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# Nature of Electronic Transitions in Trinuclear Polymethine Dyes

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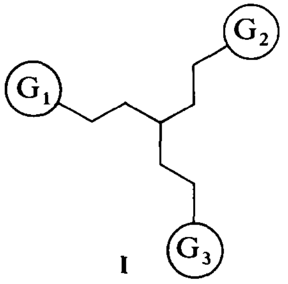
## *SUMMARY*

*Symmetric and asymmetric polymethine dyes with three end-groups have been synthesized and their absorption and fluorescence spectra investigated. The first absorption band of asymmetric dyes containing end-groups with a different effective length has been shown to split. The fluorescence spectra of trinuclear dyes have been used to assign the significant changes which occur upon excitation and, in the case of the asymmetric compounds, two conformers have been detected.*

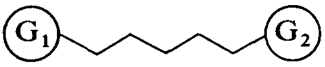
## 1 INTRODUCTION

Dyes with branched polymethine chains and three end-groups (**I**) have some special features which distinguish them from the corresponding dyes with two end-groups (**II**).

It has been shown by NMR spectroscopy that in the case where the end-groups are identical the dye molecules have $C_3$ symmetry.[1] Consequently,



**I**



**II**

the unsymmetrical levels, including the lowest unfilled MO, are degenerate. This must lead to the degeneration of the first two electron transitions corresponding to the absorption in the visible and near-IR regions.

The nature of the long-wave absorption bands of the dyes with two end-groups have been investigated in detail.[2-4] The first absorption band is related to the $\pi$-electron transition from the highest occupied energy level to the lowest unfilled one. This transition is polarized along the long axis of the molecule and is localized at the atoms of the polymethine chain. The second transition is polarized perpendicularly and may be localized at the atoms of the end-nuclei with developed conjugated systems.[5]

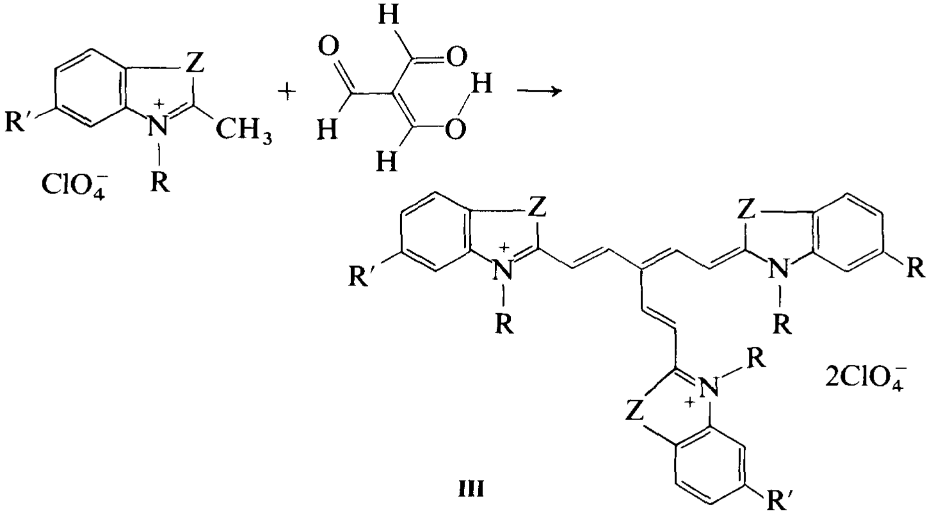
The nature of the electron transitions of the dyes with three end-groups has not been widely studied. Some investigations have been carried out, but only for dyes with identical nuclei.[6]

This present communication deals with the systematic analysis of the electron transitions in the symmetrical and the asymmetrical [2.2.2]heptamethinecyanines. To study the nature of the electron transitions, data on electronic absorption and fluorescence spectra, as well as results of quantum-chemical calculations, are utilized.

## 2 RESULTS AND DISCUSSION

### 2.1 Syntheses

Trinuclear symmetrical dyes were synthesized by the interaction of quaternary salts containing active methyl groups with triformylmethane in acetic anhydride in the presence of anhydrous sodium acetate.[7]



