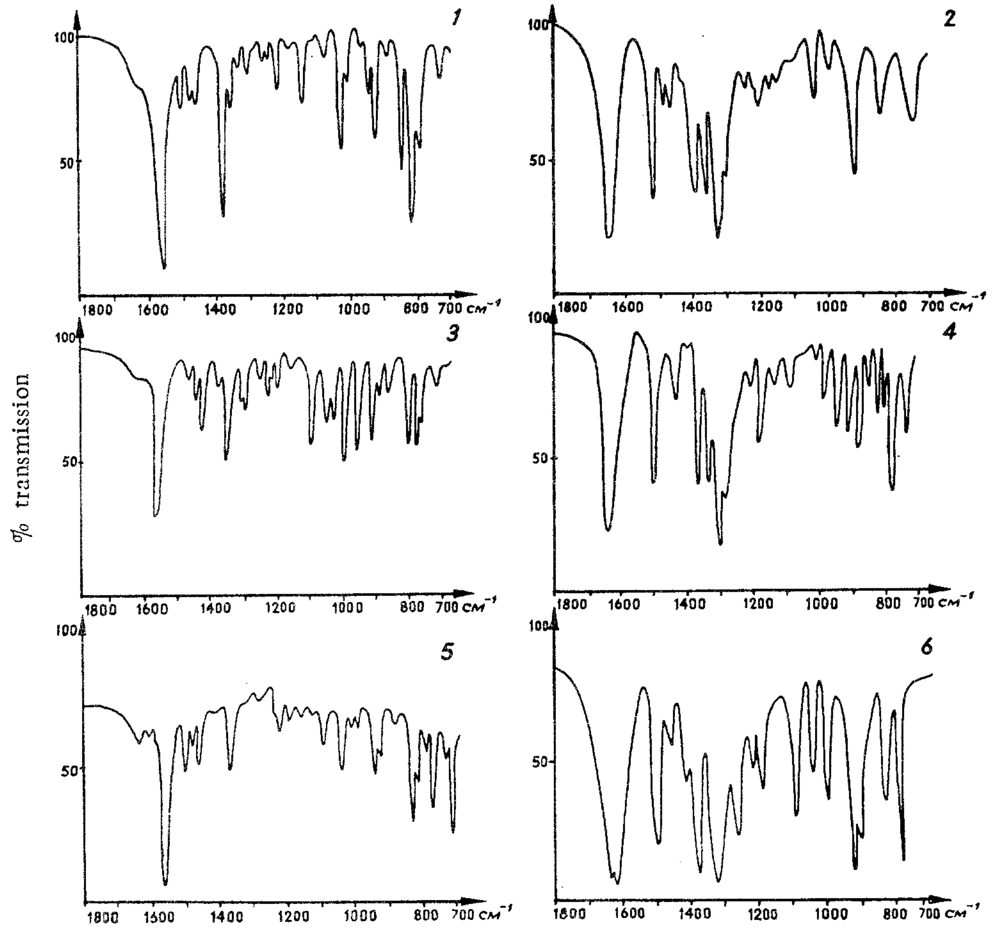
*The symbols used in Tables 1-7 have the following meanings: ν – wave number in cm^{-1}; A – total intensity in practical units ($cm^{-2} \cdot mole^{-1} \cdot l$); ε – molar extinction coefficient; l – half width of band in cm^{-1}.

IR spectra of N-oxides of nitroisoxazolines

In 3-nitroisoxazoline N-oxides, the nitro group is conjugated with the double bond in the ring, so that disturbance of the N–O valence vibrations in NO_2 would be expected. Further, it is known that conjugation with a double bond leads to change in intensity both of the double bond and of the N–O symmetric valence vibrations in the NO_2 group [3, 4]. In the spectra of unconjugated nitro compounds the valence vibrations, particularly the N–O antisymmetric valence vibration in the NO_2 group, are rather intense, and their identification is unequivocal. However, the picture changes sharply on shifting to N-oxides of 3-nitroisoxazolines (Fig. 1). The N–O antisymmetric valence vibration is lessened insignificantly in intensity, but there is a sharp growth in the intensities for the C= N bond and for the N–O symmetric valence vibration. These changes camouflage the IR spectra, and make it difficult to interpret them uniquely without further research. By way of such further research we determined the total intensities of a number of bands. Table 1* gives the results of these measurements, and our frequency assignments.



