Dyes and Pigments **18** (1992) 151–162

Synthesis, Structure, and Spectra of Merocyanines Prepared from Anionic Polymethine Dyes

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(Received 29 July 1991; accepted 3 September 1991)

ABSTRACT

A method is described for the preparation of trinuclear merocyanine dyes, involving the condensation of anionic dyes with electrophiles of a type traditionally used in polymethine-dye chemistry. Electronic and ^1H *NMR spectra data of the compounds are reported. The parameters of the first electron transition, as well as the changes in molecular electronic structure on excitation, were computed in the HMO-approximation.*

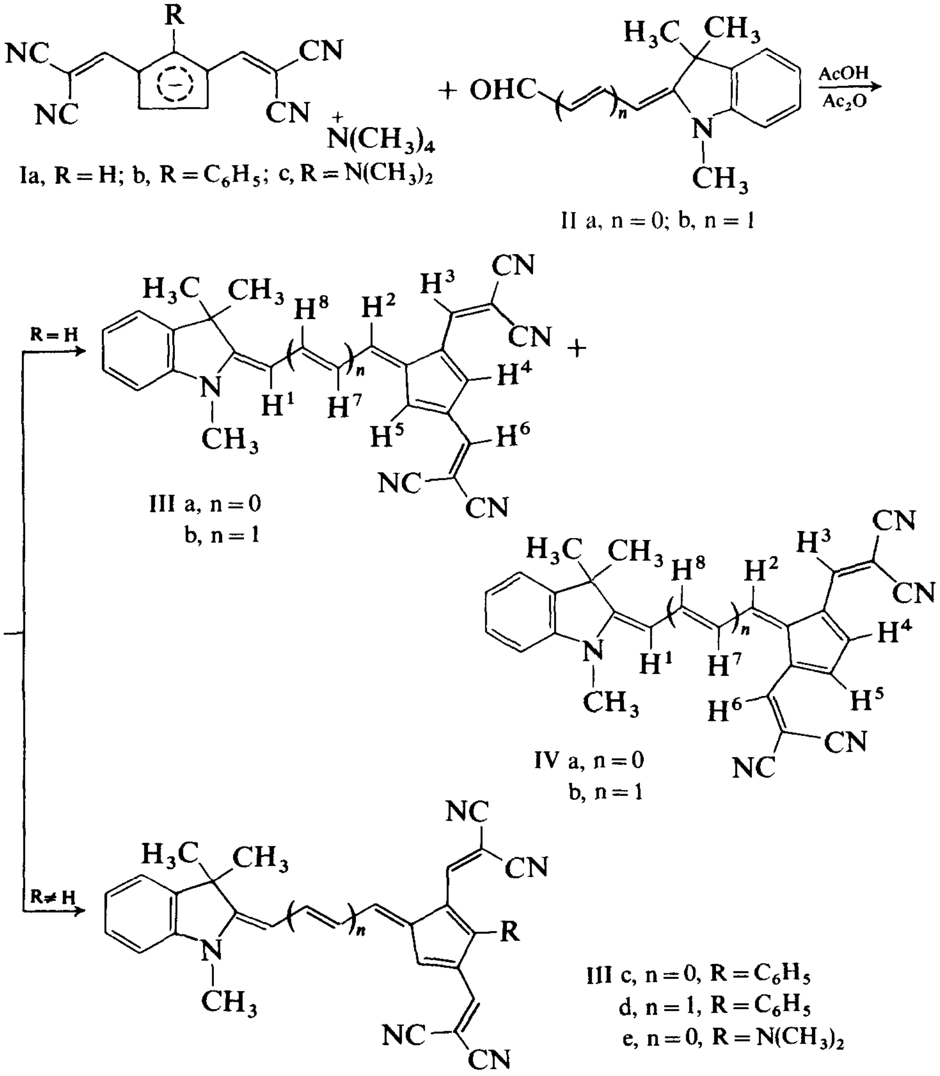
INTRODUCTION

It is known that the condensation of tetra- or dimethinemerocyanines with 2-(formylmethylene) derivatives of nitrogen-containing heterocycles or with 2-(β-chlorovinyl) derivatives of the heterocyclic quaternary salts produces trinuclear monocationic dyes.[1,2] Carbocyanines react with the electrophiles of this type to give trinuclear dicationic dyes, namely, neocyanines.[2,3] As we have described in previous papers,[4,5] anionic polymethine dyes prepared from malonitrile, and containing saturated or unsaturated bridges in their chromophores, have potential synthetic utility. We report here their condensation with some electrophiles usually used in polymethine-dye chemistry, in order to prepare the trinuclear dyes with formally uncharged molecules, i.e. merocyanines.

