VIBRATIONAL SPECTRA AND STRUCTURE OF SULFONIUM NITROIMIDES

K. I. Rezchikova, N. V. Grigor'eva, I. I. Bannova,
O. P. Shitov, and V. A. Shlyapochnikov

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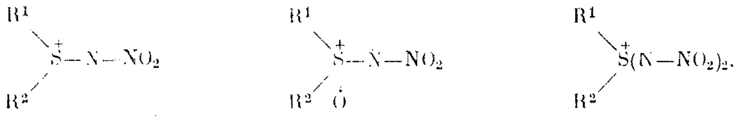
Vibrational spectroscopy and x-ray structure analysis have been used to investigate three new types of sulfonium nitroimides: N-nitrosulfylimides, N-nitrosulfoximides, and N,N'-dinitrosulfodiimides. Structural parameters have been determined for the molecules $(CH_3)_2\overset{+}{S}-\overset{-}{N}-NO_2$, $(CH_3)_2\overset{+}{S}(O)\overset{-}{N}NO_2$, and $(CH_3)_2\overset{+}{S}(\overset{-}{N}NO_2)_2$.

In the work reported here, we investigated the structure of the N-nitrosulfylimides (I)-(IV), N-nitrosulfoximides (V)-(VII), and N,N'-dinitrosulfodiimides (VIII), (IX) by methods of vibrational spectroscopy and x-ray structure analysis (XSA).



(I)—(IV) (V)—(VII) (VIII), (IX)

R^1, R^2 = Me (I), (V), (VIII); Et (II), Ph (III), (VI), (IX); R^1 = Me, R^2 = Ph (IV), (VII).

We have been able to assign the principal vibration frequencies of the molecules of these compounds by taking into account isotope effects in the replacement of hydrogen by deuterium in the CH_3 groups of (I), (V), and (VIII), by comparing the IR and Raman spectra (with measurements of the degree of depolarization of the lines in the Raman spectra), and by utilizing literature data [1-3] and our data [4] on the vibrations of the nitro group in the spectra of nitroimides.

Analysis of the spectra indicates that the stretching and bending vibrations of the CH_3 and CH groups fall within the normal ranges [5].

The stretching vibrations of the $N-NO_2$ group of the N-nitrosulfylimides are localized in the following regions: ν_{as} NO_2 1390-1430 cm^{-1}, ν_s NO_2 1260-1280 cm^{-1}, νNN 1540-1565 cm^{-1} (Table 1). In the IR spectra, the ν_{as} NO_2 and ν_s NO_2 bands are intense; in the Raman spectra, they are of medium intensity, but ν_{as} NO_2 is a depolarized line and ν_s NO_2 is a polarized line. ν_{NN} is manifested only in the Raman spectra in the form of a weakly polarized line.

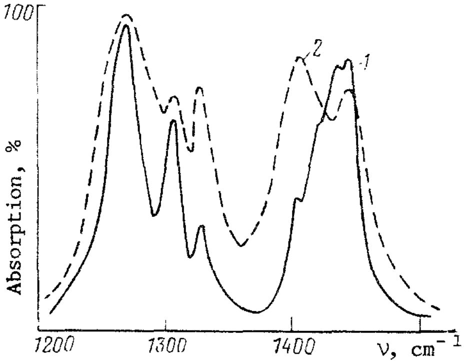


Fig. 1. IR spectra of $(CH_3)_2\overset{+}{S}-\overset{-}{N}NO$: 1) in $CHCl_3$ solution (c = 0.13 M); 2) in tablet with KBr.