IR spectra: 1) 8-nitroisoxazolizidine; 2) 3-nitroisoxazoline N-oxide; 3) 8-nitro-2-cyano-isoxazolizidine; 4) 3-nitro-4, 5-cyclohexanoisoxazoline N-oxide; 5) 8-nitro-1-phenyl-osoxazolizidine; 6) 4-hydroxy-3-nitroisoxazoline.

The strong bands in the 1500 and 1300 cm^{-1} region we ascribed to, respectively, the antisymmetric and symmetric valence vibrations of N–O in the NO_2 group. To check the correctness of these identifications we will consider the total intensities of the N–O valence vibrations of the nitro compounds, and the relationships observed on passing from an unconjugated to a conjugated nitro group (Table 2). In such a changeover, the intensity of the N–O antisymmetric valence vibration changes insignificantly (maximum deviation 1.5 fold) and without apparent regularity, whereas the intensity of the symmetric valence vibration increases with increase in degree of conjugation, upto 30-fold in isolated cases [3].

It can be seen from Table 1 that with N-oxides of 3-nitroisoxazolines the band at about 1510 cm^{-1}, which we ascribe to N–O antisymmetric valence vibration, is about half as intense as the intensity of the same vibration in the unconjugated NO_2 group. The intensity of the band at ~ 1313 cm^{-1} increases 3–3.5 fold. In other words, both the total intensities of the bands, and the nature of the change which they undergo, supports the correctness of the ascription of the bands at ~ 1510 and ~ 1310 cm^{-1} to valence vibrations of N–O in NO_2.

Table 1 shows the exceptionally high intensity of the valence vibration of the C=N bond (order of intensity of N–O symmetric valence vibrations). We consider that such an increase in intensity is due to additional interaction of the C=N and N→O bonds. This view is supported by comparison of intensities for the C=N bond in N-oxides of isoxazolines with that for the same bond in 3-nitro-5-phenylisoxazoline.

Table 2

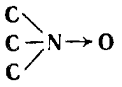
Intensities of N–O Valence Vibrations in the NO_2 Group

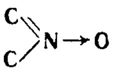
Compound	$A_s \cdot 10^{-3}$	$A_{as} \cdot 10^{-3}$
CH_3NO_2	4.0	13.3, 11.4*
$CH_3CHClNO_2$	—	11.2*
$C_6H_{11}NO_2$	3.0	13.3
$C_6H_5NO_2$	8.8	12.0
p-$ClC_6H_4NO_2$	13.3	9.2
p-$CH_3C_6H_4NO_2$	12.8	14.7
p-$IC_6H_4NO_2$	14.4	11.9
p-$OHC_6H_4NO_2$	22.2	15.7
p-$NH_2C_6H_4NO_2$	31.8	15.7
p-$N(C_2H_5)_2C_6H_4NO_2$	82.6	20.0

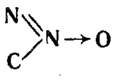
*Data taken from [5], the rest from [3].

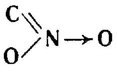
It is known from the literature that N-oxides of pyridine [6], pyrimidine [7], and pyrroline [8] exhibit intense absorption in the 1200–1300 and 820–870 cm^{-1} regions, the first of these bands relating to N → O bond vibrations [4].

Increase in multiplicity of the C–N bond in N-oxides (transition from type A to type B compounds) results in lowering of the frequency of vibration of the N → O bond to 950–970 cm^{-1}.


A


B

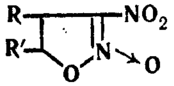

C


D

Replacement of a carbon atom at a double bond in B by a nitrogen atom (type C) leaves unchanged the region in which the N → O bond vibrations occur. Hence it was to be expected that replacement of a carbon atom at a single bond by an oxygen atom, without change in bond multiplicity will also leave unchanged the region of N → O bond valence vibrations. Actually the spectra of the N-oxides which we have investigated (Table 3) exhibit intense bands in the 1240–1300 cm^{-1} region, which we relate to valence vibrations of the N → O bond in D. Furthermore, all the spectra show an intense band in the 820–870 cm^{-1} region. These two bands can be utilized analytically, to detect the N → O bond.

