The Absorption Spectra of Styryl Dyes

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Spectroscopic properties of polymethine dyes have been the subject of repeated investigations, especially because of the interest concerning the functional relationships between the wavelength of absorption maxima and the length of conjugated systems. It has been known that the cyanine dyes show the absorption maxima that are in approximately linear relationship to the length of conjugated systems, while in the case of polyene dyes, such as diphenyl polyenes, the squares, of the wavelengths of absorption maxima are related almost linearly to the length of conjugated systems. To account for these phenomena several theories have already been proposed, among which the one set forth by Herzfeld and Sklar⁽¹⁾ seems to be most coherent and cogent.

Recently we have reported that the styryl dyes, a category of polymethine dyes which is structurally different from cyanine and polyene dyes, show an intermediate spectroscopic property between those of the latter two groups.⁽²⁾ It appears, therefore, worthwhile to investigate whether the theory of Herzfeld and Sklar might be extended also to the cases of this intermediate type of polyene dyes.

Experimental

The styryl dyes investigated are listed in Table 1. They were synthesized by the reaction of dimethylamino-benzaldehyde with mono- or di-methylpyridine-iodoethylates or mono- or di-methylquinoline-iodoethylates, using pyperidine as the condensation reagent.*

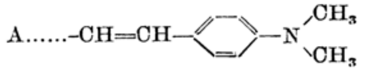
Observations of absorption spectra in a visible region were carried out by the photoelectric method, using an Adam Hilger monochrometer, the accuracy of which was about ±10 A. Throughout the experiments ethanol was used as the solvent.

Results and Discussions

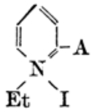
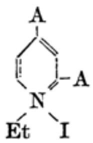
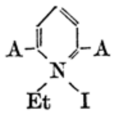
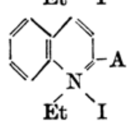
The observed values of absorption maxima of the dyes are listed in the third column of Table 1. On examining the data obtained, it becomes apparent that the disubstituted compounds (II), (III) and (VI) have two absorption bands, while monosubstituted compounds (I), (IV) and(V) have only one absorption band in the visible region.

Table 1

The Absorption Maxima of Styryl Dyes



$A\ldots\ldots\text{-}CH{=}CH\text{-}C_6H_4\text{-}N(CH_3)_2$

No.	Compounds	$\lambda_{obs.}$(in A.)	$\lambda_{cal.}$(in A.)
I		4670	4880
II		4350 5100	— —
III		4100 4970	4160 —
IV		5270	—

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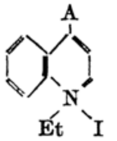
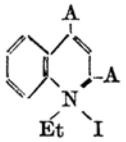
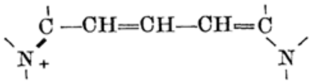
(1) Herzfeld and Sklar, *J. Chem. Phys.* **10**, 508, 521 (1942).

(2) K. Snibata, This Bulletin, **25**, 378 (1952).

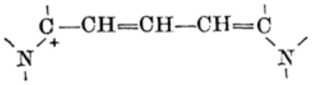
* In the synthesis of disubstituted styryl dyes such as compound (II) in Table 1, certain amounts of monosubstituted compounds were also formed as byproducts. These byproducts were removed by the chromatographic adsorption method.

V		5460	5660
VI		5000	4620
		5710	5570

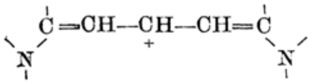
This result is of special interest from the viewpoint of the theory of Herzfeld and Sklar. According to them, the color of symmetric cyanine dyes arises from the transition between the two states caused by the resonance of two ground structures with equal energies. Let us consider trimethine dye (A) as an example of symmetric cyanine dyes. Though quite a number of resonance structures can be assumed by this substance, we may, for the present purposes, restrict our considerations to the following five structures of low energy levels.



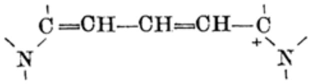
(A)



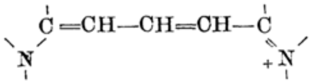
(B)



(C)



(D)



(E)

Of these resonance structures, two structures (A) and (E) have equal and lowest energies; that is, the ground level corresponding to the zero-order eigen functions is degenerate. In the first approximation by the method of valence bond eigen function, these two structures may be shown not to interact with each other directly. Their interaction results from the indirect interaction through other structures (B), (C) and (D) with higher energies; namely, (A) interacts with (B), (B) with (C), ... , and (D) with (E). As a result of these interactions, the two degenerate ground levels split into two states with different energies. The situation is graphically shown in Fig. 1. The color of symmetric cyanine dyes is attributed to the transition between these split levels.

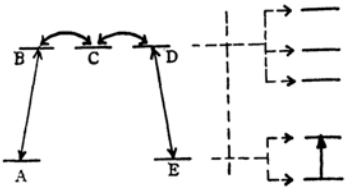
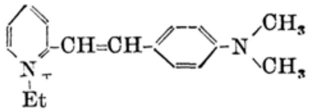
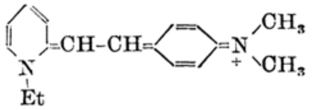


Fig. 1.

