RESEARCH ON SYNTHETIC DYES

LXXV. Condensation of α-Pyrrole Aldehyde with 1-Arylquinaldinium Salts*

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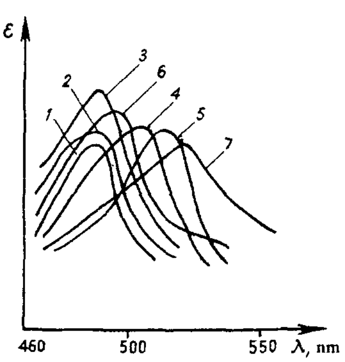
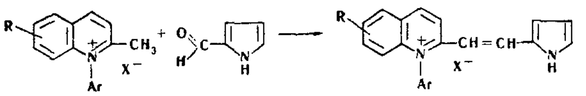
Ten new dimethine dyes of the quinostyrene type are prepared by condensing α-pyrrole aldehyde with various 1-arylquinaldinium salts. The absorption spectra of the new dyes are observed in the visible region in various neutral solvents. The dyes are shown to exhibit solvatochromism, and the spectroscopic data are analyzed.



Absorption spectra of dye I: 1) in MeOH; 2) in Me_2CO; 3) in EtOH; 4) in dioxane; 5) in $CHCl_3$; 6) in dichloroethane; 7) in benzene.

Continuing work on the synthesis of styrene dyes based on 1-arylquinaldinium salts, and on investigating their optical and biological properties [1, 2], we have condensed such salts with α-pyrrole aldehyde, and consequently obtained a series of pyrrole dimethine dyes, analogs of quinostyrenes. Equimolecular quantities of pyrrole aldehyde and the appropriate salt were reacted at 115–120° in dry pyridine, yields being 62–95%, the equation is



Dye	R	Ar	X
I	H	C_6H_5	ClO_4
II	6-CH_3	p-$CH_3C_6H_4$	ClO_4
III	5,6-benzo	C_6H_5	I
IV	5,6-benzo	p-$CH_3C_6H_4$	I
V	5,6-benzo	p-$OCH_3C_6H_4$	ClO_4
VI	5,6-benzo	o-ClC_5H_4	ClO_4
VII	5,6-benzo	β-$C_{10}H_7$	ClO_4
VIII	H	α-$C_{10}H_7$	ClO_4
IX	6-CH_3	α-$C_{10}H_7$	ClO_4
X	6-OCH_3	α-$C_{10}H_7$	ClO_4

All the new dyes were readily soluble in pyridine, ethanol, methanol, acetone, chloroform, dioxane, and dichloroethane, less soluble in benzene, and insoluble in carbon tetrachloride, hexane, ether, and water.

Solution color depended on the nature of the solvent. All the dyes exhibited negative solvatochromism, i. e., color deepening with decrease in solvent polarity (Table 1). The figure gives the absorption curves for dye I. Like the quinostyrenes, all the dyes give a single absorption maximum independent of the solvent.

Solvatochromism is known to be shown by interionic dyes, which can have two structures—one nonpolar, and the other that of a dipolar ion. The actual structure of the molecule and the color of the dye solution depending on the polarizing ability of the solvent. However a number of authors [4, 5] describe the negative centers, e. g., in the case of 1-alkylpyridinium salts. The authors explain this phenomenon by reversal of the dipole at the instant of excitation by a light quantum. The energy expended on this reversal depends on the polarizing force of the solvent, and affects the light quantum. Mushkalo [6] observed solvatochromism with cyanine dyes of noninterionic structure, with a hydrogen atom instead of a radical on the ring nitrogen atom, and explained this solely by hydrogen bonding between the NH group and the O-containing solvent, as the absorption maximum in all oxygen-containing solvents (EtOH, acetone, formamide) was the same, and higher than in chloroform. A number of other authors [7–9] regard hydrogen bonding as playing a substantial but not basic role in solvatochromism. The dimethine dyes considered in this paper do not have an interionic structure, but are dipolar compounds existing only as betaines. In addition the molecule of each dye contains the NH group of the pyrrole ring, determining the possibility of hydrogen bonding with the solvents. Analysis of the spectroscopic data of Table 1 shows that for all the dyes the deepest coloring is in benzene, and the highest in acetone. On passing from acetone to benzene the bathochromic shift of the absorption maximum is 32–40 nm. However on passing from benzene to dioxane the very small bathochromic shift of the absorption maximum which the decrease in dielectric constant (ε) would lead one to expect, is not observed, but instead a hypsochromic shift of 15–20 nm. Furthermore changing from ethanol and methanol to acetone leads to a small (3–10 nm) hypsochromic shift of the absorption maximum compared with the bathochromic shift which ε values would lead one to expect. The general relationship between the increase in absorption maximum and decrease in ε shows separation of solvents containing O, capable of hydrogen bonding with the NH group of the pyrrole ring of the molecule.

