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A Study of the Vinylene Shifts in Polymethine Dyes with Sulphur-Containing End-Groups

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ABSTRACT

A series of polymethine dyes with sulphur-containing end-groups have been investigated by spectral and quantum-chemical methods. The shift in absorption maximum with lengthening of the polymethine chain has been shown to depend on the nature of the first member of the vinylene series. Possible causes of this are discussed and a correlation between the first vinylene shift and the electron density change on excitation at the sulphur atoms has been established.

1 INTRODUCTION

Polymethine dyes (PMD) can be represented by the general formula:

$$G^{+}\text{—}(CH\text{=}CH)_{n}\text{—}CH\text{=}G \quad X^{-}$$

where n is the number of vinylene groups in the polymethine chain, G is some end-group (the nuclei) and X^{-} is an acid anion. As a rule, absorption bands of high intensity are observed in the spectra of such dyes in the visible and near-IR regions. These bands are considered to correspond on a $\pi \rightarrow \pi^{*}$ electron transition in the polymethine chromophore and a shift of the first absorption band maximum to the longer wavelength occurs with lengthening of the polymethine chain (PC). The shift produced by one vinyl group is called the 'vinylene shift' (V).

$$V = \lambda_{n} - \lambda_{n-1} \tag{1}$$

The experimental value of the vinylene shift is about 100 nm,[1] and theoretical estimations based on a direct quantum-chemical approach give the same value.[2,3] Fabian & Zahradnič[4] have made more detailed calculations of the vinylene shift and have shown that a decrease in V values, calculated via PPP and CNDO/2 approximations, occurred with PC lengthening.

Dähne & Radeclia[5] and Lemke,[6] after analysis of experimental data and estimated vinylene shifts in PMD, concluded that the vinylene shift should be slightly dependent on the number of vinyl groups and the nature of the end-nuclei for symmetrical PMD. Thus, the first electron transition wavelength can be represented by the general relationship:

$$\lambda_n = V(n + L) = Vn + \lambda_0$$

where $\lambda_0 = VL$, the transition wavelength for monomethine cyanine, and L is the effective end-group length.[7]

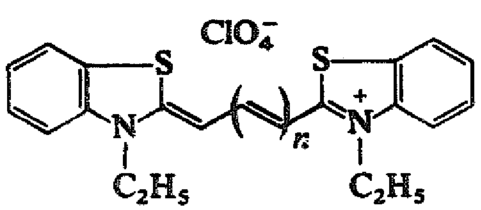
In some cases the vinylene shift differs considerably from the average value of 100 nm. For example, $V = 70$ nm for the polymethines I in which $G^+ \sim CH_2{=}CH$ and $G \sim CH{-}CH_2^-$), and $V = 30$ nm for α,ω-diphenylpolymethine anions and $V \simeq 60$ nm for the cations.[8] Such deviations from the average value have been attributed to the bond order alternation from the PC centre of the dyes to the end of the chain, this being related to the electron donor properties of the end-groups.[9] Thus, least alternation occurs with end-groups of medium basicity.

Abnormal behaviour of the vinylene shift is inherent in PMD with steric hindrance or in dyes having sulphur-containing nuclei. In these dyes, only the first vinylene shift differs from the normal one, and the shift then becomes constant again, being close to the value of 100 nm when $n \geq 2$. This present study is concerned with a detailed analysis of the effect of sulphur-containing end-groups on the first vinylene shift in the PMD series.

It is convenient to divide PMD into two classes, A and B, by the Dyadyusha classification, depending on the frontier molecular orbital (MO) symmetry.[10] Class A includes dyes having the lowest unoccupied MO (LUMO) which is asymmetric with respect to the molecule axis and has a symmetric highest occupied MO (HOMO). Class B includes dyes having inverse symmetry of the frontier levels. The first vinylene shift can be more or less than 100 nm depending on the nature of the first member of the vinylene series in dyes having a sulphur-containing end-group.

2 MATERIALS AND METHODS

Dyes of the following structures were studied.



