Dyes and Pigments **10** (1989) 111–121

Ultraviolet and Visible Absorption Spectra of Biscarbocyanine Dyes

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(Received 12 January 1988; accepted 21 March 1988)

ABSTRACT

The nature of the absorption bands of biscarbocyanine dyes has been investigated by spectral and quantum-chemical methods. Dipole–dipole approximation has been used for the analysis of the chromophore interactions. A correlation between the band intensity ratio and chromophore angle has been established. The calculated results are in good agreement with the experimental data.

1 INTRODUCTION

Cyanine dyes with a single chromophore have been widely studied with respect to the relation between the structure of organic compounds and their colour. Several papers dealing with the synthesis and electronic spectra of biscyanine dyes have appeared during the last 20 years. These dyes have two chromophores and show unusual spectral properties. Their visible spectra have two absorption bands compared to the single band for the dyes with one chromophore, i.e. the single band is split. This phenomenon is due to chromophore interaction and it may be characterised by two parameters, viz. (1) the band intensity ratio I_-/I_+; and (2) band splitting $\Delta\nu = \nu_- - \nu_+$. The shape of the band and the asymmetry of the splitting value $\delta\nu = (\nu_- + \nu_+)/2 - \nu_i$ are useful parameters in studies of these dyes.

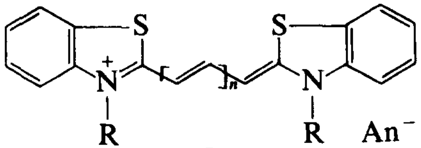
The intensity ratio has been shown to depend on the angle θ between the interacting chromophores, whilst $\Delta\nu$ depends on the type of linkage between the chromophores and on their electronic symmetry.[1] The parameter $\Delta\nu$ is proportional to the interaction energy and is highest when the chromophores of the biscyanines are equal and symmetric from an electronic viewpoint.

A convenient series of dyes for studies of chromophore interaction are the biscarbocyanines, which have a narrow absorption band of high intensity. Additionally, the structure of both the heterocyclic and aromatic nuclei, and of the substituents in the polymethine chain, may be widely varied. Some conformational problems have been successively resolved by studying the relation between θ and I_-/I_+. Thus, the all-*trans* conformation of the monocyanines has been confirmed. Replacement of the alkyl group at the nitrogen by a hydrogen atom, or introduction of a bulky substituent into the polymethine chain, facilitates the existence of mono-*cis* conformation.[2]

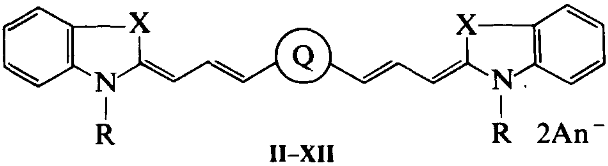
Theoretical explanations of the above experimental results have been developed by Kiprianov & Dyadyusha in terms of dipole–dipole interactions.[1] A simple expression was found to reflect the correlation between the angle formed by the directions of the chromophores and the intensity ratio of the first and the second electronic transitions. Using this correlation, it was possible to obtain angle values derived from spectral data. These angles are also available from X-ray structural data. The qualitative relationship between the 'spectral' and 'graphic' angles indicates that, in general, the dipole–dipole approximation describes the chromophore–chromophore interaction correctly.[1,2] For biscyanines, however, where the chromophore is bound by aromatic nuclei, it is also necessary to take into account this bonding. Direct quantum-chemical calculations have been found to be very useful for this purpose.

2 MATERIALS

The biscyanine dyes **I–XII** were studied in this work.

