INVESTIGATION OF AROMATIC HETEROCYCLES

XV.* COMPARISON OF THE SPECTRAL PROPERTIES OF ARENE-1,2,5-OXADIAZOLES, THEIR N-OXIDES, AND 4,5-DIHYDRO DERIVATIVES

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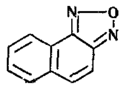
The results of an analysis of the UV and IR spectra confirm the previously drawn conclusion regarding the aromatic character of 1,2,5-oxadiazole derivatives. The spectral properties of naphth-1,2,5-oxadiazole and phenanthrene are similar; saturation of the double bond between the 4- and 5-carbon atoms of the naphthalene ring disrupts conjugation with the heterocyclic fragment. The introduction of a sulfo group into the 5-position does not substantially change the frequencies and distribution of the IR absorption bands. A difference in the effect of hydroxyl groups in the 7- or 8-positions is revealed. The spectral effects that accompany transition from arene-1,2,5-oxadiazoles to their N-oxides are analyzed.

Compounds of the oxadiazole series are currently being intensively studied. Interest in them is evoked by a number of peculiar properties. Thus 1,2,5-oxadiazoles are unusually chemically stable and have astonishingly low basicities. The peculiarities of the structures of such oxadiazoles also affect their spectral characteristics [2]. It is necessary to study the spectra of a series of compounds in order to obtain a reliable correlation of the properties of this class of compounds with the spectroscopic data. For this, we investigated the IR and UV absorption spectra of a number of naphth-1,2,5-oxadiazole (naphthofurazan) derivatives (I-IV).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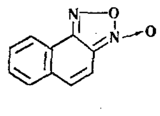
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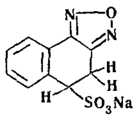
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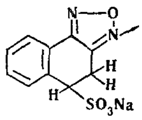
IV

In previous communications of this series we substantiated the point of view that the furazan ring condensed to the aromatic ring has a closed π-electron system. If this is, in fact, the case, naphthoflurazan(I) should be similar to phenanthrene in a π-electron sense, and the spectra of these two compounds should have much in common. It is apparent from Table 1 that three bands, which are close in position and intensity to the bands in the UV spectrum of phenanthrene [3], are observed in the UV spectrum of naphthofurazan. The Klar classification [4] was adopted to designate these bands. It is known that the expression $\lambda_\alpha/\lambda_\beta \simeq 1.35$ is satisfied for many polycyclic hydrocarbons [4]. In the case of I, II, and naphtho-1,2,5-selenadiazole, this expression lies in the same limits (1.24-1.36, Table 1). Only two bands – α and β – are most frequently seen in the spectra of these compounds. The ρ band is overlapped by the α band, and this sort of case is quite common [5]. When a hydroxyl group is introduced into the naphthalene ring, the α and β bands undergo a bathochromic shift (Table 1), which is apparently associated with their affiliation with the $\pi \rightarrow \pi^*$ transitions. Replacement of aprotic solvents by protic solvents does not induce a substantial change in the spectra: the oxadiazole ring has an extremely low basicity and, practically speaking, does not form hydrogen

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*See [1] for communication XIV.

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TABLE 1. Electronic Spectra of Furazans and Their N-Oxides in 70% Alcohol

Compound	λ_{max},nm ($\varepsilon \cdot 10^2$)			$\frac{\lambda_\alpha}{\lambda_\beta}$
	α band	ρ band	β band	
Phenanthrene [3]	344,5 (31,6)	294,5 (125,9)	254,7 (501)	1,34
Naphth-1,2,5-oxadiazole (I)	340* (31,0)	290 (32,0)	255 (255)	1,33
	325* (35,0)			1,28
				1,30
8-OH-I	360 (36)	300 (39)	265 (274)	1,36
7-OH-I	333 (48,5)	— —	265 (194)	1,29
5-SO_3Na-I	~340** (22,5)	315 (34,7)	250 (174)	1,36
8-OH-5-SO_3Na-I	360 (40)	308 (30)	264 (200)	1,36
7-OH-5-SO_3K-I	336 (46,0)	— —	270 (174)	1,24
Naphthofuroxan (II)	346 (70)	— —	260 (265)	1,29
5-SO_3Na-II	348, 365 (68)	— —	265 (221)	1,28
8-OH-5-SO_3Na-II	360 (42)	300** (42)	267 (207)	1,35
Naphtho-1,2,5-selenadiazole	331 (335)	285 (390)	255 (325)	1,30

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*Vibrational naphthalene-like structure.