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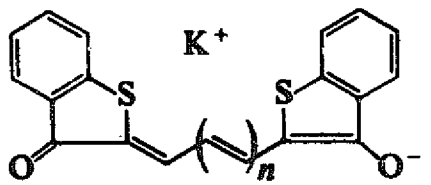

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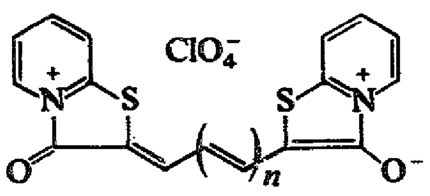

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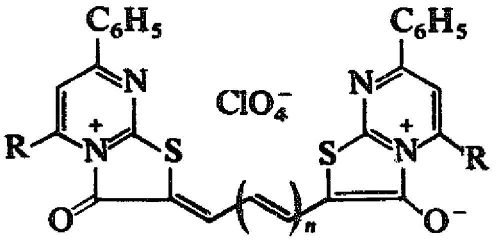
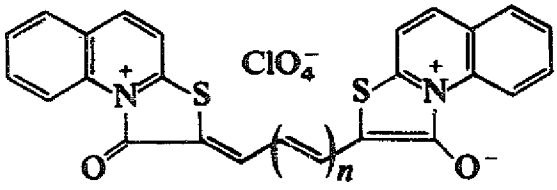


IV R = H; **V** R = C_6H_5



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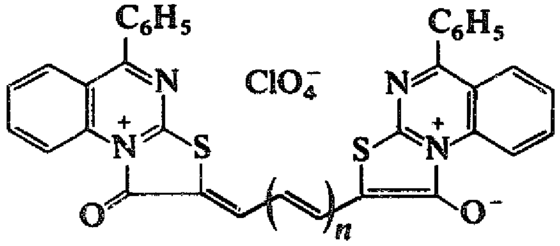

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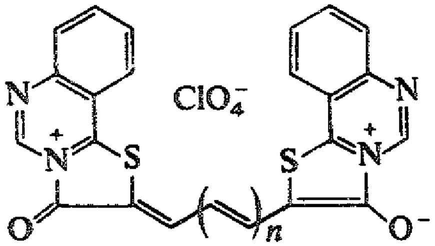

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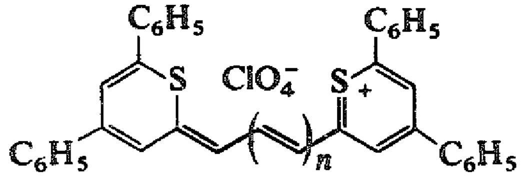

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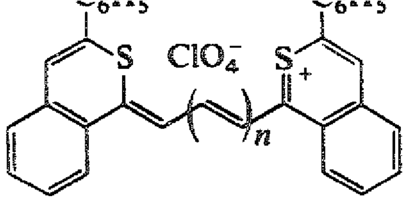

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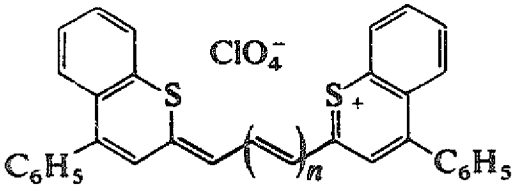


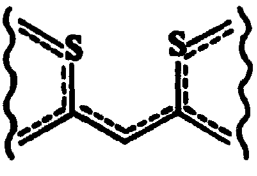
XI

The vinylene shifts observed for dyes I and II for dye solutions in methanol[11] are the same as those in acetonitrile. Dyes III–VI and IX–XI we have previously described, viz.: III,[12] IV and V,[13] VI,[14] IX,[15] X,[16] XI.[17] Dyes VII and VIII were synthesized in the same manner as V. Quantum-chemical calculations of the electron distribution for dyes I–XI were made using the PPP approximation with the same parameters as those in Ref. 18; for the C=O bond $\beta_{CO} = -1{\cdot}82\,\text{eV}$.