Dyes and Pigments 0143-7208/92/$05.00

DISCUSSION

The anionic dyes showed a high reactivity, undergoing condensation with electrophiles such as 1,3,3-trimethyl-2-formylmethyleneindoline or its vinylogue, in acetic acid in the presence of acetic anhydride. The structure of the products is determined by the bridging type in the initial anionic dye. Thus the condensation of dyes I containing a vinylene bridge with aldehydes II involves the five-membered ring and gives either a mixture of compounds III and IV or a single compound III, depending on the nature of the substituent R.



Ia, R = H; b, R = C_6H_5; c, R = $N(CH_3)_2$

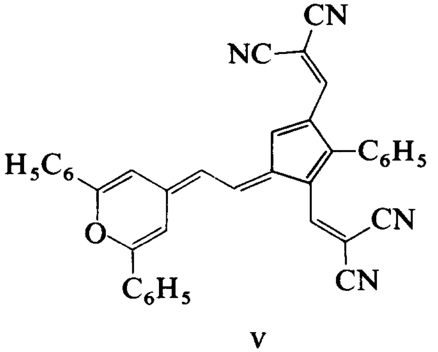
II a, n = 0; b, n = 1

III a, n = 0
b, n = 1

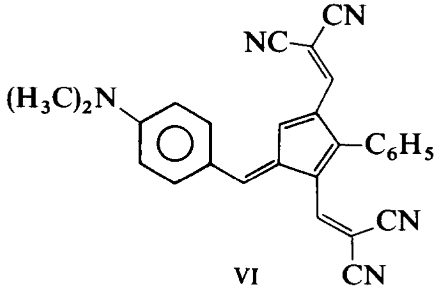
IV a, n = 0
b, n = 1

III c, n = 0, R = C_6H_5
d, n = 1, R = C_6H_5
e, n = 0, R = $N(CH_3)_2$

Similarly, dye Ib reacts with 2,6-diphenyl-4-formyl-methylene-4H-pyran or *p*-dimethylaminobenzaldehyde to yield the merocyanines V and VI.

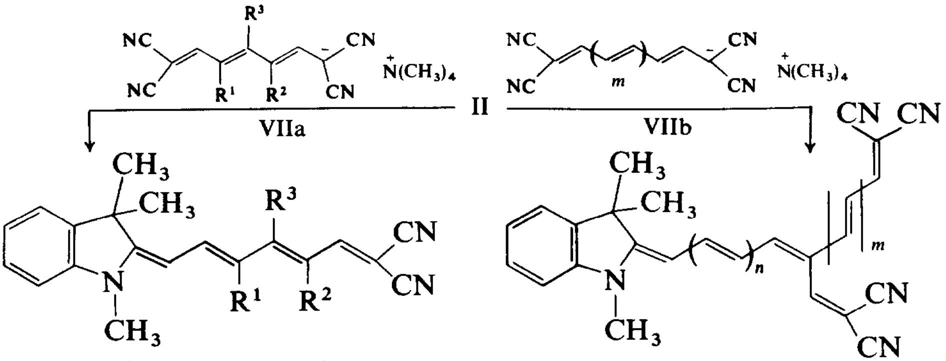


V



VI

The reaction direction and the structure of the products are controlled by the electron-density distribution in the parent anionic dye I, i.e. by the excess negative charge within the five-membered ring.[5] In contrast, for dyes VII*a* containing an ethylene or trimethylene bridge in the chromophore, the tendency is to localize the electron density predominantly at the odd atoms of the polymethine chain.[6] Therefore, the condensation of these with the aldehyde II*a* leads to the merocyanines IX–XI. Dyes of this type have been previously synthesized by other methods.[7] In the case where there is no bridge in the chromophore of the initial anionic dyes, the reaction with the electrophiles results in the formation of the trinuclear merocyanines XII–XIV with a branched polymethine chain.



