

THE STRUCTURES OF FURAZANS AND FUROXANS

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The IR spectra of furazans and furoxans are characterized by lowered values of frequencies and of integrated absorption band intensities for the C=N bands. The peculiarities of the UV absorption spectra of these compounds are similar to those of pyridine and its benzene analogs in comparison with the corresponding N-oxides. Comparison of the results with those given in the literature regarding chemical properties, delocalization energies, X-ray spectra, and quantum chemistry calculations leads to a conclusion that the 2, 1, 3-oxadiazole ring possesses a definite aromaticity.

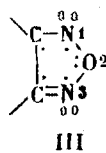
Much work has been done on determining the structures of furazans and furoxans [1]. However the sum total of chemical properties and physical data for those compounds is not in complete accord with the assumed structure.

At present the structures of furazans and aliphatic furoxans are well represented by, respectively, formulas I and II



Formula I postulates the presence of localized C=N double bonds and of single bonds C-C and N-O. But this is not in agreement with the X-ray structure results [2], which show that in the plane of the furazan ring, the bonds in benzofurazan have a length which is intermediate between those of the corresponding single and double bonds ($r_{C=N} = 1.35$; $r_{C-C} = 1.43$; $r_{N-O} = 1.25$ Å), while the valence angles are very much the same. Heats of combustion of furazans [3] are 53.8 kcal/mole less than would be expected for formula I. The difference between the found and calculated heats of combustion is 1.5 times greater than for benzene, and 2.5 times greater than for furan. In the IR and Raman spectra of furazans the C=N bond valence vibration frequency lies inside the limits $1610-1480$ cm^{-1} [4], while the frequency of the localized or conjugated aliphatic C=N bond lies in the range $1690-1640$ cm^{-1} [5]. Furazans are quite resistant to oxidation [1].

The above properties of furazans can be explained if the possibility of formation of a closed p, π electron system [3] in the furazan ring is considered. Actually there are $6p, \pi$ electrons (black dots III) in the plane furazan ring; these are the 2π electron on each carbon atom, the $2p$ electron on each nitrogen atom, and the lone pair of p electrons on the oxygen atom.



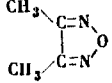
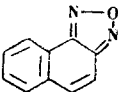
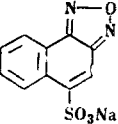
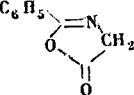

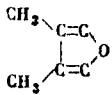
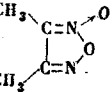
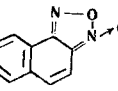
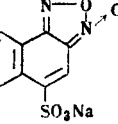
The tendency to formation of a closed p, π electron system should lead to equalizing of bond lengths and valence angles in I, to an increase in energy, to resistance to oxidation, and to a large lowering of the valence vibration frequencies of the C=N bonds due to delocalization of the latter.

Despite the generalizing of the $6p, \pi$ electrons in the furazan ring, the electron density, as in syndones, should be distributed unequally, as the ring hetero atoms have different electronegativities. The high dipole moments of furazans (~ 4.0 D) [6] indicate this.

In addition to the closed p, π electron system in the furan ring, two lone pairs of electrons (white circles in III) at N_1 and N_3 must be considered, and generally these latter are able to form coordinate links. However, furazans cannot be oxidized to furoxans [1].

Aliphatic furoxans are also characterized by resistance to oxidation [1], and lowering of the absorption frequencies in the IR and Raman spectra [3]. There the exocyclic oxygen powerfully affects the aromatic system of the ring, and this shows itself by increase in frequency, intensity, and number of C=N bond absorption bands in comparison with

Integrated Intensities of Absorption Bands of Ring C=N Bond Valence Vibrations in IR Spectra

Expt. No.	Compound	In chloroform		in KBr tablets	
		$\nu_{C=N}$ (cm^{-1})	$A_{C=N} \cdot 10^{-2}$ $\text{mole}^{-1} \cdot \text{L} \cdot \text{cm}^{-2}$	$\nu_{C=N}$ (cm^{-1})	$A_{C=N} \cdot 10^{-2}$ $\text{mole}^{-1} \cdot \text{L} \cdot \text{cm}^{-2}$
1		1594	3		
2		1611	12**		
3				1604	11**
4		1647	200		
5		1603/1589	56**		
6		1576***	20****		
7		1617	145		
8				1635	100**
9				1622/1614	100**

* Intensity refers to one C=N group.

