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Nature of Absorption Bands of Thiazolopyrimidinium Polymethine Dyes

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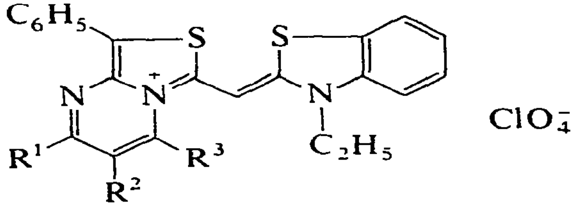
SUMMARY

Both symmetric and asymmetric thiazolopyrimidinium monomethine-, carbo- and dicarbo-cyanines have been synthesized. The wavelengths of the first two long-wave absorption bands have been investigated by physical and quantum-chemical methods. Electron density distributions for the ground, the first excited and second excited singlet states have been calculated. The electron redistribution diagrams were used to analyse the localization of electron transitions. The first band has been shown to be localized in the polymethine chain (Kühn's chain) while the second band is mainly localized in the thiazolopyrimidinium end-group.

1. INTRODUCTION

Thiazolopyrimidinium polymethine dyes (I) are very convenient subjects for the elucidation of a number of colour theory problems. As a rule two absorption bands are observed in the spectra of such dyes in their visible



I

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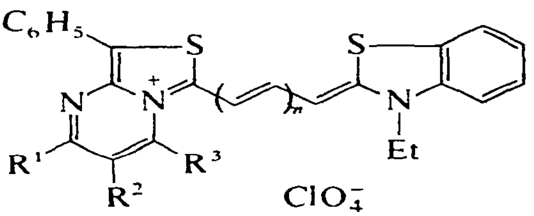
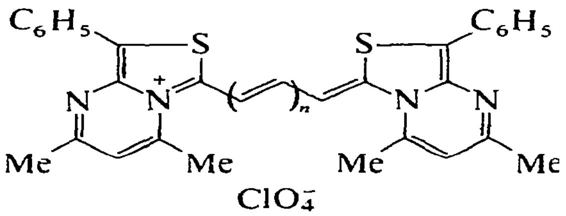
and near-IR regions. This is rather atypical for polymethine dyes having nitrogen heterocycles as the end-groups. We have shown[1] previously that in the asymmetric monomethine cyanine (**I**) the first long-wave absorption band is related to a $\pi \rightarrow \pi^*$-transition in a polymethine chain (Kühn's chain), while the second band is caused by the local transition of π-electrons within the thiazolopyrimidinium nucleus together with the shift of π-electron density from the thiazole ring to the pyrimidine one. The highest vinylog cyanines of the asymmetrical series (**II**, **III**) as well as the symmetrical dyes (**IV**–**VI**) were synthesized to investigate the relation between the position of the first two absorption bands and the chemical structure of the dye molecules.



II, III

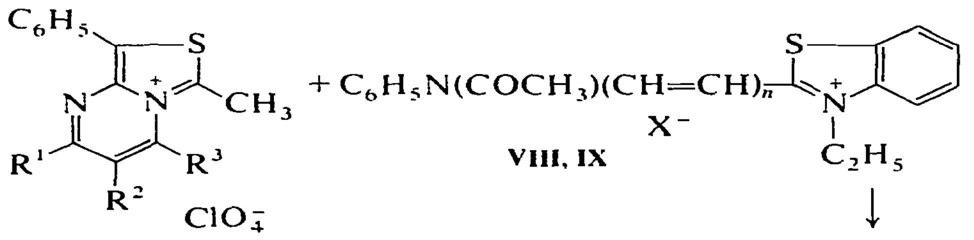


IV–VI

IV: $n = 0$
II, V: $n = 1$
III, VI: $n = 2$

2. MATERIALS

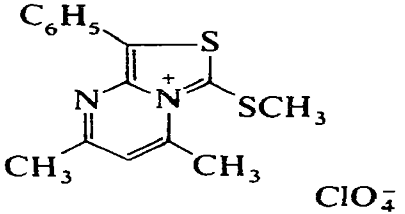
Asymmetric dyes were synthesized by the interaction of substituted 6-methylthiazolo[3,4-*a*]pyrimidinium perchlorate (**VIIa–d**) with salts of 3-ethyl-2-(2-acetanilidovinyl) benzothiazole (**VIII**) or 3-ethyl-2-(4-acetanilido-1,3-butadienyl)benzothiazole (**IX**).



VIIa-d **VIII, IX** **IIa, b, d, IIId**

a: $R^1 = R^2 = R^3 = H$; b: $R^1 = R^3 = H$, $R^2 = C_6H_5$; c: $R^1 = R^3 = CH_3$, $R^2 = H$;
d: $R^1 = C_6H_5$, $R^2 = H$, $R^3 = CH_3$.

Monomethinecyanine (IV) was obtained by condensation of 2,4,6-trimethyl-8-phenylthiazolo[3,4-*a*]pyrimidinium perchlorate (**VIIc**) with the 6-methylthio derivative (X) of the same heterocycle.