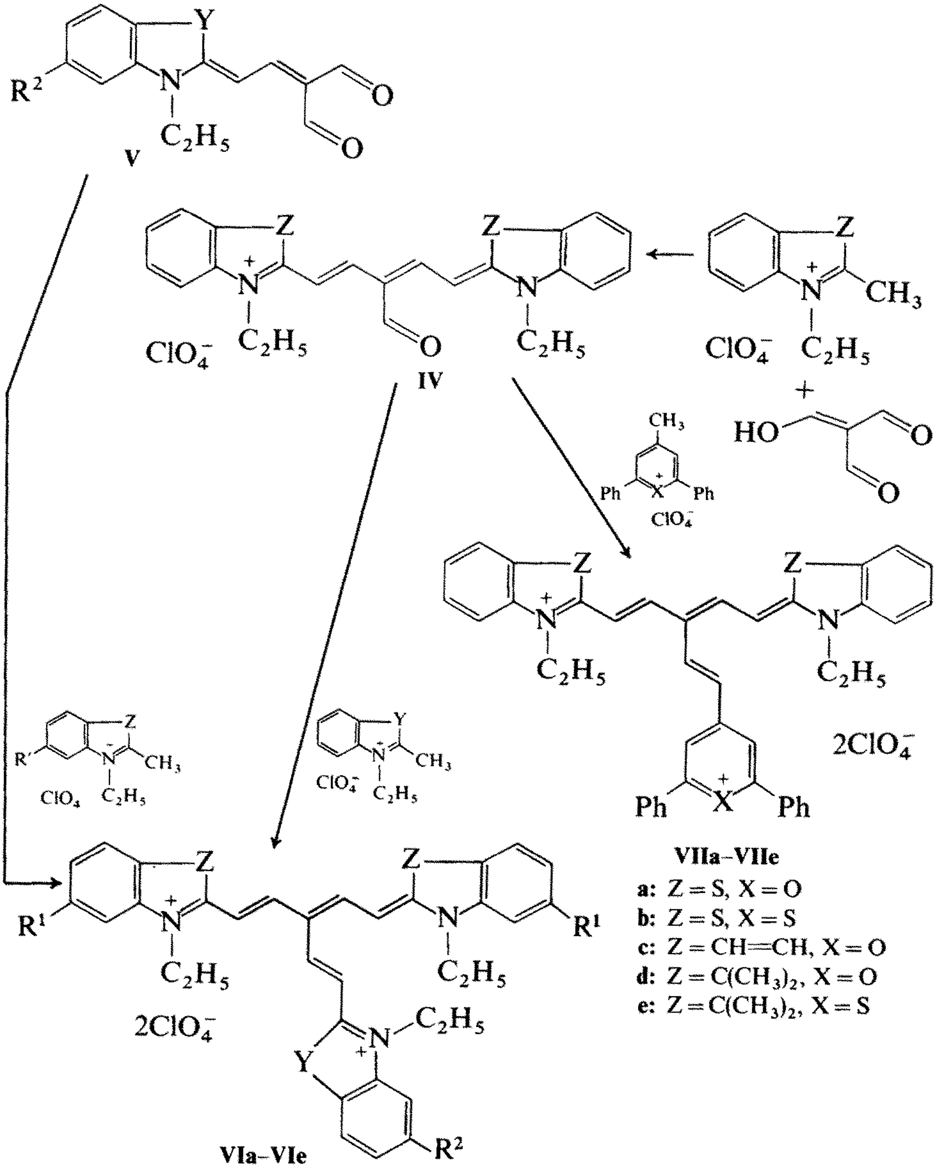
III

**IIIa**: Z = S, R = Et, R′ = H

**IIIb**: Z = C(CH$_3$)$_2$, R = Me, R′ = H

**IIIc**: Z = CH=CH, R = Et, R′ = H

**IIId**: Z = NPh, R = Et, R′ = CN



**V**

**IV**

**VIa–VIe**

**a:** $Z = Y = S$, $R = NO_2$, $R^1 = R^2 = H$

**b:** $Z = S$, $Y = CH{=}CH$, $R = R^1 = R^2 = H$

**c:** $Z = CH{=}CH$, $Y = S$, $R = R^1 = R^2 = H$

**d:** $Z = C(CH_3)_2$, $Y = NPh$, $R = R^1 = H$, $R^2 = CN$

**e:** $Z = NPh$, $Y = C(CH_3)_2$, $R = R^2 = H$, $R^1 = CN$

**VIIa–VIIe**

**a:** $Z = S$, $X = O$

**b:** $Z = S$, $X = S$

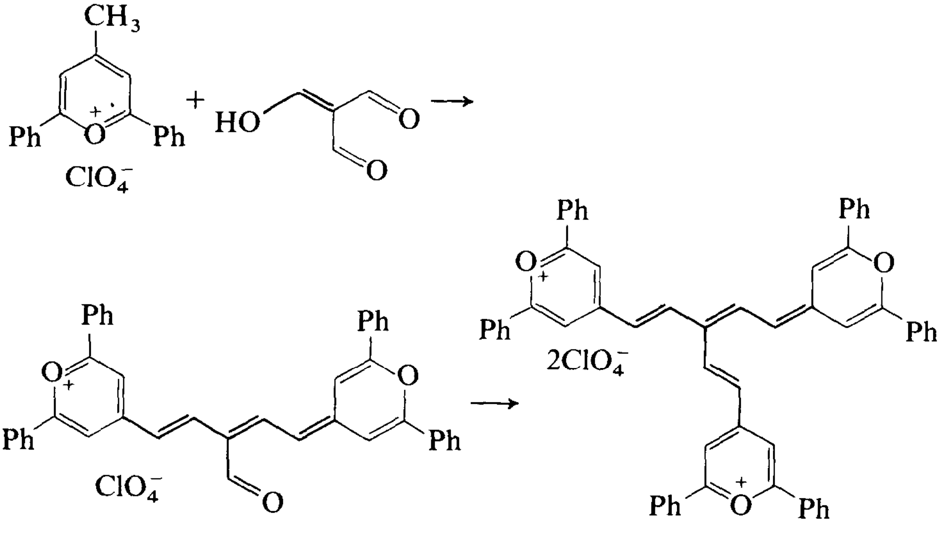
**c:** $Z = CH{=}CH$, $X = O$

**d:** $Z = C(CH_3)_2$, $X = O$

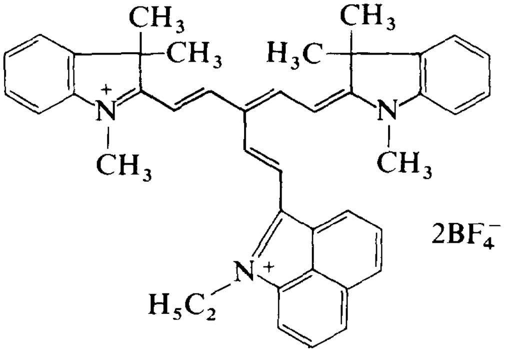
**e:** $Z = C(CH_3)_2$, $X = S$

Trinuclear asymmetrical dyes were obtained by condensation of the γ-formyl-substituted pentamethinecyanines **IV** with the nitrogen-containing heterocyclic salts as well as 4-methyl-2,6-diphenylpyrylium and 4-methyl-2,6-diphenylthiopyrylium perchlorates in acetic anhydride.