Table 3

Some Vibration Frequencies in the Spectra of N-Oxides of Isoxazolines*



R	R′	ν_{N-O}	$\nu_{N\to O}$	NO_2 group		$\nu_{C=N}$
				ν_s	ν_{as}	
H	H	830(37)	1292(62)	1310(80)	1510(67)	1640(76)
H	CH_3	830(60)	1300(80)	1315(86)	1510(62)	1645(90)
CH_3	H	860(56)	1280(74)	1310(77)	1510(70)	1640(78)
OH	H	830(66)	1270(78)	1320(92)	1505(80)	1620(94) 1640(92) d
C_6H_5	H	870(30)	1270(60) 1282(68) d	1316(78)	1515(57)	1630(70) 1650(88) d
H	CH_3OCO	835(38)	1240(68)	1315(74)	1530(52)	1660(70)
$-(CH_2)_3-$		830(32)	1290(70)	1325(72)	1505(68)	1640(90)
$-(CH_2)_4-$		830(30)	1285(68)	1305(83)	1508(62)	1635(78)

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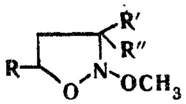
*Tables 3–5 give frequencies in cm^{-1}, intensities as % absorptions shown in parentheses.

Table 4

Some Frequencies for Isoxazolidine Derivatives



R	R'	R''	ν_{O-N-O}	$C-(NO_2)_2$ group ν_s	$C-(NO_2)_2$ group ν_{as}	$\nu_{C=O}$
H	NO_2	NO_2	1030(48)	1330(35)	1590(60)	—
CH_3	NO_2	NO_2	1033(48)	1326(41)	1590(77)	—
CH_2OH	NO_2	NO_2	1035(63)	1330(47)	1590(86)	—
CH_2Cl	NO_2	NO_2	1030(50)	1335(50)	1595(70)	—
CH_3COO	NO_2	NO_2	1030(56)	1328(50)	1595(80)	1765(73)
CH_3OCO	NO_2	NO_2	1030(52)	1330(50)	1595(75)	1760(70)
CH_3CO	NO_2	NO_2	1025(57)	1330(48)	1590(82)	1732(64)
a			1030(54)	1330(65)	1585(79)	—
C_6H_5	NO_2	NO_2	1030(82)	1330(80)	1590(90)	—
H	H	C_2H_5OCO	1040(57)	—	—	1745(76)
C_6H_5	H	C_2H_5OCO	1040(60) 1060(73) d	—	—	1748(75)
CH_3COO	H	C_2H_5OCO	1065(54)	—	—	1720(78)
CN	H	C_6H_5	1032(68)	—	—	—
CH_3OCO	H	C_6H_5	1040(78)	—	—	1730(86)

a)

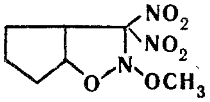
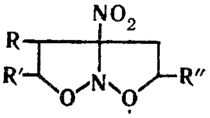


Table 5

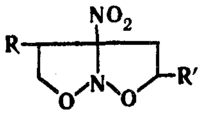
Some Frequencies for Isoxazolizidine Derivatives



R	R'	R''	ν_{O-N-O}	$-NO_2$ group ν_s	$-NO_2$ group ν_{as}	$\nu_{C=O}$	$\nu_{C\equiv N}$
H	H	H	1030(47)	1355(34) 1360(72) d	1560(90)	—	—
H	H	CN	1015(48)	1360(48)	1570(71)	—	2230(30)
OH	H	H	1010(68)	1370(92)	1540(92) 1560(92) d	—	—
H	H	CH_3COO	1030(42)	1365(44)	1570(60)	1745(56)	—
OH	H	CH_3COO	1035(28)	1370(42)	1570(82)	1750(72)	—
OH	H	CN	1040(30)	1370(38)	1570(75)	—	2235(35)
H	H	C_6H_5	1015(42)	1365(48)	1565(80)	—	—
C_6H_5	H	H	1040(50)	1362(52)	1560(93)	—	—
C_6H_5	H	C_6H_5	1035(36)	1360(39) 1370(39) d	1565(78)	—	—
CH_3	H	C_6H_5	1015(30) 1030(30) d	1370(34)	1565(75)	—	—
C_6H_5	H	CH_3	1030(38)	1370(40)	1560(70)	—	—
C_6H_5	H	CH_3COO	1030(36)	1360(40)	1568(65)	1742(60)	—
H	CH_3	C_6H_5	1035(32)	1360(35)	1560(77)	—	—

