

## Solvent Shifts of Certain Aminoarylpyrylium Salts

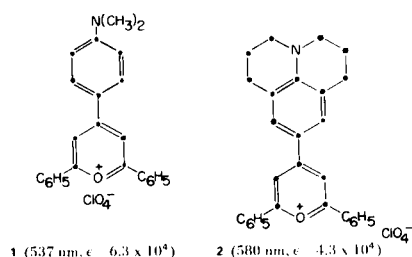
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The incorporation of the julolidine ring system into a wide variety of dyes leads to a large bathochromic shift of the longest-wavelength absorption band in comparison to other dialkylamino groups (1-3). This shift is usually ascribed to the improved conjugation brought about by the methylene bridges in the julolidine rings (3). The explanation does not seem sound to us, since any dialkylamino group in the absence of undue steric effects should show complete overlap of the nitrogen free electrons with the  $\pi$  system. We now offer a different possibility for this bathochromic shift that applies to at least one type of dye.

In a continuation of the study of pyrylium dyes containing amino functions (4), we prepared **1** and its julolidyl counterpart **2** and, as expected, **2** showed absorption at longer wavelengths (spectrum in acetonitrile).



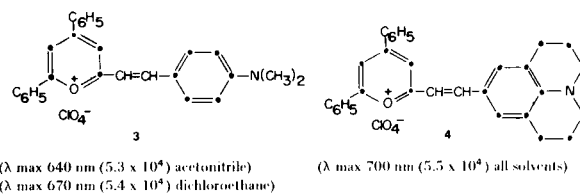
We ran the spectra of **1** and **2** in a variety of solvents and found that the position of the long-wavelength absorption of **2** was completely insensitive to the polarity of the solvent, while the  $\lambda$  max of **1** varied from 537 nm in polar solvents such as alcohol, acetonitrile, and dimethylsulfoxide to 554 nm in relatively nonpolar solvents such as chloroform and dichloroethane. The limited solubility of **1** in nonpolar solvents precluded a more thorough study of solvent effects. Dyes corresponding to **1**, with diethylamino and dipropylamino groups, showed absorptions identical with that of **1**.

A model of **2** shows that one of the saturated rings of the julolidine is puckered above the plane of the benzene ring and the other below the plane. The nitrogen atom is indeed constrained to complete planarity with the benzene ring, but it is also apparent that the free electrons of the nitrogen atom are well shielded by an extremely bulky

group. This suggests the possibility that the nitrogen electrons in **2** cannot interact with the solvent, and that the absence of these interactions causes the bathochromic shift. On the other hand, **1** is susceptible to solvation, and this is reflected in the variation of  $\lambda$  max with solvents of different polarity. An extreme case of a solvent interaction is demonstrated when the spectra of **1** and **2** are run in formic acid. The  $\lambda$  max of **1** is not changed from its value in polar solvents, but  $\epsilon$  is only  $2.2 \times 10^3$  owing to appreciable protonation of the amino group. The spectrum of **2** in formic acid is identical with the one in acetonitrile showing that protonation of the nitrogen does not take place.

The effects of solvents on the absorption of **1** and **2** could also be explained on the basis of the complete delocalization of the nitrogen free pair in **2**. However, steric inhibition of solvation should not be overlooked, since the bathochromic shift caused by the julolidyl group may be due to a combination of effects.

Another example which compares the spectra of a dimethylamino with a julolidyl dye is given for **3** and **4**. The solvent shifts are more pronounced because the dyes absorb at considerably longer wavelengths than **1** and **2**.



## EXPERIMENTAL

The spectra were determined on a Model 15 Carey spectrometer. Compound **1** was prepared as described previously (5) and **2** was prepared by the same procedure; m.p. 290-291° (from acetonitrile).

*Anal.* Calcd. for  $\text{C}_{29}\text{H}_{26}\text{ClNO}_5$ : C, 69.2; H, 5.2; N, 2.8. Found: C, 68.9; H, 5.0; N, 2.7.

Compound **3** was prepared by the published procedure (6), and **4** was prepared in an analogous way, m.p. 220-221° (from acetonitrile).

*Anal.* Calcd. for  $\text{C}_{31}\text{H}_{28}\text{ClNO}_5$ : C, 70.3; H, 5.3; N, 2.7. Found: C, 70.5; H, 5.1; N, 2.5.

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