IX, $R^1 + R^2 = (CH_2)_2$, $R^3 = H$
X, $R^1 + R^2 = (CH_2)_2$, $R^3 = C_6H_5$
XI, $R^1 + R^2 = (CH_2)_3$, $R^3 = CH_3$

XII, n = 0, m = 0
XIII, n = 0, m = 1
XIV, n = 1, m = 1

The ^1H NMR spectroscopy involving the homonuclear Overhauser effect (HOE) was applied to ascertain the structure of the isomeric compounds III*a* and IV*a* (see Table 1). Positive HOE-values were observed for the resonance signals H^1 and H^5, H^2 and H^3, H^4 and H^6 of dye III*a*, suggesting the close

TABLE 1

^1H NMR Spectral Assignment of Dyes III*a*,*b* and IV*a*,*b* (δ, ppm; J_{HH}, Hz)

Proton No. / *No. Comp.*	*1*	*2*	*3*	*4*	*5*	*6*	*7*	*8*	*Indolenine ring*	$C(CH_3)_2$	NCH_3
III*a*[1]	7·22 d $J=15$	8·53 d $J=15$	8·25 s	8·13 d $J=1·5$	7·96 d $J=1·5$	7·95 s	—	—	7·50–7·80	1·85 s	4·04 s
III*b*[2]	7·05 d $J=15$	8·08 d $J=15$	7·94 s	7·88 d $J=1·5$	7·35 d $J=1·5$	7·54 s	8·45 dd $J^1=15\,J^2=12$	7·23 dd $J^1=15\,J^2=12$	7·50–7·80	1·82 s	4·02 s
IV*a*[1]	6·81 d $J=15$	8·69 d $J=15$	8·15 s	7·63 s	7·63 s	8·15 s	—	—	7·50–7·80	1·89 s	4·15 s
IV*b*[3]	7·39 d $J=15$	8·36 d $J=15$	8·03 s	7·48 s	7·48 s	8·03s	8·49 dd $J^1=15\,J^2=12$	7·25 dd $J^1=15\,J^2=12$	7·50–7·90	1·83 s	4·08 s

[1] In acetone-D_6; [2] In DMSO-D_6; [3] In DMFA-D_7.

disposition of the corresponding H-atoms,[8] whereas dye IV*a* shows the same effect for the signals H^1 and H^6, H^2 and H^3. In addition, the structure of the latter dye is confirmed by the equivalence in pairs of protons H^3 and H^6, H^4 and H^5, as well as by the absence of the positive HOE when irradiating the dye sample with the resonance frequencies $H^{4,5}$. The isomers were also analysed in terms of molecular mechanics, by taking into account the conjugation effect,[9] in order to optimize their geometrical parameters. The distances between the H-atoms showing positive HOE were found to be as follows: $H^{1,5}$—2·15 Å, $H^{2,3}$—2·26 Å, $H^{4,6}$—2·65 Å (III*a*), and $H^{1,6}$—2·35 Å, $H^{2,3}$—2·31 Å (IV*a*).

TABLE 2

Electronic-Absorption Spectra of Merocyanines III–VI and IX–XIV

N	λ_{max} ($\varepsilon \cdot 10^{-4}$) *nm*		
	DMFA	*Methanol*	*Benzene*
III*a*	450 (3·92)	445 (4·07)	447 (4·28)
	589 (7·44)	590 (7·95)	620 (8·11)
III*b*	484 (3·43)	465 (3·43)	463 (2·50)
	664 (6·25)	671 (8·35)	725 (14·08)
III*c*	442 (4·28)	437 (4·48)	441 (4·04)
	608 (5·41)	609 (6·08)	626 (7·96)
III*d*	457 (3·62)	454 (3·67)	452 (2·92)
	682 (5·20)	688 (6·79)	720 (13·49)
III*e*	429 (5·06)	425 (5·33)	425 (4·96)
	651 (4·38)	644 (4·58)	656 (4·28)
IV*a*	365 (2·24)	365 (2·55)	370 (2·24)
	589 (4·23)	613 (4·81)	635 (5·72)
IV*b*	400 (3·25)	400 (3·05)	400 (2·70)
	429 (3·17)	426 (2·85)	446 (3·43)
	658 (5·17)	602 (4·72)	742 (12·60)
V	412 (3·61)	407 (3·62)	400 (3·62)
	454 (3·41)	444 (3·40)	444 (3·20)
	686 (8·13)	684 (8·35)	712 (9·05)
VI	384 (2·60)	380 (3·03)	384 (3·44)
	431 (2·30)	428 (2·67)	428 (2·55)
	660 (7·90)	654 (7·54)	660 (8·08)
IX	626 (7·25)	611 (7·31)	596 (6·27)
X	647 (8·22)	628 (8·42)	612 (7·00)
XI	650 (8·13)	631 (8·22)	615 (7·08)
XII	462 (1·93)	454 (1·86)	443 (1·47)
	560 (5·21)	560 (5·55)	577 (4·58)
XIII	504 (2·53)	494 (2·41)	482 (2·34)
	618 (5·91)	610 (5·58)	615 (3·78)
XIV	548 (3·40)	533 (3·14)	512 (2·44)
	716 (10·17)	709 (10·08)	720 (6·65)

