

THE EFFECT OF *N*-METHYLATION (QUATERNIZATION) ON THE ELECTRONIC SPECTRA OF SOME *N*-HETEROAROMATIC CATIONS*

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On replacement of an NH_2 proton in aniline by methyl the absorption bands near 285 and 234 $\text{m}\mu$ are displaced to longer wavelengths by about 11 $\text{m}\mu$; the band near 197 $\text{m}\mu$ is almost unaffected (Ley and Specker 1939; Tunnicliff 1948; Robertson and Matsen 1950); the shifts may be attributed to enhancement of the electron-donating effect of the amino group by the electron-donating effect of the methyl group (Robertson and Matsen 1950).

It seemed of interest to examine the somewhat different situation encountered in the comparison between *N*-protonated and quaternary *N*-methylated *N*-heteroaromatic cations. The ultraviolet spectra of the pyridinium, quinolinium, and isoquinolinium ions and of their *N*-methyl derivatives were therefore studied. Reasonably detailed spectra of the isoquinolinium ion and its *N*-methyl derivative were previously recorded by Osborne, Schofield, and Short (1956). The spectral shifts due to the methyl group in these ions (Table 1) are found to be in the same direction as, but smaller than, those observed for *N*-methylanilines.

Proton addition to pyridine shifts the α -band (Andon, Cox, and Herington 1954) slightly (by 1.5 $\text{m}\mu$) to shorter, and the p -band, by ~ 3 $\text{m}\mu$, to longer wavelengths (Pickett *et al.* 1956; Schubert *et al.* 1959). The replacement of the proton attached to nitrogen by methyl shifts both bands to longer wavelengths, by greater amounts. Proton addition to quinoline (Albert, Brown, and Cheeseman 1951) and to isoquinoline (Ewing and Steck 1946) shifts all bands to somewhat longer wavelengths, and *N*-methylation in the ions produces further (usually smaller) shifts in the same direction.

In the absence of steric complications methyl groups normally produce bathochromic shifts of $\pi \rightarrow \pi^*$ bands (the hypsochromic shift of the α -band due to the methyl group in γ -picoline and in the γ -picolinium ion (Andon, Cox, and Herington 1954) being exceptional). Such shifts have been variously attributed to inductive and hyperconjugation effects (Mulliken 1939; Walsh 1947) or to the fact that a methyl group constitutes an additional polarizable unit (Spinner 1961).

The shifts observed among the ions studied here are not likely to arise simply from alterations in charge distribution due to the extra methyl group. In view of the smallness of the shift obtained when the heterocyclic nitrogen atom acquires a positive charge as a result of protonation, the slight reduction in this charge that results from the replacement of the *N*-proton by the (inductively) electron-donating

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methyl group should not produce any appreciable shift. Hyperconjugated structures such as $\text{H}^+\text{CH}_2 = \text{N}^+(\text{CH})_5^-$ leave the nitrogen atom positively charged and should not play an appreciable part.

An alternative explanation in terms of steric hindrance to solvation is equally unsatisfactory: the *N*-protonated ions are much more strongly solvated than the un-ionized bases, yet the shift resulting from cation formation is small; that due to interference with solvation by the *N*-methyl group should be negligible.

TABLE 1
WAVELENGTHS AND INTENSITIES OF BAND MAXIMA* OF CATIONS IN WATER

Ion†	Wavelengths and Intensities	β -Band‡	<i>p</i> -Band‡	α -Band‡
Pyr	λ		200.5§	251, 255.5, 261
	Log ϵ			3.63, 3.70, 3.53
<i>N</i> -Me- Pyr	λ		208	254, 259, 263, 265
	Log ϵ		3.51	3.56, 3.65, 3.54, 3.52
Qui	λ	233, 236		307, 313
	Log ϵ	4.50, 4.45		3.76, 3.79
<i>N</i> -Me- Qui	λ	234.5, 236.5		310, 315
	Log ϵ	4.47, 4.48		3.86, 3.88
i-Qui	λ	226.5	266, 274, 285	325, 332
	Log ϵ	4.57	3.29, 3.30, 3.01	3.61, 3.64
<i>N</i> -Me- i-Qui	λ	231	269, 276, 289	327, 335
	Log ϵ	4.70	3.41, 3.42, 3.10	3.60, 3.63

* Wavelengths, λ , are in $\text{m}\mu$, intensities in molecular extinction coefficients, ϵ .
Inflexions in italics.

† Pyr, pyridinium; qui, quinolinium; i-qui, isoquinolinium; *N*-Me-, *N*-methyl derivative.

‡ Clar's(1952) nomenclature.

§ Not accessible on instruments used by author; value quoted from Schubert *et al.* (1959).

|| It is debatable whether this band may legitimately be compared with the *p*-bands in polycyclic systems.

The vibrational structure of the electronic absorption bands is a little more clearly developed for the *N*-methylated than for the *N*-protonated ions, presumably because solute/solvent interaction is a little weaker in the former. The α -band systems of the pyridinium and isoquinolinium ions and their *N*-methyl derivatives show appreciable vibrational anharmonicity, the second interval always being smaller (in cm^{-1}) than the first one. The vibrational structure is, however, not sufficiently well resolved for detailed comparisons between the *N*-protonated and the *N*-methylated ions to be profitable.

The quaternary salts chosen for examination were the chlorides, rather than the much more readily manipulable iodides, so that no complications due to possible

formation of complexes would arise. However, the spectrum of *N*-methyloquinolinium iodide was found to be identical with that of the chloride (if the absorption by iodide ion was compensated for in the reference cell); thus, no complex is formed in aqueous solution, even in the case of the iodide. The spectra of the quaternary ions were, furthermore, found to be unaffected by the pH value over the range 0 to 14.

The quaternary chlorides were prepared from the iodides by ion exchange with silver chloride or lead chloride; analysis showed them to be anhydrous (they were all highly deliquescent unless pure and dry). *N*-Methylpyridinium chloride (deliquescent), *ex isopropanol*, had m.p. 110–112°C; *N*-methylquinolinium chloride (nonhygroscopic), *ex dioxan/ethanol* (2 : 1 by vol.) had m.p. 170·5–172°C; *N*-methylisquinolinium chloride (somewhat hygroscopic), *ex isopropanol*, had m.p. 80·5–81°C.

Spectra were measured with a Perkin–Elmer spectracord model 4000-A and peak intensities checked with an Optica CF4 manual spectrophotometer. All solutions were examined at pH = 1.

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