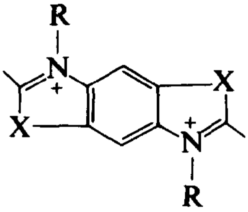


I

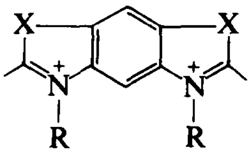


II–XII

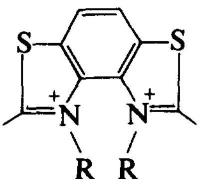
where Q is:



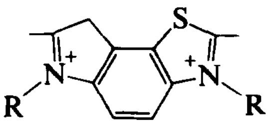
II X = S
III X = O
IV X = CMe$_2$



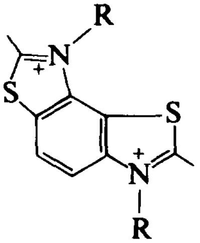
V X = S
VI X = 0
R = Me



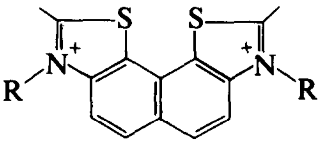
VII



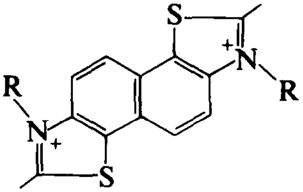
VIII



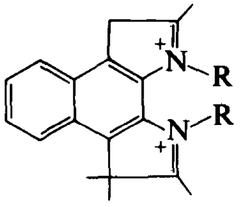
IX



X



XI



XII

3 QUANTUM CALCULATIONS

The electron transition energies of the dyes were calculated by means of the standard SCF–PPP approximation. The parameters for the atoms and bonds, together with intaratomic distances, are listed in Table 1. The two-centre electron repulsion integrals were calculated by the Mataga–Nishimoto formula.[3] Twenty-five singly excited configurations were used. Steric effects in the dye molecules were not taken into consideration. The relationship between the calculated transition energies and the observed values is shown to be reduced with lengthening of the conjugated chain. This is a common defect of the standard PPP method, where the excited state is calculated using only the single excited configuration expansion.[4]

TABLE 1
Atomic and Bond Parameters[a]

Atom X	U_X (*eV*)	γ_{XX} (*eV*)	l_{CX} (*Å*)	β_{CX} (*eV*)
C	−11·42	10·83	1·40	−2·318
N	−23·13	12·98	1·35	−2·318
S	−20·27	9·80	1·75	−1·660
O	−27·70	15·58	1·28	−1·850
CMe_2	−29·00	10·00	1·50	−0·464

[a] Bond length, l; core integral, $U_\mu = \langle \mu | \hat{H}_{core} | \mu \rangle$; resonance integral, $\beta_{\mu\nu} = \langle \mu \hat{H}_{core} | \nu \rangle$; one-centre integral of electron interaction, $\gamma_{\mu\mu} = \langle \mu\mu | \mu\mu \rangle$.

4 DISCUSSION

The nature of the splitting of the absorption maxima of the biscarbocyanines compared with the maxima of the parent monochromophore dye may be interpreted by the same model which has been developed for the excited states of molecular crystals.[5]

If we denote the wave functions of the parent dyes A and B in the ground state as ϕ_a° and ϕ_b° and in an excited state as ϕ_a^* and ϕ_b^*, the energies being ε_a°, ε_b°, ε_a^* and ε_b^*, respectively, then, in the zero-order approximation, wave functions of the compounds with two chromophores are the antisymmetrical products of the initial ones:

$$\Psi_0 = \hat{A}\phi_a^\circ\phi_b^\circ; \quad \Psi_a = \hat{A}\phi_a^*\phi_b^\circ; \quad \Psi_b = \hat{A}\phi_a^\circ\phi_b^* \tag{1}$$

where $\hat{A}$ is the antisymmetrisation operator.

