



Anionic Polymethine Dyes Containing a Vinylene Bridge

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ABSTRACT

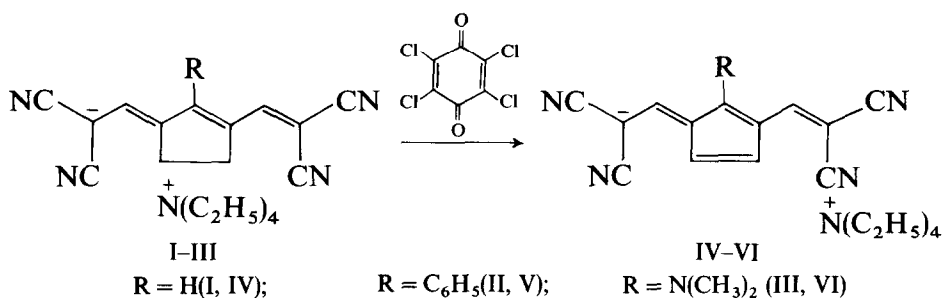
A method for the synthesis of anionic polymethine dyes which contain a vinylene bridge in the chromophore is described. It involves the dehydration of malonocyanines containing an ethylene bridge in the polymethine chain. The UV-VIS-, ^1H and ^{13}C -NMR spectra of the dyes are reported and quantum-chemical calculations of the electronic structure of the compounds were carried out using the PPP approximation. The theoretical prediction of the hypsochromic effects in the spectra of the dyes is in good agreement with the results of studies of their oxidation potentials ($E_{1/2}^{\text{ox}}$).

1 INTRODUCTION

We have previously described the synthesis^{1,2} and spectra^{2,3} of cationic and anionic polymethine dyes containing either an ethylene or trimethylene bridge in the chromophore. Anionic dyes such as trimethine- and pentamethine cyanines,⁴ and also tricarbocyanines^{5,6} and hexamethine merocyanines⁷ with an o-phenylene bridge in the polymethine chain have also been reported. In a number of cases the colour of dyes containing an o-phenylene bridge has been shown to be determined not only by electronic effects, but also by a change in the three-dimensional structure of the dye molecule due to steric effects.⁴ It was, therefore, of interest to develop a method of synthesis, and to study the properties of anionic dyes containing a vinylene bridge in the chromophore.

2 DISCUSSION

Dehydration of dyes I–III was carried out in order to obtain compounds having an unsaturated bridge in the polymethine chain. It was found that anionic dyes containing an ethylene bridge, when heated with benzoquinone or chloranil in acetonitrile or benzonitrile, gave dyes IV–VI.



The structure of these new anionic dyes having a vinylene bridge in the polymethine chain, was confirmed by NMR spectroscopy. Thus, the singlet originating from the hydrogen atoms of the ethylene bridge of dye I is absent in the ^1H -NMR spectrum of dye IV. The spectrum of dye IV shows a singlet at 7.51 ppm ($\text{H}^{4,4}$) and a broad singlet at 6.96 ppm ($\text{H}^{6,7,7}$). The fusion of the signals of the latter protons into a broad singlet gives evidence for the conformational inhomogeneity of dye IV; a similar effect has been previously observed in analogous compounds.² The ^{13}C -NMR spectrum of this dye gives data in accord with the postulated structure. Thus, it should be noted that the resonances of dye IV are at 61.67 ppm whereas the resonances of the same carbon atoms of dye I containing an ethylene bridge are at 52.78 ppm.⁹ Such a weak polar shift of resonances ($\Delta\delta \approx 9$ ppm) confirms that the negative charge on the $\text{C}^{2,2'}$ atoms of dye IV is decreased. Quantum-chemical calculations carried out using the PPP approximation predict such a pattern of electron density shift. The molecular diagrams (Fig. 1(a) and (b)) show that in the dye containing the vinylene bridge, the π -charges are reduced on the indicated atoms.

Whilst the ethylene bridge leads to an equalization of charges in the polymethine chain,⁹ introduction of a vinylene bridge conjugated with the chromophore is accompanied by an unequal distribution of the electron density. The essential negative charge (-0.45) primarily localizes in the five-membered cyclic system of dyes IV–VI due to a considerable increase of electron density at the meso-carbon atom. This carbon atom carries a positive charge ($+0.07$, Fig. 1(a)) in the unsubstituted dye VII and a negative one (-0.07 , Fig. 1(b)) in dye IV. A considerable negative charge (-0.08) is predicted for the $\text{C}^{7,7'}$ atoms of the vinylene bridge, whereas the charges