The pentamethinecyanines **IV** were prepared from appropriate quaternary salts and triformylmethane (2:1). The symmetrical [2.2.2]heptamethinecyanine **IX** with three pyrylium nuclei was obtained by the same procedure. The γ-formyl-substituted pyrylo-4-pentamethinecyanine **VIII** was initially prepared by condensation of 4-methyl-2,6-diphenylpyrylium perchlorate with triformylmethane in acetic anhydride in the presence of sodium acetate, and this dye was then reacted with a small excess of 4-methyl-2,6-diphenylpyrylium perchlorate in a mixture of benzonitrile and acetic anhydride.



**VIII** **IX**



**X**

Some asymmetrical dyes were found to be more conveniently obtained by heating 2 moles of a corresponding salt with 1 mole of the 3-alkyl-2-(3,3-diformylallylidene) derivative of an appropriate heterocycle **V**. Thus, dye **X** with benz[*c*,*d*]indole nuclei was synthesized by both the described methods.

### 2.2 Methods

Electronic absorption spectra of the dyes were recorded on an SF-8 spectrophotometer and the fluorescence spectra on an SDL-1 fluorimeter.

Quantum-chemical calculations were carried out by means of the HMO method, as well as by the PPP method, using parameters given in a previous paper.[8]

Two parameters, namely effective length $L$ and electron donor ability $\Phi_0$, were used as end-group characteristics. The first parameter characterizes an additional bathochromic shift of the long-wave band influenced by the end-groups. It is expressed by the equivalent number of the vinyl groups,[8,9] so $\lambda_n = V(n + L)$, where $n$ is the number of vinyl groups in the polymethine chain and $V \simeq 100$ nm, the so-called 'vinylene shift'. The second parameter, $\Phi_0$, determines the position of the frontier MO relative to the Fermi level ($\alpha$) of the $\pi$-electrons and is the quantitative characteristic of nuclei 'basicity'.[2] Both parameters can be theoretically calculated using the first coefficients of the nuclei polynomials. Calculated values of $L$ and $\Phi_0$ of some end-groups used in this paper are listed in Table 1.

For the quantitative estimation of the absorption bandwidth of dyes the parameter $\sigma$, calculated on the basis of the second central moment (dispersion) of the band,[10] was used. This parameter allows a quantitative comparison of the bands with different forms in contrast to the halfwidth traditionally used for this purpose. The values of $\sigma$ are listed in Table 2.

### 2.3 Electronic structure of the trinuclear dyes

Examples of the frontier and neighbouring MO positions of dyes with two and three end-groups are shown in Fig. 1. Apparently, branching of the polymethine chain leads to an energy decrease of the symmetrical ($y$) occupied levels and to an energy increase of asymmetrical ($x$) unfilled ones. Asymmetrical levels ($x$), characterized by the molecular function with a node on the central carbon atom of the polymethine chain, do not show a change in energy. In the case of trinuclear dyes with the same end-groups, the asymmetrical levels are doubly degenerate. Due to these energy levels, the first absorption band of the dyes **I** with branched polymethine chains must be shifted to shorter wavelength in comparison with the corresponding dinuclear dyes **II**. In the case of the trinuclear dyes with different end-groups,

TABLE 1
Electron Donor Ability $\Phi_0$ and Effective Length $L$ of End-Groups of Polymethine Dyes: $G^+\!\left(CH{=}CH\right)_n CH{=}G$

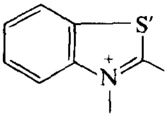
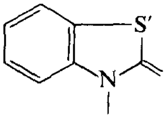
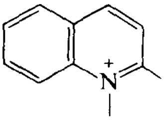
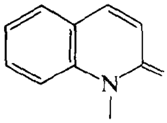
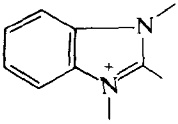
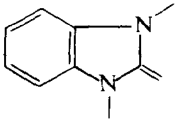
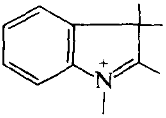
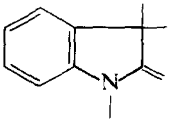
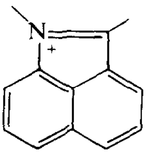
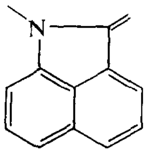
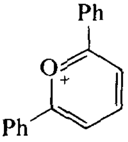
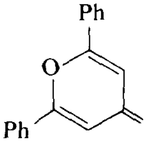
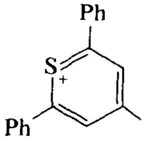
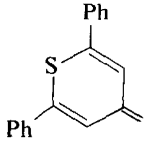
| $G^+$ | $G$ | $\Phi_0$ (deg.) | $L$ |
|---|---|---|---|
|  |  | 47 | 3·06 |
|  |  | 66 | 3·23 |
|  |  | 76 | 2·59 |
|  |  | 34 | 2·76 |
|  |  | 33 | 6·50 |
|  |  | 44 | 6·06 |
|  |  | 42 | 7·26 |

