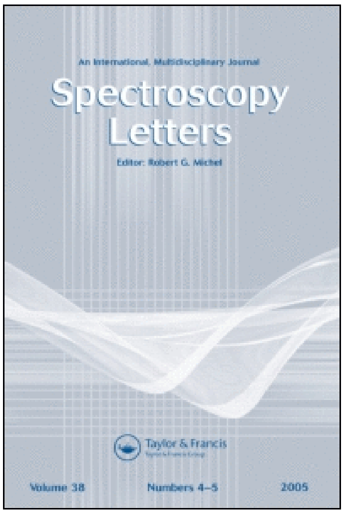

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STUDIES OF THE ELECTRONIC STRUCTURES IN MONONITRONAPHTHOL-2 DERIVATIVES BY THE UV AND VIS SPECTROSCOPIC METHODS

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A shift of the K band in the spectrum of monosubstituted benzene C_6H_5-X may by to some extent considered a measure of the electron donor or acceptor strength of the X substituent[1]. However, it should be emphasized that the knowledge of only $\Delta\lambda^{exp.}_{H,X}$ value does not allow to determine the spectral nature of a certain unknown X substituent since the bathochromic shift of the K band occurs both - when this substituent is auxochromic /electron donor/ or when it is anti-auxochromic /electron acceptor/.

It was found in many instances[2] that the K band is particularly sensitive to the substitution of the aromatic ring. On substituting the ring with the X and Y substituent of opposite natures the K band shift is large, larger than the additive effect of the substituent. These deviations are the larger, the more pronounced are the electron donor or acceptor properties of the substituent. It seems[3] that in the case of disubstituted benzene derivatives only the para isomers absorb as single chromophores owing to maximum coupling between the substituent and the ring. On the other hand, in the meta and ortho isomers the monosubstituted chromophores are partially isolated and, hence, the spectra of these disubstituted benzene derivatives are hybrid spectra of monosubstituted compounds. A convenient measure of deviations from additivity is the value[2]:

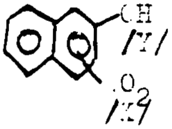
$$\frac{\Delta\lambda^{\text{exp.}}_{X,Y}}{\Delta\lambda^{\text{calc.}}_{X,Y}} = \frac{\lambda^{\text{exp.}}_{X,Y} - \lambda^{\text{exp.}}_{H,H}}{/\lambda^{\text{exp.}}_{H,X} - \lambda^{\text{exp.}}_{H,H}/ + /\lambda^{\text{exp.}}_{H,Y} - \lambda^{\text{exp.}}_{H,H}/} \lessgtr 1$$

The ratio $\Delta\lambda^{\text{exp.}}_{X,Y}/\Delta\lambda^{\text{calc.}}_{X,Y}$ is lower than unity if $X=Y$, or, if X and Y have the same spectral nature. On the other hand, it is higher than unity if X and Y differ in their spectral natures.

The results of calculations with the above assumption in mind, for the nitro derivatives of naphthol-2 are summarized in Table 1.

TABLE 1

Calculation of the measure of deviation from additivity for mononitro derivatives of naphthol-2



NO_2	OH	$\lambda^{exp.}_{X,Y}$ /nm/ /lg ε/	$\Delta\lambda^{exp.}_{X,Y}$	$\Delta\lambda^{calc.}_{X,Y}$	$\frac{\Delta\lambda^{exp.}_{X,Y}}{\Delta\lambda^{calc.}_{X,Y}}$
-	-	275 /5,068/	-	-	-
-	2	286 /3,518/	11	-	-
1	-	327 /3,623/	52	-	-
2	-	303 /3,908/	28	-	-
1	2	370 /3,344/	95	63	1,51
3	2	323 /3,873/	48	39	1,12
4	2	340 /3,480/	65	63	1,03
5	2	336 /3,592/	61	63	0,97
6	2	341 /3,981/	66	39	1,69
7	2	308 /3,916/	33	39	0,85
8	2	380 /3,642/	105	63	1,67

As shown, the results obtained confirm the considerations carried out for the benzene derivatives[1-3]. Nitronaphthols-2 with conjugated systems absorb as one chromophore as evidenced by the high ratio of $\Delta\lambda_{X,Y}^{exp.}/\Delta\lambda_{X,Y}^{calc.}$ whereas for the other isomers their absorption is similar to the additive model of single chromophores, although the overall nature of the spectrum demonstrates quite clearly the domination of the nitro chromophore /FIG.1/. The K bands found are merely the ones corresponding to the K bands of nitronaphthalenes absorptions and only some of them exhibit shoulders corresponding to the residual absortion of naphthol-2.