†Shoulder in the spectrum.

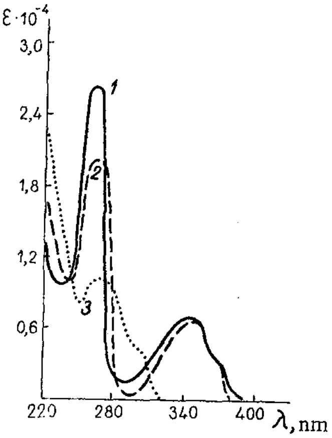

Fig. 1

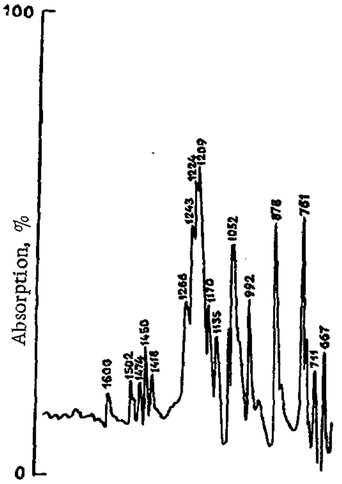

Fig. 2.

Fig. 1. UV spectra in 70% alcohol: 1) naphthofuroxan; 2) sodium salt of naphthofuroxan-5-sulfonic acid; 3) sodium salt of 4,5-dihydronaphthofuroxan-5-sulfonic acid.

Fig. 2. IR spectrum of the sodium salt of naphthofurazan-5-sulfonic acid (KBr pellet).

bonds. A hydroxyl group attached to $C_{(8)}$ of the naphthalene ring causes a stronger bathochromic shift in the spectrum than a hydroxyl group in the 7-position. The positions of both absorption bands (both α and β) remain virtually constant when a sulfo group is introduced into the 5-position, but this sort of substitution sometimes causes a decrease in the intensity of the long-wave α band. The UV spectra of N-oxides for the investigated substituted naphthofurazans [substituted naphthofuroxans (II)] are characterized by the same principles as the N-bases (Fig. 1). However, the transition from the furazan to the furoxan ring causes a general shift of the maxima of the bands to the long-wave region, thereby causing a small intensification of the short-wave band and a substantial increase in the intensity of the long-wave band. It is characteristic that the vibrational structure of the naphthofurazans is washed out in the process. In the case of 4,5-dihydronaphthofuroxan-5-sulfonic acid (IV), the long-wave band vanishes, and the intensity of the short-wave band decreases (Table 2). This band is simultaneously shifted to higher wavelengths. Thus, according to the spectral data, saturation of the bond in one of the benzoid rings leads to disruption of the unit of the π-electron system as a whole, although, as follows from the formula of III, it would seem that conjugation of the heterocycle with the more far-removed aromatic ring is also retained.

TABLE 2. Electronic Spectra of the Bisulfite Compounds in 70% Alcohol

Compound	λ_{max}, nm ($\varepsilon \cdot 10^2$)	
III	257, 280	(106; 24,8)
IV	270, 305	(105; 38,8)
8-OH-IV	225, 272, 325	(32; 75,5; 42,3)
7-OH-IV (salt)	240, 285, 310	(125; 112; 82,5)

TABLE 3. Frequencies of the Absorption Bands in the IR Spectra of Solutions in CCl_4 (cm^{-1})

Phenanthrene [3]			Naphth-1,2,5-oxadiazole			Naphtho-1,2,5-selenadiazole		
709	733	814	696	718	744	686	704	698
865	876	949	755	812	840	742	750	788
1001	1038	1089	879	896	972	815	794	822
1140	1200	1219	997	1024	1069	872	977	965
1243	1301	1420	1109	1150	1212	982	1009	1100
1451	1462	1490	1248	1300	1315	1154	1139	1204
1504	1527	1600	1429	1454	1481	1233	1309	1349
1617	1644	1673	1506	1520	1595	1464	1523	3112
1725	1753	1808	1622	1636	1678	3084	3042	
1922	1952	3099	1706	1776	1844			
			1974	1954	1970			
			3085					