Assuming that the chromophore interaction is small, then the energy operator of the compound containing two chromophores $\hat{H}$ differs from the sum of the initial operators $\hat{H}_a$ and $\hat{H}_b$ by a small interaction operator $\hat{H}_{ab}$, i.e.

$$\hat{H} = \hat{H}_a + \hat{H}_b + \hat{H}_{ab} \tag{2}$$

The wave functions of the excited states of the biscyanines in the first-order approximation can be represented by eqn (3).

$$\Psi_i = C_{ia}\Psi_a + C_{ib}\Psi_b \tag{3}$$

The energies of the two transitions for a compound with two chromophores may then be determined and they may be expressed as eqn (4).

$$\Delta E_- \simeq \Delta E_a - \frac{H_{ab}^2}{\Delta E_a - \Delta E_b}; \qquad \Delta E_+ \simeq \Delta E_b + \frac{H_{ab}^2}{\Delta E_a - \Delta E_b} \tag{4}$$

where $\Delta E_a = \varepsilon_a^* - \varepsilon_a^\circ$, $\Delta E_b = \varepsilon_b^* - \varepsilon_b^\circ$, and $H_{ab} = \langle \Psi_a | \hat{H} | \Psi_b \rangle$ is the interaction term.

It is apparent from eqn (4) that if the difference of the transition energies in the parent dyes becomes comparable with the interaction energy H_{ab}, then splitting of the absorption maxima should be observed. The maxima of the parent dye will separate from one another, the longer-wavelength absorption band undergoing a bathochromic shift and the shorter-wavelength band a hyposochromic shift. The closer disposed are the maxima of the parent dyes, the more this splitting is observed.

Equation (4) becomes inapplicable if the transition energies of the parent dyes coincide or are very close. In that case eqn (5) must be used.

$$\Delta E_{\pm} = \frac{\Delta E_a + \Delta E_b}{2} \pm \tfrac{1}{2}\sqrt{(\Delta E_a + \Delta E_b)^2 + 4H_{ab}^2} \qquad (5)$$

If $\Delta E_a = \Delta E_b$, then it is no longer possible to assign one band or another to a specific chromophore, both chromophores being excited to the same degree in these transitions. However, in the first case they are excited in the same phase, whereas in the second case they are excited in opposite phases. The wave function of the first state is given by the sum of the wave functions of the locally excited states [i.e. eqn (6)]

$$\Psi_+ = \frac{1}{\sqrt{2}}(\Psi_a + \Psi_b) \qquad (6)$$

and the wave function of the second state, by the difference:

$$\Psi_- = \frac{1}{\sqrt{2}}(\Psi_a - \Psi_b) \qquad (7)$$

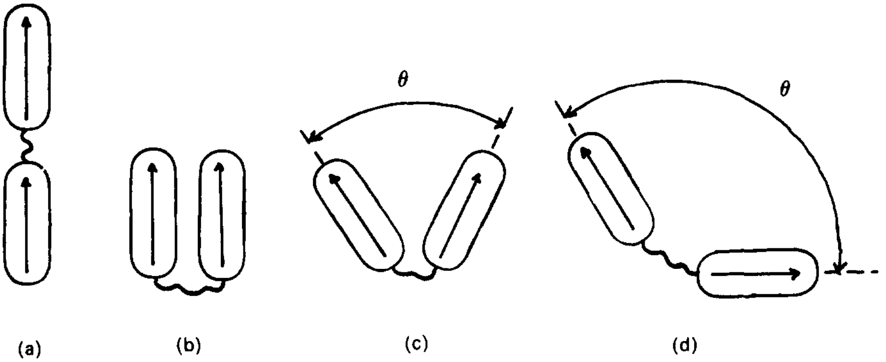
Strictly speaking, both local excited states take part in the electronic transitions of biscyanines in cases where the transition energies of the parent dyes do not coincide. The contributions of these are estimated by the coefficients shown in eqn (8).

$$C_i^2 = \frac{(\Delta E_+ - \Delta E) \pm (\Delta E_a - \Delta E_b)}{2(\Delta E_+ - \Delta E_-)} \qquad (8)$$

To calculate the interaction energy of the chromophores H_{ab}, the simplest way is to use the dipole–dipole approximation [eqn (9)].

$$H_{ab} = \frac{e^2}{R^5}\{(\vec{M}_a\vec{M}_b)R^2 - 3(\vec{M}_a\vec{R}_{ab})(\vec{M}_b\vec{R}_{ab})\} \qquad (9)$$

where $\vec{M}_a$ and $\vec{M}_b$ are the transition moments of the parent compounds, $\vec{R}_{ab}$ is a distance vector between the chromophores and R is the vector length.