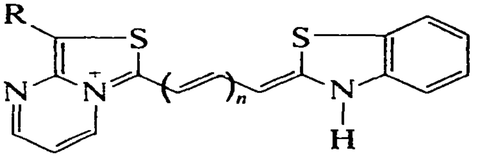


X

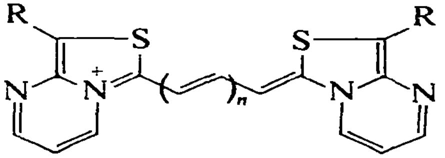
Trimethinecyanine (V) and pentamethinecyanine (VI) were synthesized by condensation of salt **VIIc** with diphenylformamidine (XI) or with (3-anilino-2-propenylidene)phenylammonium (XII) respectively.

3. METHOD

In the present work the standard method of self-consistent field in the PPP-approximation[2] was used to analyse the electron structure of the model dye cations **XIII–XVIII**.



XIII–XV



XVI–XVIII

XIII, **XVI**: $n = 0$
XIV, **XVII**: $n = 1$
XV, **XVIII**: $n = 2$

Atomic and bond parameters as well as values of interatomic distances and bond angles were used as in our previous paper:[3] C(trtrtrπ), $U_\mu = -11{\cdot}42$ eV, $\gamma_{\mu\mu} = 10{\cdot}83$ eV; N(trtrtrπ^2), $U_\mu = -23{\cdot}13$ eV, $\gamma_{\mu\mu} = 12{\cdot}98$ eV; N(tr^{2}trtrπ), $U_\mu = -14{\cdot}12$ eV, $\gamma_{\mu\mu} = 12{\cdot}34$ eV; S(tr^{2}trtrπ^2), $U_\mu = -20{\cdot}27$ eV, $\gamma_{\mu\mu} = 9{\cdot}80$ eV; $\beta_{CC} = -2{\cdot}32$ eV, $\beta_{CN} = -2{\cdot}53$ eV, $\beta_{CS} = -1{\cdot}65$ eV. Double-centre integrals of electron interaction were calculated using the Mataga–Nishimoto formula.[4]

Correlation between calculated absorption maxima and those observed is reduced on polymethine chain lengthening. It is a common defect of the standard PPP method where the excited state is calculated using only the singly excited configuration expansion.[5]

The electron density redistribution diagrams were used to analyse the localization of electron transitions. The diagrams describing the electron density changes along the conjugated system upon excitation clearly indicate the atoms involved in these transitions. The electron density changes enable the energy changes in the dye spectra to be determined. In this respect, these diagrams have a great advantage over other approaches to the analysis of electron excitation localization.[6]

4. RESULTS AND DISCUSSION

4.1. Asymmetrical dyes

Consider firstly the vinylog series of the asymmetrical dyes (**I**–**III**). These dyes have benzothiazole as one end-group. The absorption band of this nucleus is localized in the short-wave region of the spectrum.

In the visible part of the spectra of the dyes **I**–**III** two absorption bands are observed (Figs. 1 and 2; Table 1). Both bands are shifted to the long-wave region on polymethine chain lengthening. The first absorption band shift (120–130 nm) corresponds to the usual vinylog shift in case of polymethine dyes.[7] The long-wave band intensity also rises with the increase in the number of vinyl groups. The intensity of the

TABLE 1
Experimental Absorption Band Wavelengths of Asymmetrical Dyes

Dye	*n*	*R^1*	*R^2*	*R^3*	λ_{max} *(nm) (log ε)*	*Solvent*
Ia	0	H	H	H	420 (4·26), 440 (4·27), 534 (4·39)	DMF[a]
Ib	0	H	Ph	H	428 (4·31), 448 (4·33), 552 (4·35)	DMF[a]
Ic	0	Me	H	Me	420 (4·04), 440 (4·04), 540 (4·46)	DMF[a]
Id	0	Ph	H	Me	478 (4·47), 545 (4·34)	DMF[a]
IIa	1	H	H	H	496 (4·14), 520 (4·16), 655 (4·34)	CH_3CN
IIb	1	H	Ph	H	496 (4·19), 530 (4·19), 672 (4·75)	CH_3CN
IId	1	Ph	H	Me	560 (4·27), 678 (4·71)	CH_3CN
IIId	2	Ph	H	Me	480 (4·15), 790 (4·91)	CH_3CN

[a] DMF, dimethylformamide.