In analyzing the UV absorption spectra of naphthofurazan, naphthoselenadiazole, and phenanthrene, we noted their similarity. This sort of similarity is also observed for the IR spectra of these compounds. In the 1350-1716 cm^{-1} region, where vibrations of the C–C and C–N vibrations appear, solutions of naphthofurazan and phenanthrene in CCl_4 each display an intense band at 1595 cm^{-1} and four bands of average intensity at 1506, 1481, 1454, and 1419 cm^{-1} (Table 3). Both phenanthrene and naphthofurazan each give two intense bands in the region of the CH ($\delta_{\parallel}$) in-plane deformation vibrations (1200-1212 and 1234-1248 cm^{-1}). In the region of the out-of-plane deformation vibrations ($\delta_{CH\perp}$), phenanthrene and naphthofurazan each display very intense bands at 709-718 and 744-755 cm^{-1} (four C–H bonds in the unsubstituted ring of the naphthalene fragment) and an intense band at 812-814 cm^{-1} (the vibrations of two adjacent hydrogen atoms in the angularly substituted ring).

According to the data in [6], the oxadiazole ring is characterized by nine fundamental vibrations: one completely symmetric valence vibration (ω_s 889 cm^{-1}), four asymmetric valence vibrations (ω_{as} 1546, 1418, 1316, and 1006 cm^{-1}), and four deformation vibrations (Δ 952, 872, 640, and 631 cm^{-1}). When the furazans are substituted, the 1407-1418, 950-952, 889-902, and 622-631 cm^{-1} bands retain their satisfactory constancy. We note that for arene furazans (i. e., for benzo and naphtho derivatives), these bands may be overlapped by the vibrational bands of the aromatic C–C and C–H bonds. The vibrational bands of the oxadiazole ring at 1300-1610, 992-1006, 952, 889, and 872 cm^{-1} are overlapped by the corresponding bands of phenanthrene.

An examination of the IR spectrum of naphtho-1,2,5-selenadiazole demonstrates that this spectrum is essentially similar to the IR spectra of both phenanthrene and naphthofurazan. It follows from Table 3 that naphthoselenadiazole also displays a similar distribution of the absorption bands in those regions of the spectrum where phenanthrene and naphthofurazan absorb in similar fashion.

Introduction of a sulfo group in the 5-position of naphth-1,2,5-oxadiazole (Fig. 2) shifts somewhat the bands associated with the vibrations of the C–C and C–N bonds (Table 4). A strong sulfo group effect is detected for the in-plane C–H deformation bands: sulfonic acids have more intense bands at 1266, 1243, 1224, 1170, and 1135 cm^{-1}, and the intense band at 812 cm^{-1} vanishes completely. Since this band vanishes precisely during substitution of the hydrogen atom in the 5-position, there is no doubt that it is correct to assign it to the vibrations of adjacent 4- and 5-hydrogen atoms. The vibration of the residual methylidyne group is apparently observed as a shoulder on the 878 cm^{-1} band. The bands associated with the out-of-plane vibrations of the four CH groups of the unsubstituted ring (748-761 cm^{-1}) in the spectra of derivatives

TABLE 4. Frequencies of the Absorption Bands in the IR Spectra of Some Naphth-1,2,5-oxadizoles and Their N-Oxides in Mineral Oil

Compound	Frequencies of the Absorption bands, cm^{-1}							
5-SO$_3$Na-I	16006 1209 776	1502 1170 771	1474 1135 667	1450 1041	1418 1052	1266 992	1243 878	1224 761
III	1652 1186 786	1520 1156 727	1447 1050 696	1457 1005	1430 987	1404 950	1304 873	1206 850
II	1627 1273 778	1605 1209 759	1585 1160 745	1546 1099 682	1505 1078 662	1484 1963	1436 829	1353 805
5-SO$_3$Na-II	1624 1255 944	1614 1231 861	1576 1219 853	1505 1177 781	1486 1109 732	1442 1065 692	1295 1037 655	1270 997
IV	1646 1159 724	1605 1103 675	1574 1053 665	1491 1032 615	1435 995 590	1304 852 519	1259 829 497	1205 770 774 478
7-OH-IV (salt)	1646 1268 1000 676	1608 1243 952 646	1560 1224 890 618	1484 1190 864 606	1438 1180 830 588	1412 1168 778 552	1307 1108 752 533	1280 1050 703 495
8-OH-IV	1644 1330 1007 620	1622 1300 988 602	1578 1280 952 573	1506 1241 879 542	1484 1223 847 478	1442 1180 813	1548 1164 753	1423 1044 689
7-NO$_2$-IV (salt)		1660 1325 1130 755	1628 1300 1050 684	1590 1270 990 593	1538 1231 950 538	1490 1200 910 485	1410 1190 870	1356 1165 835
Naphtho-1,2,5-selenadiazole-5-SO$_3$Na	527	1608 1250* 890	1507 1205 868	1474 1160 725	1396 1120 675	1360 1060 620	1325 1020 540	1275 950 465