Spectral parameters of the dyes are shown in Table 2. Several transitions with rather close energies are typical of all the merocyanines having a branched chromophore. This is consistent with the quantum-chemical estimates in the HMO-approximation given in Table 3.

The calculated data indicate that the first transition of a trinuclear merocyanine is not strictly localized in a specific structural fragment of the dye molecule. In fact, for both dyes III*a* and XIV, the projections M_x and M_y of the transition dipole moment are comparable. Although the maximum change in charge on excitation occurs in the polymethine chain between the heterocyclic residue and the chromophore branching point, this effect is of the same order of magnitude for the rest of the atoms, except the β-carbon atom of the heterocycle (see Fig. 1).

For compound IV*a* the projection M_y is zero, but nevertheless excitation is accompanied by a considerable change in charge at all the atoms of the branched chromophore.

Lengthening the section of the polymethine chain between the heterocyclic residue and the chromophore branching point by a vinylene group causes a bathochromic shift of *c*. 100 nm for dyes containing the five-membered ring (III*a* and III*b*, III*c* and III*d*, IV*a* and IV*b*), as well as for those without it (XIII and XIV). Other sections of the polymethine chain are not so spectroscopically sensitive to their lengthening. For example, on comparing the merocyanine XII and its vinylogue XIII, the bathochromic shift is *c*. 50 nm.

As can be seen from Table 2 and Fig. 2, the merocyanines III and IV, both containing a fulvene-like fragment, have a pronounced negative solvatochromism. In dimethylformamide (DMF), their absorption bands are rather wide and bell-shaped, and their vinylene shifts are *c*. 100 nm. In benzene, however, the dye colour deepens, the absorption bands narrow, and the molar-absorption coefficients increase. Thus, in a non-polar solvent, spectral

TABLE 3

Wavelengths of the First Two Electronic Transitions (λ^1_{ex}, λ^2_{ex} for Observed, λ^1_{HMO}, λ^2_{HMO} for Calculated Values) and Electron-Donor Ability ϕ_0 of Merocyanines

Compound	λ^1_{ex} (*nm*)	λ^1_{HMO} (*nm*)	λ^2_{ex} (*nm*)	λ^2_{HMO} (*nm*)	ϕ_0 (*degrees*)
III*a*	620	497	447	437	26
IV*a*	635	613	370	326	24
XIV	720	674	512	560	39

The Coulomb α_N and the resonance β_{CN} integrals of the nitrogen atom and its bonds are taken as $\alpha + 1{\cdot}5\beta$ and β, respectively for the indolenine ring, and $\alpha + 0{\cdot}5\beta$ and $1{\cdot}4\beta$, respectively, for the cyano group.