(a) (b) (c) (d)

Fig. 1. Mutual arrangement of two chromophores of biscyanines.

This approximation gives good results if the distance between the chromophores exceeds their own dimensions. If the chromophores are arranged linearly (Fig. 1a), the transition moments are summated on transition to the Ψ_- state. But if the chromophores are parallel (Fig. 1b) they are subtracted and the intensity of the longer-wavelength transition will be lowered.

When equal dipoles are oriented arbitrarily at an angle (Fig. 1c), the ratio of the intensities of the longer-wavelength transition I_- and the shorter-wavelength one I_+ is given by eqn (10).

$$\frac{I_-}{I_+} = \frac{\nu_- M_-^2}{\nu_+ M_+^2} = \frac{\nu_-}{\nu_+}\tan^2\frac{\theta}{2} \tag{10}$$

Herewith, it is presumed that the dipole force must be constant, i.e. $M_a^2 + M_b^2 = M_-^2 + M_+^2$, or more exactly, the oscillator strength would be constant, i.e. $f_a + f_b = f_- + f_+$, thus giving the relationship shown in eqn (11).

$$\frac{I_-}{I_+} = \tan^2\theta \tag{11}$$

This approximation is valid only when the chromophores are weakly conjugated. Dyes **II**–**XII**, however, have two chromophores linked by a conjugated system. The wave functions of both chromophores overlap significantly and in this case chromophore interaction differs from the dipole–dipole interaction at the expense of both multiple interaction and interaction of the molecular orbitals which are delocalised throughout the molecule of the biscarbocyanines **II**–**XII**. Further, it is apparent that interactions with higher configurations cannot be ignored and the energies of these can be close to the energies of the first and the second transition. First of all, these are charge transition states. In the first-order approximation, if a configurational interaction is taken into account, it can be assumed that the molecular orbitals of a biscyanine having identical chromophores are given by symmetrical and asymmetrical combination of the orbitals of the parent dyes, i.e.

$$\phi_i^+ = \frac{1}{\sqrt{2}}(\phi_{ia} + \phi_{ib}); \qquad \phi_i^- = \frac{1}{\sqrt{2}}(\phi_{ia} - \phi_{ib}) \tag{12}$$

They are degenerate and in this case pairs of configurations of the same symmetry

$$\Psi_{i}{}^{+}{}_{j}{}^{+},\ \Psi_{i}{}^{-}{}_{j}{}^{-} \text{ and } \Psi_{i}{}^{+}{}_{j}{}^{-},\ \Psi_{i}{}^{-}{}_{j}{}^{+} \tag{13}$$

would be degenerate and strongly interacting. This interaction results in the states corresponding to symmetrical and asymmetrical combinations of the configurations (13); for example,

$$\Psi_s^+ = \frac{1}{\sqrt{2}}(\Psi_{i}{}^{+}{}_{j}{}^{+} + \Psi_{i}{}^{-}{}_{j}{}^{-}); \quad \Psi_a^- = \frac{1}{\sqrt{2}}(\Psi_{i}{}^{+}{}_{j}{}^{+} - \Psi_{i}{}^{-}{}_{j}{}^{-}) \tag{14}$$

The former equation corresponds to the symmetrical combination of degenerate configurations of the parent dyes:

$$\Psi_s^+ = \frac{1}{\sqrt{2}}(\Psi_{ia\,ja} + \Psi_{ib\,jb}) \tag{15}$$

and the latter corresponds to the electron transition between the chromophores:

$$\Psi_a^+ = \frac{1}{\sqrt{2}}(\Psi_{ia\,jb} + \Psi_{ib\,ja}) \tag{16}$$

If configurational interactions are correctly taken into account (for example, by PPP approximation), then orbital degeneration vanishes, but this effect is small (Fig. 2c). The resulting states are close to those which could be expected to be obtained in a zero-order approximation. For example, for dye **XII** they are equal (Fig. 3):