*A shoulder in the spectrum.

with a sulfo group in the 5-position do not undergo shifts. The position and intensity of the vibrational band of the oxadiazole ring at 992 cm^{-1} also remain constant. The strongest bands in the IR spectra of the investigated sulfonic acids pertain to the vibrations of the SO$_3^-$ group at 1209 and 1052 cm^{-1}, the asymmetric and symmetric valence vibrations, respectively.

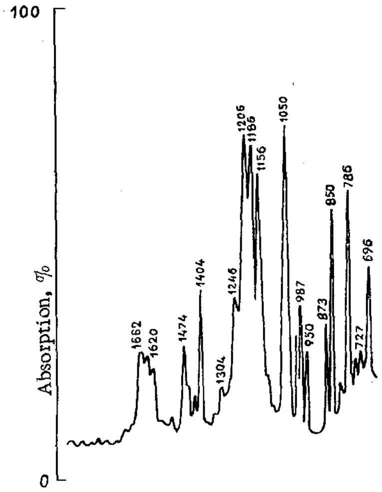

Fig. 3. IR spectrum of the sodium salt of 4,5-dihydronaphthofurazan-5-sulfonic acid (KBr pellet).

The UV spectral data (Table 2) demonstrate that hydrogenation of the double bond between C$_{(4)}$ and C$_{(5)}$ in naphth-1,2,5-oxadiazole-5-sulfonic acid leads to considerable disturbance of the π-electron interaction of the oxadiazole ring with the more far-removed aromatic ring. 4,5-Dihydronaphthofurazan-5-sulfonic acid (III) should therefore be considered to consist of 1,2-disubstituted benzene and 1,2-disubstituted oxadiazole. The band of the valence vibrations of the C–C and C–N bonds in the spectrum of this sort of "hydrogenated" sulfonic acid (Fig. 3) is shifted by ~ 20 cm^{-1} to the high-frequency region, and the intensity of the band in the 1500 cm^{-1} region drops markedly. The band of the deformation vibrations of the four CH groups of the benzoid ring previously located at 761 cm^{-1} is shifted by 25 cm^{-1} to the high-frequency region in the hydrogenated derivative. At the same time, the intensity of the $\delta_{\mathrm{CH}\perp}$ bands (1304, 1425, 1186, and 1156 cm^{-1}) increases. The bands of the deformation vibrations of the CH$_2$ group are overlapped by the band of the C–C vibrations, while the bands of the valence vibrations ($\lambda_{\mathrm{SO}_3^-}^{as}$ and $\lambda_{\mathrm{SO}_3^-}^{s}$) for the dihydro derivative acquire somewhat higher intensity. Thus the UV and IR spectra consistently attest to the fact that conjugation of the heteroring with the aromatic benzoid ring is not effective in 4,5-dihydronaphthofurazan.

The N-oxidation of the investigated furazans, i.e., transition to the corresponding furoxans, has an extremely pronounced effect on the spectrum (Table 4). This is manifested in a sharp reinforcement of the intensity and number of bands related to the valence vibrations of the benzoid and oxadiazole rings: the frequencies at 1590-1630 cm^{-1} increase by 20-40 cm^{-1}, and their intensities increase by a factor of 10-20. In addition, additional bands at 1530-1570 cm^{-1} appear in the spectrum of naphthofuroxans. Of the four bands at 1418-1480 cm^{-1}, which we noted for the spectrum of naphth-1,2,5-oxadiazole, only three bands remain in the spectrum of naphthofuroxan, while the low-frequency band at 1395-1418 cm^{-1} vanishes. The changes in the absorption at 1395-1630 cm^{-1} noted above are associated with N-oxidation of the furazan ring; the same changes accompany transition from dimethylfurazan to dimethyl-6-furoxan. The N-oxidation is also associated with a sharp reinforcement of the bands of the in-plane deformation vibrations of the CH bonds (1078, 1099, 1160, and 1209 cm^{-1}). The bands at 992 and 870 cm^{-1}, which are characteristic for naphthofurazans, vanish in the spectra of naphthofuroxans; a triplet appears in place of the $\delta_{\perp}$ doublet of the four adjacent CH bonds. The two adjacent CH groups in the angular ring appear as a doublet (829/809 cm^{-1}) with an average frequency of 814 cm^{-1}.