TABLE 2
Spectral Characteristics of Dyes

| *Compound* | *CH$_2$Cl$_2$* | | | *CH$_3$CN* | | | *CH$_3$OH* | | $\lambda_{max}^{fluor}$ *(nm)* | $\Delta S$ *(cm$^{-1}$)* |
|---|---|---|---|---|---|---|---|---|---|---|
| | $\lambda_{max}^{abs}$ *(nm)* | *(ε × 10$^{-4}$)* | *σ (cm$^{-1}$)* | $\lambda_{max}^{abs}$ *(nm)* | *(ε × 10$^{-4}$)* | *σ (cm$^{-1}$)* | $\lambda_{max}^{abs}$ *(nm)* | *(ε × 10$^{-4}$)* | | |
| **IIIa** | 640(—) | | 1 472 | 632(11·0) | | 1 309 | 634(—) | | 699 | 1 466 |
| **IIIb** | 635(11·4) | | 1 446 | 628(11·4) | | 1 251 | 636(15·1) | | 698 | 1 597 |
| **IIIc** | 660(9·12) | | 1 495 | 690(9·90) | | 1 344 | 686(—) | | 759 | 1 317 |
| **IIId** | 620(5·80) | | 1 807 | 605(6·20) | | 1 582 | 615(6·74) | | 652 | 1 191 |
| **VIa** | 640(—) | | 1 230 | 640(—) | | 1 353 | 645(11·4) | | — | — |
| **VIb** | 645(—) | | 1 328 | 636(11·5) | | 1 406 | 650(10·5) | | 709 | 1 619 |
| **VIc** | 670(—) | | 1 464 | 666(—) | | 1 493 | 674(10·8) | | 735 | 1 390 |
| **VId** | 645(—) | | 1 731 | 630(—) | | 1 773 | 630(9·12) | | 654[a] 694 | 1 513 |
| **VIe** | 580(—) | | 1 873 | 556(—) | | 2 032 | 550(3·60) | | 626[b] 663 | 2 903 |
| **VIIa** | 735(6·70) | 628(5·10) | 2 351 | 724(5·60) | 652(5·50) | 2 317 | 720 | 650[c] | — | — |
| **VIIb** | 780(7·50) | 620(5·00) | 2 640 | 781(—) | 610(—) | 2 633 | 770 | 640[c] | — | — |
| **VIIc** | 730(5·80) | 635(7·10) | 2 469 | 700(6·50) | | 2 333 | 710 | 660 | — | — |
| **VIId** | 740(—) | 635(—) | 2 159 | 730(2·20) | 625(5·00) | 2 125 | 720(—) | 640 | — | — |
| **VIIe** | 780(7·10) | 635(6·00) | 2 180 | 770(6·00) | 630(5·20) | 2 286 | 770 | 635[c] | — | — |
| **IX** | 800(—) | 710(—) | 1 359 | 820(11·7) | 775(12·4) | 1 387 | — | — | — | — |
| **X** | — | — | — | 760(7.21) | 625(5·47) | — | 760 | 640[c] | — | — |

[a] Excitation wavelength 628 nm for the first maximum, 660 nm for the second.
[b] Excitation wavelength 556 nm for the first maximum, 620 nm for the second.
[c] The more intensive maximum.

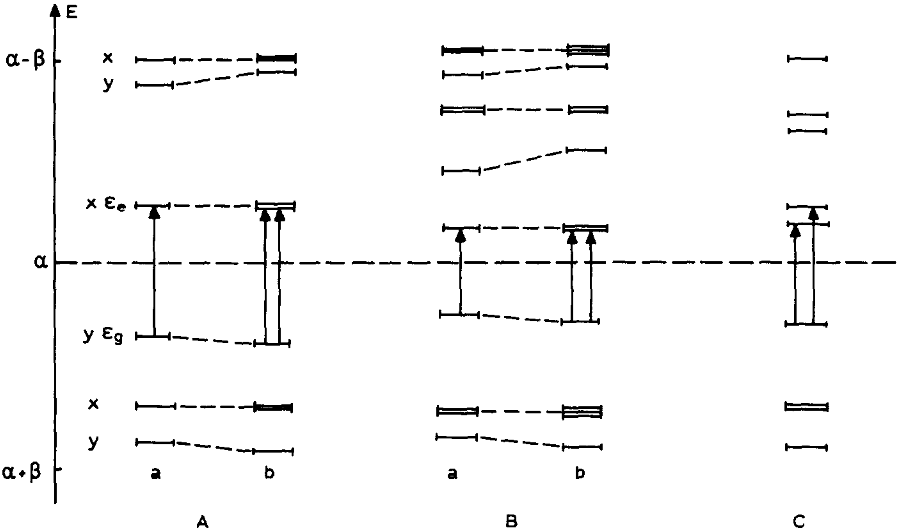


**Fig. 1.** The electronic energy levels of dinuclear (a) and trinuclear (b) dyes calculated by the HMO method; A, B, symmetrical dyes; C, asymmetrical dye.

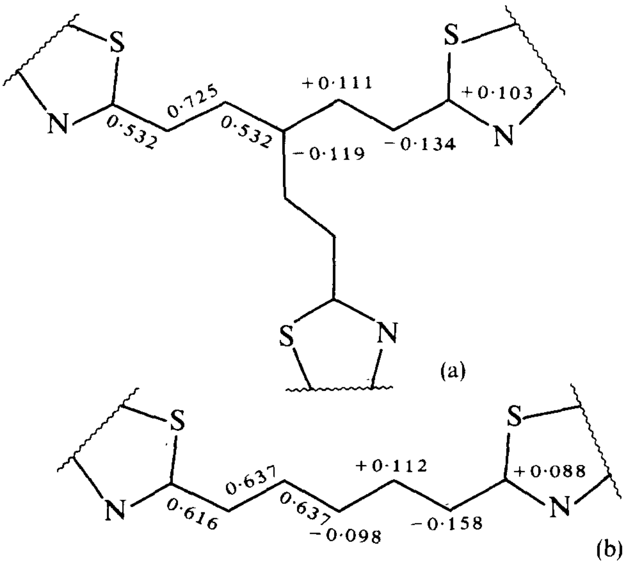
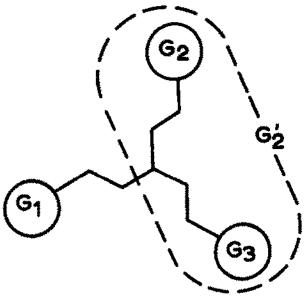


**Fig. 2.** Bond-orders and charges in the ground state of trinuclear [2.2.2]heptamethinecyanine (a) and dinuclear pentamethinecyanine (b) calculated by the PPP approximation.

the degeneracy of the levels must disappear (Fig. 1(C)). The splitting value must be proportional to the effective length difference of the end-groups. If this difference is significant, two long-wave absorption bands should be observed in the spectrum. These bands are caused by different electronic transitions. If the values of the parameter $L$ for the different end-nuclei are nearly the same, only a band expansion is observed.