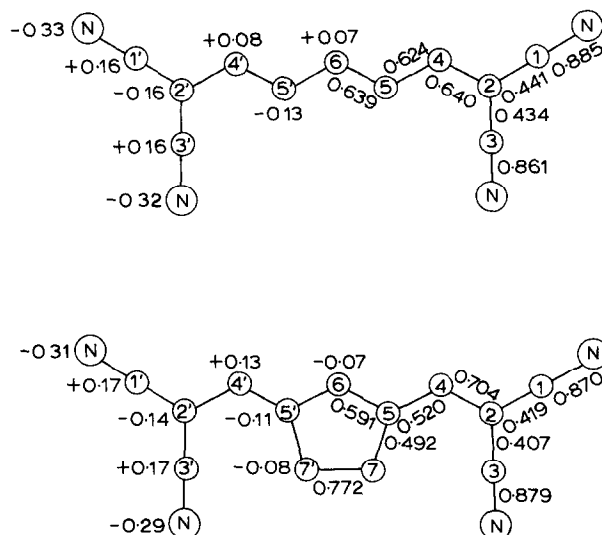
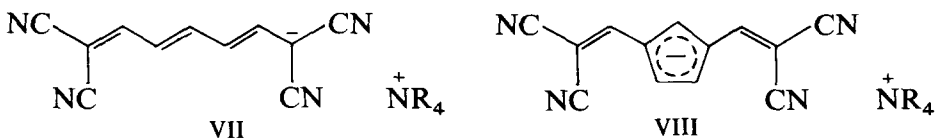


Fig. 1. Molecular diagrams of dyes VII (a) and IV (b).

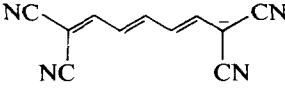
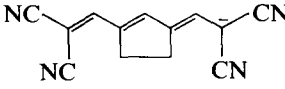
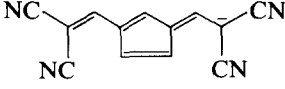
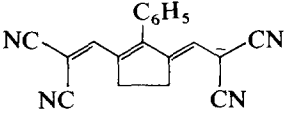
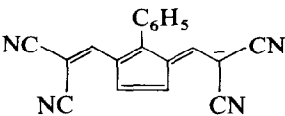
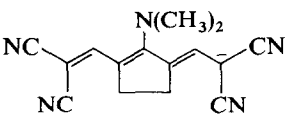
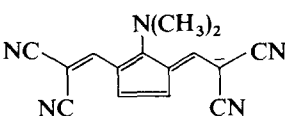
decrease to some extent on the $C^{5,5'}$ atoms. Such a shift in electron density to the five-membered cycle is due to the formation of a stable sextet of π -electrons and causes an increase of positive charge on the $C^{4,4'}$ atoms and also an alternation of the bond orders. The order of the C^4-C^5 bond decreases, while that of the C^2-C^4 bond increases, the difference being 0.18, compared to 0.02 in the unsubstituted dye.



The data of Table 1 show that the introduction of the ethylene bridge results in a bathochromic shift of the absorption maxima by 46 nm.² A vinylene bridge in the same position in the anionic dye IV leads to a hypsochromic shift of similar order ($\Delta\lambda = -52$ nm). Since the effect of these bridging groups on the colour of the dye is opposite, then the transition from the anionic dye with an ethylene bridge to a dye with a vinylene bridge is accompanied by considerably larger hypsochromic shifts (from -84 up to -103 nm).

The effect of the vinylene bridge on the colour of the anionic dyes may be interpreted using perturbation theory.¹⁰ The conjugation between the vinylene bridge and the π -electron system of the polymethine chromophore should lead to changes in the electronic energy transitions due to the mutual repulsion between levels. Since the dye molecule and the cyclization

TABLE 1
Spectral and Electrochemical Characteristics of Anionic Dyes

<i>N</i>	<i>Dye</i>	λ_{\max} , (nm) ^a ($\epsilon \times 10^{-4}$)	$E_{1/2}^{\text{ox}}$, <i>B</i>	<i>Id</i> (μA)
VII		$\text{N}^+(\text{C}_2\text{H}_5)_4$ 538 (17.8)	0.51	32.8
I		$\text{N}^+(\text{C}_2\text{H}_5)_4$ 584 (17.5)	0.29	41.5
IV		$\text{N}^+(\text{C}_2\text{H}_5)_4$ 486 (6.9)	0.73 ^b 0.89	7.6 29.6
II		$\text{N}^+(\text{C}_2\text{H}_5)_4$ 594 (16.0)	0.32	38.5
V		$\text{N}^+(\text{C}_2\text{H}_5)_4$ 491 (8.4)	0.90	44.6
III		$\text{N}^+(\text{C}_2\text{H}_5)_4$ 540 (18.1)	0.32	35.6
VI		$\text{N}^+(\text{C}_2\text{H}_5)_4$ 456 (4.6)	0.31	34.6

^a In methanol.

