

Condensation Products of Dibenzophenoxaz-5-ones with Aromatic Amines and Their Physicochemical Investigation

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The reaction of 5*H*-dibenzo[*aj*]phenoxaz-5-one and 5*H*-dibenzo[*ah*]phenoxaz-5-one with aromatic amines and their hydrochlorides in melt was investigated. The proper arylamines of the mentioned dibenzophenoxazones were isolated from the reaction mixture. Of the obtained products, infra-red, ultra-violet and visible spectra were measured and also ionization constants in 50% ethanol were estimated by a spectrophotometric method.

Only one arylamino derivative of dibenzophenoxazone has been so far reported by Goldstein and co-workers [1], namely 9-anilino-5*H*-dibenzo[*aj*]phenoxaz-5-one, prepared by condensation of 4-anilino-1-amino-2-naphthol with 2-hydroxynaphtho-1,4-quinone. We tried to prepare the same compound by reaction of aniline with 5*H*-dibenzo[*aj*]phenoxaz-5-one, we attempted to find out reaction conditions for synthesis of further arylamino derivatives and we investigated these compounds by physicochemical methods.

Experimental

5*H*-Dibenzo[*aj*]phenoxaz-5-one and 5*H*-dibenzo[*ah*]phenoxaz-5-one were prepared according to [2]; aromatic amines and their hydrochlorides were either commercial products (Lachema), or preparations made by routine laboratory methods.

Preparation of arylamino derivatives of dibenzophenoxaz-5-ones

Dibenzophenoxaz-5-one (300 mg, *ca.* 1 milimole) was mixed with aromatic amine (2 milimoles) and its hydrochloride (1 milimole) in a testing tube and heated in an oil bath at 220°C for 10 minutes. The cooled melt, violet in colour and solid in nature was then extracted with benzene. When checking its purity by thin layer chromatography on silicagel in the solvent system acetone—benzene (1 : 3) it was found out that the obtained product is not an individual compound. There were three stains visible on the chromatogram: orange-red ($R_F = 0.80$) attributable to the unreacted dibenzophenoxaz-5-one, violet-red ($R_F = 0.30$) and blue-violet sticking on the starting point. Chromatography over silicagel afforded the residue of the starting dibenzophenoxazones by elution with benzene, a violet-red product with acetone—benzene (1 : 3) and finally a blue substance with 96% ethanol. The proper arylamino derivatives, yielding 65—80 mg (15% of the calculated amount) were obtained from the violet effluents by evaporation of the solvent. Compounds isolated from the ethanolic effluents have not been satisfactorily identified.

Table 1
List of prepared substances and their elemental analyses

No.	Compound	Molecular formula	M	Calculated (Found)		
				% C	% H	% N
<i>I</i>	9-anilino-5 <i>H</i> -dibenzo[<i>aj</i>]phenoxaz-5-one	C ₂₆ H ₁₆ N ₂ O ₂	388.4	80.41	4.16	7.22
<i>V</i>	13-anilino-5 <i>H</i> -dibenzo[<i>ah</i>]phenoxaz-5-one			(78.99)	(4.50)	(7.17)
				(79.80)	(4.30)	(7.24)
<i>II</i>	9-(<i>p</i> -tolylamino)-5 <i>H</i> -dibenzo[<i>aj</i>]phenoxaz-5-one	C ₂₇ H ₁₈ N ₂ O ₂	402.6	80.58	4.51	6.96
<i>VI</i>	13-(<i>p</i> -tolylamino)-5 <i>H</i> -dibenzo[<i>ah</i>]phenoxaz-5-one			(81.52)	(4.79)	(7.11)
				(81.30)	(4.70)	(7.18)
<i>III</i>	9-(<i>N</i> -1-naphthylamino)-5 <i>H</i> -dibenzo[<i>aj</i>]phenoxaz-5-one	C ₃₀ H ₁₈ N ₂ O ₂	438.5	82.15	4.14	6.39
<i>VII</i>	13-(<i>N</i> -1-naphthylamino)-5 <i>H</i> -dibenzo[<i>ah</i>]phenoxaz-5-one			(81.70)	(4.18)	(6.10)
<i>IV</i>	9-(<i>N</i> -2-naphthylamino)-5 <i>H</i> -dibenzo[<i>aj</i>]phenoxaz-5-one			(82.33)	(4.36)	(6.19)
<i>VIII</i>	13-(<i>N</i> -2-naphthylamino)-5 <i>H</i> -dibenzo[<i>ah</i>]phenoxaz-5-one			(80.98)	(4.20)	(6.02)
				(81.31)	(4.30)	(6.11)