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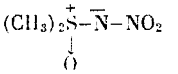
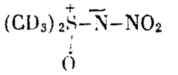
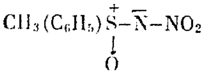
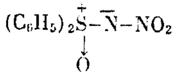
TABLE 1. Frequencies of Stretching Vibrations of Nitro Groups in Vibrational Spectra of N-Nitrosulfylimides, N-Nitrosulfoximides, and N,N'-Dinitrosulfodiimides (solid substances, ν, cm^{-1})

Compound	$\nu_{as}NO_2$		ν_sNO_2		νNN
	IR	Raman	IR	Raman	Raman
N-Nitrosulfylimides					
$(CH_3)_2\overset{+}{S}-\bar{N}-NO_2$	1402	1405	1273	1263	1540
$(CD_3)_2\overset{+}{S}-\bar{N}-NO_2$	1408	1390	1283	1270	1555
$(C_2H_5)_2\overset{+}{S}-\bar{N}-NO_2$*	1408	–	1268	–	–
$(C_6H_5)_2\overset{+}{S}-\bar{N}-NO_2$	1420	1426	1260	1256	1552
$(CH_3)C_6H_5\overset{+}{S}-\bar{N}-NO_2$	1398	1402	1274	1260	1562
N-Nitrosulfoximides					
 $(CH_3)_2\underset{\downarrow}{\overset{+}{S}}-\bar{N}-NO_2$, $\downarrow O$	1482	1490	1273	1285	1575
 $(CD_3)_2\underset{\downarrow}{\overset{+}{S}}-\bar{N}-NO_2$, $\downarrow O$	1478	1485	1292	1290	1560
 $CH_3(C_6H_5)\underset{\downarrow}{\overset{+}{S}}-\bar{N}-NO_2$, $\downarrow O$	1490	1494	1282	1283	1585
 $(C_6H_5)_2\underset{\downarrow}{\overset{+}{S}}-\bar{N}-NO_2$, $\downarrow O$	1500	1497	1282	1283	1582
N,N'-Dinitrosulfodiimides					
$(CH_3)_2\overset{+}{S}(\bar{N}NO_2)_2$	1515 1502	1510 1500	1283	1280	1540
$(CD_3)_2\overset{+}{S}(\bar{N}NO_2)_2$	1515 1500	1495 1490	1292	1290	1530
$(C_6H_5)_2\overset{+}{S}(\bar{N}NO_2)_2$	1512 1502	1510 1500	1272	1270	1580

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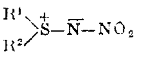
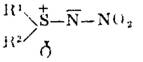
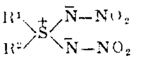
*No satisfactory Raman spectrum could be obtained.

TABLE 2. Frequencies of Stretching Vibrations of Nitro Groups in IR Spectra of N-Nitrosulfylimides, N-Nitrosulfoximides, and N,N'-Dinitrosulfodiimides ν, cm^{-1}

Compound	$\gamma_{as}NO_2$	ν_sNO_2
 $R^1R^2\overset{+}{S}-\bar{N}-NO_2$	1420–1390	1280–1260
 $R^1R^2\underset{\downarrow O}{\overset{+}{S}}-\bar{N}-NO_2$	1500–1480	1290–1270
 $R^1R^2\overset{+}{S}(\bar{N}-NO_2)_2$	1515–1500	1290–1270

The stretching vibrations of the N—NO$_2$ group of the N-nitrosulfoximides (Table 1) are manifested in the regions ν_{as} NO$_2$ 1480-1500 cm^{-1}, ν_s NO$_2$ 1270-1290 cm^{-1}, νNN 1560-1590 cm^{-1}. The bands of ν_s NO$_2$ and ν_{as} NO$_2$ in the IR spectra are strong; in the Raman spectra they are of strong and medium intensity, respectively. In comparison with the spectra of the N-nitrosulfylimides, the ν_{as} NO$_2$ vibration of the N-nitrosulfoximides is localized and is located in a higher-frequency region. The νNN vibration of the N-nitrosulfoximides, the same as for the N-nitrosulfylimides, is manifested only in the Raman spectra in the form of a weak line. In the IR spectra of the N,N'-dinitrosulfodiimides, the stretching vibra-