^b The values of $E_{1/2}^{\text{ox}}$ are given for two conformers.

positions are symmetrical, then only levels with the same type of symmetry interact (Fig. 2). The vinylenic group has two π -levels with energies $\epsilon_1 = \alpha + \beta$, $\epsilon_2 = \alpha - \beta$ (Fig. 2(b)). In this case, the highest occupied level has symmetry b_2 , whilst the lowest unoccupied level is a_2 . The anionic dye VII, which has no bridging group, is related to class B;¹¹ its HOMO is antisymmetrical (a_2) and its LUMO is symmetrical (b_2).

Since the LUMO coefficients in the positions at which cyclization has been effected are virtually equal to zero, then the interaction of this boundary MO (ϵ_e) with the symmetrical MO of the bridge (ϵ_1) is negligible. And *vice versa*, i.e. the repulsion of antisymmetrical levels (ϵ_0 and ϵ_2) should

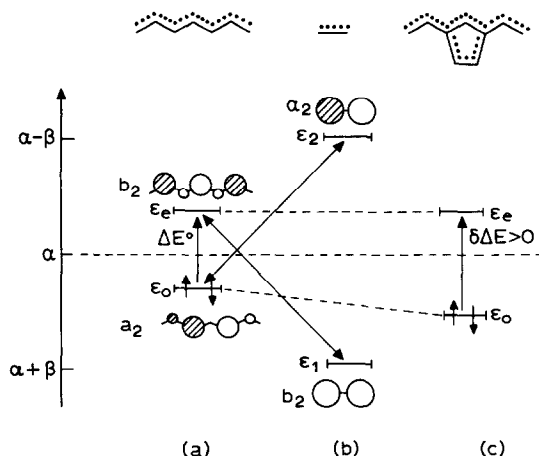


Fig. 2. Location and shape of the interacting boundary levels of the dye (class B) with the π -levels of ethylene: (a) levels of the unsubstituted dye; (b) vinylene bridge levels; (c) dye levels with the bridge in the polymethine chain.

be substantial, with lowering of the HOMO energy. In this case the energy gap increases (Fig. 2(b)) and hypsochromic shifts of the absorption maxima should be observed. Figure 2 shows that the effect of the vinylene group is opposite to that of the ethylene bridge whose two levels are located lower than the boundary MO of the dye, and hence the repulsion of the antisymmetrical levels increases the HOMO energy. In addition, the ethylene bridge levels are located considerably deeper ($\epsilon_{1,2} \simeq \alpha + (2 \pm \eta)\beta$) and are lower in energy than the boundary MO of the dye. Therefore, such a cyclization is accompanied by smaller spectral effects. Thus, comparing dye **VII** with the anionic dye **I** containing an ethylene bridge, the bathochromic shift is $\Delta\nu = 1464 \text{ cm}^{-1}$, and on comparing it to the dye with a vinylene bridge, the hypsochromic shift is much larger ($\Delta\nu = -3453 \text{ cm}^{-1}$).

In order to experimentally demonstrate the decrease in the HOMO energy of the anionic dyes due to the effect of the vinylene bridge (Fig. 2(c)), we measured the oxidation potentials ($E_{1/2}^{\text{ox}}$) of dyes **I–VII**. The data in Table 1 show that introduction of the ethylene bridge shifts the oxidation potential towards the cathode region, whereas the presence of the vinylene bridge leads to higher anode oxidation potentials. The increase in the oxidation potential is considerable when comparing dyes **I** and **IV**, and this is expressed in the larger hypsochromic shift which is observed. A similar effect is observed when comparing dyes **II** and **V**. It should be noted that two anode waves are observed in the voltamograms for the electrochemical oxidation of dye **IV**. This is explained by the presence of two conformers in the solution, in agreement with $^1\text{H-NMR}$ spectra data. The same values of $E_{1/2}^{\text{ox}}$ for dyes **III** and **VI** confirm that a pair of electrons of the nitrogen atom

of the dimethylamino group participates in the oxidative process, rather than the delocalized pair of the dye HOMO.

However, in the electronic spectrum of the latter, there is a transition between HOMO and LUMO, but by analogy with the other anionic dyes under discussion, this is not an $n \rightarrow \pi^*$ transition and it exhibits a shift to lower wavelength, in agreement with the Forster-Dewar-Knott rule.¹²⁻¹⁴ This shift can also be more simply explained using perturbation theory. Figure 1(a) shows that LUMO in the meso-position has a non-zero coefficient and hence it will interact effectively with the energy levels of the substituent. The antisymmetrical HOMO has a node in the meso-position and its interaction in the first approximation is equal to zero. A small bathochromic shift induced by the phenyl group, which is not coplanar with the rest of the molecule, is explained by a negative inductive effect. The strong electron-donating dimethylamino group, whose interacting level is below the boundary MO ($\varepsilon = \alpha + h\beta$, where h is a correction to the Coulomb integral of the nitrogen atom: $\alpha_N = \alpha + h\beta$) should lead to repulsion of the LUMO and hence to an increase in the transition energy.

