



Nature of the Absorption Bands of Pyrylocyanines: Heteroanalogues and Isomers

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ABSTRACT

The investigation of electron transition nature in pyrylocyanines and their heteroanalogues was carried out by spectral and quantum-chemical methods. The electron distribution diagrams have been used in order to determine the transition localization. The first transition is localized within the polymethine chain, and the higher ones are mainly localized within the end groups. It has been shown that the D_{2h} symmetry of the Hückel hamiltonian of γ -isomeric dyes had lead to quasi-generation of higher electron transitions, contrary to α -isomers being of C_{2v} symmetry.

1 INTRODUCTION

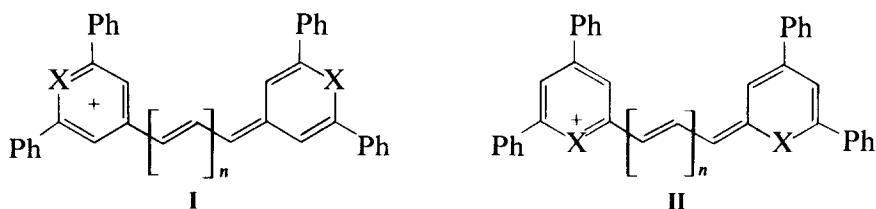
Pyrylocyanines and their heteroanalogues are convenient structural systems for the investigation of colour theory relationships. As a rule some absorption bands are observed in the spectra of such dyes in both the visible and near-IR region, these bands being of high intensity and well separated.^{1,2} This feature allows the interpretation of the electron transitions within the molecule to be made, using quantum-chemical methods. These dyes are therefore excellent models for evaluating the influence of the nature of the heteroatom within molecules with the same molecular geometry.

We have previously estimated the relative and absolute positions of the frontier energy levels of γ -pyrylocyanines and their heteroanalogues.² This

paper is concerned with the nature of the long-wavelength absorption as well as the higher-energy electron transitions within dye molecules of this type and also their α -isomers.

2 MATERIALS AND QUANTUM CALCULATIONS

The polymethine dye cations studied were those of general structures **I** and



II, and in which the following terminology is used throughout the text of this paper:

	X = O	X = S	X = Se	X = NMe
Dye I	4-O _n	4-S _n	4-Se _n	4-N _n
Dye II	2-O _n	2-S _n	2-Se _n	2-N _n

where n is the number of vinylene groups in the polymethine chain (PC). The synthesis and some properties of compounds **I** and **II** have been described previously.^{2,3}

The electron energy levels of the dye molecules were calculated by means of the molecular method within the framework of the Hückel approximation (HMO). The transition energies were calculated by means of the PPP method. The atomic and bond parameters, as well as the interatomic distances, have been reported previously.² Steric effects in the molecules were taken into consideration, thus phenyl groups are considered to be out of the plane with respect to the rest of the molecule.² These phenomena were simulated by variation of the bond parameter: $\beta_{\text{CPh}} = \beta \cos \theta$.

3 SPECTRAL DATA AND DISCUSSION

3.1 γ -Isomer dyes **I**

Polymethine dyes with pyrylium residues and their heteroanalogues as end-groups have an intense absorption band in the long-wavelength region

although they have a short PC. For illustration, the spectra of a vinyllogous series of pyrylocyanines and thiapyrylocyanines are shown in Figs 1 and 2.

The long-wavelength absorption is due to the large bathochromic effect of these residues. The influence of the configuration of the end-groups on the spectra can be characterized by means of their effective length L .⁴ The long-wavelength band maximum is defined by the relationship

$$\lambda_{\max,n} = V(n + L)$$

where V , the vinylene shift, is approximately 100 nm. The greater the parameter L , the more the absorption of the corresponding polymethine dye is shifted to longer wavelength. The pyrylium residues and their heteroanalogues have a comparatively large effective length, which depends on the nature of the heteroatom X (Table 1). The parameter L increases in the series N_n , O_n , S_n , Se_n . Experimentally observed maxima of the long-wavelength absorption band undergo bathochromic shifts in the same series provided there is a constant PC length² (Table 2).

