# POLYMETHINE DYES — JULOLIDINE DERIVATIVES

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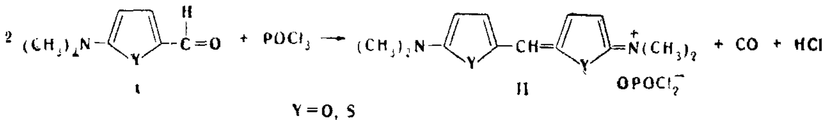
It is shown that 9-formyljulolidine reacts with phosphorus oxychloride with splitting out of the formyl group to give a symmetrical diphenylmethane dye. A comparison of data from the absorption spectra of polymethine dyes that are derivatives of dimethylaniline and julolidine indicates that the latter has greater electron-donor character.

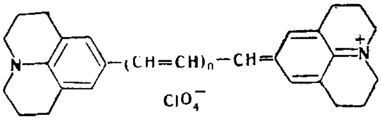
Heterocyclic analogs of p-dimethylaminobenzaldehyde, viz., 2-formyldimethylaminofurans and 2-formyldimethylaminothiophenes (I), react with phosphorus oxychloride with the evolution of carbon monoxide to give bisheteroarylmethininium salts (II) [1].



Y = O, S

p-Dimethylaminobenzaldehyde itself does not react in this way, although it readily forms a p-dimethylaminobenzal chloride [2] that is similar to the electrophilic intermediates formed from aldehydes I in the first step of the condensation [3]. This is probably explained by the lower nucleophilicity of p-dimethylaminobenzaldehyde as compared with its heteroanalogs I as a consequence of the greater aromatic character of the benzene ring as compared with the furan and thiophene rings [4].

Julolidine, which is an analog of dimethylaniline with a fixed amino group, has high electron density in the para position of the benzene ring [5], and one therefore might have expected that 9-formyljulolidine would react with phosphorus oxychloride to give a dye of the II type. The reaction does not take place under ordinary conditions (in methylene chloride at 20°C [1]), but dye IIIa is formed in appreciable yield in nitromethane. It has been previously shown from the absorption spectrum [6] that a dye with a structure of this type is formed from the corresponding hydrol in acetic acid.



III a–c

a n = 0; b n = 1; c n = 2

The higher nucleophilicity of julolidine makes it possible to obtain polymethine dyes with various electrophilic partners, with which dimethylaniline does not react under similar conditions. Thus the same dye IIIa was obtained in high yield in the reaction of julolidine with formyljulolidine, whereas its higher vinylene homologs IIIb,c are formed with malonic and glutaconic aldehyde dianil hydrochlorides. Unsymmetrical dyes IVa,b were obtained in high yields from julolidine. (See top, following page.)

Compounds III and IV make it possible to supplement the conclusions regarding the chromaticity of dyes with a julolidine ring that were drawn in [6].

Thus the approximately equal vinylene shifts of dyes IIIa-c constitute evidence that the steric hindrance in the central part of dye molecule IIIa, i.e., diphenylmethane dyes in

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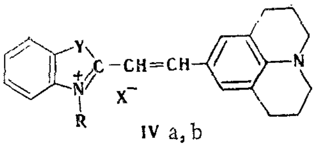
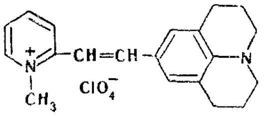


IV a,b

a $Y=C(CH_3)_2$, $R=CH_3$; b $Y=S$, $R=C_2H_5$

general, is so insignificant that it does not affect the chromaticity. In the opposite case the first vinylene shift is usually anomalous [7]. These ideas are in agreement with the high extinction of dye IIIa, as well as the hydrol of Michler's blue ($\varepsilon$ = 147,500 [6]) with the same chromophore as their analog with a fixed isopropylidene group in the plane [6].

An increase in the deviation, i.e., the deviation from the arithmetic means of the maxima of the corresponding symmetrical dyes, is observed for dyes IV on passing from the indolenine to the benzothiazole dye ($\Delta\lambda_{max}$ 7 and 12 nm). From the magnitude of the deviation one can form a judgement regarding the Brooker basicity [8] of the rings of the dyes or regarding their electron-donor character [9], i.e., regarding the tendency of the ring to transmit the electron density to the chromophore and the second ring. The indolene ring is less basic than the benzothiazole ring [8], and the greater deviation of dye IVb indicates that the julolidine ring is less basic than these rings. Dye V with a strongly basic 2-pyridine ring was obtained in order to determine the location of the 9-julolidine ring in the ring-basicity series [10].



V

Judging from the deviation of this dye ($\Delta\lambda_{max}$ 80 nm) the julolidine ring occupies a position that is intermediate between the indolenine ($\Delta\lambda_{max}$ 43 nm [11]) and 5-dimethylamino-2-thiophene ($\Delta\lambda_{max}$ 50 nm [12]) rings and the dimethyl-4-aniline ring ($\Delta\lambda_{max}$ 127 nm [8]), which is the least basic of the nitrogen-containing rings. Thus fixing of the amino group in the plane of the benzene ring in julolidine improves the conjugation of the pair of electrons of the nitrogen atom with the benzene ring.

The 9-julolidine and 4-dimethylaniline rings graphically illustrate the difference between the Brooker basicity and ordinary basicity, i.e., the ease of the addition of a proton by the bases from which these rings are constructed. In contrast to the rings in the dyes, in julolidine the greater shift of the electron density to the benzene ring lowers the basicity ($pK_a$ 3.6 [13]) as compared with dimethylaniline ($pK_a$ 3.8 in 50% ethanol [4]).