3 DISCUSSION

Table 1 shows the values of the long-wavelength absorption maxima for dyes I–XI. The first vinylene shift is seen to differ frequently from the average value of 100 nm and from the value of the second vinylene shift. For example, the first vinylene shift is much larger than 100 nm in the thiacyanines I and the thiopyrylocyanines IX, as well as in some other cases when the monomethine cyanine belongs to class A. The value is much less than 100 nm for the oxonole dyes II and their heteroanalogues III–VI. The transition energy in monomethine cyanine molecules is affected either by the steric hindrance or by resonance interaction or by the Coulomb repulsive forces of the valency non-bonding sulphur atoms, and these factors are responsible for changes in the first vinylene shift values. PC lengthening weakens the influence of these factors and other factors determining the spectral characteristics of the dyes such as an effective chain length and the electron donor ability of the end-groups are practically the same for all the series.

The first members of dyes I–XI have the same sulphur-containing fragment in their molecules, i.e.



Compounds of this type have been shown by X-ray analysis for dyes I[19] and by the PMR method for dyes IX[20] to exist in this conformation, i.e. where the sulphur atoms are in closest proximity. The effects described above are likely to affect the colour of the first members of the vinylene series.

Removal of steric hindrance in polymethine dyes by the molecule fragments twisting around the PC bonds results in decrease in conjugation and is energetically advantageous. In accordance with perturbation theory,[21] the first transition-energy change ($\delta\Delta E$) is expressed by:

$$\delta\Delta E = -2(p^{*}_{\mu\nu} - p^{0}_{\mu\nu})\,\partial\beta_{\mu\nu} \equiv 2\,\Delta_{\mu\nu}\,\partial\beta_{\mu\nu} \qquad (2)$$

where $\Delta_{\mu\nu}$ is the bond-order change for the molecular transition to the excited state and $\partial\beta_{\mu\nu}$ is the change of resonance integral characterizing quantitatively the decrease in conjugation. The bond-order changes may be described in a single configurational MO approximation as follows.

$$\Delta_{\mu\nu} = C_{e\mu}C_{e\nu} - C_{0\mu}C_{0\nu} \qquad (3)$$

where $C_{e\mu}$ is the LUMO coefficient and $C_{0\mu}$ is the HOMO coefficient.

In cases where bond twisting occurs, $\partial\beta_{\mu\nu} < 0$, the signs of the frontier MO coefficients determine the spectral effect sign. Figure 1 represents the frontier MO of class A and class B dyes. Bond orders of the PC of symmetric monomethine cyanines on excitation decrease independently of the dye class.[21] Steric hindrance in the monomethine cyanines therefore may result in a bathochromic shift in the absorption spectra and hence a decrease of the first vinylene shift value. The results given in Table 1 show however that the value V may decrease or increase, the increase being observed for class A monomethines. Therefore steric effects cannot be the main cause of the abnormal behaviour of the vinylene shifts, although they may distort the spectral picture.

Resonance interaction between the orbitals of valency non-bonded sulphur atoms, which are spaced from each other at a distance more or less than the Van der Waal's combined radii, is the second important factor in monomethine cyanines which may considerably influence the colour. The radii sum is 3·70 Å[22] and the distance between the sulphur atoms in the thiamonomethine cyanine **I** is about 2·9 Å, as determined by X-ray analysis.[19] In monomethine cyanines having thiopyridyl groups (**IX**), the distance between the sulphur atoms is even lower and Fabian *et al.*[11] has discussed this interaction in detail.

In this present work we consider the possible causes of this effect and its connection with the monomethine cyanine class. The interaction can be