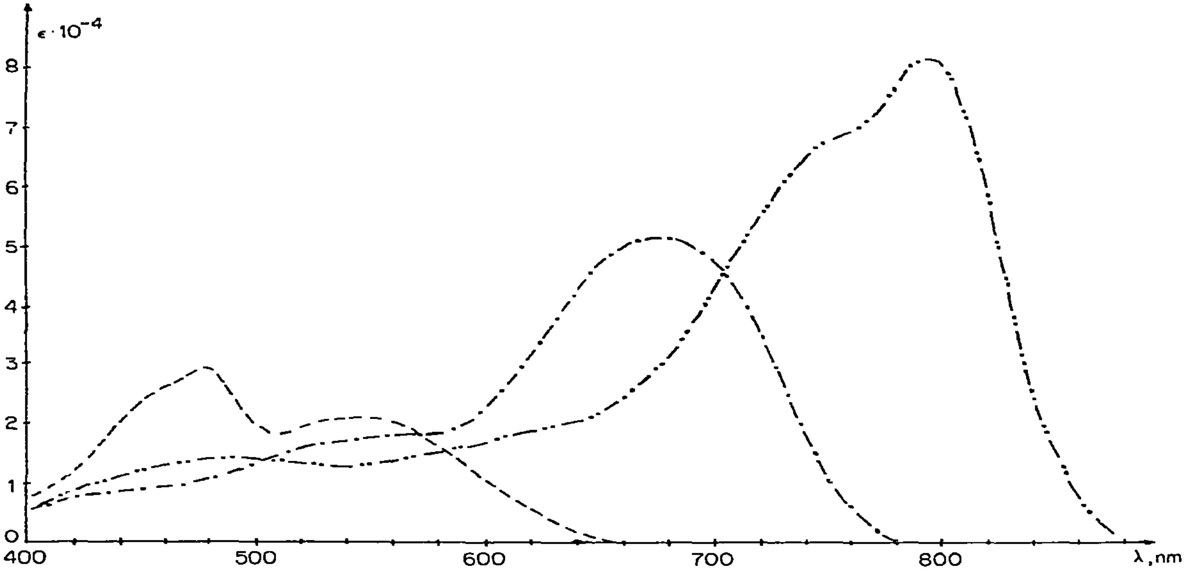


Fig. 1. Absorption spectra of dyes in CH_3CN. ———, **Id**; —·—·—, **IId**; —··—··—, **IIId**.

short-wave band depends very much on the substituent and it may exceed that of the first band in dyes having a short polymethine chain ($n = 0$). The distance between the bands increases on chain lengthening; they become more independent and the second band intensity decreases, in contrast to the chromophore interaction.[8]

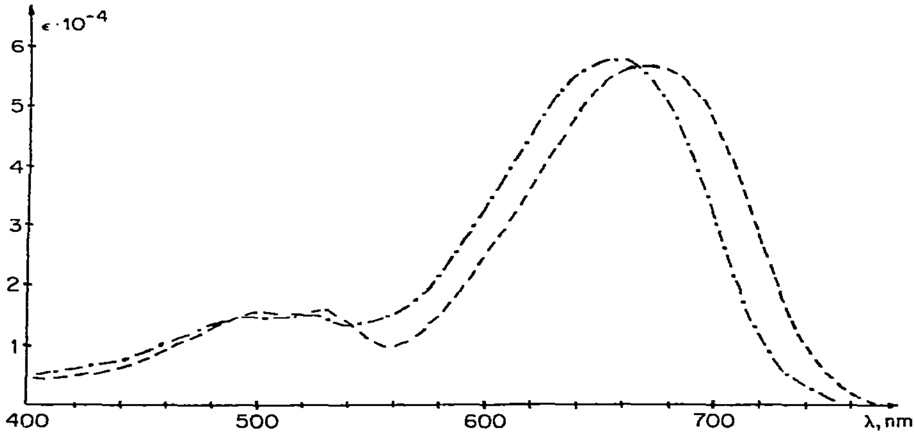


Fig. 2. Substituent effect on absorption bands of dyes. —·—·—, **IIa**; ———, **IIb**.

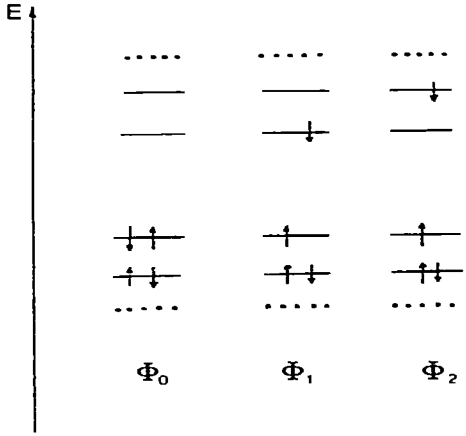


Fig. 3. Ground (Φ_0) and two excited (Φ_1, Φ_2) electron configurations of dyes.