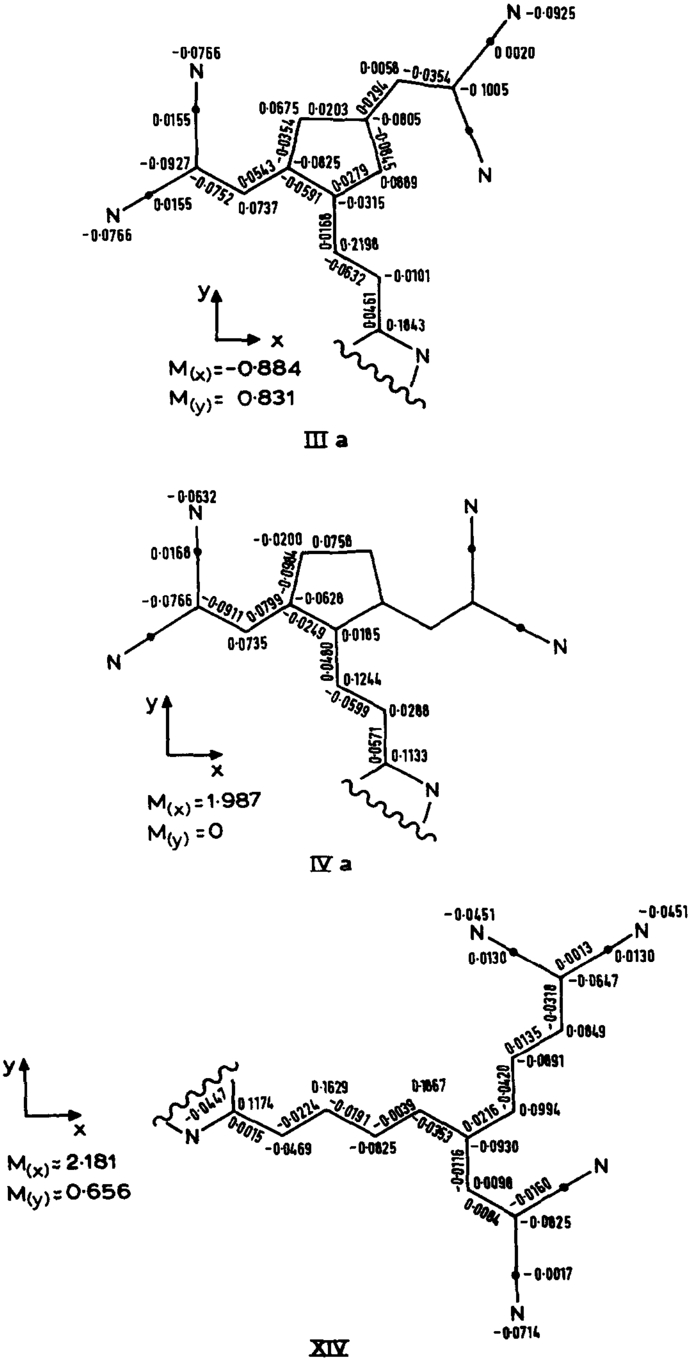


Fig. 1. The change of π-electron charges on the atoms and bond orders in the merocyanine molecules on excitation.

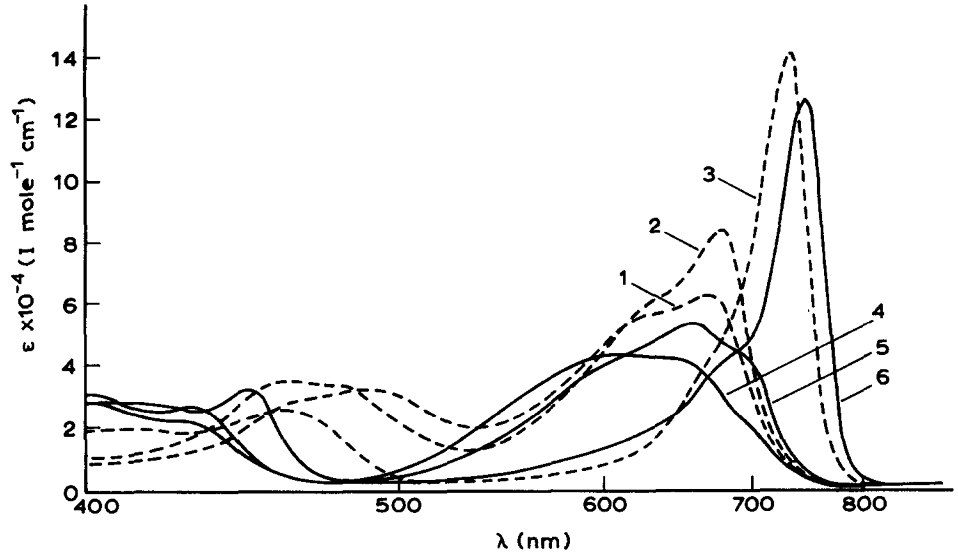
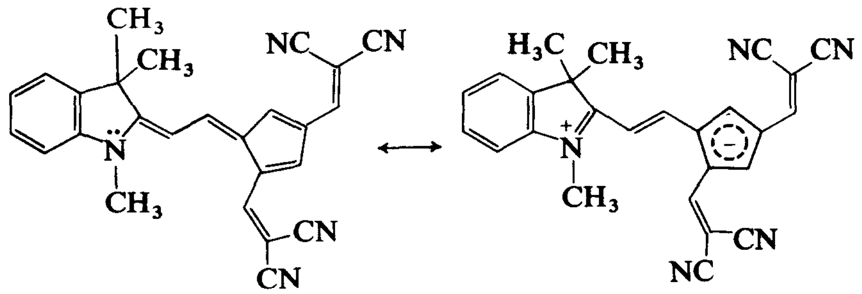