The effect of solvent polarity on the positions and intensities of the absorption bands in the UV and Vis spectra of mononitronaphthols-2 and their acylated derivatives seems to be interesting. During preliminary studies a highly-coloured solution was found to be formed during dissolution of samples in the concentrated sulphuric acid. However, the product obtained was too unstable /the "life-time" of the product was shorter than the period necessary to measure a full UV-Vis spectrum/. This suggested that the product obtained

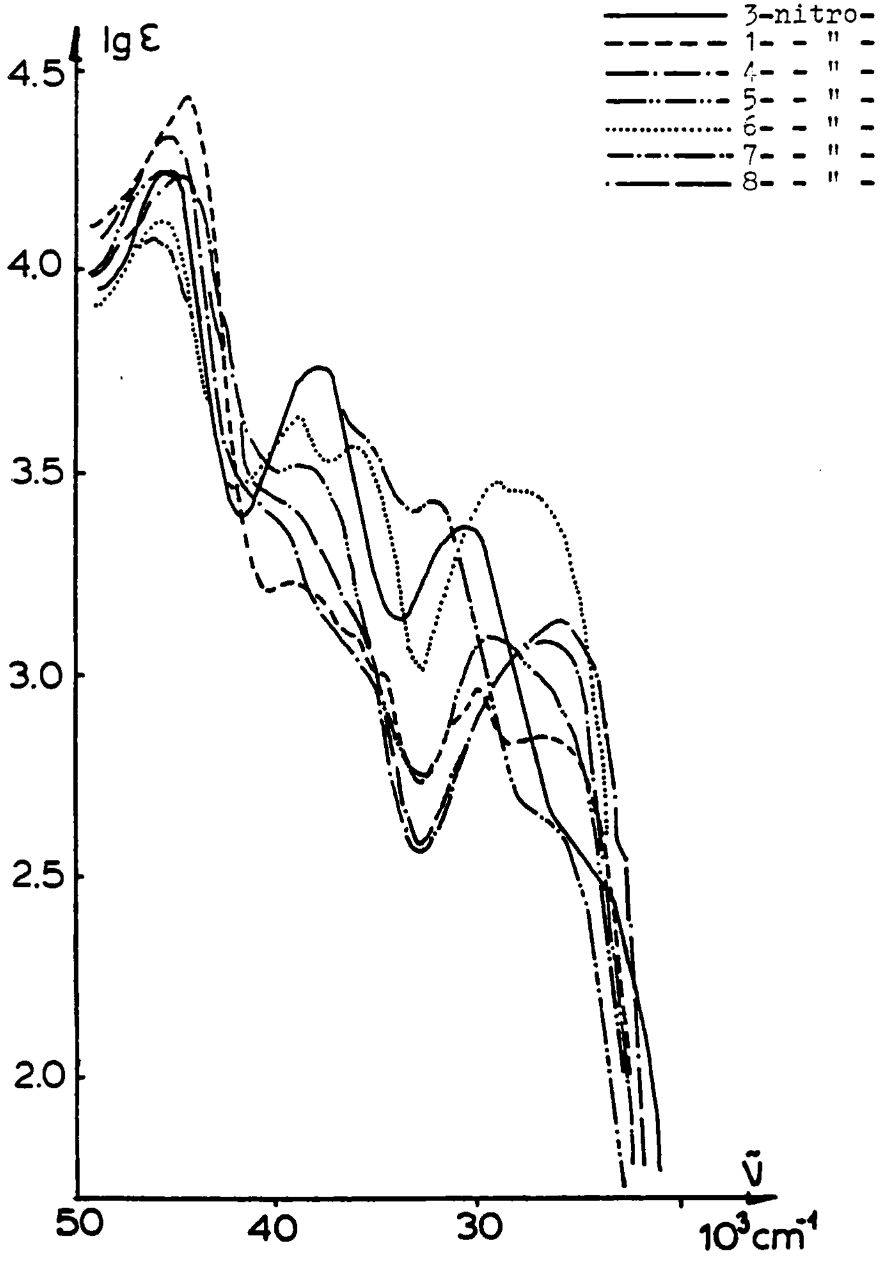


FIG.1

Electronic spectra of nitronaphthols-2.

TABLE 2

The absorption bands for 1-nitronaphthyl-2-derivatives: 1/ 2-hydroxy, 2/ 2-acetoxy, 3/ 2-mesyloxy - depending of solvents.

No.	n-hexane						
1/	220	249	275s	285s	305s	320	337,5 385
2/	220	244	260s	275s	285s		
3/	221	295s	320	350			
	dioksane						
1/	223	251	275s	285s	337,5	385	
2/	222	253	290s	307,5	321	350s	
3/	208s	223	252	280s	290s	310s	320 350
	$HClO_4$ 72%						
1/	194,5	207,5s	221	254	288s	410	600
2/	207,5s	221	253	300	410	610	700
3/	193	207,5s	221,5	260	328	353	
	conc. H_2SO_4						
1/	200^{*} ε_i	$227,5^{*}$ D	$252,5^{*}$ ε_i	$292,5s^{*}$ ε_d	313^{*} ε_d	395^{**} ε_d	475^{***} D
2/	195	202,5	252,5	290	292,5 490	322s 540	400 700
3/	195s	208s	221	248	325	375	

Remarks: s = shoulder; ε: i = increases, d = decreases; D = disappears; * - after 24h, ** - after 10min. up to $\varepsilon_2=1/2\varepsilon_1$, *** - after 10min.

is an ion-radical. This supposition was confirmed by a typical EPR spectrum measured.

Studies were also initiated on the effect of acidic groups in the acylated derivatives of mononitronaphthols-2 on their UV-Vis spectra. Preliminary results obtained for 1-nitro-2-oxynaphthalenes are summarized in Table 2.

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