

ELECTRONIC SPECTRA OF PHENOXAZINE DYESTUFFS AND SUBSTITUENT EFFECTS ON THE POSITION OF LONG-WAVE ABSORPTION BANDS

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Dedicated to Professor Dr S. Stankoviansky on the occasion of his 70th birthday.

The most characteristic band in electronic spectra of the measured substances is the long-wave band due to intramolecular electron transfer. The whole quinoid ring is the acceptor in the charge transfer, the rest of the molecule being the donor. The position change of the long-wave band is discussed in the terms of the change of donor and acceptor strength of the respective parts of the molecule, which varies with the presence of substituents.

In previous papers we studied protonation equilibria of phenoxazine dyestuffs¹⁻⁴, their infrared spectra^{5,6}, and their use as acid-base indicators^{7,8}. The present paper deals with the electronic spectra measured in ethanol and with the substituent effects on position of the long-wave absorption bands. Recently several authors studied electronic spectra of orceine and similar compounds⁹⁻¹³.

EXPERIMENTAL

Preparation of the Substances

The following substances were prepared according to literature data: phenoxaz-3-one¹⁴ (*I*; m.p. 216–217°C), benzo[*a*]phenoxaz-5-one¹⁵ (*II*; m.p. 194.5°C), benzo[*c*]phenoxaz-9-one¹⁶ (*III*; m.p. 233–235°C), benzo[*a*]phenoxaz-9-one¹⁷ (*IV*; m.p. 227–228°C), 5-aminobenzo[*a*]phenoxaz-9-one¹⁷ (*XIII*; m.p. > 350°C), dibenzo[*a,j*]phenoxaz-5-one¹⁸ (*V*; m.p. 287–288°C), dibenzo[*a,h*]phenoxaz-5-one¹⁸ (*VI*; m.p. 291–292°C), 8-methylphenoxaz-3-one¹⁹ (*VII*; m.p. 204–205°C), 2-aminophenoxaz-3-one²⁰ (*VIII*; m.p. 249°C), 8-methylphenoxaz-3-one-*N*-oxide¹⁹ (*XIV*; m.p. 251–253°C) >9-hydroxybenzo[*a*]phenoxaz-5-one (*IX*; m.p. 305–307°C), 5-ethoxybenzo[*a*]phenoxaz-9-one (*X*, m.p. 225–6°C), by condensation of 4-nitrosoresorcinol with 1-naphthol in ethanol in the presence of sulphuric acid and by chromatographical separation²¹, 2-hydroxybenzo[*a*]phenoxaz-9-one²² (*XI*; m.p. > 350°C), 9-diethylaminobenzo[*a*]phenoxaz-5-one²³ (*XII*; m.p. 200–201°C), 1,7,9-trihydroxyphenoxaz-3-one²⁴ (*XV*; m.p. > 350°C), 7,9-dimethoxyphenoxaz-3-one²⁴ (*XVI*; m.p. 280–286°C), 1-methoxycarbonyl-7-dimethylaminophenoxaz-3-one²⁵ (*XVII*; m.p. 194°C), 7-aminophenoxaz-3-imine²⁶ (*XVIII*; m.p. > 350°C), 9-dimethylaminobenzo[*a*]phenoxazonium chloride²⁷ (*XIX*), 5-amino-9-diethylaminobenzo[*a*]phenoxazonium sulphate (*XX*) was a commercial product (Lachema) which was recrystallized and washed with ether.

The melting points were determined with a Kofler apparatus with the accuracy $\pm 2^\circ\text{C}$ up to 200°C , and they are not corrected. The non-substituted phenoxazones were chromatographed on a silica gel CH (Spolana Neratovice) thin layer with 10% gypsum using benzene-ethanol (8:2) eluent system. The other substances were chromatographed on silica gel or alumina thin layer. Before measurement the substances were dried at 60°C at 0.1 Torr to constant weight. The non-substituted phenoxazones *I*–*VI* were sublimed at 100°C at 0.1 Torr. Purity of the compounds was checked by elemental analysis (C, H, N) using the Perkin Elmer 240 Elemental Analyser.