** $A_{C=N}$ intensity includes vibration bands of aromatic rings, as they cross.

*** Vibrations of the ring multiple bond.

**** Intensity refers to one C=C group.

the corresponding furazans (table). Moreover, reduction of the dimethylfuroxan takes place at a more positive potential ($E_{1/2} = -1.52$ V, pH = 8.0) than dimethylfurazan ($E_{1/2} = -2.12$ V, pH = 8.0) [8].

PMR spectra [9] and X-ray structure studies [10] show that a type II formula for furoxans condensed with an aromatic ring must be rejected. A fuller understanding of the structure of aromatic furoxans must include the idea of the heterocyclic ring's possessing a certain aromaticity. Thus benzofuroxan is not oxidized by performic and peracetic acids, which convert nitrosobenzene into nitrobenzene [1]. Oxidation of benzofuroxan to o-dinitrobenzene occurs when trifluoroperacetic acid is the oxidizing agent, though despite precautions, the yield is slight. Under the same conditions naphtho-1, 2- and phenanthro-1, 2-furoxans are unchanged [11]. It is of interest to note that attempts to prepare benzofuroxan from dehydrobenzene and nitrogen oxides proved unsuccessful [12]. Furthermore, reduction of aromatic furoxans takes place under milder conditions than are required for aliphatic ones. If dimethylfuroxan is reduced at $E_{1/2} = -1.52$ V (pH = 8.0), aromatic furoxans start to reduce at much lower potentials ($E_{1/2} = -0.1$ to -0.15 V at pH = 8.0), with decomposition of the furan ring [8].

The present authors consider that if the assumption regarding the aromatic character of the furan ring is correct, additional data in support of it can be derived from IR and UV spectra. In such a case the C=N bond in the furan ring must be considerably delocalized, giving rise to an appreciable reduction in ν_{C-N} , and to a sharp decrease in band intensity. It is also to be expected that the UV spectra of the furazans and furoxans will be rather similar to the UV spectra of aromatic N-heterocyclic rings and N-oxides.

Hence, the IR and UV spectra of some furazans and furoxans were observed, and the total intensities of absorption bands due to valence vibrations of C=N bonds in the ring measured. The IR spectra were measured with an IKS-14 spectrophotometer. Total intensities were measured by Ramsay's method, using the formula

$$A = \frac{\pi}{2} \cdot \frac{1}{c \cdot e} \cdot \ln \left(\frac{T_0}{T} \right) \frac{\Delta \nu_{1/2}^2}{\nu_{max}}$$

To investigate the compounds in the crystalline state, tablets were prepared from 500 mg KBr and 2-3 mg compound. The specimen pieces were 22 mm in diameter. Tablet thickness, calculated taking the density of KBr as 2.75 g/cm³ and tablet volume as 0.182 cm³, was 0.048 cm. Intensities are given in practical units mole⁻¹ · L · cm⁻². UV spectra were measured with a SF-4 spectrophotometer.

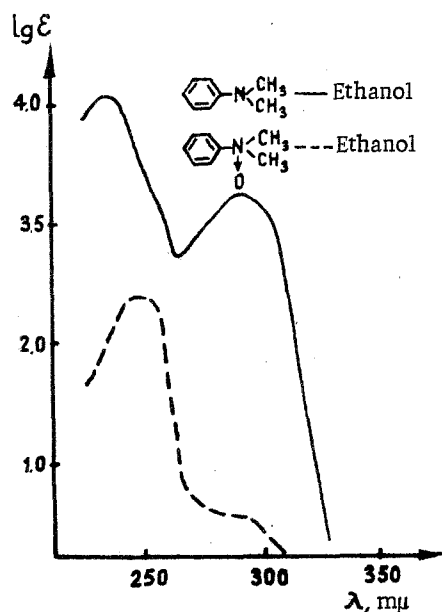


Fig. 1. UV spectra of dimethylaniline and its N-oxide.