The same line of reasoning may be applied to the interpretation of the number of absorption bands of styryl dyes. For monosubstituted styryl dyes, we may consider two structures with lowest energies apart from the other levels. In contrast to the case of symmetric cyanine dyes, these two structures have slightly different energies, because the molecules are asymmetric. For example, the two resonance structures to be assumed for compound (I) will be

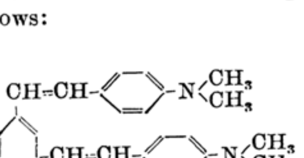


(F)

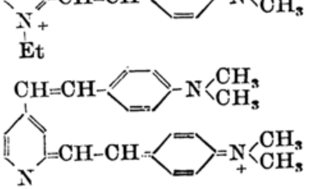


(G)

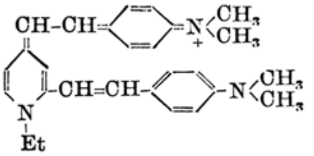
As a result of resonance, the height of energy levels will be changed, but the resulting levels of these two structures may be considered to be by far lower than those of other higher levels, since we may assume that the levels corresponding to the structure with the formal charge at the carbon atom is sufficiently higher than the levels of the structure with the charge at the nitrogen atom. The same consideration will lead to the inference that the number of levels with rather low energies must be three in disubstituted styryl dyes; for example, the structures to be assumed for compound (II) are as follows:



(H)



(J)



(K)

The absorption of light caused by the transitions between (F) and (G) as well as between (H), (J) and (K) may all be in the visible region. Thus, the fact that the monosubstituted dyes show one absorption band and the disubstituted dyes two in the visible region has received a rational explanation.

On inspecting the data given in Table 1, the following facts will also be noticed.

i) The wavelengths of absorption maxima of the dyes having quinoline nucleus are always greater than those of the corresponding dyes with pyridine nucleus.

ii) The bathochromic effect of the redical A at position 4 of pyridine or quinoline nucleus is always stronger than the effect of the same radical at position 2.

In the preceding paper these relations have been explained on the basis of the "color factor", which was proposed as a convenient parameter to account for the spectral denpendency on the lengths of conjugated systems of many cyanine and polyene dyes. In the following an attempt will be made to elucidate quantitatively the spectroscopic properties of these substances from the viewpoint of the method of valence bond eigen function. It should be noted in advance that we are obliged to make a rather crude approximation because of the complex nature of the molecules of styryl dyes.

Let us consider compound (I) and assume that the energies of the eigen functions corresponding to the structures (F) and (G) are e and f, respectively. We shall neglect the interactions between many states other than (F) and (G) and assume the effective interaction energy between (F) and (G) to be α, though more precisely, these stepwise interactions must be taken into account. The height E of the levels resulting from the resonance in question can be obtained by solving the following secular determinant;

$$\begin{vmatrix} e-E & \alpha \\ \alpha & f-E \end{vmatrix} = 0 \qquad (1).$$

The same assumption will lead to the following equation* (2) for the energy of compound (III).

$$\begin{vmatrix} f-E & \alpha & 0 \\ \alpha & e-E & \alpha \\ 0 & \alpha & f-E \end{vmatrix} = 0 \qquad (2).$$

For compound (II), the interaction energy between (H) and (J) will also be α, but the interaction energy between (H) and (K), which may be denoted by β, must be assumed to be smaller than α, if we take into account the length of the conjugated double bond. Hence, the equation for the energy of the states of compound (II) will be

$$\begin{vmatrix} f-E & \alpha & 0 \\ \alpha & e-E & \beta \\ 0 & \beta & f-E \end{vmatrix} = 0 \qquad (3).$$

The solutions of equations (1), (2) and (3) are graphically shown in Fig. 2, in which dotted arrows indicate resonance.

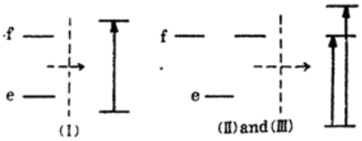


Fig. 2.

Using equations (2) and (3), the values of parameters, α, β and f-e, were calculated from the data of the two absorption bands of compound (II) and the band at the longer wavelength of compound (III). The obtained values ($\alpha=6258\ \text{cm}^{-1}$., $\beta=5207\ \text{cm}^{-1}$. and $f-e=16228\ \text{cm}^{-1}$.) were used for the calculation of the wavelength of the absorption maximum of compound (I) and that of compound (III) at a shorter wavelength.

As to compounds (IV), (V) and (VI), we assumed that the interaction energies α and β are the same as in the above cases but the energy difference f-e has a different value, which was calculated from the data of compound(IV). This value of f-e ($f-e=14261\ \text{cm}.^{-1}$) was assumed to be applicable also to compounds (V) and (VI).

The calculated value of the wavelength of absorption maximum of each compound is shown in the fourth column of Table 1. As will be seen, the coincidence between calculated and observed values is fairly good in spite of the crude approximation we have made. These results seem to substantiate the theory of Herzfeld and Sklar, showing that it may well be applied also to the cases of asymmetric conjugated systems. The results obtained give us also ground for the conclusion that the absorption bands shown by styryl dyes in a

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* In this equation, the interaction between the two states, which have the positive charge at the nitrogen atom of amino group, was ignored.

visible region are due to the transition between electronic levels, and not to the transition to the split levels of one electronic level caused by the vibrational splitting.

The author wishes to express his earnest thanks to Dr. M. Katayanagi for his generous gift of the intermediate compounds for the synthesis of dyes, and to Prof. H. Tamiya for his valuable guidance and his constant interest in this study.

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