Spectrophotometric Measurements

Samples of 0.10 to 0.15 mg of the compounds were weighed and dissolved in 10 ml ethanol. Positions and intensities of the absorption bands are summarized in Table I. The spectra were measured with a recording ultraviolet spectrophotometer Unicam SP 1800 with a linear recorder Unicam AR 25 in 1.00 or 0.20 cm cells. The spectral slot width was 0.25 mm for 0.8 nm wave length range.

RESULTS

The most characteristic absorption band of phenoxazine dyestuffs is the long-wave one. It is due to an intramolecular electron transfer, the whole quinoid system being the acceptor in the charge transfer, and the donor is the rest of the molecule. The most long-wave band of the non-substituted compounds is situated in the region 428–504 nm, that of the substituted ones is in the region 428–612 nm (Table I). The simplest compound measured is phenoxaz-3-one (*I*) with the long-wave band at 448 nm. A fused benzene ring at position a (*II*) converts the system into a naphthoquinoid one which is a weaker electron acceptor than the benzoquinoid system. This structural change not concerning the donor part of the molecule causes a hypsochromic shift of the long-wave band by 20 nm. Similarly, the aminobenzoquinoid system of the compound *VIII* represents a weaker electron-acceptor than the benzoquinoid system of the compound *I*, and the long-wave band is hypsochromically shifted, too. According to an obvious intensity increase of the both last bands in spectrum of the compound *VIII* an intramolecular hydrogen bond is formed causing the bathochromic shift ($\Delta 70$ nm) of the last but one band. We presume that hydrogen bond has a large effect on this band, a quasiaromatic ring being formed. A methyl group at 8 position of the compound *VII* strenghtens little the donor part of the molecule, which is manifested by a not large bathochromic shift.

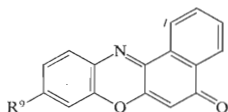
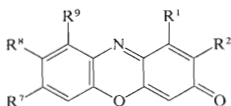
Comparison of spectra of the compounds *IX* and *II* shows that substitution by —OH group at position 9 causes a bathochromic shift (by 35 nm) of the absorption maximum of the long-wave band. This shift is due by strenghtening of the donor molecule part by —OH substituent. Substitution by methoxyl in the compound *X* causes a hypsochromic shift (by 43 nm) of the longest-wave band as compared with the compound *IV*. The ethoxyl group here does not contribute to the

donor influence of the donor part of the molecule. Substitution by —OH group at 2 position (*XI*) causes a not large bathochromic shift of the longest-wave band.

TABLE I
Electronic Spectra of Phenoxazine Dyestuffs in Ethanol

Compound	λ_{max} , nm (log ϵ)				
<i>I</i>		246 (4.19)	252 (4.17)	350 (3.98)	448 (3.94)
<i>II</i>	218 (4.19)	235 (4.44)	243 (4.30) 258 (4.16)	363 (4.03)	428 (4.05)
<i>III</i>	214 (4.52)	228 sh	290 (4.21)	304 (4.23) 363 (4.03)	504 (4.10)
<i>IV</i>	216 (4.55)	253 (4.33)	289 (4.09)	310 (3.95)	497 (4.12)
<i>V</i>	214 (4.57)	244 (4.46) 253 (4.38)	292 (4.18)		482 (4.25)
<i>VI</i>	214 (4.54)	245 (4.43) 252 (4.48)	307 (4.26)	356 (4.06) 370 (4.06)	480 (4.17)
<i>VII</i>	210 (4.68)	249 (4.46)	255 (4.45)	354 (4.28)	465 (4.20)
<i>VIII</i>		237 (4.47)		420 (4.39)	434 (4.40)
<i>IX</i>		242 sh	248 (4.49)		463 (4.35)
<i>X</i>		230 (4.43) 241 (4.46)	247 (4.48)		454 (4.40)
<i>XI</i>	226 (4.51)		256 (4.40)	315 (4.16)	514 (4.31)
<i>XII</i>	222 (4.19)		265 (4.56)	307 (3.78)	552 (4.41)
<i>XIII</i>	219 (4.42)	250 sh	258 (4.37) 273 (4.41)	307 (3.93) 319 (3.95)	571 (4.51) 592 (4.64) 612 (4.73)
<i>XIV</i>		236 (4.39)	257 (4.11) 267 (4.12)	362 (4.07)	492 (4.02) 526 sh
<i>XV</i>			263 (4.15)	465 (4.22)	575 (3.51)
<i>XVI</i>	220 (4.45)		258 (4.24)		463 (4.31)
<i>XVII</i>			250 (4.28)		591 (4.33)
<i>XVIII</i>	230 (4.42)	248 (4.55)	270 sh	301 (3.89)	589 (4.96)
<i>XIX</i>	217 (4.37)		266 (4.21) 274 sh	321 (4.02) 432 (3.93)	573 (4.32)
<i>XX</i>	228 (4.47)		276 (4.47)	324 (4.02)	624 (4.64)