Considering the differences in the electron distributions on the atoms and the bonds of the polymethine chain in trinuclear dye molecules and corresponding dinuclear ones, the molecular diagrams (Fig. 2) show that the polymethine chain branching does not lead to an essential change of the charges on the carbon atoms. Considerable alternation of positive and negative charges on the polymethine chain in the case of the trinuclear dyes is the same as that in dyes with two end-groups. This fact has also been demonstrated using $^{13}$C-NMR spectroscopy.[1]

Bond-order changes are more significant. In the dyes with two end-groups all bond-orders in the polymethine chain are practically equal (Fig. 2(a)). In the case of the trinuclear dyes the calculations predict a considerable bond alternation in the ground state. To interpret this alternation in the simplest way, we may consider the trinuclear dye as a normal asymmetrical polymethine dye with two end-groups, one of which is part of the molecule with two branches of the polymethine chain:



Then the electron donor ability $\Phi'_0$ of this modified nucleus will decrease. If all three nuclei are the same, with an electron donor ability $\Phi_0$, one obtains $\tan \Phi'_0 = 2 \cot \Phi_0$, i.e. each branch of a trinuclear dye can be described as a polymethine chain of an asymmetrical dye with two end-groups. Consequently, bond alternation occurs. According to PPP calculations, the central bonds are characterized by the lowest order (Fig. 2(b)). The decrease of the order of some bonds in a polymethine chain of the trinuclear dyes should facilitate twisting around these bonds. This factor can explain the presence of twisting isomers distinguished by the absorption spectra. As previously mentioned, $^{13}$C-NMR spectroscopy investigations have predicted a $C_3$ symmetry for the dye molecules I. Nevertheless, we believe that, in solution, some isomers can exist in which out-of-plane twistings of one heterocycle with respect to the others occur. Hence, the additional absorption bandwidth expansion should appear in spectra.

## 2.4 Absorption spectra

In the visible spectra of the dyes containing the same three end-groups, one absorption band is observed. However, the bandwidth of the trinuclear dyes considerably exceeds that of their dinuclear analogues, as shown by the method of moments[10] (Fig. 3; Table 2) ($\sigma = 1251$–$1807\,\mathrm{cm}^{-1}$ for the trinuclear dyes and $\sigma = 774$–$1000\,\mathrm{cm}^{-1}$ for the dinuclear dyes). The most probable causes of this phenomenon appear to be the increase of the vibrational interaction in the dye molecules and the presence of twisting isomers in solution.

The bond-order alternation in the polymethine chain of the trinuclear dyes leads to a marked increase in the vibrational interactions. In order to estimate these, it is possible to use the relationship between the quadratic bond-order variations and the excitation $\delta$:[12]

$$\delta = \sqrt{\sum_i (p_i^* - p_i^0)^2}$$

where $p_i^0$ and $p_i^*$ are bond-orders for the $i$th bond in the ground state and in the excited state, respectively. The parameter $\delta$ correlates with experimental long-wave absorption bandwidths when strong solvation effects are absent.[12] Quantum-chemical calculations in the HMO approximation show that the value $\delta$ of the trinuclear dye exceeds that of the dinuclear dye: $\delta = 0{\cdot}1168$ for the thiapentamethinecyanine and $\delta = 0{\cdot}1614$ for the dye **IIIa**. This

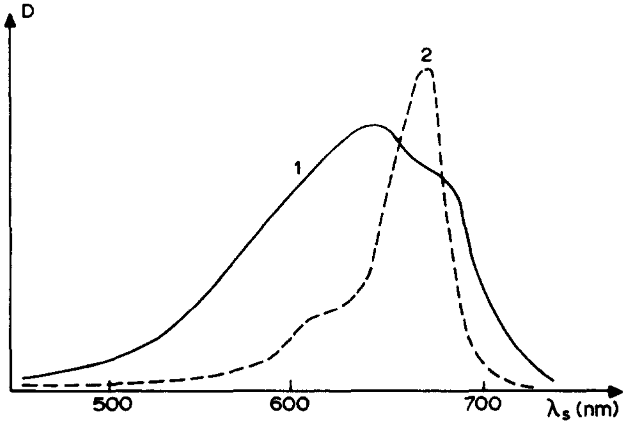


**Fig. 3.** Absorption spectra of dye **IIIa** (1) and its dinuclear analogue (2).

change of $\delta$ agrees well with the bandwidth expansion observed in the absorption spectra. Not only bandwidth expansion but also the unusual dependence on the band maximum and width in the case of some trinuclear dyes with end-groups differing from one another by electron donor ability $\Phi_0$ can confirm the existence of twisting isomers (Table 2). For example, a significant hypsochromic shift of the absorption maximum is observed comparing the spectra of the quinocyanine **IIIb** and pyrylocyanine **IX** (30 and 65 nm), and a strong band narrowing for dyes **IIIa** and **IIIb** in $CH_3CN$ compared with $CH_2Cl_2$. The reverse relation would be expected since the former solvent has a larger refractive index and lower polarity. Probably, in the case of a more polar solvent, the band of the twisting isomer is observed due to the ability of such a solvent to stabilize the isolated positive charge on one of the dye branches, thus enabling this isomer to exist.[6]

A more noticeable splitting of the degenerated electron transitions may be achieved in asymmetrical dyes in which one of the end-groups differs from the other two. It was observed, however, that the dyes with benzothiazole, quinoline, indolenine and benzimidazole nuclei have absorption bands similar to those of symmetrical dyes. Therefore, the levels splitting is negligible and the first two electron transitions do not result in separate bands in the absorption spectra.