Fig. 2. The electronic-absorption spectra of merocyanines III*b* (curves 1, 2, 3) and IV*b* (curves 4, 5, 6) in DMF (1, 4), methanol (2, 5), and benzene (3, 6).

curves take on a shape characteristic of the symmetric polymethine dyes, with vinylene shifts approximating to 100 nm. Furthermore, the negative solvatochromism attenuates, as the Brooker basicity of the heterocyclic residue[10] lowers. Thus, in γ-pyranylidene (dye V) this effect is much less than in indolenine (dyes III and IV) and is absent for the *p*-dimethylaminophenyl group (dye VI).

This phenomenon can be clarified by taking into account the intramolecular charge-transfer inherent in merocyanines in general:



The negative solvatochromism results from the fact that the molecule in the ground state is polarized to a greater degree than in the excited state. Hence, the larger the difference in basicities of the dye end-groups,[10] the stronger should be the solvatochromic effect. With an allowance for the rather low basicity of the indolenine residue in dyes III*a* and IV*a*, it is reasonable to suppose that the second residue, i.e. the dicyanovinylcyclopentadienylidene group, can exhibit a considerable electron-withdrawing ability. It could then be responsible for a charge separation in the ground state that is sufficient for the negative solvatochromism to appear. In fact, the fulvene-like fragment exceeds its acyclic analogue in electron-acceptor property, which is demonstrated by the increasing proton-chemical shifts for the *N*-methyl group of the indolenine ring in the dye series: 3·75 ppm (XIV) < 4·04 ppm (III*a*) < 4·15 ppm (IV*a*).

The compounds can also be characterized by their electron-donor ability ϕ_0. This parameter was introduced in terms of the approximation of a quasi-long polymethine chain, in order to estimate the disposition of the dye-frontier molecular orbitals relative to the Fermi level:[11,12]

$$\phi_0 = 90^\circ \lim_{n \to \infty} \frac{E_{\text{LUMO}}}{E_{\text{LUMO}} - E_{\text{HOMO}}}$$

(n is the number of vinylene groups in the polymethine chain, and E_{HOMO} and E_{LUMO} are the energies of the highest-occupied and the lowest-unoccupied molecular orbitals, respectively). As expected, the electron-donor ability decreases in the series of dyes XIV, III*a*, and IV*a* (see Table 3), according to the regularity found in their ^{1}H NMR spectra.

It is of interest to note that the acyclic end-residue in dye XIV is not sufficiently acceptor in nature to cause a pronounced negative solvatochromic effect, in spite of the presence of four cyano groups in the molecule. Similarly, this effect is negligible for the merocyanine XII, and even touches on the inverse for the merocyanine XIII. Additionally, these dyes in benzene show notable widening of their absorption bands and a decrease in ε values, unlike compounds III*a* and IV*a*.

As Fig. 2 indicates, the band shapes of trinuclear merocyanines are influenced both by the dye structure and by the nature of the solvent; the vibronic interactions are of prime importance in the former case, and the specific solvation of the dye in the latter. To estimate the degree of vibronic interactions, we have used the total square change of bond orders on excitation,[13] δ, calculated in the HMO-approximation:

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

with p_i^0 and p_i^* denoting bond orders in the ground and excited states, respectively.