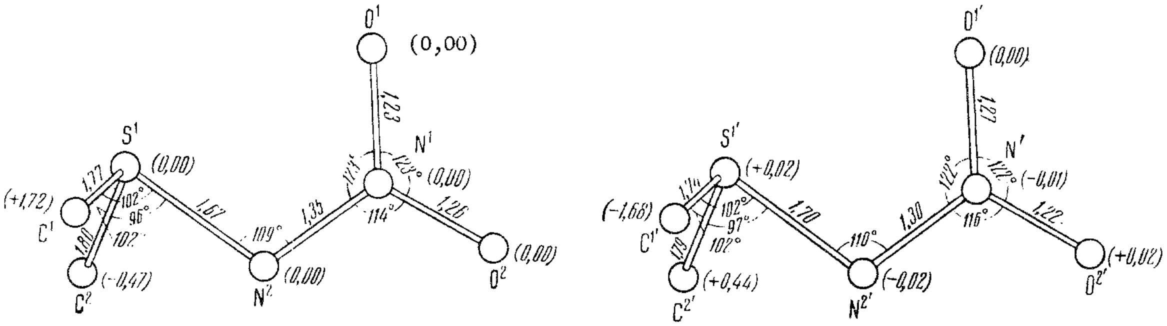


Fig. 2. Structure of crystallographically independent molecules $(CH_3)_2\overset{+}{S}-\overset{-}{N}NO_2$.

tions of the $N-NO_2$ group are manifested in the form of three strong bands in the regions 1500-1515 cm^{-1} (ν_{as} NO_2), 1272-1292 cm^{-1} (ν_s NO_2) (see Table 1). In the Raman spectra, the ν_s NO_2 band is strong, and ν_{as} NO_2 is medium intensity. The νNN vibrations are manifested in the form of a weak line in the 1530-1580 cm^{-1}, in the Raman spectra only.

A comparison of the frequencies of the stretching vibrations ν_{as} NO_2 and ν_s NO_2 in the spectra of the N,N'-dinitrosulfodiimides, N-nitrosulfylimides, and N-nitrosulfoximides (Table 2) shows that these bands for the dinitro derivatives lie in the region of absorption of the nitrosulfoximide groups, and are observed at higher frequencies in comparison with the N-nitrosulfylimides.

Such a relative position of the bands of stretching vibrations of the nitro groups in the spectra of N,N'-dinitrosulfodiimides can be explained by the lower degree of delocalization of the negative charge of each imide atom through the anionoid fragment, which is possible as a consequence of deviation of the nitro groups from the SNN plane.

Thus, the sequence of bands of NO_2 group stretching vibrations in the spectra of the sulfonium nitroimides is the same as for nitroylids [6] and ammonium nitroimides [4], and is considerably different from the spectra of nitro compounds and their salts [7].

It is difficult to make an unambiguous assignment of the bending vibrations of the $N-NO_2$ group on the basis of the experimental material alone, and it would be necessary to bring in additional data.

The stretching vibrations of the S–N bond are evidently noncharacteristic, which makes them difficult to assign. Using material from [8, 9], in the spectra of the N-nitrosulfylimides, we have made a preliminary assignment of the band in the 1037-1045 cm^{-1} region to νS–N vibrations; this band is strong in the Raman spectra but very weak in the IR spectra.

The intense bands in the 1012-1015 cm^{-1} region of the spectra of the N-nitrosulfoximides have been assigned to νSO vibrations, by analogy with literature data [5]; and bands in the 1214-1230 cm^{-1} region have been assigned to νS–N [6]. The νS–N band in the IR spectra is strong; in the Raman spectra, it is of medium intensity. In comparison with the N-nitrosulfylimides, it is localized in a higher-frequency region of the spectrum. This indicates strengthening of the S–N bond, possibly because of an increase in electrostatic interaction of charges when their magnitude increases [9].

In the spectra of the N,N'-dinitrosulfodiimides, we were unable to assign the νS–N band on the sole basis of the available experimental material.

The character of the spectra of the N-nitrosulfylimides depends on their state of aggregation and on the temperature. The spectra of the crystalline substances differ from those of solutions, in both the number and intensity of the bands.