$$\left.\begin{aligned}
\Psi_1 &= 0{\cdot}82\Phi_1 + 0{\cdot}55\Phi_4 + 0{\cdot}14\Phi_7 + \cdots \\
\Psi_2 &= 0{\cdot}66\Phi_2 + 0{\cdot}73\Phi_3 + \cdots \\
\Psi_3 &= 0{\cdot}68\Phi_2 - 0{\cdot}68\Phi_3 + \cdots \\
\Psi_4 &= 0{\cdot}49\Phi_1 + 0{\cdot}74\Phi_4 + 0{\cdot}38\Phi_5 + 0{\cdot}08\Phi_6 + \cdots
\end{aligned}\right\} \tag{17}$$

The wave functions Ψ_1 and Ψ_4 are antisymmetrical, but functions Ψ_2 and Ψ_3 are symmetrical, because of the symmetrical structure of the dye **XII**. Therefore, transitions between such pairs of states are mutually per-

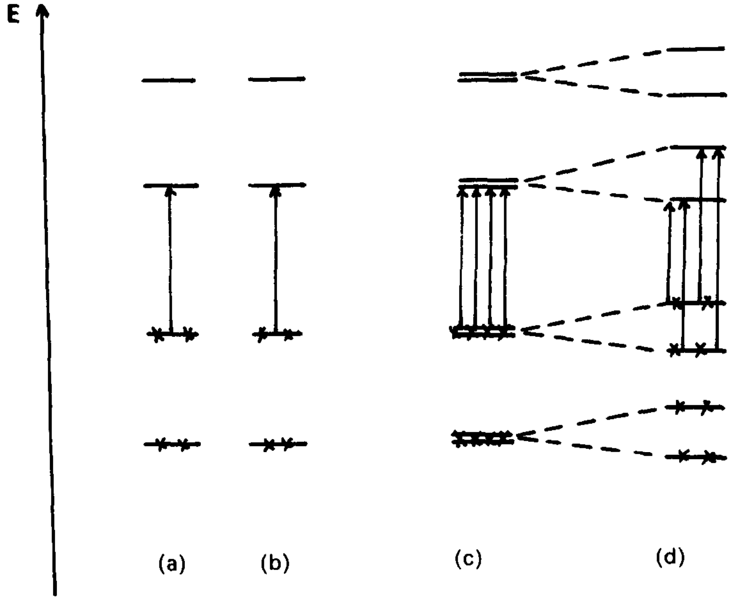


Fig. 2. Schematic positions of frontier energy levels: (a, b) dye with one chromophore; (c) biscyanine without MO interaction; (d) biscyanine with MO interaction.

pendicular. Theory predicts that the transition from the ground state to the electron transfer state is of low intensity.

If the functions (17) are used, then the transitions are equally localised in both chromophores. Moreover, a redistribution of electron density occurs at the atoms of the polymethine chain, similarly to typical monocyanines. The changes of electron density in biscyanine and monocyanine are shown in Fig. 4.