For the three dyes considered above, this parameter changes in the order: 0·114 (XIV) < 0·199 (III*a*) < 0·269 (IV*a*). The vibronic effects are therefore presumed to be enhanced, and the first absorption bands should widen. This is, in fact, the case in a polar medium such as DMF, which weakens the dye intermolecular interactions. Moreover, this solvent stabilizes the structure with separated charges, owing to nucleophilic solvation, and thus additionally favours the alternation of bond orders in the ground state and their change on excitation. In contrast to this, in benzene the absorption bands of dyes III*a*–*d* and IV*a*,*b* become markedly narrower, which may be accounted for by dispersion interactions. Analogous phenomena have been previously observed in investigations of unsymmetric cationic dyes.[13]

In the absorption spectra of compounds XII–XIV, free of the pronounced negative solvatochromism, such a band-narrowing is not observed in benzene. The merocyanines IX–XI display positive solvatochromism, their band shapes being practically unchanged on passing from a non-polar to a polar solvent.

In this present paper, we do not discuss in detail the intensity ratio for the short- and long-wavelength absorption bands of the trinuclear merocyanines. However, it should be mentioned that this is greatly influenced by the dye constitution. Thus, in the dye series III*a*, III*c*, III*e*, the two absorption bands undergo increasing band separation, the short-wavelength band intensifying while the long-wavelength band weakens.

EXPERIMENTAL

Electronic-absorption spectra were recorded by using a Specord M-40; ^{1}H NMR spectra were measured on a Varian VXR-300 (299·96 MHz) with TMS as an internal standard. The HOE was determined by the difference method, involving the selective frequency saturation of multiplet components, with the use of a composite rectangular-reading pulse.[8,14]

All the merocyanines were prepared by the general procedure. An anionic dye (0·0010 mol) was mixed with the appropriate aldehyde (0·0012 mol) in acetic anhydride (2 cm^3) and acetic acid (2 cm^3). After standing at 20–60°C for 10 min, the mixture was cooled to room temperature and diluted with methanol. After 1 h, the dye was filtered, washed with methanol, and recrystallized. Dyes III*a* and IV*a*, III*b* and IV*b* were separated by chromatography on alumina with acetone used as eluent.

^{1}H NMR spectra in acetone-d$_6$, δ_{ppm}, J_{Hz}: *1,3-dihydro-1,3,3-trimethyl-2-[7,7-dicyano-3,5-(ethylene)hepta-2,4-6-trien-1-ylidene]-2H-indole* (IX)—1·77 s (6H, C(CH$_3$)$_2$), 2·80–3·10 m (4H, CH$_2$CH$_2$), 3·35 s (3H, N(CH$_3$)), 5·52 d (1H, CH, $J = 13·2$), 7·27 s (1H, CH), 7·45 d (1H, CH, $J = 13·2$), 7·56 s (1H, CH), 6·93–7·01 m (2H, ring CH), 7·23 d (1H, ring CH, $J = 7·8$), 7·33 d (1H, ring CH, $J = 7·8$); *1,3-dihydro-1,3,3-trimethyl-2-[7,7-dicyano-3-(2,2-dicyano-ethene-1-yl)hepta-2,4,6-trien-1-ylidene]-2H-indole* (XIII)—1·77 s (6H, C(CH$_3$)$_2$), 3·81 s (3H, N(CH$_3$)), 6·64 d (1H, CH, $J = 14·3$), 6·95 dd (1H, CH, $J = 14·3$),

TABLE 4
Yields, Melting Points, and Analytical Data of Compounds III–VI and IX–XIV