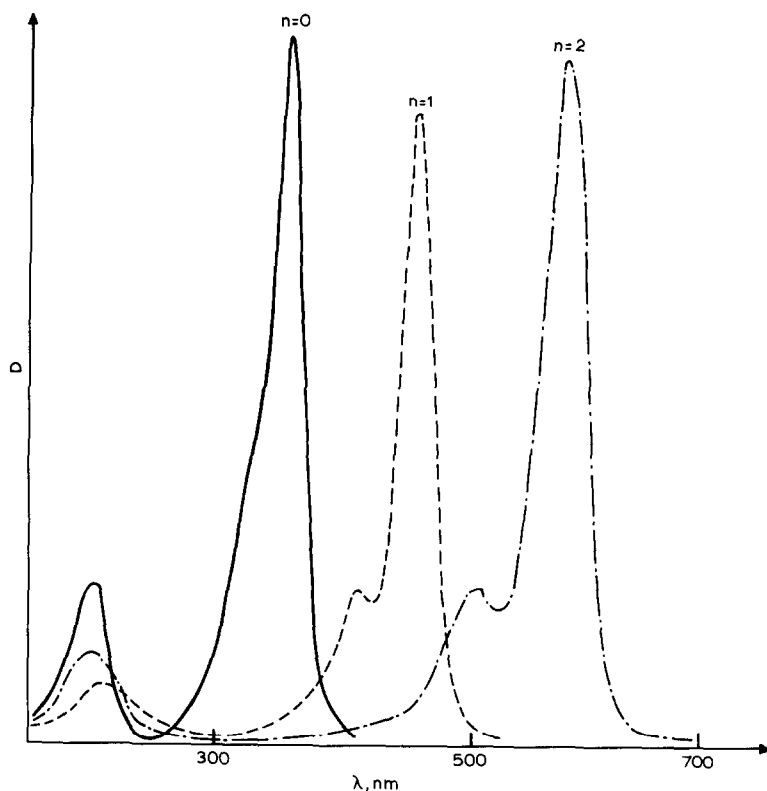


Fig. 1. Absorption spectra of γ -pyrylocyanines 4- O_n : —, $n=0$; ---, $n=1$; - · -, $n=2$.

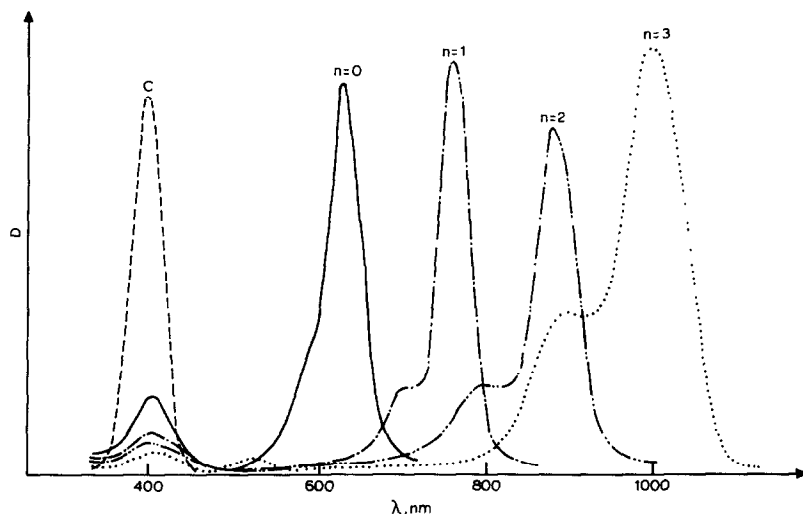


Fig. 2. Absorption spectra of the thiapyrylium cation **III** (C) and γ -thiapyrylocyanines **4-S_n**. ---, C; —, $n=0$; - · - ·, $n=1$; ···, $n=2$.

This long-wavelength transition is typical for polymethines. As a rule the polymethine transition is accompanied by a considerable change in the electron density. Figure 3a shows the π -electron redistribution at the atoms on the excitation $S_0 \rightarrow S_1$. This transition is seen to be localized mainly in the polymethine chromophore. Similar diagrams were retained from calculations for other dyes.