The intensity of the band of stretching vibrations of the NO_2 group ν_{as} NO_2 in the IR spectra of the solutions increases upon dilution and upon raising the temperature (Fig. 1). This suggests the existence of strong intermolecular interactions for the N-nitrosulfylimides. On the basis of analysis of the vibrational spectra, we can state that the oxygen atom of the nitro group participates in the formation of intermolecular bonds. Unfortunately, we have been unable to make any quantitative evaluation of such interactions, owing to the very pronounced overlap of the absorption bands of the bound and free forms.

With the aim of establishing the structure of the N-nitrosulfylimides, N-nitrosulfoximides, and N,N'-dinitrosulfodiimides, we carried out an x-ray structure analysis (XSA)

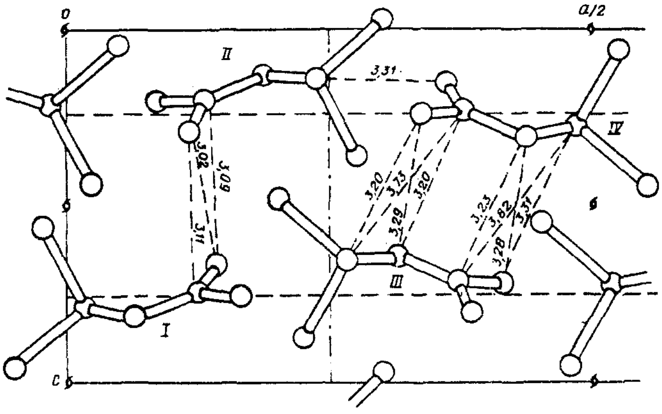


Fig. 3. Projection of structure of $(CH_3)_2\overset{+}{S}-\overset{-}{N}NO_2$ on ac plane.

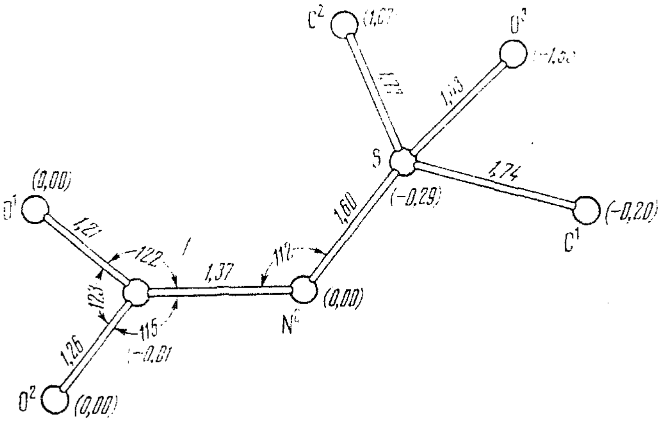


Fig. 4. Structure of $(CH_3)_2\overset{+}{S}(O)\overset{-}{N}NO_2$.

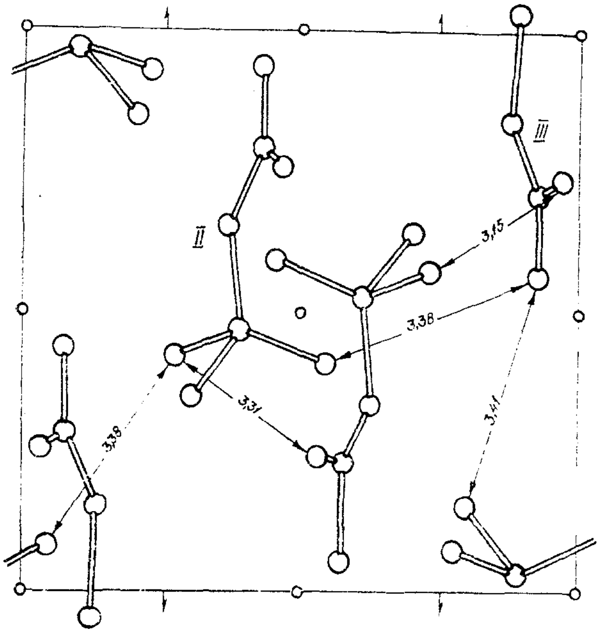


Fig. 5. Projection of structure of $(CH_3)_2\overset{+}{S}(O)\overset{-}{N}NO_2$ on yz plane.