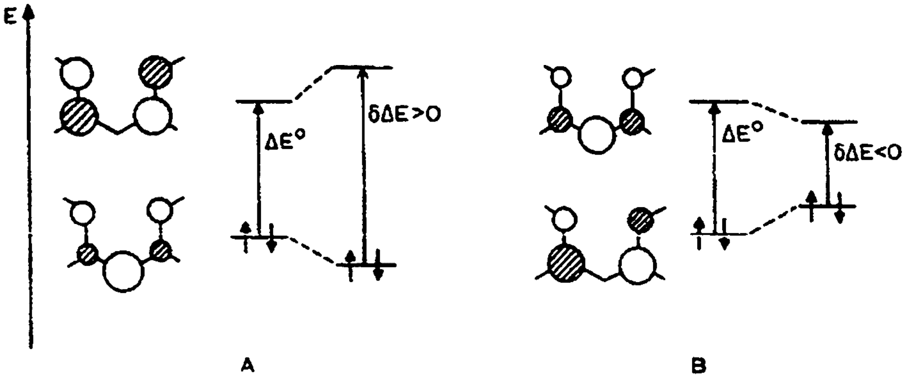


Fig. 1. Part of the frontier MOs of the class A (A) and class B (B) monomethines, and energy-level changes on resonance SS-interaction.

TABLE 1

Absorption Maxima (λ), Vinylene Shifts (V), Bond-Order Change ($\Delta_{SS'}$) and Electron Density Change (Δq) at Sulphur Atoms for the Transition of Dye Molecules into the Excited State

Compound	*n*	λ_{max}(*nm*)	V (*nm*)	$\Delta_{SS'}$	Δq_S
II	0	585	—	0·0456	−0·0304
	1	650	65	—	—
III	0	608		0·0583	−0·0165
	1	685	77	—	—
	2	786	101	—	—
IV	0	683		0·0498	−0·0179
	1	764	81	—	—
	2	886	122	—	—
VI	0	644		0·0600	−0·0124
	1	738	94	—	—
	2	843	105	—	—
VII	0	695		0·0553	−0·0096
	1	810	115	—	—
VIII	0	603		0·1011	0·0026
	1	700	97	—	—
I	0	420		—	0·0126
	1	555	135	—	—
	2	658	103	—	—
IX	0	598		−0·0915	0·0204
	1	780	182	—	—
X	0	615		−0·1199	0·0282
	1	820	205	—	—
XI	0	646		−0·1058	0·0333
	1	845	219	—	—

modelled by increasing the resonance integral between the sulphur atoms from zero to a value $\partial\beta_{SS'}$. If $\partial\beta_{SS'}$ is considered to be small, we may use the perturbation theory formulae for intramolecular perturbation, particularly eqn (3). In this case $\Delta_{\mu\nu}$ is equal to $\Delta_{SS'}$, i.e. the change of bond order between valency non-bonded sulphur atoms on excitation.

Figure 1 shows that for class A dyes the sulphur atom coefficients are of identical sign for the symmetric HOMO, and opposite signs for the asymmetric LUMO. Therefore, $\Delta_{SS'} < 0$. Since the resonance integral change is always negative ($\partial\beta_{SS'} < 0$), the interaction of the sulphur atoms causes an increase in transition energy and the first absorption band shifts to shorter wavelength. Hence, the first vinylene shift increases in this series of dyes. The experimental results for dyes I and IX–XI are in agreement with this conclusion (see Table 1). For class B monomethine cyanine dyes the frontier MO symmetry is opposite (Fig. 1B) and the bond order of the sulphur atoms increases; i.e. $\Delta_{SS'} > 0$. In accordance with this, the transition energy decreases for the monomethine cyanine, the long-wavelength band thus undergoes a bathochromic shift, and the first vinylene shift decreases. Experimental results for dyes II–VI (class B dyes) illustrate this. Attempts to obtain a correlation between the first vinylene shift values and the sulphur atoms bond-order change, calculated by PPP approximation, in the case of the transition of the monomethine cyanine molecule to the first excited state, failed.