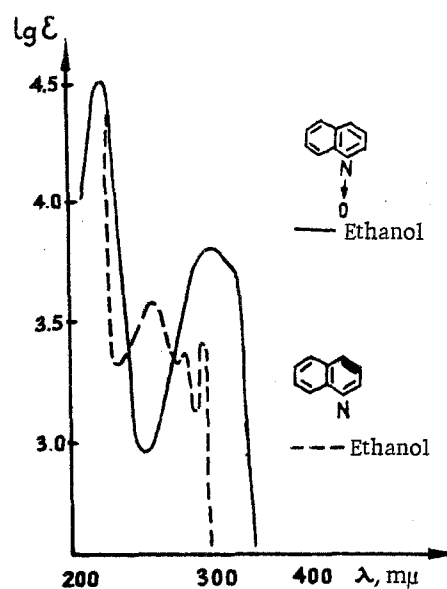


Fig. 2. UV spectra of quinoline and its N-oxide.

The table shows that ν_{C-N} for furazans (nos. 1-3) lies in the region 1590-1610 cm⁻¹, and the integrated intensity of the $A_{C=N}$ band for chloroform solutions and for KBr tablets is 3-12 units, which is far lower than for the model compound 3-phenyloxazolone (table, no. 4), which lacks the aromatic character of the ring, where $\nu_{C=N}$ is 1647 cm⁻¹ and the intensity 200 units. For pyridine the intensity of the bands of the aromatic bonds C=N and C=C is 56 units (bands at 1603 and 1598 cm⁻¹) (table, no. 5), but the vibrations of the multiple bond in 3, 4-dimethylfuran appear at 1576 cm⁻¹ and are characterized by 20 units of intensity (table, no. 6).

In the IR spectra of the furoxans the frequency of the C=N bond is increased to 1620-1640 cm⁻¹, and the intensity

of the bond rises to 100-140 units (table, nos. 7-9). These frequency and intensity values of the bands of the C=N bonds are intermediate between the values for 3-phenyloxazolone and furazans. It should be mentioned that the intensities of the bands of the aromatic C-C bonds (1600 cm^{-1}) in aromatic furoxans are also much greater (100 units).

So the positions of the frequencies and the values of the integrated intensities of the C=N bonds' vibration bands are in accord with existing ideas regarding the aromatic character of the furazan ring.

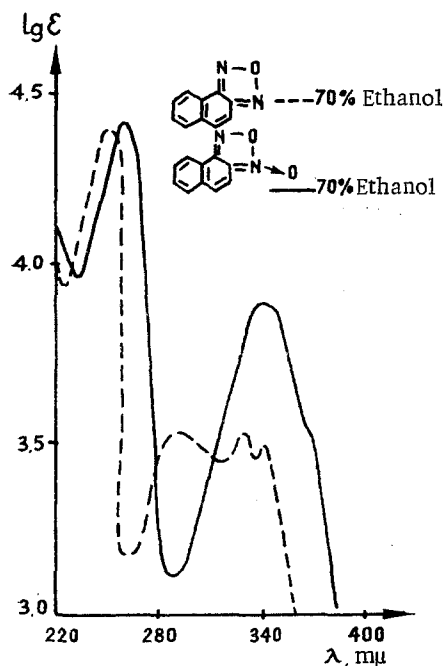


Fig. 3. UV spectra of naphthofurazan and naphthofuroxan.