It might be expected that the levels splitting would be more apparent where there is a considerable increase in the effective length of one of the end-groups (Fig. 1(C)). In this case the first two electron transitions are observed in the absorption spectra as two separate bands. Table 1 shows that dyes with the pyrylium, thiapyrylium and benz[*c*,*d*]indolium nuclei are characterized by a large effective length (6·06, 7·23 and 6·50, respectively). Large values of the parameter $L$ are thus in good agreement with experimental data. Absorption bands of the polymethine dyes containing these nuclei show large red-shifts compared with analogous thia- and quinocyanines having the same polymethine chain length. For example, the spectra of 2,6,2′,6′-tetraphenyl-substituted pyrylo-4- and thiapyrylo-4-pentamethinecyanines in $CH_2Cl_2$ are characterized by absorption maxima at 805 and 888 nm, respectively,[14] and the pentamethinecyanine benz[*c*,*d*]-indole derivative absorbs at 850 nm,[15] whilst the absorption maxima of thiapentamethinecyanine, indopentamethinecyanine and quino-2-pentamethinecyanine occur at 665, 665 and 705 nm, respectively.

We have synthesized the asymmetrical dyes **VIIa**–**VIIe** and **X** containing the above-mentioned heterocycles as one of the end-groups. Their absorption spectra are shown in Fig. 4. As was expected, two maxima occur in the long-wave region, as in dye **VIIa**, which has $\lambda^1_{max}$ at 628 nm ($\varepsilon = 5{\cdot}1 \times 10^4$) and $\lambda^2_{max}$ at 730 nm ($\varepsilon = 6{\cdot}7 \times 10^4$). These maxima correspond only to two electron transitions since the distance between them is much more than

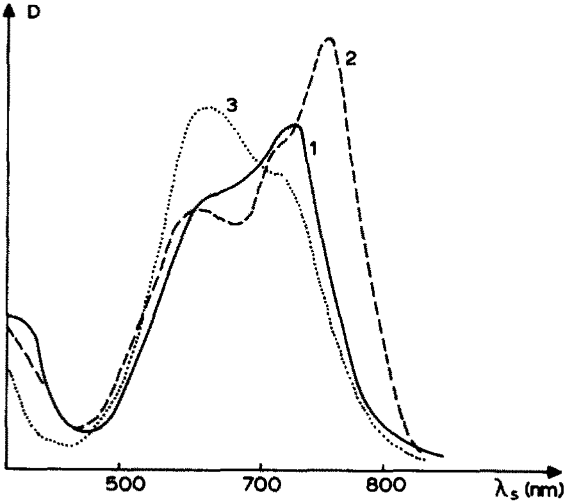


**Fig. 4.** Absorption spectra of asymmetrical dyes with pyrylium and thiapyrylium end-groups in $CH_2Cl_2$: 1, **VIIa**; 2, **VIIb**; 3, **VIIc**.

the 1200–1300 cm$^{-1}$ typical for the oscillating structure;[4] for example, for the dye **VIIa**, $\Delta\nu = 2225\,\mathrm{cm}^{-1}$, and for the dye **VIIb**, $\Delta\nu = 3309\,\mathrm{cm}^{-1}$. The change in the nature of the remaining two nuclei leads to a significant difference between the intensity ratios of the first and second bands. For example, the short-wave band is more intensive in the case of the dye **VIIc** containing two 2-quinoline nuclei (Fig. 4). The same phenomenon is observed for the dyes **VIId** and **VIIe** (Table 2).

Thus, in the case of asymmetrical trinuclear dyes containing end-groups with a different effective length, degeneracy of the electron transitions was found to be removed. Therefore, two maxima in the absorption spectra of these dyes are observed, in contrast with trinuclear dyes containing end-groups with nearly the same effective length, where only one wide band is observed.

## 2.5 Excited states and fluorescence spectra

As has been previously discussed, the energy levels of the excited states in symmetrical trinuclear dyes are degenerate. Upon excitation of the dye molecule, occupation of one of the degenerate lowest vacant levels occurs and the molecule becomes unstable, according to the Jahn–Teller rule. If the lifetime of the excited state is sufficiently large, twisting around the bond with the lowest bond-order could occur. It has been shown[16] that one of the polymethine chain branches is tilted out of the molecule plane, thus decreasing the symmetry of the molecule.