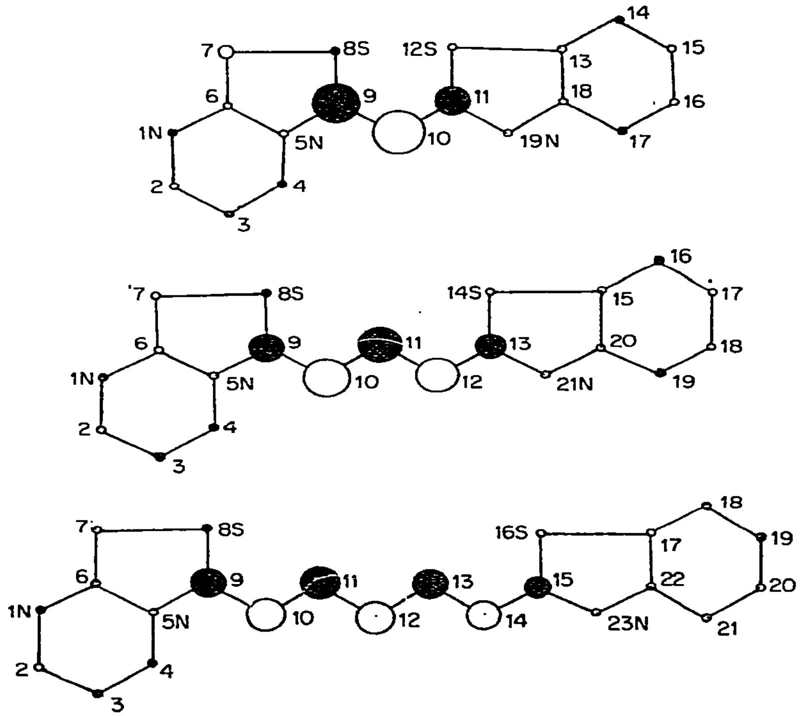


Fig. 4. Electron density redistribution of model asymmetrical dyes for molecular transition from ground state to first excited state. ○, Electron density decreases; ●, electron density increases; radii are proportional to electronic density changes.

Quantum analysis using MO approximation shows both bands to be caused by electronic transition from the same highest field molecular orbital (Fig. 3). That is why their intensities are so closely related.

Calculated electron density distributions for the ground (S_0), first (S_1) and second (S_2) excited singlet states of model dye cations XIII–XV are listed in Table 2. Figures 4 and 5 show electron density changes on atoms upon excitation. The main centre of the electron redistribution is seen to be localized mainly in Kühn's chain, if the first transition occurs. Similar changes upon excitation are typical for cyanine dyes (e.g. streptocyanine or thiacyanine[1]). Consequently, the bands mentioned above are of the same nature.

The first excited state is described mainly as a Φ_1-configuration in which two orbitals are singly occupied (Fig. 3). The wave function

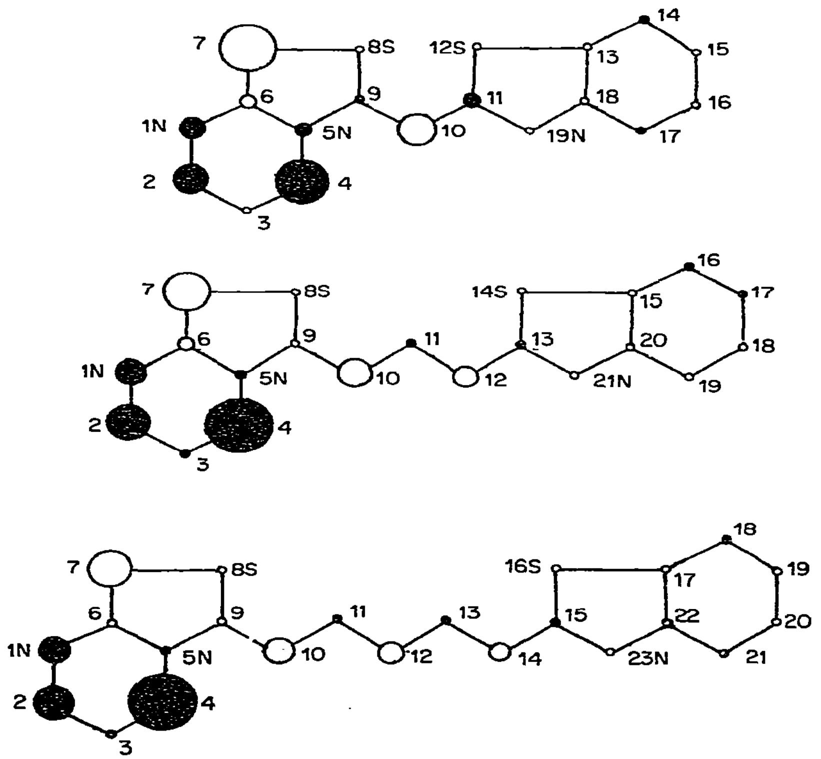


Fig. 5. Electron density redistribution of model asymmetrical dyes: molecular transition from ground state to second excited state. Symbols as in Fig. 4.