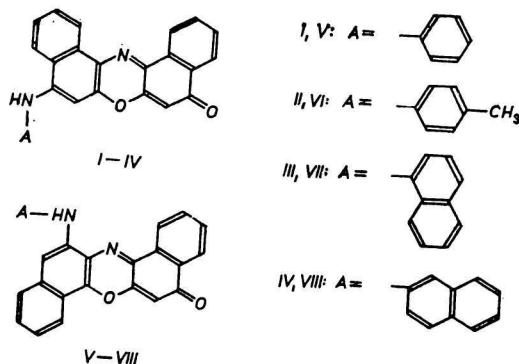
Characterization of compounds *I* – *VIII*:

The compounds as listed above did not melt up to 300°C. They are soluble in benzene, 96% ethanol, glacial acetic acid and chloroform to give violet-red solutions. They behave as acid-base indicators: acid solutions are yellow, neutral and basic solutions red-violet. With concentrated sulfuric acid the solution is intensive green-blue which, upon dilution with water turns blue, then violet and finally yellow.

Note

As far as the general use of this method is concerned it should be mentioned that good results were obtained with aromatic amines as follows: aniline, *p*-toluidine, 1-naphthylamine, 2-naphthylamine. Other aromatic amines (nitroaniline, haloanilines) either failed to react under the given reaction conditions, or a mixture of chromatographically difficultly separable coloured substances (*e.g.* anisidines) was obtained. Upon melting with their hydrochlorides many amines (aminophenol, *p*-phenylenediamine) furnish blue-violet products which make the isolation of the desired compound impossible. The reaction with *p*-aminobenzenecarboxylic acid resulted in decarboxylation.

Characteristic data and elemental analyses of the prepared compounds are listed in Table 1.



Spectral measurements

Infra-red spectra were taken with a Hilger—Watts Infracan H-900 apparatus (calibration with a polystyrene foil at 1601.4 cm^{-1}) in $4000\text{--}650\text{ cm}^{-1}$ range using KBr technique.

Ultra-violet and visible spectra were taken with a Beckman DU spectrophotometer in 96% ethanol in 1 cm cells of silica. All compounds exhibit a similar pattern in the visible region of spectra, the main maximum being at about 525 nm (ϵ_{max}) and the additional two maxima at about 495 and 565 nm (Table 2).

The ionization constant values were determined in 50% ethanol as described in [3]. The ethanol stock solutions were $1 \times 10^{-4}\text{ M}$ and to be measured they were diluted with a Sørensen buffer solution ($\text{pH} = 1.15\text{--}3.68$, $\mu = 0.1$) in a 1 : 1 ratio. Moreover, spectra were taken in an ethanolic 0.2 N-HCl and 0.2 N-NaOH, respectively. To get pH curves the absorbancies were measured at properly selected wavelengths and pH values (intervals 0.1—0.3 of the pH unit). Absorbancy values for plotting the horizontal section of the pH curves in acid medium were obtained in ethanolic solutions of hydrochloric acid at various concentrations (2 N, 1 N and 0.5 N); these values were compared with those calculated always from two points at the steep section of the pH curve and from the absorbance of a neutral molecule.

All measurements were run with a Beckman DU spectrophotometer in 1.00 cm glass cells. Solutions consisting of all components in the same proportion excepting the dyestuff

Table 2

Absorption maxima in ethanol

λ , nm	$\log \epsilon$	λ , nm	$\log \epsilon$	λ , nm	$\log \epsilon$	λ , nm	$\log \epsilon$
I		II		III		IV	
250	4.30	247	4.54	232	4.56	245 _s	4.60
276	4.28	276	4.38	260 _s	4.00	268	4.58
345	4.05	350 _s	4.02			340 _s	4.02
363	4.02						
390	3.60	390 _s	3.78				
495	3.95	495	3.99	490	3.70	495	3.95
525	4.08	525	4.08	525	3.80	525	4.04
565	3.93	565	3.90	562	3.62	565	3.88
V		VI		VII		VIII	
				232	4.60		
262	4.51	258	4.66	260	4.30	250 _s	4.48
330	4.34	330	4.38			330	4.03
490 _s	3.95	495 _s	4.02	495	3.56	495	3.59
525	4.05	525	4.10	525	3.63	525	3.75
560	3.93	560	3.95	560	3.50	560	3.51

s = shoulder

as those being measured were always used as comparison samples. pH Values were measured with a Beckman-G pH meter, tested with a 0.01 N-HCl + 0.09 N-KCl solution (pH = 2.075).