Fluorescence spectra give useful information about conformational

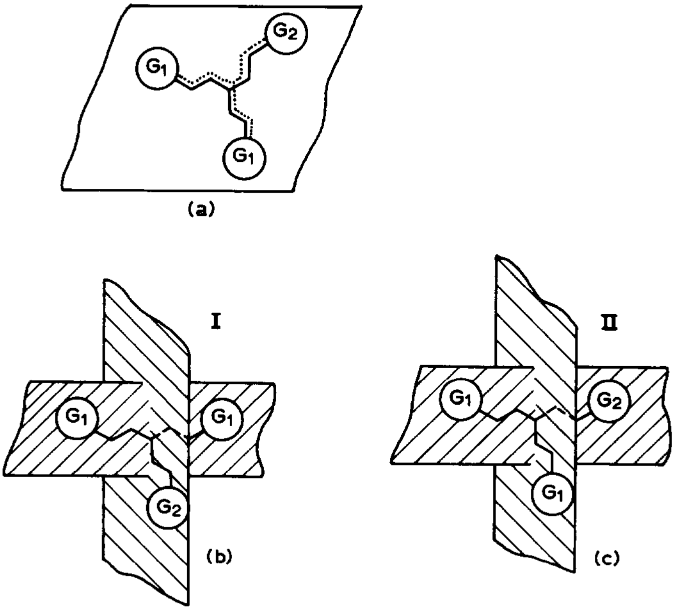


**Fig. 5.** The conformations of the trinuclear dyes in the ground (a) and excited (b, c) states. In the ground state the projection on the plane is represented.

isomers in the excited states. In this case, the electronic transitions occur when the molecule has the equilibrium geometry of the excited state. In the case of a symmetrical trinuclear dye, however, the presence of conformational isomers should not substantially influence the fluorescence spectra because the structure of all three possible conformers is similar and their fluorescence maxima will also be the same. Fluorescence spectra are only characterized by very large Stokes' shifts compared with those of the dinuclear homologues because the geometrical structure of a molecule in the ground state and the excited state is different. In the case of asymmetrical dyes containing at least one different nucleus, the presence of two distinct conformers is possible (Fig. 5). One conformer corresponds to the symmetrical pentamethinecyanine with the substituent in the $\gamma$-position (Fig. 5(b)) and the other to the substituted asymmetrical dye (Fig. 5(c)).

To support the existence of conformers in solutions of trinuclear dyes in excited states, their fluorescence spectra have been investigated. The quantum yield of the fluorescence was not quantitatively measured, but qualitative observations imply that the trinuclear dyes are much weaker luminophores than the dinuclear dyes. It was not possible to measure the fluorescence spectra of dyes with pyrylium end-groups.

Absorption and fluorescence maxima and Stokes' shifts ($\Delta S$) of trinuclear dyes and corresponding dinuclear dyes are listed in Table 2. Stokes' shifts of all trinuclear dyes are considerably larger compared with those of the dinuclear homologues. The large Stokes' shifts confirm the assumption that significant changes of the geometrical structure occur upon electron excitation. The magnitude of the quadratic changes of the bond-orders on excitation ($\delta$), which correlated with bond-length changes and is proportional to the bandwidth $\sigma$ as well as to the Stokes' shift $\Delta S$,[12] is substantially larger than those of the dinuclear dyes. This fact is in good agreement with the observed Stokes' shifts. It is important to note that the absorption spectra of the trinuclear dyes correspond to the ground-state propeller-like conformations with $C_3$ symmetry (Fig. 5(a)), whereas the fluorescence spectra reflect the excited-state conformations (Fig. 5(b,c)) attributed to substituted pentamethinecyanines.

The fluorescence spectra of the asymmetrical dyes **VId** and **VIe** are of special interest. In these examples end-groups are characterized by very different electron donor abilities $\Phi_0$. A significant asymmetry in electron density distribution must occur in the case of the asymmetrical conformer (Fig. 5(c)) and thus the electron transitions in those two conformers substantially differ in energy. Indeed, in the case of dyes **VId** and **VIe** two fluorescence maxima can be observed, with a difference of approximately 40 nm. We believe that these two maxima can be attributed to two possible conformers (Fig. 5(b,c)). In the case of the conformer A, corresponding to the symmetrical pentamethinecyanine, the electron density distribution should be more uniform. The longer-wave fluorescence maximum should thus correspond to this conformer. In the case of the conformer B, corresponding to the asymmetrical dye with considerable bond-order alternation in the polymethine chain, the fluorescence maximum should be observed at shorter wavelengths compared with the conformer A.

Thus, the fluorescence and absorption spectra data of dyes with branched chromophores can be used to study the significant changes which occur on excitation. In the case of asymmetrical dyes with end-groups differing considerably in electron donor ability $\Phi_0$, conformers characterized by different fluorescence maxima can be detected.

## 3 EXPERIMENTAL (Table 3)

### 3.1 2,6-Diphenyl-4-[3-formyl-5-(2,6-diphenylpyranylidene-4)]-1,3-pentadienyl pyrylium perchlorate (VIII)

A mixture of 0·173 g (0·5 mmol) 2,6-diphenyl-4-methylpyrylium perchlorate, 0·025 g (0·25 mmol) triformylmethane and 0·03 g sodium acetate was heated in 5 ml of acetic anhydride for 10 min at 100°C. The precipitated dye was filtered, washed initially with acetic anhydride and then with ether and crystallized. Yield: 0·108 g.

TABLE 3
Analytical Characteristics of Dyes

| *Compound* | *Melting point (°C)* | *Solvent* | *Found (%)* | | | |
|---|---|---|---|---|---|---|
| | | | *C* | *H* | *Cl(F)* | *N(S)* |
| **VId** | 250–252 | $C_2H_5OH$ | — | — | 8·4 | 8·3 |
| **VIe** | 177–179 | $C_2H_5OH$ | — | — | 7·2 | 10·3 |
| **VIId** | 181–183 | $CH_3CN$ | 65·6 | 5·5 | 8·5 | — |
| **VIIe** | 194–195 | $CH_3CN$ | 64·8 | 4·9 | 8·4 | — |
| **VIII** | 243 | $CH_3CN$ | 72·8 | 4·5 | 5·4 | — |
| **IX** | 284–285 | $CH_3CN$ | 70·7 | 4·3 | 6·9 | — |
| **X** | 235–236 | $CH_3CN$ | — | — | (20·0) | 5·3 |