TABLE 2

Electron Density Distribution in Asymmetrical Dyes

$n = 0$				$n = 1$				$n = 2$			
Atom number	P_i^0	P_i^*	P_i^{**}	*Atom number*	P_i^0	P_i^*	P_i^{**}	*Atom number*	P_i^0	P_i^*	P_i^{**}
N-1	1·1773	1·2084	1·2693	N-1	1·1796	1·1948	1·3032	N-1	1·1812	1·1900	1·3155
C-2	0·8532	0·8505	1·0054	C-2	0·8549	0·8493	1·0212	C-2	0·8562	0·8512	1·0207
C-3	0·9906	1·0441	0·9803	C-3	1·0279	1·0279	1·0039	C-3	1·0001	1·0219	1·0195
C-4	0·9910	1·0413	1·2111	C-4	0·9846	1·0058	1·2513	C-4	0·9819	0·9946	1·2612
N-5	1·5134	1·4727	1·5807	N-5	1·5109	1·4837	1·5511	N-5	1·5119	1·4920	1·5334
C-6	1·0352	0·9902	0·9633	C-6	1·0345	1·0064	0·9700	C-6	1·0347	1·0149	0·9769
C-7	1·0633	0·9725	0·8285	C-7	1·0654	1·0092	0·8649	C-7	1·0692	1·0289	0·8983
S-8	1·7339	1·7621	1·6852	S-8	1·7306	1·7539	1·6775	S-8	1·7328	1·7807	1·6820
C-9	0·9866	1·1857	1·0133	C-9	0·9887	1·1591	0·9854	C-9	0·9916	1·1302	0·9868
C-10	1·2180	0·9972	1·0582	C-10	1·1534	0·9616	1·0184	C-10	1·1421	0·9878	1·0193
C-11	0·9245	1·0782	0·9981	C-11	0·9084	1·0841	0·9308	C-11	0·9093	1·0698	0·9181
S-12	1·8017	1·7761	1·7783	C-12	1·1653	0·9899	1·0535	C-12	1·0975	0·9334	0·9935
C-13	1·0442	1·0155	1·0262	C-13	0·9169	1·0383	0·9350	C-13	0·8993	1·0394	0·9080
C-14	1·0000	1·0059	1·0025	S-14	1·7975	1·7803	1·7772	C-14	1·1561	1·0226	1·0829
C-15	0·9772	0·9693	0·9690	C-15	1·0421	1·0235	1·0324	C-15	0·9184	1·0112	0·9235
C-16	0·9755	0·9647	0·9702	C-16	1·0015	1·0064	1·0022	S-16	1·7982	1·7835	1·7813
C-17	1·0272	1·0352	1·0275	C-17	0·9806	0·9752	0·9742	C-17	1·0416	1·0284	1·0341
C-18	1·0611	1·0315	1·0478	C-18	0·9784	0·9708	0·9752	C-18	1·0024	1·0059	1·0028
N-19	1·6262	1·5991	1·5852	C-19	1·0282	1·0348	1·0262	C-19	0·9831	0·9791	0·9786
				C-20	1·0586	1·0386	1·0517	C-20	0·9802	0·9749	0·9782
				N-21	1·6239	1·6064	1·5957	C-21	1·0293	1·0338	1·0276
								C-22	1·0569	1·0425	1·0523
								N-23	1·6260	1·6130	1·6055

Atom numbering is shown in Fig. 4. P_i^0, electron density at *i*th atom when dye cation is in the ground state; P_i^*, in the first excited state; P_i^{**}, in the second excited state.

expansion by singly excited configurations for this state may be written as (in the case when $n = 0$):

$$|S_1\rangle = 0{\cdot}9873|\Phi_1\rangle + \sum_{i \geq 2} T_i|\Phi_i\rangle$$

where $T_i < 0{\cdot}1$, i.e. the contribution of the highest Φ_i-configurations is negligible compared with that of the main Φ_1.

The second transition of asymmetrical dyes is localized mainly on the thiazolopyrimidinium end-group and on the carbon atom in the 10-position in monomethinecyanine (Fig. 5). In this case the electron density transfers from the thiazole ring and atom at position 10 to the pyrimidinium ring. Qualitatively, the electron density changes correspond to those upon the first $\pi \rightarrow \pi^*$-transition within the 6-methylthiothiazolopyrimidinium cation.[9] The second state is mainly described as a Φ_2-configuration (Fig. 3):

$$|S_2\rangle = 0{\cdot}9835|\Phi_2\rangle + \sum_{i \neq 2} T_i|\Phi_i\rangle, \qquad (T_i < 0{\cdot}1)$$

Atoms of an external polymethine chain are involved in an electron redistribution when a dye cation is raised to the second excited state. They are in vinylogous positions with the respect to the α-atom of a polymethine chain in the case of dyes with longer chains ($n = 1, 2$). Therefore, the lengthening of the second transition chromophore occurs. In the experiment, this phenomenon corresponds to the second band shift to the long-wave region of the spectrum (Fig. 1; Table 1).

The diagrams (Fig. 5) show the largest shift of the second band to be expected if chemical structure changes occur in the positions 2, 4, 7. On the other hand, the first band is very sensitive to chemical structure perturbations in a polymethine chain. However, the wavelengths and band shapes are non-sensitive to chemical changes in the 3 position. Experimental studies based on an introduction of the phenyl group have supported this conclusion (Fig. 2).

4.2. Symmetrical dyes

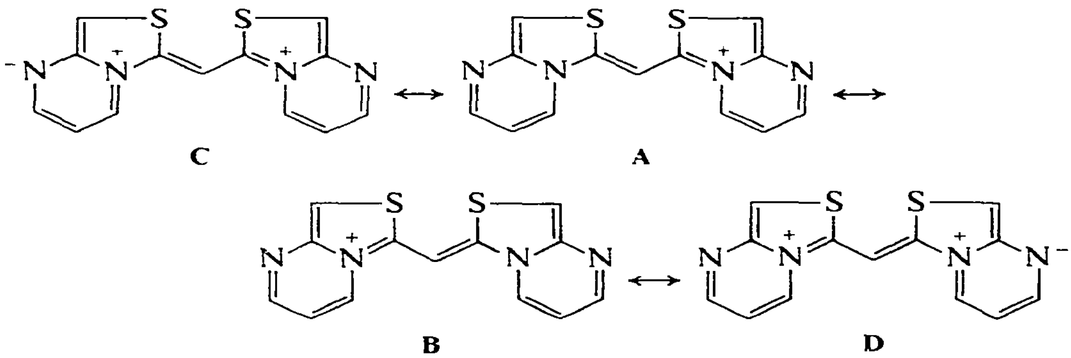
Spectra of symmetrical dyes have a similar appearance as those of asymmetrical cyanines. However, the first band is strongly red-shifted