## EXPERIMENTAL

The absorption spectra of the dyes were measured with SF-10 and SF-8 spectrophotometers.

2,3,5,6,7,9-Hexahydro-9-[(2,3,6,7-tetrahydro-1H,5H-benzo[i,j]quinolizin-9-yl)methylene]-1H-benzo[i,j]quinolizinium Perchlorate (IIIa). A) A 154-mg (1 mmole) sample of phosphorus oxychloride was added to a solution of 603 mg (3 mmole) of 9-formyljulolidine [15] in 5 ml of nitromethane, and the mixture was allowed to stand for 24 h. The solvent was removed by distillation *in vacuo*, the residue was dissolved in 10 ml of boiling absolute ethanol containing several drops of acetic acid, and 500 mg of sodium perchlorate was added. The mixture was cooled, and the dye crystals were removed by filtration to give 160 mg (35%) of a product with mp 207°C (dec., from acetic acid). UV spectrum (in nitromethane), $\lambda_{max}$ $(\varepsilon\cdot 10^{-4})$: 637 nm (18.6). Found: Cl 7.9; N 6.5%. $C_{25}H_{29}ClN_2O_4$. Calculated: Cl 7.8; N 6.1%.

B) A mixture of 100 mg (0.3 mmole) of julolidine perchlorate, 60 mg (0.3 mmole) of 9-formyljulolidine, and 3 ml of methanol was refluxed for 3 min, after which it was cooled, and the precipitated crystals were removed by filtration to give 80 mg (47%) of a product with mp 207°C (dec., from acetic acid). The quantitative absorption spectra of samples obtained by the two methods coincided.

2,3,5,6,7,9-Hexahydro-9-[3-(2,3,6,7-tetrahydro-1H,5H-benzo[i,j]-quinolizin-9-yl)-2-propenylidene]-1H-benzo[i,j]quinolizinium Perchlorate (IIIb). A mixture of 100 mg (0.5 mmole) of julolidine, 150 mg (0.5 mmole) of julolidine perchlorate, 130 mg (0.5 mmole) of malonic aldehyde dianil hydrochloride, and 3 ml of acetic anhydride was refluxed for 3 min, after which it was cooled, and the precipitated crystals were removed by filtration to give 120 mg (50%) of a product with mp 239°C (dec., from nitromethane). UV spectrum (in nitromethane), $\lambda_{max}$ ($\varepsilon \cdot 10^{-4}$): 740 nm (21.8). Found: Cl 7.2; N 6.0%. $C_{27}H_{31}ClN_2O_4$. Calculated: Cl 7.4; N 5.8%.

2,3,5,6,7,9-Hexahydro-9-[5-(2,3,6,7-tetrahydro-1H,5H-benzo[i,j]quinolizin-9-yl)-2,4-pentadienylidene]-1H-benzo[i,j]quinolizinium Perchlorate (IIIc). A mixture of 300 mg (1 mmole) of julolidine perchlorate, 140 mg (0.5 mmole) of glutaconic aldehyde dianil hydrochloride, 100 mg of sodium acetate, and 3 ml of acetic anhydride was refluxed for 3 min, after which it was cooled, and the precipitated crystals were removed by filtration to give 125 mg (50%) of a product with mp 244°C (dec., from nitromethane). UV spectrum (in nitromethane), $\lambda_{max}$ ($\varepsilon \cdot 10^{-4}$): 849 nm (22.0). Found: Cl 7.0; N 5.7%. $C_{29}H_{33}ClN_2O_4$. Calculated: Cl 7.0; N 5.5%.

2-[2-(2,3,6,7-Tetrahydro-1H,5-H-benzo[i,j]quinolizin-9-yl)ethyl]-1,3,3-trimethyl-3H-indolium Perchlorate (IVa). A mixture of 150 mg (0.5 mmole) of julolidine perchlorate, 100 mg (0.5 mmole) of 1,3,3-trimethyl-2-formylmethyleneindoline, and 3 ml of acetic anhydride was heated to the boiling point, after which it was cooled, and the precipitated crystals were removed by filtration and washed with boiling ethanol and ether to give 165 mg (72%) of a product with mp 242°C (dec.). UV spectrum (in nitromethane), $\lambda_{max}$ ($\varepsilon \cdot 10^{-4}$): 580 nm (10.7). Found: Cl 7.8; N 6.1%. $C_{25}H_{29}ClN_2O_4$. Calculated: Cl 7.8; N 6.1%.

2-[2-(2,3,6,7-Tetrahydro-1H,5H-benzo[i,j]quinolizin-9-yl)-ethenyl]-3-ethylbenzothiazolium Perchlorate (IVb). A mixture of 150 mg (0.5 mmole) of julolidine perchlorate, 170 mg (0.5 mmole) of 2-methyl-3-ethylbenzothiazolium tosylate, 150 mg (1 mmole) of ethyl orthoformate, and 5 ml of acetic anhydride was refluxed for 5 min, after which it was cooled, and the precipitate was removed by filtration to give 115 mg (51%) of a product with mp 231°C (dec. from acetonitrile). UV spectrum (in nitromethane), $\lambda_{max}$ ($\varepsilon \cdot 10^{-4}$): 572 nm (8.8). Found: Cl 7.8; S 6.6%. $C_{23}H_{25}ClN_2O_4S$. Calculated: Cl 7.7; S 6.9%.

2-[2-(2,3,6,7-Tetrahydro-1H,5H-benzo[i,j]quinolizin-9-yl)ethenyl]-1-methylpyridinium Perchlorate (V). This compound was obtained by the method in [5]. UV spectrum (in nitromethane), $\lambda_{max}$ ($\varepsilon \cdot 10^{-4}$): 510 nm (3.8).

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