Table 6

Intensities of N–O Valence Vibrations in the NO_2 Group



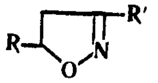
R	R′	ν_s	$A_s \cdot 10^{-3}$	ε_s	l_s	ν_{as}	$A_{as} \cdot 10^{-3}$	ε_{as}	l_{as}
H	H	1360	4.3	135	18	1560	11.8	435	18
C_6H_5	H	1362	3.2	100	18	1565	10.6	345	18.5
C_6H_5	C_6H_5	1365	3.1	98	18	1565	10.2	287	20
C_6H_5	CH_3COO	1360	4.8	153	18	1568	10.7	394	18

IR spectra of isoxazolidine and isoxazolizidine derivatives

Tables 4 and 5 give frequencies characterizing functional groups in both of these series of compounds, and also of the O–N–O portion. Table 6 gives results for total intensities of valence vibrations of the nitro group for some isoxazolizidine derivatives. Comparison of intensity values with the results in Table 2 shows that the intensity of N–O valence vibrations in nonconjugated nitro compounds is practically constant, and independent of group structure. Hence constancy of intensity of N–O bond vibrations in IR spectra can be successfully employed for identification of the nitro group in these compounds.

Table 7

Frequencies of Valence Vibrations of N–O, C= N, C=O



R	R′	ν_{N-O}	$\nu_{C=N}$	$\nu_{C=O}$
C_6H_5	COOH	1060(40)	1600(60)	1700(90)
C_6H_5	C_2H_5OCO	1036(64)	1598(68)	1730(87)
C_6H_5	NO_2	1040(30)	1610(55)	—

The given assignments of absorption bands (see Tables 4 and 5) to valence vibrations of functional groups does not call for comment; these bands are sufficiently intense and characteristic.

All the compounds investigated had an intense absorption band in the 1010–1060 cm^{-1} region, which we ascribed to the O–N–O segment [9]. The band of the N–O bond in isoxazoline derivatives (see Table 7) lies in the same region. N-oxide derivatives of isoxazolines lack a band in the 1010–1060 cm^{-1} region, but absorb in the 1240–1300 and 820–870 cm^{-1} regions. Isoxazoline, isoxazolidine, and isoxazolizidine derivatives do not, in this connection, have absorption bands in the 1200–1300 cm^{-1} region. In other words, the regions mentioned can be utilized for analytical purposes, to identify the series which we have investigated.

The IR spectra were measured with a UR-10 instrument, on tablets with KBr, and total intensities were measured on chloroform solutions. Layer thickness 0.01 cm.

UV spectra of N-oxides of nitroisoxazolines and isoxazolizidines

Investigation of the UV spectra shows that N-oxides of isoxazolines have an absorption maximum in the 320 mμ region with a molar extinction coefficient of ~ 8500. It is of interest to compare these results with the absorption of conjugated nitro groups and of the O-methyl ether of dinitroacetonitrile (Table 8). Table 8 shows that isoxazoline N-oxides and dinitroacetonitrile O-methyl ether absorb at practically the same wavelength, with about the same molar extinction coefficient. In other words the absorptions of these compounds are basically conditioned by the segment RO–N(O)= C–NO_2. Nitroolefins absorb at much lower long wavelengths, and only the introduction of halogen atoms (Cl, Br) into nitrostyrene results in a bathochromic shift of λ_{max} to values of 320–324 mμ.

The UV spectra of isoxazolizidines do not show selective absorption in the 320 mμ region and above. λ_{max} ~ 260 mμ (ε ~ 100) is due to the nitro group.

Table 8

UV Spectra of Isoxazoline N-oxides, Dinitroacetonitrile O-methyl Ether and Nitroolefins.

Compound	Solvent	λ_{max}, mμ	ε_{max}
3-Nitroisoxazoline N-oxide	H_2O	320	8366
3-Nitro-5-methylisoxazoline-N-oxide	"	320	8448
3-Nitro-4-methylisoxazoline N-oxide	"	320	8300
4-Hydroxy-3-nitroisoxazoline	"	315	8370
Dinitroacetonitrile O-methyl ether [10]	MeCN	315	11296
	Glacial AcOH	315	9796
1-Nitroprop-1-ene [11]	EtOH	229 235	9400 9700
1-Nitro-1-bromoprop-1-ene [11]	"	225 269	4000 4800
1-Nitro-penta-1,3-diene [11]	"	226 298	5500 12000
β-Nitrostyrene [11]	"	227 309	9500 16500
β-Chloro-β-nitrostyrene [11]	"	226 320	10600 13600
β-Bromo-β-nitrostyrene [11]	"	226 324	8700 12000

The UV spectra were measured with an SF-4 instrument. Table 8 gives the exposure conditions.

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