The Effect of Methyl Substitution on the Absorption Maxima of Quinoline Derivatives

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In 1947, Herzfeld(1) proposed a theory dealing with the effect of various kinds of substitutions on the position of the electronic absorption maxima of conjugated systems. According to his theory, the effect of substitution by the radicals containing two $2p\pi$ electrons as in the case of -Cl, -NH_2, -OH, etc. must always be bathochromic. Along the line of his reasoning, the effect of methyl substitution must be expected also to be more or less bathochromic, since the two bonding electrons between C and H will interact with the electrons of conjugated systems. In conformity with this expectation, there are extensive data showing that the absorption bands of $2p\pi$ electron systems are shifted redward by the effect of the methyl substitution.

In the course of our systematic study on spectroscopic properties of some conjugated systems, we have found, however, that some conjugated systems having quinoline nucleus represent exceptions to the above rule. The object of this paper is to present such examples and to describe some rule governing the effect of substitution on the position of absorption maxima of these compounds.

Experimental

The compounds investigated were methyl derivatives of quinocyanines, tetrahydro-quinolines, benztetrahydro-quinolines and their picrates. Absorption spectra were measured by photoelectric method, with an Adam Hilger monochrometer. The solvent used was ethanol, and the thickness of the cell compartment was 1 cm.

Results

The data obtained for quino-cyanines are listed in Table 1. As may be seen from this table, the substitution of methyl group in position 2 of quinoline nucleus shifts the absorption maxima redward, while the reverse is the case when the substitution is made at position 4. The absolute values of the shift caused by the substitution into position 2 are larger than those caused by the substitution in position 4.

With methyl derivatives of benztetrahydroquinoline, we obtained the results given in Table 2. Since the methyl groups in positions 5, 6, 7 and 8 will not directly interact with the conjugated system, the effect of the substitution into these positions is expected to be less than the effect of the 2-, 3- and 4-substitutions. The data obtained confirmed this expectation. It may be remarked that the absorption maxima of 2-

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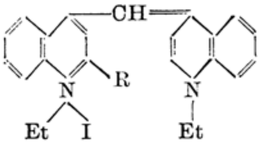
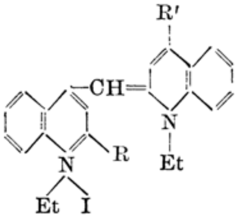
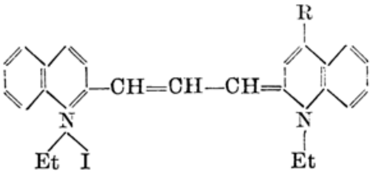
(1) K. F. Herzfeld, *Chem. Rev.*, **41**, 233 (1947).

Table 1

Absorption Maxima of Methyl Substituted Quino-cyanines

Compounds	*R*	*R'*	λ(A.)	Δλ
	$-H$	—	5910	0
	$-CH_3$	—	5980	+70
	$-H$	$-H$	5580	0
	$-CH_3$	$-H$	5600	+20
	$-H$	$-CH_3$	5570	−10
	$-H$	—	6070	0
	$-CH_3$	—	6030	−40

methyl derivatives are situated at longer wavelengths than the maxima of 2, 4-dimethyl derivatives.

In table 3, are shown the data obtained for the picrates of methyl substituted benztetrahydro-quinolines. These compounds have two absorption bands, of which the one situated at longer wavelength is obviously due to the picric acid which is either in combined or in free state in the solution investigated. (See Table 3) In respect to the second absorption bands, the effects of methyl substitutions in various positions were found to follow virtually the same rule as was the case with benztetrahydro-quinolines.

These findings tell us that the same rule found for the absorption maxima of quino-cyanines may be applicable to benztetrahydro-quinolines and their picrates, and it may be that this behavior of the shift of absorption band by methyl substitution is the charateristic of the conjugated system having pyridine ring as a part.

In connection with the above data, it seems worthwhile to present the data of the melting points and the solubilities (%) in water of methyl derivatives of quinoline-iodoethylate. They are listed in Table 4, which shows that a rule analogous to the above mentioned one is found also in respect to these physical quantities; namely (1) the methyl substitution into position 2 enhances the melting point but lowers the solubility of quinoline-iodoethylate, while the substitution into position 4 shows the contrary effect, and (2) the

Table 2

Methyl Derivatives of Benztetrahydro-quinoline

Positions of methyl groups.	λ(A.)	ε
2, 7-	2840	18, 000
2-	2800	16, 000
2, 4, 6-	2800	13, 000
2, 4-	2760	14, 000
none	2730	12, 000
Pyridine	2550	9, 000

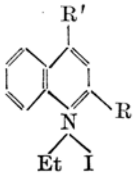
Table 3

The Picrates of Methyl Derivatives of Benztetrahydro-quinoline

Position of Methyl Groups	First Band (A.)	Second Band (A.)	ε (Second Band)
2, 7-	3630	2810	21, 000
2-	3630	3810	20, 000
2, 4-	3620	2780	21, 000
None	3640	2730	14, 000
8-	3630	2690	16, 000
Picric Acid	3630	—	—

Table 4

Melting Points and Solubilities of Quinoline-iodoethylates

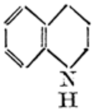
Compounds	*R*	*R'*	m.p.(°C.)	Solubility at 25°C.(%)
	$-H$	$-CH_3$	141	19.8
	$-H$	$-H$	156—157	8.1
	$-CH_3$	$-CH_3$	222—224	1.6
	$-CH_3$	$-H$	237—238	0.6

magnitude of the former effect is larger than that of the latter effect, as will be seen from the data of 2, 4-dimethyl-quinoline.

In contrast to the cases described above, the effect of methyl substitution in tetrahydroquinoline is always bathochromic as is shown in Table 5. This may be explicable if we realize that in these compounds the pyridine moiety in quinoline nucleus is saturated and, therefore, they may be regarded as alkyl derivatives of aniline from the viewpoint of conjugated system. In these compounds, the magnitude of bathochromic shift caused by methyl substitution is most pronounced in position 6, followed by 7 and then 8. It should also be remarked that the values of molar extinction coefficient ε of these compounds decrease with the shift of absorption maxima to longer wave-lengths, a phenomenon which is in quite reverse direction to that observed in the case of benztetrahydro-quinolines.

Table 5

Methyl Derivatives of Tetrahydro-quinoline



Positions of Methyl Groups.	λ(A.)	ε
2, 6-	3100	1, 100
2, 4-	3040	1, 600
2, 4, 6-	3030	800
2, 7-	3030	1, 900
2, 4, 7-	3000	1, 300
7-	3000	1, 600
8-	2990	2, 000
2, 4, 8-	2950	2, 600
2, 8-	2920	3, 000
Aniline	2840	—

Conclusion

The effect of methyl substitutions on the position of absorption maxima of some quinoline derivatives was investigated and it was found that there exists a certain empirical rule governing the relationship between the position of substitution and the shift of absorption band. Attention was called to the fact that in some quinoline derivatives the methyl substitution causes a hypsochromic shift of absorption band, a fact which is contrary to the expectation based on the now prevailing theory. The analysis of this phenomenon may be highly relevant from the standpoint of the theory of hyperconjugation.

The writers wish to express their earnest thanks to Prof. Eiji Ochiai and Mr. Yoshihisa Mizuno for the samples of quinoline derivatives used in the present investigation and also to Prof. Hiroshi Tamiya for his guidance and special interest in our study.

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