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*For part LXXIV see [1].

Table 1
Absorption Maxima of Dyes I–X in Various Solvents (nm)*

Solvent	Dielectric constant	Dye									
		I	II	III	IV	V	VI	VII	VIII	IX	X
Dioxane	2	503	503	510	511	510	520	506	508	508	508
Benzene	2.23	519	518	528	528	524	—	527	526	522	523
Chloroform	5.1	514	511	521	520	521	525	515	519	517	518
Dichloroethane	10.16	493	490	504	502	498	492	503	502	496	499
Acetone	21.45	484	482	490	488	492	493	490	489	490	489
Ethanol	25.8	490	494	497	496	494	503	495	498	493	498
Methanol	33.7	488	483	492	494	493	500	491	495	495	496

*A SF-2M instrument was used to measure the spectra.

Table 2
Properties of Dyes

Dye	Heating time, min	Appearance	Mp, °C (decomp.)	Formula	N, %		Yield, %
					Found	Calculated	
I	60	Dark cherry red crystals, with reflex	204–205	$C_{21}H_{17}ClN_2O_4$	7.08, 7.10	7.05	78.5
II	60	Cherry red needles	234–235	$C_{23}H_{21}ClN_2O_4$	6.50, 6.52	6.60	86
III	60	Brown powder	225–227	$C_{25}H_{19}IN_2$	5.79, 5.90	5.91	62.6
IV	60	Brown crystals	257–259	$C_{26}H_{21}IN_2$	5.72, 6.05	5.75	95
V	50	Dark green shining needles	258–260	$C_{26}H_{21}ClN_2O_5$	5.87, 5.90	5.88	88
VI	60	Dark red crystals with glitter	>300	$C_{25}H_{18}Cl_2N_2O_4$	5.74, 5.96	5.81	62.5
VII	120	Brown powder	211–217	$C_{29}H_{21}ClN_2O_4$	5.62, 5.85	5.77	82.7
VIII	90	Dark cherry red crystals, with reflex	210–215	$C_{25}H_{19}ClN_2O_4$	6.15, 6.34	6.27	95.5
IX	60	Dark green shining needles	221–223	$C_{26}H_{21}ClN_2O_4$	5.73, 6.00	6.08	87
X	120	Brown powder	205–208	$C_{26}H_{21}ClN_2O_5$	5.70, 5.98	5.88	95

*Crystallized from iso-BuOH; compounds V and VI can also be crystallized from EtOH, and VI and IX from acetone.

So we are inclined to explain the solvatochromism of the dyes prepared by, on the one hand, reversal of the dipole of the molecule when excited by a light quantum whose value will be less, the smaller the ε of the solvent. In other words with decrease in the solvent ε, the dye solution absorption maximum is displaced towards the longer wavelengths region. This was also found on passing from methanol to benzene. On the other hand, a considerable part is played by hydrogen bonds requiring for the same ε value, expenditures of more energy, i. e., large light quanta, resulting in a hypsochromic shift of the absorption maximum. This is particularly clearly evident in the case of benzene—dioxane, where the dielectric constant is practically the same, but there is a hypsochromic shift of the absorption maximum (Table 1).

EXPERIMENTAL

For the preparation of the 1-arylquinaldinium salts see [10–20].

α-(1-Phenylquinolyl-2)-β-(pyrrolyl-2)ethylene perchlorate (I). A mixture of 0.3 g (0.001 mole) 1-phenylquinaldinium perchlorate, 0.1 g (0.0011 mole) α-pyrrole aldehyde [13], and 2 ml dry pyridine was refluxed for 1 hr. The dye was precipitated with ether, washed with hot water, and crystallized from EtOH. Recrystallization from isobutanol gave minute dark cherry red crystals exhibiting a glitter, mp 204° (decomp), yield 0.31 g (78.5%).

The other dyes were obtained similarly. Dyes II and VI crystallized out on cooling the reaction products, and were washed with ether to remove traces of aldehyde.

Table 2 gives all the experimental results and dye properties.

The solvents for spectroscopy were purified as described in [14].

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