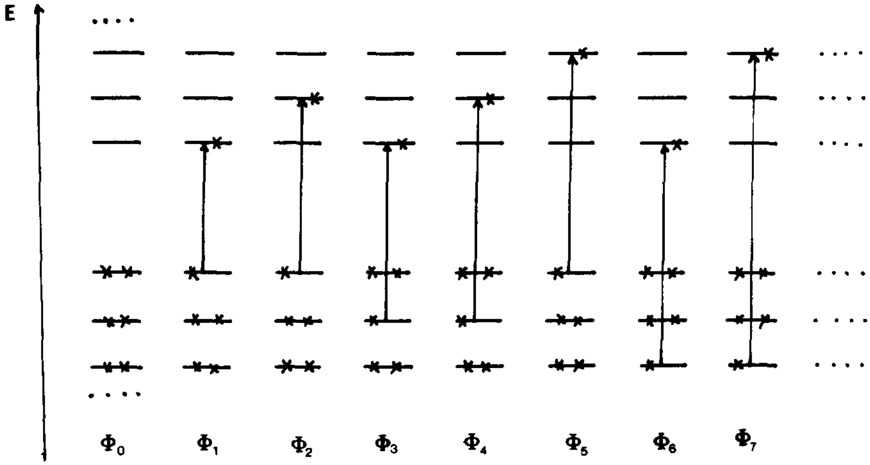
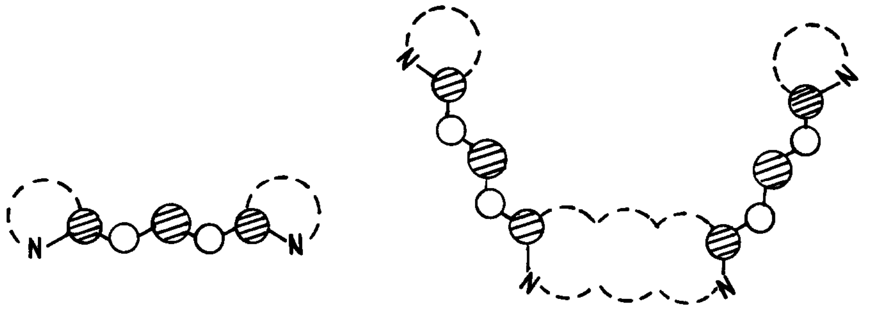


Fig. 3. Scheme of electronic configurations.



(a) (b)

Fig. 4. Electron density redistribution for the transition to the first excited state. (a) Dye **I**; (b) dye **X**; ○, electron density decreases; ⊜, electron density increases.

Analysis of the moments of these four transitions shows that practically all the intensity must be concentrated in the longer-wavelength transition when both chromophores are arranged linearly. The second transition is forbidden, but the intensity of the third and the fourth transition must be essentially smaller. Moments calculated by the PPP method are $\mu_1 = 2{\cdot}697$, $\mu_2 = 0{\cdot}039$, $\mu_3 = 0{\cdot}326$, $\mu_4 = 0{\cdot}559$. The calculations predict further that the energies of the third and the fourth transition should practically coincide: $\lambda_3 = 347$ nm and $\lambda_4 = 345$ nm.

The experimentally observed UV and visible absorption spectrum of dye **XI** is shown in Fig. 5. An intense band is observed near 610 nm. Quantum-chemical calculations give smaller values (Table 1). This result is due to the limited number of configurations used, and to the NDO approximation, which, in the case of chromophore interactions, should overestimate the transition energy. The second transition is not observed, but a less intense band arises at 390–400 nm which corresponds to $S_0 \rightarrow S_3$ and $S_0 \rightarrow S_4$ transitions. The band at 330 nm presumably corresponds to the intrinsic absorption of the central nucleus.

When the directions of the interacting chromophores form an acute angle, the second band must be more intense, in accord with eqn (11). Dyes with parallel chromophores were not synthesised in this work. Quantum-chemical calculations of dye **X**, modelling such a situation, gave the following results: $\mu_1 = 1{\cdot}013$, $\mu_2 = 2{\cdot}639$, $\mu_3 = 0{\cdot}246$, $\mu_4 = 0{\cdot}337$. The calculated energies of the third and the fourth transition were almost coincident, viz. $\lambda_3 = 387$ nm, $\lambda_4 = 386$ nm. Whilst the experimentally observed absorption spectra qualitatively agree with those results (Fig. 5), the calculated transition energies considerably exceed the observed values. Two intense bands ($\lambda_1 = 620$ nm and $\lambda_2 = 520$ nm) and a less intense inflexion near 400 nm are also observed; the latter corresponds to the charge transfer transition $S_0 \rightarrow S_3$ and $S_0 \rightarrow S_4$.