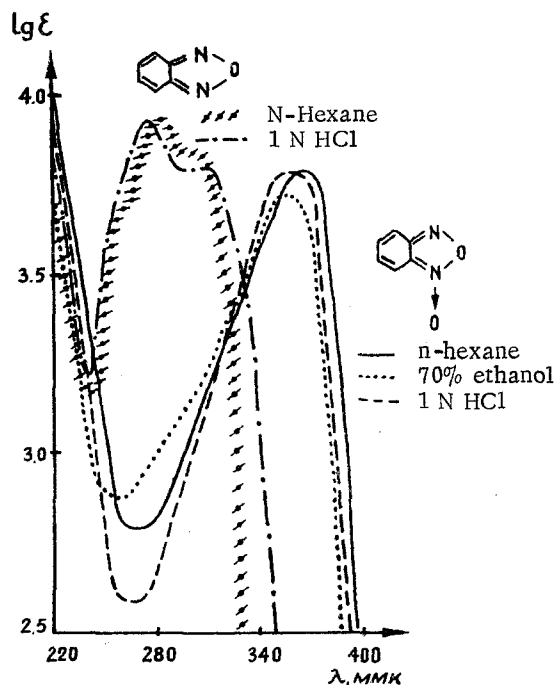


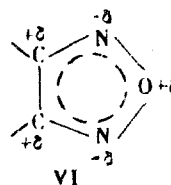
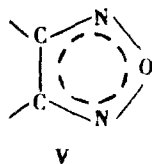
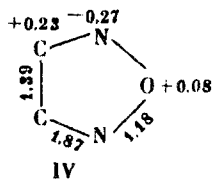
Fig. 4. UV spectra of benzofurazan and benzofuroxan.

It is known [7] that the presence of the NO group in N-oxides results in a different shift in the UV spectra of aromatic or aliphatic N-oxides compared with those of the starting bases. (Figs. 1 and 2). The spectrum of dimethylaniline N-oxide lies below the absorption curve of dimethylaniline base, and resembles that of benzene. On the other hand, in the spectrum of quinoline N-oxide the long wave band is appreciably shifted towards the high values side and its intensity increased in comparison with that of the spectrum of the quinoline base. Similar changes in UV spectra are called forth by aprotic solvents as compared with protonating ones. This kind of behavior of aromatic N-oxides is explained by conjugation of the electron pair of the exocyclic oxygen with the aromatic ring, repressed in acid medium through interaction with a proton.

The UV spectra of dimethylfuran in alcohol (λ_{max} 252 mμ, $\lg \epsilon$ 3.71) resemble the spectrum of γ -picoline N-oxide (λ_{max} 264 mμ, $\lg \epsilon$ 4.059) [13]. The spectrum changes on passing from solutions of dimethylfuroxan in aprotic solvents (λ_{max} 265 mμ in cyclohexane) to spectra in protonating solvents (λ_{max} 252 mμ and 251 mμ in H_2O and 1 N HCl solution, respectively) are characterized by a shift of the absorption maximum towards the shortwave region. The UV spectrum of γ -picoline N-oxide behaves in the same way [7]. In the spectra of naphtho- and benzofuroxans the long-wave band is shifted bathochromically in comparison with the spectra of naphtho- and benzofurazans (Figs. 3, 4), like the UV spectra of quinoline and its N-oxide (Fig. 2). In the case of naphthofuroxan this band is also intensified (Fig. 3). On passing from solutions of benzofuroxan in aprotic solvents to those in protonating solvents, some shift of the longwave absorption maximum in the direction of lower wavelengths and a small decrease in band intensity (Fig. 4) are observed. As was previously indicated, this effect of a shift of maximum depending on solvent nature is characteristic of aromatic N-oxides (quinoline N-oxide). So the large agreement between the UV spectra of furazans and furoxans and those of ordinary aromatic N bases and N-oxides is also in agreement with the hypothesis regarding the definite aromatic character of these compounds.

Such a conclusion is arrived at from quantum chemistry calculations for furazans using the method of molecular orbitals (see the molecular diagram IV) [14], though the method of arriving at the numerical results, assumed in the work mentioned, is open to criticism [15, 16].

Thus, the structure of the furazan can be represented by formulas V or, more precisely, VI, which reflect the partially aromatic character of the ring



Furoxans are characterized by significant disturbance of the aromatic oxadiazole rings, especially, apparently, where such a ring is condensed with a benzene or naphthalene one.

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