TABLE 3
Experimental Absorption Band Wavelengths of Symmetrical Dyes

Dye	*n*	λ_{max} *(nm) (log ε) in MeCN*	$\Delta\lambda^1$ *(nm)*^{a}	$\Delta\lambda^2$ *(nm)*
IV	0	430 (3·69), 625 (4·37)	—	—
V	1	470 (3·99), 805 (4·76)	40	180
VI	2	498 (4·10), 895 (4·92)	28	90

[a] $\Delta\lambda^1$, $\Delta\lambda^2$, vinylog shift of first and second band, respectively.

(Table 3). This deepening of colour is caused by the large effective length[10,11] of the thiazolopyrimidinium end-group: $L^{theor} = 6{\cdot}89$. According to the valence bond theory, the resonance structures **C** and **D** have considerable importance. These structures bear a negative charge on the nitrogen atom in position 1.



The PPP calculations give the following values for the charge on the nitrogen atom in the ground and the first excited states: $q_0 = -0{\cdot}178$ and $q^* = -0{\cdot}201$, respectively. Therefore, the presence of the structures **C** and **D** (Sachs graphs having non-zero weight[11]) results in the lengthening of total chromophore, responsible for the first electron transition.

Symmetrical dyes have a large first vinylog shift of the first band ($\Delta\lambda = 180\,\mathrm{nm}$, $n = 0$ and $n = 1$). Perhaps this fact may be accounted for by the interaction of sulphur atoms in positions 8 and 8′ in monomethinecyanines ($n = 0$). This interaction in conjugated systems having an odd number of π-electron pairs must cause a hypsochromic shift.[12,13] However, we have not taken into consideration the above interaction in our model calculations. The model has resulted in a lower theoretical value of the first vinylog shift (Table 4). The experimental

TABLE 4
Theoretical Wavelengths of Electron Transitions of Dyes

n	*R*	*Asymmetrical*		*Symmetrical*	
		Dye	λ_{max} (*nm*)	*Dye*	λ_{max} (*nm*)
0	H	**XIII**	389, 499	**XVI**	445, 572
0	Ph	**XIII**	—	**XVI**	490, 667
1	H	**XIV**	416, 580	**XVII**	552, 650
1	Ph	**XIV**	444, 625	**XVII**	498, 756
2	H	**XV**	437, 662	**XVIII**	469, 727
2	Ph	**XV**	464, 700	**XVIII**	512, 797

second vinylog shift agrees with that of the typical polymethine dyes.[7] The second band is also shifted if the number of vinyl groups increases. This spectral effect is quite similar to that of asymmetrical dyes.

Table 5 presents electron density distribution data in the ground, first and second excited states. The redistribution diagrams are shown in Figs. 6 and 7. Atom charges on the polymethine chain are seen to

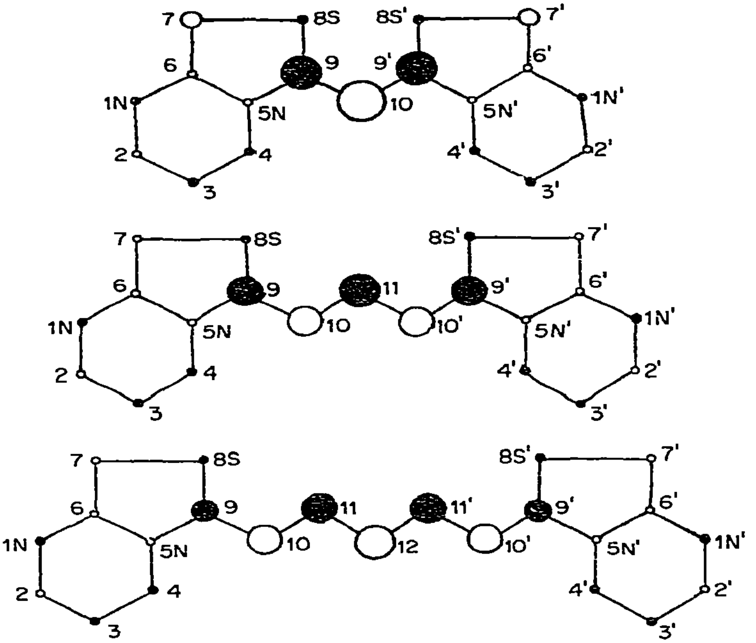


Fig. 6. Electron density redistribution of model symmetrical dyes for molecular transition from ground state to first excited state. Symbols as in Fig. 4.