We now consider the effect of the Coulomb repulsive forces on the sulphur atoms of neighbouring end-groups having the same charge in monomethine cyanines. It can be assumed that, provided other conditions are equal, the electronic state energy change should be proportional to the charge of the atoms in such interactions. Increase in the electronic density on the sulphur atoms on excitation increases the energy difference between the excited state and ground state (Fig. 2A), and similarly, decrease in the electron density lowers the energy difference. In accord with this, the first transition energy change should be proportional to the change in the charge on the sulphur atoms on excitation. The latter is the difference between the frontier MO square coefficients in single configurational MO LCAO theory:

$$\Delta_{\mu\mu} = C_{e\mu}^2 - C_{0\mu}^2 \qquad (4)$$

Figure 1 shows that $\Delta_{\mu\mu}$ for the sulphur atoms depends on the dye class, viz. A or B. Analysis shows that the direction of the shift in the long-wavelength band should be the same as in the case of resonance interaction, and should depend on frontier MO symmetry. On comparing the electron density change at the sulphur atoms, calculated by PPP approximation for dyes I–XI with the absorption maximum of the first vinylene shifts, a satisfactory linear relationship is observed (Fig. 3), as described by eqn (5) (correlation coefficient $r = 0{\cdot}957$):

$$V = 127 + 2470\,\Delta q \qquad (5)$$

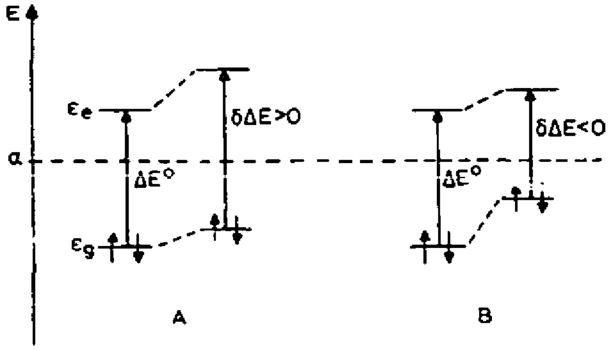


Fig. 2. The energy-level changes on Coulomb SS-interaction.

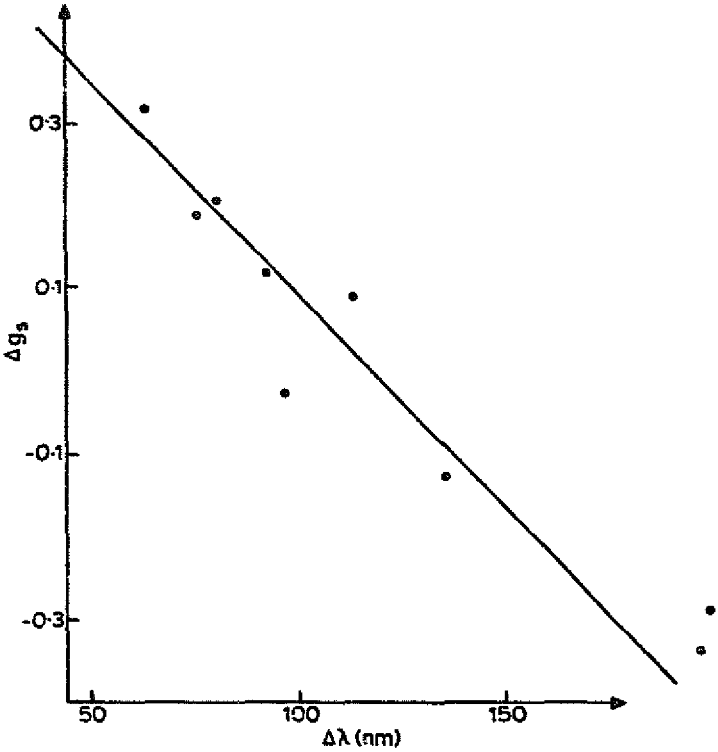


Fig. 3. The correlation between vinylene shifts ($\Delta\lambda$) and electron density changes on the excitation at sulphur atoms (Δq_S).

This correlation clearly shows that the observed change in the first vinylene shift of sulphur-containing dyes is dependent on the molecular structure and this allows a prediction of the spectral properties to be made in dyes of this type.

Steric hindrance is not the main cause of the vinylene shift change, since the spectral effect is independent of the dye class. The effect of resonance interaction and Coulomb repulsive forces cannot be separated because of their close relationship, although Coulomb interaction of the sulphur atoms shows a satisfactory correlation between the first vinylene shift and the electronic density changes on excitation in corresponding monomethine dyes.

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