The introduction of a sulfo group into the 5-position of naphthofuroxan does not have a substantial effect on the vibrations of the naphthalene ring and the heteroring. Much greater changes are observed in the region of the in-plane and out-of-plane deformation vibrations of the CH bonds: the number of intense bands at 1000-1300 cm^{-1} increases by at least three; at 700-1000 cm^{-1} the very intense bands at 963 and 829/806 cm^{-1} vanish, and bands at 861 and 732 cm^{-1} remain in place of the $\delta_{CH\perp}$ triplet of the four adjacent bonds. The band at 861 cm^{-1} that reappears is related to $\delta_{CH\perp}$ of an isolated CH bond. The absorption bands of the valence vibrations of the sulfo group are 12-15 cm^{-1} higher than those in the spectra of the corresponding naphth-1,2,5-oxadiazoles. The hydrogenation of the 4,5- C= C bond in naphthofuroxan-5-sulfonic acids causes the most substantial changes in the $\delta_{\parallel}$ region of the CH bonds, and the intensities of the bands at 1259 and 1159 cm^{-1} increase sharply. As expected, the band at 861 cm^{-1}, related to $\delta_{\perp}$ of an isolated CH bond, vanishes on passing to the hydrogenated derivative. The bands of the deformation vibrations of the ring methylene group are overlapped by the bands of the vibrations of the carbon-carbon ring bonds. It is interesting that the introduction of a hydroxyl group into the benzoid ring of 4,5-dihydronaphthofuroxan-5-sulfonic acid causes changes in the spectrum that differ for the 7- and 8-positions. The derivative with a hydroxyl group in the 8-position is characterized by the most intense band in the IR spectrum at 813 cm^{-1} ($\delta_{\perp}$ of two adjacent CH groups), while the most intense band for the 7-hydroxyl derivative is the band at 864 cm^{-1}, which is characteristic for $\delta_{\perp}$ of an isolated CH bond. The spectrum of the 7-hydroxyl derivative contains two very intense bands at 1646 and 1608 cm^{-1}, while the 8-hydroxyl isomer has one band of high intensity at 1644 cm^{-1}. In addition, an intense band at 1506 cm^{-1} is characteristic for the 8-hydroxyl derivative, while the 7-hydroxyl isomer has a band at 1484 cm^{-1}. Finally, the 7-hydroxyl derivative displays four very intense bands at 1224, 1190, 1180, and 1168 cm^{-1} and four bands of medium intensity at 1307, 1280, 1268, and 1243 cm^{-1} in the region of the CH in-plane deformation vibrations and asymmetric valence vibrations of the SO_3 group; in the case of the 8-hydroxyl derivative, two very intense bands at 1123 and 1180 cm^{-1} and one band of medium intensity at 1280 cm^{-1} are observed in this region. These differences in the spectra of the 7- and 8-hydroxyl derivatives of 4,5-dihydronaphthofuroxan-5-sulfonic acid can be used for analytical determinations. If a nitro group is introduced into the 7-position of this sulfonic acid in place of the hydroxyl group, a very intense band at 1660 cm^{-1} and a band of medium intensity at 1628 cm^{-1} appear in place of the bands at 1646 and 1608 cm^{-1}. The vibrations of the nitro group are displayed by bands at 1538 and 1356 cm^{-1}. The effect of the nitro group is also exerted in the fact that the bands noted for the 7-hydroxyl derivative at 1248-1307 cm^{-1} are shifted to the low-frequency region with a simultaneous reduction in their intensities.

EXPERIMENTAL

The synthetic methods and the characteristics of the compounds studied are presented in [7,8]. The spectra were recorded with IKS-14 and SF-4 spectrometers.

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