TABLE 5

Electron Density Distribution in Symmetrical Dyes

Atom number	*n = 0*			*n = 1*			*n = 2*		
	P_i^0	P_i^*	P_i^{**}	P_i^0	P_i^*	P_i^{**}	P_i^0	P_i^*	P_i^{**}
N-1	1·1784	1·2006	1·2485	1·1810	1·1897	1·2496	1·1825	1·1876	1·2531
C-2	0·8547	0·8533	0·9299	0·8565	0·8516	0·9502	0·8577	0·8541	0·9470
C-3	0·9971	1·0287	1·0111	1·0018	1·0217	1·0005	1·0051	1·0170	1·0084
C-4	0·9910	1·0255	1·1482	0·9838	0·9982	1·1151	0·9809	0·9893	1·1126
N-5	1·5189	1·4772	1·4898	1·5153	1·4891	1·4933	1·5155	1·4960	1·4981
C-6	1·0357	1·0015	0·9896	1·0353	1·0127	1·0016	1·0355	1·0189	1·0075
C-7	1·0720	0·9964	0·9316	1·0730	1·0232	0·9829	1·0759	1·0413	1·0075
S-8	1·7448	1·7565	1·7070	1·7391	1·7515	1·7108	1·7398	1·7488	1·7109
C-9	1·0014	1·1558	1·0068	0·9947	1·1322	1·0028	0·9950	1·1080	1 0045
C-10	1·2122	1·0088	1·0753	1·1558	0·9878	1·0320	1·1453	1·0088	1·0392
C-11				0·9276	1·0846	0·9224	0·9185	1·0566	0·9134
C-12							1·0967	0·9471	0·9956

Atom numbering is shown in Fig. 6.

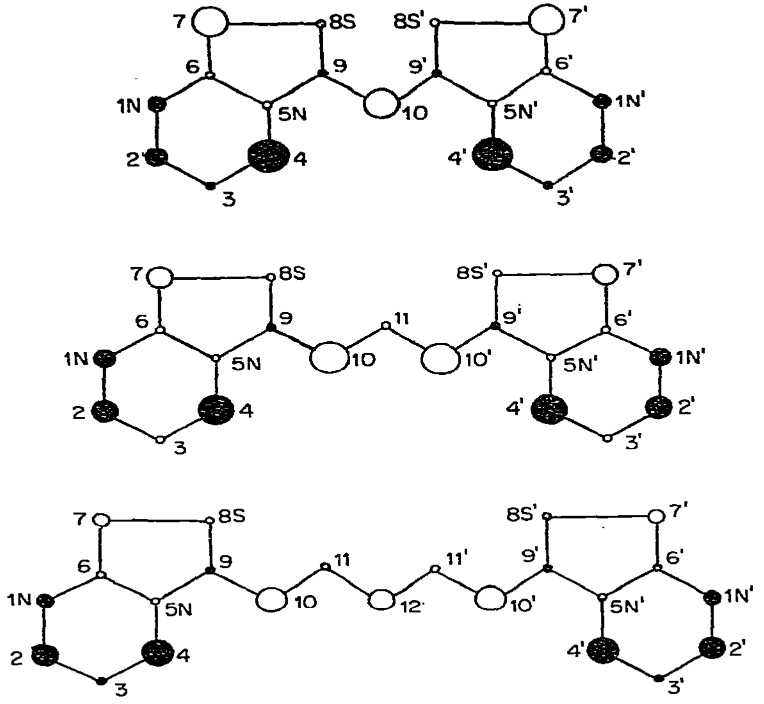


Fig. 7. Electron density redistribution of model symmetrical dyes for molecular transition from ground state to second excited state. Symbols as in Fig. 4.

alternate: the sign of the charges is opposite on the same chain position in the first excited state. Therefore, the dyes under consideration are in the polymethine state in correspondence with the Dähne hypothesis.[14] The diagrams (Figs. 6 and 7) are similar to those of the asymmetrical dyes. The first electron transition is seen to be localized in Kuhn's chain. The second transition is localized in the end-groups and in odd-numbered positions of the chain. It is interesting to note that the values of electron density changes in thiazolopyrimidinium end-groups are about half of those in asymmetrical cyanine series. As a first approximation, the same spectral effects are to be observed for disubstituted symmetrical dyes and for monosubstituted asymmetrical cyanines.

Thus, the analysis of absorption spectra and quantum calculation lead to an understanding of the nature of the first two bands of thiazolopyrimidinium polymethine dyes.

TABLE 6
Thiazolopyrimidiniumcyanines

Compound	*M.p.* (°C)	*Solvent*	*Found*			*Formula*	*Required*			*Yield* (%)
			Cl	*S*	*N*		*Cl*	*S*	*N*	
IIa	223–224	CH_3CN	6·7	—	8·0	$C_{24}H_{20}ClN_3O_4S_2$	6·9	—	8·2	32
IIb	242–243	CH_3CN	5·8	—	7·4	$C_{30}H_{24}ClN_3O_4S_2$	6·0	—	7·1	31
IId	219–220	CH_3CN, C_2H_5OH (1:1)	5·4	—	6·6	$C_{31}H_{26}ClN_3O_4S_2$	5·8	—	6·9	30
IIId	200–201	CH_3CN	5·7	10·1	—	$C_{33}H_{28}ClN_3O_4S_2$	5·6	10·1	—	39
IV	241–242	$CH_3(O))_2O, (CH_3)_2NCHO$ (3:1)	5·6	10·8	—	$C_{29}H_{25}ClN_4O_4S_2$	5·9	10·8	—	84
V	243–244	—	6·0	10·2	—	$C_{31}H_{27}ClN_4O_4S_2$	5·7	10·3	—	25
VI	296–297	—	5·4	9·8	—	$C_{33}H_{29}ClN_4O_4S_2$	5·5	9·9	—	28