| *Compound* | *Formula* | *Required (%)* | | | | *Yield (%)* |
|---|---|---|---|---|---|---|
| | | *C* | *H* | *Cl(F)* | *N(S)* | |
| **VId** | $C_{45}H_{45}Cl_2N_5O_8$ | — | — | 8·3 | 8·2 | 57 |
| **VIe** | $C_{50}H_{45}Cl_2N_7O_8$ | — | — | 7·5 | 10·4 | 27 |
| **VIId** | $C_{46}H_{44}Cl_2N_2O_9$ | 65·8 | 5·3 | 8·5 | — | 95 |
| **VIIe** | $C_{46}H_{44}Cl_2O_8S$ | 64·5 | 5·2 | 8·3 | — | 90 |
| **VIII** | $C_{40}H_{29}ClO_7$ | 73·1 | 4·5 | 5·4 | — | 63 |
| **IX** | $C_{58}H_{42}Cl_2O_{11}$ | 70·7 | 4·3 | 7·2 | — | 34 |
| **X** | $C_{42}H_{43}N_3B_2F_8$ | — | — | (19·9) | 5·5 | 60 |

### 3.2 Symmetrical trinuclear [2.2.2]heptamethinecyanines

The synthesis of dyes **IIIa–IIId** has been described previously.[7]

2,6-Diphenyl-4-{5-(2,6-diphenylpyranyliden-4)-3-[2-(2,6-diphenylpyrylio-4)vinyl]}-1,3-pentadienylpyrylium diperchlorate **IX** was obtained by heating of a mixture of 0·22 g (0·3 mmol) dye **VIII** and 0·116 g (0·3 mmol) of 4-methyl-2,6-diphenylpyrylium perchlorate in a mixture of 7 ml of benzonitrile and 2·5 ml of acetic anhydride for 40 min at 80°C. The precipitated dye was filtered, washed with ether and crystallized. The IR spectrum of the product showed no $\nu_{C=O}$ in the 1680–1660 $cm^{-1}$ region but the pyrylium ring stretching band was present at 1630 $cm^{-1}$.

### 3.3 Asymmetrical trinuclear [2.2.2]heptamethinecyanines

The synthesis of dyes **VIa–VIc** and **VIIa–VIIc** has been described previously.[7]

(a) 1,3,3-Trimethyl-2-{5-(1,3,3-trimethyl-1,2-dihydro-3*H*-indolylidene)-3-[2-(1-phenyl-3-ethyl-5-cyanobenzimidazolio-2-yl)vinyl]}-1,3-pentadienylindolium diperchlorate **VId** was obtained by heating a mixture of 0·172 g (0·5 mmol) of 1-phenyl-5-cyano-2-(3,3-diformylallylidene)benzimidazole prepared according to known synthetic procedure[6] and 0·274 g (1 mmol) of 1,2,3,3-tetramethylindolinyl perchlorate for 30 min at 100°C. Yield: 0·245 g.

(b) 1-Phenyl-3-ethyl-5-cyano-2-{5-(1,3,3-trimethyl-1,2-dihydro-3*H*-indolyliden)-3-[2-(1-phenyl-3-ethyl-5-cyanobenzimidazolio-2-yl)vinyl]}-1,3-pentadienylbenzimidazolium diperchlorate **VId** was obtained by heating a mixture of 0·362 g (1 mmol) of 1-phenyl-2-methyl-3-ethyl-5-cyanobenzimidazolium perchlorate and 0·127 g (0·5 mmol) of 1,3,3-trimethyl-2-(3,3-diformylallyliden)-1,2-dihydro-3*H*-indolylidene **V**[6] for 1 h at 110–115°C. Yield: 0·125 g.

(c) 1,3,3-Trimethyl-2-{5-(2,6-diphenylpyranyliden-4)-3-[2-(1,3,3-trimethyl-3*H*-indolio-2-yl)vinyl]}-1,3-pentadienylindolium diperchlorate **VIId** and 1,3,3-trimethyl-2-{5-(2,6-diphenylthiopyranyliden-4)-3-[2-(1,3,3-trimethyl-3*H*-indolio-2-yl)vinyl]}-1,3-pentadienylindolium diperchlorate **VIIe** were obtained by condensation of $\gamma$-formylindopentamethinecyanine **IV**[6] (0·6 mmol) with 0·5 mmol 2,6-diphenyl-4-methylpyrylium or thiopyrylium salts in acetic anhydride at 125°C.

(d) 1,3,3-Trimethyl-2-{5-(1,3,3-trimethyl-1,2-dihydro-3*H*-indolyliden)-3-[2-(1-ethylbenz[*c*,*d*]indolio-2-yl)vinyl]}-1,3-pentadienylindolium ditetrafluoroborate **X**.

*Method A:* A mixture of 0·25 g (0·5 mmol) $\gamma$-formylindopentamethinecyanine tetrafluoroborate and 0·145 g (0·5 mmol) 1-ethyl-2-methylbenz[*c*,*d*]-indolium tetrafluoroborate was heated in 5 ml of acetic anhydride for 40 min at 120°C. The precipitated dye was filtered and washed with ether. Yield: 0·26 g (68%).

*Method B:* A mixture of 0·130 g (0·5 mmol) 1,2,3,3-tetramethylindolium tetrafluoroborate and 0·065 g (0·25 mmol) 1-ethyl-2-(3,3-diformylallylidene)-benz[*c*,*d*]indole was heated in 3 ml of acetic anhydride for 30 min at 120°C. The precipitated dye was filtered and washed with ether. Yield: 0·15 g (79%).

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