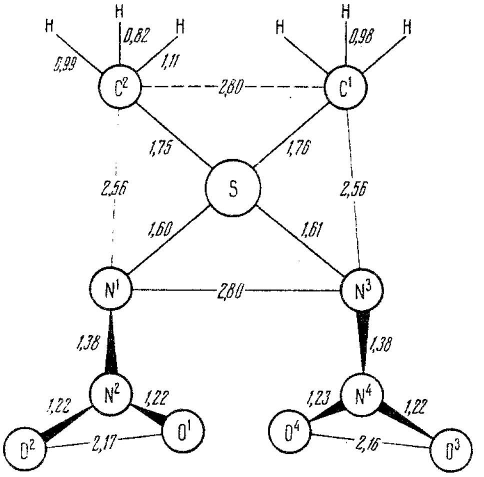


Fig. 6

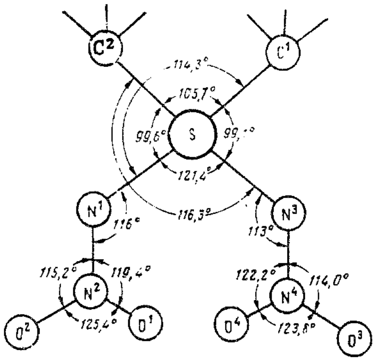


Fig. 7

Fig. 6. Structure of $(CH_3)_2\overset{+}{S}(\bar{N}NO_2)_2$ molecule (bond lengths given in Å).

Fig. 7. Structure of $(CH_3)_2\overset{+}{S}(\bar{N}NO_2)_2$ molecule, with an indication of bond angles.

of the simplest representatives of these types of compounds, specifically (I), (V), and (VIII).

It was established that the nitroimide fragment of the molecule (I) has a planar structure. The N–NO_2 bond in both crystallographically independent molecules is shortened (Fig. 2), the NO bonds are lengthened, and the ONO angle is decreased in comparison with the corresponding parameters in the molecules of nitramines [12]. The S^1 and $S^{1'}$ atoms are positioned at the vertices of triangular pyramids formed by the bonds S^1C^1–S^1C^2–S^1N^2 and $S^{1'}C^{1'}$–$S^{1'}C^{1'}$–$S^{1'}N^{2'}$. In the crystal lattice of the substance (I) (Fig. 3), the distance between the sulfur atom of one molecule and the oxygen atom of another molecule is less than the sum of the van der Waals radii, indicating the existence of strong intermolecular interactions, which we had predicted from our study of the vibrational spectra of the N-nitrosulfylimides.

The principal results of the x-ray structure analysis of (V) are presented in Figs. 4 and 5. The data indicate that the nitroimide fragment of (V) also has a planar structure. The shortening of the nonvalence distance C^2–O^1 in the molecule produces a considerable distortion of the O^1–N^1–N^2 angle and deformation of the tetrahedron in which the sulfur atom is centered. The S–N and N–O bonds are shorter, and the N–N bond longer, than the corresponding bonds in the molecule (I). This explains the high-frequency absorption of ν_{as} NO_2 and νS–N in the spectra of the N-ntirosulfoximides in comparison with the spectra of the N-nitrosulfylimides, if we start with the known correlations between the NN bond length and ν_{as} NO_2 (the longer the NN bond, the higher is ν_{as} NO_2) [13] and between the vibrational frequencies and bond lengths [7].