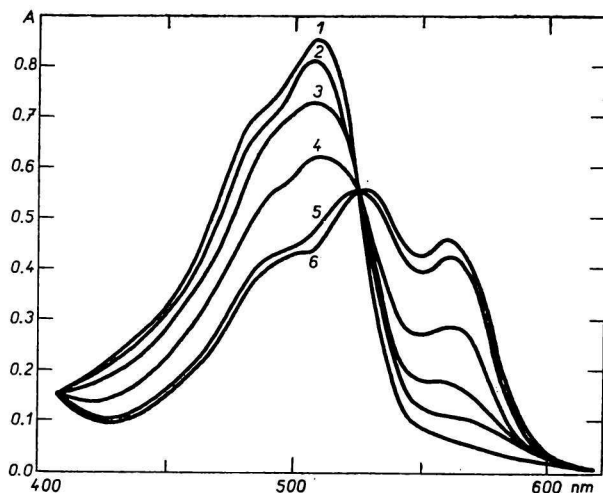


Fig. 1. Absorption curves of 9-anilino-5H-dibenzo[a,j]phenoxaz-5-one (I); 5×10^{-5} M solutions in 50% ethanol.

1. pH = 1.35; 2. pH = 1.63; 3. pH = 2.00; 4. pH = 2.51; 5. pH = 3.20; 6. pH = 4.20.

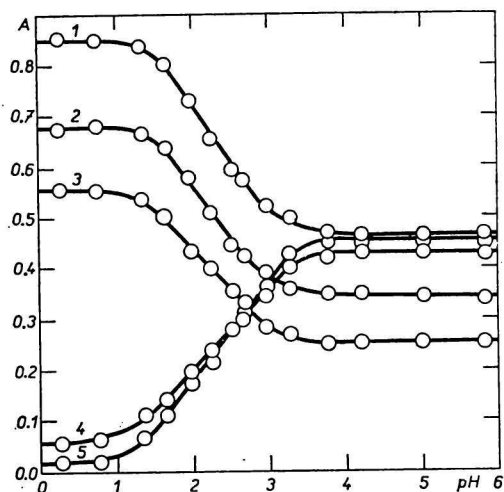


Fig. 2. pH Curves of 9-anilino-5H-dibenzo[aj]phenoxaz-5-one (I); 5×10^{-5} M solutions in 50% ethanol.

1. 505 nm; 2. 480 nm; 3. 470 nm; 4. 545 nm; 5. 560 nm.

Absorption curves of compound I at various pH values and pH curves at various wavelengths are plotted in Fig. 1 and 2. The remaining arylamino derivatives of dibenzophenoxaz-5-ones reveal a quite analogous pattern.

Table 3

Ionization constants of arylamino derivatives of dibenzophenoxaz-5-ones

Compound	$K \times 10^3$	pK
I	6.918	2.16
II	4.169	2.38
III	14.45	1.84
IV	8.318	2.08
V	9.333	2.03
VI	6.310	2.20
VII	12.05	1.72
VIII	19.05	1.92

pH Values were calculated according to [4] from the equation

$$\text{pK} = \text{pH} - \log \frac{A_1 - A}{A - A_m},$$

where A_1 stands for absorbancy of the ionized molecule, A_m is the absorbance of a neutral molecule and A is the absorbance of a mixture for a given pH of the solution; these values, representing the average of 20–25 measurements (accuracy ± 0.05) are listed together with K values in Table 3.

Furthermore, absorption curves of substances *I–VIII* were measured in various concentrated sulfuric acid. The absorption maxima were shifted in this solvent towards longer wavelengths when compared with those measured in other solvents (*e.g.* in ethanol). Absorption curves of compound *V* in various concentrated sulfuric acid are plotted in Fig. 3. The other compounds disclose a similar pattern of the absorption curves.