5. EXPERIMENTAL (Table 6)

5.1. 2-R^1-3-R^2-4-R^3-8-Phenyl-6-[3-(3-ethyl-2(3H)-benzothiazolyliden)-1-propenyl]thiazolo[3,4-a]pyrimidinium perchlorate (II a, b, d)

A mixture of 1 mmol of the respective perchlorate **VII**, 0·41 g (1 mmol) of perchlorate **VIII** and 2 mml acetic anhydride was heated to the boiling point and 0·1 g (1 mmol) triethylamine added. The precipitated dye was filtered and crystallized.

5.2. 4-Methyl-2,8-diphenyl-6-[5-(3-ethyl-2(3H)-benzothiazolylidene)-1,3-pentadienyl]thiazolo[3,4-a]-pyrimidinium perchlorate (III)

Perchlorate **IX** (0·43 g; 1 mmol) was dissolved in 5 ml alcohol and a solution of 0·35 g (1 mmol) perchlorate **VIId** in 3 ml acetonitrile was added. The solution was heated to boiling and 0·1 g (1 mmol) of triethylamine added. The precipitated dye was filtered and crystallized. Yield: 0·24 g.

5.3. 2,4-Dimethyl-8-phenyl-6-[(2,4-dimethyl-8-phenyl-6(6H)-thiazolo-[3,4-a]pyrimidiniliden)methyl]thiazolo[3,4-a]pyrimidinium perchlorate (IV)

A mixture of 0·35 g (1 mmol) perchlorate **VIIc**, 0·38 g (1 mmol) perchlorate **X** in 7 ml of alcohol and 6 ml of dimethylformamide was heated to dissolve the components and 0·1 g (1 mmol) of triethylamine added. The precipitated dye was filtered and crystallized. Yield: 0·5 g.

5.4. 2,4-Dimethyl-8-phenyl-6-[3-(2,4-dimethyl-8-phenyl-6(6H)-thiazolo-[3,4-a]pyrimidiniliden)-1-propenyl]thiazolo[3,4-a]pyrimidinium perchlorate (V)

A mixture of 0·35 g (1 mmol) perchlorate **VIIc** and 0·25 g (1·3 mmol) of compound **XI** was heated in 3 ml of acetic anhydride over 1 h at 110 °C. The product was precipitated with ether, ground with alcohol and filtered. Salt **VIIc** (0·35 g; 1 mmol) and 2 ml of acetic anhydride were added to the filtered precipitate and the mixture heated to the boiling point; 0·1 g (1 mmol) triethylamine was added and the precipitated dye (0·15 g) filtered.

5.5. 2,4-Dimethyl-8-phenyl-6-[5-(2,4-dimethyl-8-phenyl-6(6H)-thiazolo-[3,4-a]pyrimidinyliden)-1,3-pentadienyl]thiazolo[3,4-a]pyrimidinium perchlorate (VI)

A mixture of 0·75 g (2 mmol) perchlorate **VIIc**, 0·26 g (1 mmol) chloride **XII** and 5 ml acetic anhydride was heated to the boiling point and 0·1 g (1 mmol) triethylamine added. The precipitated dye was filtered. Yield: 0·18 g.

REFERENCES

1. A. D. Kachkovski, E. K. Mikitenko and N. N. Romanov, *Khim. Geterotsikl. Soedin.*, 639 (1982).
2. M. J. S. Dewar, *The molecular orbital theory of organic chemistry*. New York, McGraw-Hill Book Company (1969).
3. G. G. Dyadyusha, N. N. Romanov, A. D. Kachkovski and A. I. Tolmachev, *Khim. Geterotsikl. Soedin.*, 1618 (1980).
4. N. Mataga and K. Nishimoto, *Z. Phys. Chem.*, Neue Folge, **13**, 140 (1953).
5. J. Fabian and R. Zahradnic, *Wiss. Z. Tech. Univ. (Dresden)*, **26**, 315 (1977).
6. A. V. Lusanov, *Usp. Khim.*, **49**, 2086 (1980).
7. S. Dahne and R. Radeglia, *Tetrahedron*, **27**, 3673 (1971).
8. A. I. Kiprianov and G. G. Dyadyusha, *Ukr. Khim. Ž.*, **35**, 608 (1969).
9. E. K. Mikitenko, A. D. Kachkovski and N. N. Romanov, *Khim. Geterotsikl. Soedin.*, 634 (1982).
10. G. G. Dyadyusha and A. D. Kachkovski, *Ukr. Khim. Ž.*, **43**, 948 (1978).
11. G. G. Dyadyusha and A. D. Kachkovski, *Theoret. i Experim. Khim.*, **17**, 393 (1981).
12. J. Fabian, H. Hartman and K. Fabian, *Tetrahedron*, **29**, 2209 (1973).
13. G. G. Dyadyusha, *Ukr. Khim. Ž.*, **31**, 1171 (1965).
14. S. Dahne, *Z. Chem.*, **10**, 168 (1970).