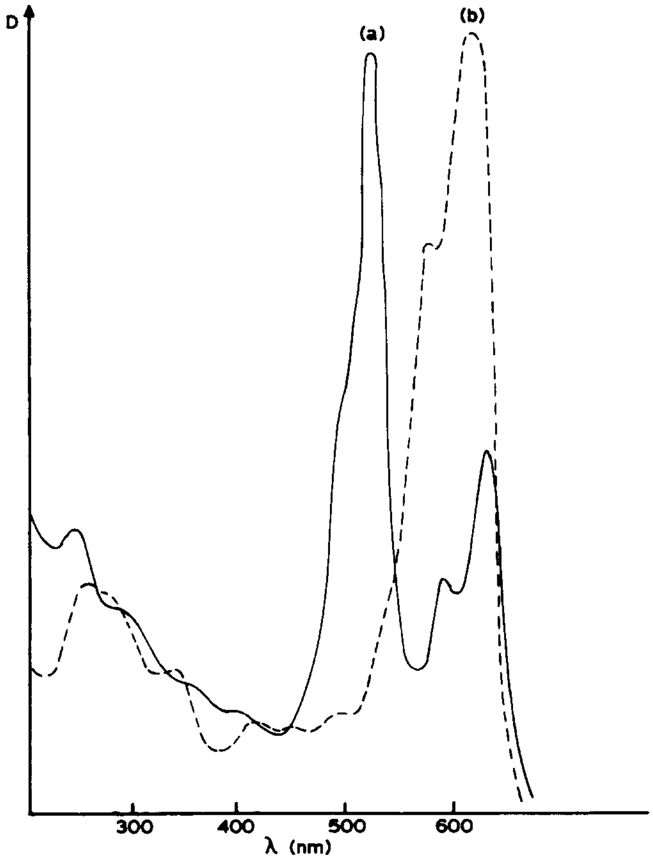


Fig. 5. Absorption spectra of the dyes **X** (a) and **XI** (b).

TABLE 2
Spectral Characteristics of Biscyanines II–XII

Dye	λ^{exp} (*nm*)	$\Delta\nu^{exp}$ (cm^{-1})^{a}	λ^{calc} (*nm*)	$\Delta\nu^{calc}$ (cm^{-1})^{a}	θ^{exp} (*degree*)	θ^{calc} (*degree*)
II	498,634	4 307	476,548	2 760	160	180
III	469,598	4 600	470,546	2 962	160	180
IV	506,642	4 186	475,560	3 195	155	180
V	510,629	3 710	470,540	2 758	146	147
VI	469,590	4 373	476,544	2 626	113	106
VII	516,591	2 459	478,536	2 264	143	144
VIII	505,618	3 621	474,543	2 680	93	89
IX	511,591	2 649	477,537	2 342	121	116
X	516,625	3 380	480,567	3 196	56	39
XI	518,610	2 912	485,539	2 066	160	180
XII	520,596	2 452	500,560	2 143	145	154

[a] $\Delta\nu = \lambda_1 - \lambda_2$.

The results of the spectral measurements and quantum-chemical calculations of some other biscyanines are presented in Table 2. The PPP calculations correctly reproduce the chromophore interactions and predict a splitting of transitions, as well as the relationship between the intensities of the two long-wavelength bands and the chromophore angle. However, the precision of the prediction of the positions of the absorption maxima is relatively poor. This is due to the neglect of overlap between the orbitals of the unbonded atoms, since it is the resonance interaction which is the main contribution to the split. The use of the PPP method for the study of dyes with one chromophore results in a smaller deviation from experimental data, but in this case the deviation for the longer-wavelength absorbing dyes becomes apparent also.[4]

REFERENCES

1. Kiprianov, A. I. & Dyadyusha, G. G., *Ukr. Khim. Zh.*, **35** (1969) 608.
2. Dyadyusha, G. G., Kolesnikov, A. M. & Mikhailenko, F. A., *Zh. Org. Khim.*, **18** (1982) 206.
3. Mataga, N. & Nishimoto, K., *Z. Phys. Chem. (BRD)*, **13** (1953) 140.
4. Fabian, J. & Zahradnic, R., *Wiss. Z. Techn. Univ. (Dresden)*, **26** (1977) 315.
5. Davidov, A. S., *Zh. Experim. Theoret. Phys.*, **18** (1948) 200.