XSA results on (VIII) are presented in Figs. 6 and 7. According to these data, the molecule of (VIII) is built up symmetrically. The sulfur atom is positioned within a tetrahedron formed by the atoms $N^1N^3C^1C^2$ at the vertices of the tetrahedron. The edges of the tetrahedron are equal in pairs. The C^1–C^2 and N^1–N^3 pair, and the N^1–C^1 and N^3–C^2 pair, are very similar in magnitude. All of the faces of the tetrahedron are very nearly mutually perpendicular (89.3-89.7°). The symmetry of the molecule is not related to the symmetry of the crystal lattice: The molecule is entirely positioned in an independent part of the elementary cell.

The angle between the SN^1N^2 and $N^2O^1O^2$ planes is 66°, and the angle between the SN^3N^4 and $N^4O^3O^4$ planes is 67°; this prevents complete delocalization of the negative charge of the imide atoms and is responsible for the high-frequency absorption of ν_{as} NO_2 in the spectra of the N,N'-dinitrosulfodiimides in comparison with the spectra of the N-nitrosulfylimides.

EXPERIMENTAL

The N-nitrosulfylimides that were studied in this work were obtained by the interaction of the corresponding sulfoxides with nitramide in the presence of acetic anhydride. The N-nitrosulfoximides were obtained by oxidation of the corresponding N-nitrosulfylimides. The N,N'-dinitrosulfodiimides were obtained by nitration of the unsubstituted sulfodiimides or their N,N'-bis(trimethylsilyl) derivatives [14].

The IR spectra were taken in a UR-20 spectrometer, the Raman spectra in a RAMANOR HG-2S spectrometer (with an argon laser as the excitation source, λ_{exc} = 5145 Å), following standard procedures.

The elementary cell constants of the crystals of compounds (I), (V), and (VIII) and the intensities of the independent reflections obtained in a Weissenberg camera (hk0–hk6) were measured in an MF-4 microphotometer. All of the structures were deciphered by the direct method, using the Roentgen-75 program in a BÉSM-6 computer. The refinement of the structures was performed by the least-squares method in the isotropic approximation. The coordinates of the atoms of the structures and their isotropic constants are listed in Table 3. The error in determining bond lengths was no greater than 0.02 Å, angles 2°.

The crystals of (I) are orthorhombic ($Pn2_1a$), a = 20.00(2), b = 7.58(1), c = 6.93(1) Å, $d_{x\text{-}ray}$ = 1.55 g/cm³, Z = 8. Used 872 independent reflections. Hydrogen atoms were not determined. Final value R = 0.094.

TABLE 3. Relative Coordinates of Atoms in Structures, and Their Isotropic Thermal Constants