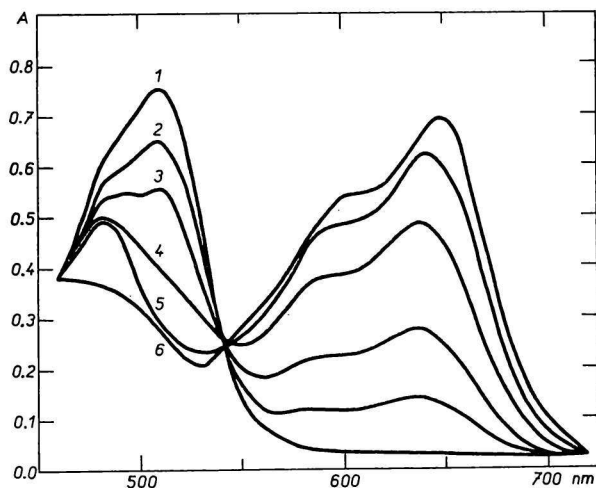


Fig. 3. Absorption curves of 13-anilino-5*H*-dibenzo[*ah*]phenoxaz-5-one (*V*) in sulfuric acid; 1×10^{-5} M solutions in various concentrated sulfuric acid.

1. 20%; 2. 30%; 3. 35%; 4. 40%; 5. 45%; 6. 95% H_2SO_4 .

It was impossible to measure absorbance in this case when the concentration of sulfuric acid was less than 20% since the dyestuff was precipitated from the solution within few minutes.

Discussion

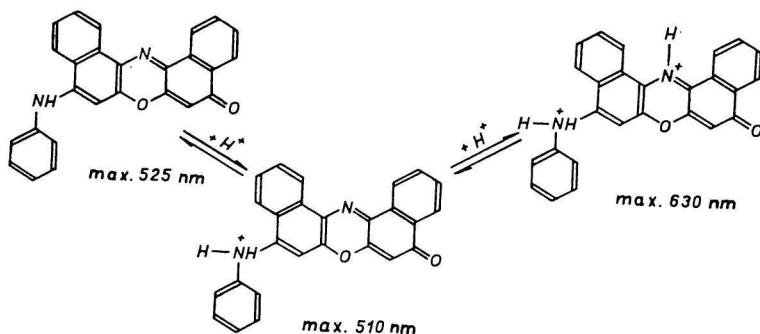
As known, the active positions of phenoxazones and benzophenoxazones are at C_5 , C_7 and C_5 , C_9 respectively, *i.e.* in *p*-positions regarding the heterocyclic nitrogen [5]. This phenomenon was evidenced by the evaluation of all experimental data so far reported by mathematical methods used in quantum chemistry and for 5*H*-dibenzo[*ah*]phenoxaz-5-one the position C_{13} was found to be significantly preferred for all types of reaction [6]. Compounds prepared as given in the present paper are the 9-arylamino derivatives of 5*H*-dibenzo[*aj*]phenoxaz-5-one (substances *I–IV*) and 13-arylamino derivatives of 5*H*-dibenzo[*ah*]phenoxaz-5-one (*V–VIII*).

The stretching vibration of the secondary amino group of the prepared substances occurred at $3380\text{--}3230\text{ cm}^{-1}$ in the infra-red spectrum, while those of anilino and *p*-tolylamino derivatives *I*, *II*, *V*, *VI* at 3380 and 3240 cm^{-1} and those of naphthylamino derivatives *III*, *IV*, *VII*, *VIII* at 3370 and 3230 cm^{-1} [7]. An intensive band in the $1636\text{--}1590\text{ cm}^{-1}$ region can be attributed to the vibration of a quinone

carbonyl group. The lowered position is explained by the polarity of the C=O bond. The vibration of the aromatic skeleton and the $\nu(\text{C}=\text{N})$ vibration appears at 1580–1490 cm^{-1} [8].

The compounds under study reveal a weak basic character and their pK values were found to vary at about 2 in 50% ethanol. The basicity increases in series *III*, *IV*, *I*, *II* and *VII*, *VIII*, *V*, *VI* similarly as it does with 1-naphthylamine, 2-naphthylamine, aniline and *p*-toluidine.

Aqueous-ethanolic solutions of compounds *I*–*VIII* are violet-red in colour showing a maximum at 525 nm. Due to protonation of arylamino group in acid solutions the maximum is hypsochromically shifted to 510 nm (see Fig. 1). On the other hand, in a strong acid medium a significant bathochromic shift is observed the maximum being at 630–650 nm associated probably with the second protonation at the heterocyclic nitrogen. The consecutive protonation of compound *I* can be demonstrated as in Chart 1:



The other compounds disclose an analogous protonation.

A continuous attention is being paid to arylamino derivatives of dibenzophenoxaz-5-ones especially from the view-point of their utilization in analytical chemistry.

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