When comparing dyes **I** and **III** (which contain the ethylene bridge) with dyes **IV** and **VI** (which contain the vinylene bridge) it follows that the spectral effects depend only slightly on the nature of the bridging group ($\Delta\nu = 1395 \text{ cm}^{-1}$ and $\Delta\nu = 1354 \text{ cm}^{-1}$). However, it must also be considered that corresponding dyes without substituents in the meso-position differ considerably in their absorption characteristics (almost 100 nm). The spectral effects resulting from the introduction of the phenyl group, although being more sensitive to the nature of the bridging group (dyes **1**, **2** and **IV**, **V**), show considerably smaller shift values.

3 EXPERIMENTAL

Electron absorption spectra were recorded on a Specord M 40, and NMR spectra on a Bruker WP 200 (TMS as internal standard).

Oxidation potentials were determined using a Polarographical PA-3 analyzer (ČSSR). A rotating disk electrode made of platinum wire (2 mm diameter) pressed into fluoroplast was used as working electrode. The angular rate of electrode rotation was $3 \times 10^3 \text{ rev/min}$. When recording voltammograms, the potential sweep rate was 20 mV/s. A platinum spiral, separated from the working volume of a cell by a porous glass membrane, served as an auxiliary electrode. A saturated calomel electrode was employed as reference. The background electrolyte was 0.1M solution of tetrabutylammonium boron fluoride in acetonitrile. The concentration of depolarizer, when recording the voltammograms, was $1 \times 10^{-3} \text{ mol/l}$. The cell

design and procedure for recording the voltamograms were as previously reported.⁸

The electronic structure and transition energies were calculated by means of the PPP method. The atomic and bond parameters, and interatomic distances, were taken from reported values.⁹ Steric effects were not taken into consideration.

Tetraethylammonium 1,1,7,7-tetracyano-3,5-(vinylene)-1,3,5-heptatrienide (IV)

0.001 mole of malonocyanine I and 0.002 mole of 1,4-benzoquinone were heated to reflux in 2 cm³ of benzonitrile for 1 min (up to the disappearance of the violet colour of the solution). After standing at room temperature for 1 h, the semiquinone crystals were filtered and the dye in the mother liquor was precipitated by addition of diethyl ether. Purification was performed by reprecipitation from ethylacetate with ether. The yield was 33%, m.p. 100–102°C. ¹H-NMR spectrum in acetone—d₆; δ ppm: 1.37 t (12H, CH₃), 3.45q. (8H, CH₂), 6.96 broad singlet (3H, H^{6,7,7}), 7.51 s (2H, H^{4,4}). ¹³C-NMR spectrum in acetonitrile—d₃, δ ppm: 6.69 (CH₃), 51.50 (CH₂), 61.61 (C^{2,2}), 117.97 (C^{5,5}), 117.35 and 118.18 (C^{1,1,3,3}), 127.88 (C^{7,7}), 138.85 (C⁶) and 151.47 (C^{4,4}). (Found: C, 72.6; H, 7.2; N, 19.8. C₂₁H₂₅N₅ calculated: C, 72.6; H, 7.25; N, 20.2%.)

Tetraethylammonium 1,1,7,7-tetracyano-3,5-(vinylene)-4-phenylhepta-1,3,5-trienide (V)

This was similarly obtained; yield, 27%, m.p. 140–142°C. Found: C, 76.6; H, 6.7; N, 16.3. C₂₇H₂₉N₅ calculated; C, 76.6; H, 6.9; N, 16.5%.

Tetraethylammonium 1,1,7,7-tetracyano-3,5-(vinylene)-4-dimethylaminohepta-1,3,5-trienide (VI)

Yield 34%. m.p. 122–124°C. Found: C, 70.9; H, 7.8; N, 21.25. C₂₃H₃₀N₆ calculated: C, 70; H, 7.7; N, 21.5%.

CONCLUSIONS

Introduction of a vinylene bridge into the chromophore of pentamethine cyanides leads to a considerable hypsochromic shift of the absorption maxima. This is related to a decrease in the HOMO energy due to repulsion of the antisymmetric levels of the vinylene bridge and polymethine

chromophore. Based on the experimental data it is concluded that the new dyes contain a stable Huckel 6 π -electron system as a result of the concentration of electron density at the five-membered cyclic moiety. The synthetic method used may be extended with synthesis of cationic dyes containing a vinylene bridge in the chromophore, using an appropriate selection of oxidation potential values of the system. The results obtained make it possible to predict that the introduction of a vinylene bridge at the same positions in the polymethine chain of dyes possessing opposite symmetry of boundary levels will result in a bathochromic effect.

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