Atom	x	y	z	B
$(CH_3)_2\overset{+}{S}-\overline{N}-NO_2$				
S^1	0,0157(2)	0,0500(0)	0.7808(5)	2,34
$S^{1'}$	0,2364(2)	0,2735(7)	0,1542(5)	2,23
O^1	0,1397(4)	0,0633(14)	0,6569(13)	3,58
O^2	0,1619(4)	0,3331(13)	0,7509(13)	3,67
$O^{1'}$	0,1159(4)	0,2743(15)	0,2930(12)	3,34
$O^{2'}$	0,0870(4)	0,0081(14)	0,2090(13)	3.62
N^1	0,1231(5)	0,2033(17)	0,7341(17)	2.38
N^2	0,0618(5)	0,2316(17)	0,8100(17)	2.87
$N^{1'}$	0,1288(5)	0,1258(18)	0,2174(17)	2.73
$N^{2'}$	0,1865(5)	0,0924(17)	0,1393(16)	2,54
C^1	−0,0238(6)	0,0892(19)	0,5566(21)	3.30
C^2	−0,0491(6)	0,1094(20)	0,9497(20)	3,38
$C^{1'}$	0,2770(6)	0,2395(20)	0,3725(21)	3,17
$C^{2'}$	0,2984(6)	0,2013(19)	−0,0147(21)	3,29
$(CH_3)_2\overset{+}{S}(O)\overline{N}NO_2$				
S	0,26179(6)	0,53064(22)	0,60791(23)	1.39
O^1	0,1166(6)	0,2374(8)	0,5292(8)	2,66
O^2	0,2952(9)	0,0560(8)	0,5671(9)	3,98
O^3	0,2374(7)	0,5888(8)	0,4468(8)	3,16
N^1	0,2392(7)	0,2075(8)	0,5727(8)	1,97
N^2	0,3269(6)	0,3363(7)	0,6345(8)	1,75
C^1	0,4007(9)	0,6486(10)	0.6998(11)	2,65
C^2	0,1065(8)	0,5684(10)	0,7290(11)	2,31
$(CH_3)_2\overset{+}{S}(\overline{N}NO_2)_2$				
S	0,2466(2)	0,5101(3)	0,3178(3)	1,78
O^1	0,4130(5)	0,6315(9)	0,5261(9)	2,80
O^2	0,3884(6)	0,4495(10)	0,7426(9)	2.98
O^3	0,1182(6)	0.9300(9)	0,3704(10)	3,01
O^4	0,0691(6)	0,6721(9)	0,4531(10)	2,94
N^1	0,2746(6)	0.4361(10)	0,5121(10)	2,26
N^2	0,3643(6)	0,5120(9)	0,5981(10)	2,34
N^3	0,2218(6)	0,7131(9)	0,2849(10)	2,00
N^4	0,1317(6)	0,7723(10)	0,3776(10)	2,18
C^1	0,3523(7)	0.4809(11)	0,1631(13)	2,57
C^2	0,1420(8)	0,3646(11)	0,2539(13)	2,21
H^{21}	0,178(7)	0,238(12)	0,212(13)	1,01
H^{22}	0,099(9)	0,399(14)	0,176(15)	2,28
H^{23}	0,143(7)	0,479(10)	0,315(12)	0,43
H^{11}	0,340(16)	0,458(24)	0.130(28)	9,44
H^{12}	0,420(12)	0,484(18)	0,237(18)	4,49

Compound (II) crystallizes in space group $P2_1/c$ with the following dimensions of the elementary cell: a = 9.22(1), b = 7.55(1), c = 8.30(1) Å, β = 90.0(2)°, Z = 4, $c_{x\text{-ray}}$ = 1.60 g/cm³. The final values of the R-factor, on the basis of 671 reflections, was 0.082.

Compound (III) crystallizes in space group $P2_1/c$ with the following dimensions of the elementary cell: a = 12.14(3), b = 7.66(2), c = 7.52(2) Å, β = 91.0(5)°, Z = 4, $d_{x\text{-ray}}$ = 1.74 g/cm³. Registered a total of 770 independent reflections. The R-factor on the basis of these reflections was 0.102. The positions of the hydrogen atoms were determined by a difference synthesis of electron density. Five hydrogen atoms were defined. When these atoms were taken into account, R = 0.079.

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^{13}C NMR SPECTRA OF POLYCYCLIC DIAZIRIDINES

G. Kaupp, S. N. Denisenko, G. V. Shustov,
and R. G. Kostyanovskii

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A significant difference between experimental ^{13}C NMR chemical shifts and those predicted from the ^{13}C NMR/IR databank was found for bi- and tricyclic diaziridines. Quantum chemical (AM1) and molecular-mechanical (MMX) calculations showed that the relative chemical shift of the nodal C atom is dependent mainly on deformations of the C—C—C valence angle at this atom.

Bi- and tricyclic diaziridines (Ia)-(IIIb) [1-3] vary significantly in chemical properties and spectral parameters in dependence on the size of the ring joined to the diazirdine ring. We have investigated the effect of this structural factor on the chemical shifts of the ^{13}C nuclei which change significantly for the nodal C atom from five- to six-membered rings. Quantum chemical calculations of diaziridines (Ia)-(IIIb) by the AM1 method [4] with full optimization geometry were conducted to ascertain the nature of this effect. This is the best of the semiempirical methods [4], but in order to exclude the possibility of

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N. N. Semenov Institute of Chemical Physics, Academy of Sciences of the USSR, Moscow. Oldenburg University. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 11, pp. 2496-2499, November, 1991. Original article submitted February 7, 1991.