The compound *XII*, carrying a diethylamino group at 9 position, has its long-wave absorption maximum bathochromically shifted by 124 nm as compared with the compound *II*. The electron-donor group $\text{—N}(\text{C}_2\text{H}_5)_2$ causes a great increase in the effect of the donor molecule part. The energy necessary for the transfer of a π electron to the lowest unoccupied π^* molecular orbital is considerably lowered. A similar situation is encountered with the compound *XIII*. As compared with the compound *IV*, the long-wave band is strongly bathochromically shifted (by 115 nm) and split into three bands.



I; R¹, R², R⁷, R⁸, R⁹ = H

VII; R¹, R², R⁷, R⁹ = H, R⁸ = CH₃

VIII; R¹, R⁷, R⁸, R⁹ = H, R² = NH₂

XIV; R¹, R², R⁷, R⁹ = H, R⁸ = CH₃, N → O

XV; R¹, R⁷, R⁹ = OH, R², R⁸ = H

XVI; R¹, R², R⁸ = H, R⁷, R⁹ = OCH₃

XVII; R¹ = COOCH₃, R², R⁸, R⁹ = H, R⁷ = N(CH₃)₂

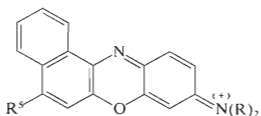
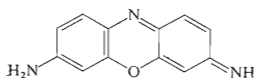
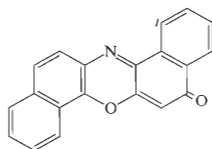
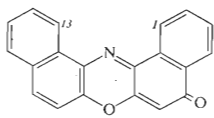
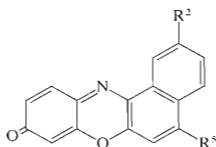
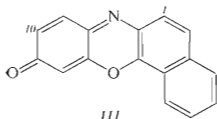
II; R⁹ = H

IX; R⁹ = OH

XII; R⁹ = N(C₂H₅)₂

The compound *XIV* slightly deviates from the rest of the series. Compared with the compound *VII*, the N-oxide has its absorption band bathochromically shifted by 61 nm, and in addition to it formation of a new band can be observed.

Introduction of three hydroxyl groups (*XV*) causes a bathochromic shift of the both long-wave bands by 127 and 115 nm, respectively. If methoxyl groups are at positions 7 and 9 (*XVI*), the last but one band completely disappears, and the longest-wave band is shifted only slightly bathochromically as compared with the compound *I*. Effect of the methoxyl groups in the compound *XVI* on its absorption spectrum is similar to that of ethoxyl group in the compound *X*. In spectrum of the compound *XVII* the last but one band disappears, too, and the longest-wave band is strongly bathochromically shifted (by 143 nm as compared with the compound *I*) due to the effect of diethylamino group on the donor part of the molecule. If spectra of this compound and *XII* are compared, methoxycarbonyl group at 1-position being replaced by fused benzene ring at position *a*, a bathochromic shift by 39 nm with respect to the compound *XII* is observed, too. In the compound *XVIII* the quinoid group is replaced by quinoneimine group. A further substitution by —NH_2 group at position 7 causes a strong bathochromic shift of the long-wave band. The interlocking of =NH and —NH_2 groups results in a strong mesomeric effect,



as it was the case with the compound XIII having the $-NH_2$ group interlocked with carbonyl. The expected bathochromic shift of the long-wave band of the compound XX as compared with XIX was confirmed ($\Delta 51$ nm). Comparison of the compounds IV and XIX shows a bathochromic shift of XIX by 76 nm. It was confirmed that the $=N^+(R)_2$ group, having positive charge, has a greater electron-attracting ability than quinoide $C=O$ group.

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