No.	*Yield* (%)	*Melting point* (°*C*)	*Found* (%)			*Formula*	*Requires* (%)		
			C	*H*	*N*		*C*	*H*	*N*
III*a*	12	294–295	77·73	4·61	17·48	$C_{26}H_{19}N_5$	77·78	4·77	17·45
III*b*	6	275–277	78·85	5·09	16·29	$C_{28}H_{21}N_5$	78·66	4·95	16·38
III*c*	35	275–276[a]	80·72	5·07	14·43	$C_{32}H_{23}N_5$	80·48	4·85	14·67
III*d*	37	295–297[b]	82·34	5·41	12·97	$C_{34}H_{25}N_5 \cdot 1/2C_6H_6$	81·89	5·20	12·91
III*e*	33	251–252[b]	75·97	5·46	18·96	$C_{28}H_{24}N_6$	75·65	5·44	18·91
IV*a*	15	285–286	77·73	5·01	17·37	$C_{26}H_{19}N_5$	77·78	4·77	17·45
IV*b*	9	303–305	78·93	5·12	16·28	$C_{28}H_{21}N_5$	78·66	4·95	16·38
V	17	297–299[c]	83·04	4·07	9·85	$C_{38}H_{22}N_4O$	82·89	4·03	10·18
VI	21	235–237[a]	79·21	4·65	16·33	$C_{28}H_{19}N_5$	79·04	4·50	16·46
IX	23	212–213	80·75	6·45	12·79	$C_{22}H_{21}N_3$	80·70	6·47	12·83
X	27	239–241	83·47	6·00	10·17	$C_{28}H_{25}N_3$	83·34	6·25	10·41
XI	17	217–219	80·93	7·07	11·73	$C_{24}H_{25}N_3$	81·09	7·09	11·82
XII	37	266–267	75·26	4·81	19·79	$C_{22}H_{17}N_5$	75·19	4·88	19·93
XIII	33	220–221	76·16	5·07	18·69	$C_{24}H_{19}N_5$	76·34	5·07	18·56
XIV	21	217–219[d]	77·12	5·14	17·42	$C_{26}H_{21}N_5$	77·39	5·25	17·36

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[a] Recrystallized from the mixture pyridine–benzene.

[b] From the mixture DMFA–benzene.

[c] From DMFA.

[d] From pyridine, other compounds were recrystallized from the mixture pyridine-isopropanol.

7·87 d (1H, CH, $J = 11{\cdot}7$), 7·96 d (1H, CH, $J = 14{\cdot}3$), 8·07 s (1H, CH), 8·50 d (1H, CH, $J = 14{\cdot}3$), 7·30–7·70 m (4H, ring CH).

The structures of the other merocyanines were similarly confirmed. Other characterisation for parameters of the compounds is shown in Table 4.

CONCLUSIONS

Starting from anionic cyanine dyes, novel trinuclear merocyanines were synthesized, their structures being dependent on the nature of the bridging system in the anionic dyes. Several transitions with rather close energies were observed in the electronic-absorption spectra of the compounds. The first transition proved not to be strictly localized in a specific part of the molecule. Negative solvatochromism was observed for the trinuclear merocyanines containing a fulvene-like fragment.

REFERENCES

1. Coenen, M., *Ann. Chem.*, **633** (1960) 92.
2. Shirokova, N. I., Sveshnikov, N. N. & Levkoev, I. I., *Dokl. AN SSSR, Ser. Khim.*, **162** (1965) 603.
3. Kendall, J. D. & Mazer, J. R., *J. Chem. Soc.*, (1948) 690.
4. Slominsky, Yu. L., Popov, S. V., Ilchenko, A. Ya. & Tolmachev, A. I., *Zh. Org. Khim.*, **21** (1985) 1294.
5. Slominsky, Yu. L., Kachkovski, A. D., Popov, S. V., Nechitailo, L. A. & Ignatiev, N. V., *Dyes and Pigments*, **15** (1991) 247.
6. Slominsky, Yu. L., Popov, S. V., Repyakh, I. V., Povolotsky, M. I., Kachkovsky, A. D. & Dyadyusha, G. G., *Theoret. Experim. Khim.*, **23** (1987) 687.
7. Slominsky, Yu. L., Popov, S. V. & Kachkovsky, A. D., *Zh. Obshch. Khim.*, **59** (1989) 459.
8. Derome, A. E., *Modern NMR Techniques for Chemistry Research*. Pergamon Press, Oxford, 1987, p. 280.
9. Clark, T., *A Handbook of Computational Chemistry*. John Wiley & Sons, New York, 1985.
10. Brooker, L. G. S., *Rev. Mod. Phys.*, **14** (1942) 275.
11. Dyadyusha, G. G. & Kachkovsky, A. D., *Ukr. Khim. Zh.*, **44** (1978) 948.
12. Dyadyusha, G. G. & Ushomirsky, M. N., *Theoret. Experim. Khim.*, **21** (1985) 268.
13. Ishchenko, A. A., Derevyanko, N. A. & Tolmachev, A. I., *Dokl. AN SSSR, Ser. Fizich. Khim.*, **274** (1984) 106.
14. Kinns, M. & Sanders, J. K., *J. Magn. Res.*, **56** (1984) 518.