According to PPP calculations configuration $\Phi_{m,m+1}$, corresponding to the electron transition from HOMO ϕ_m to LUMO ϕ_{m+1} , derives mainly from the expansion of the first excited function $S_1 = \sum_i T_{1,i} \Phi_i$, so that $T_{1,1} > 0.95$. This fact allows the use of the HMO approximation in investigations of the relationship between molecular configuration and the position of the long-wavelength absorption maximum.

Dyes **I** also have several low-intensity absorption bands in the short-wavelength region, these transitions usually being related to the localized or

TABLE I
Effective Length (L) and Electron Donor Ability (Φ_0) of the
End-Groups of Dyes **I** and **II**

X	Dyes	L	Φ_0
NMe	4-N _n , 2-N _n	3.30	69 ^c
O	4-O _n , 2-O _n	6.07	44 ^d
S	4-S _n , 2-S _n	7.24	42 ^c
Se	4-Se _n , 2-Se _n	7.94	37 ^e

TABLE 2
Long-Wavelength Absorption Maxima of Dyes I and II (nm)

<i>X</i>	<i>n</i>	<i>Dyes I</i>		<i>Dyes II</i>	
		λ_{\max}	V^a	λ_{\max}	V^a
NMe	0	512	—	540	—
	1	638	126	630	90
	2	748	110	728	98
O	0	552	—	640	—
	1	676	124	806	166
	2	798	122	910	104
S	0	627	—	646	—
	1	755	128	865	119
	2	879	124	1000	135
	3	1000	121	—	—
Se	0	672	—	—	—
	1	795	123	—	—
	2	910	115	—	—
	3	1035	125	—	—

^a $V = \lambda_n - \lambda_{n-1}$.

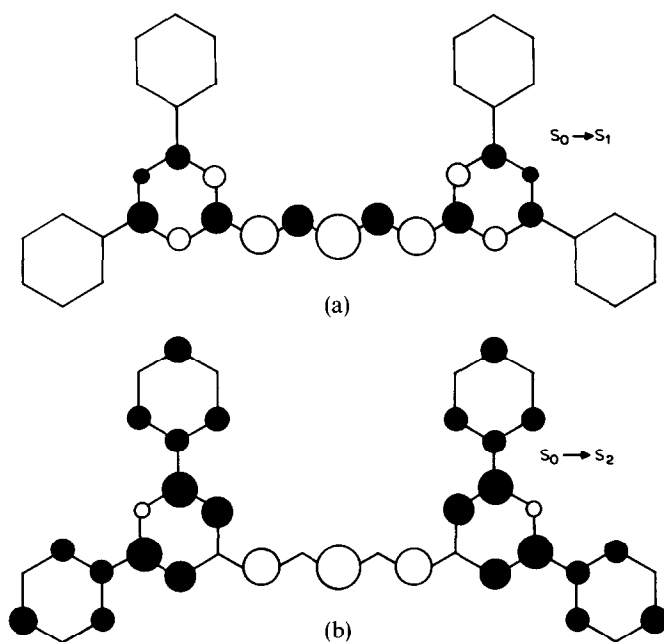
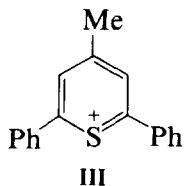


Fig. 3. Electron density redistribution on excitation of dyes 4-O₂. (a) First excited state; (b) second excited state.

end-group chromophores,⁵ which have their own intense absorption. For example, an absorption maximum at 410 nm is observed in the spectrum of the thiapyrylium cation **III** (Fig. 2). Heteroanalogues of this compound also absorb in a similar region.



Interaction between the two end-group chromophores and the polymethine moiety results in an additional bathochromic shift in the long-wavelength band, as well as the separation of the localized transition bands. As a result the short-wavelength band can either broaden or split into separate absorption bands. There is one comparatively weak band in the absorption spectra of the vinyllogous series of the γ -pyrylocyanines 4-O_n and of the thiapyrylocyanines 4-S_n (Fig. 2) when $n = 0-2$, but the thiapyrylotri-carbocyanine ($n = 3$) has two pronounced maxima at 420 and 530 nm. Hence the localized chromophore interaction is not strong.

To interpret the correct nature of the bands of dyes **I**, calculated levels can be used (Fig. 4). Considering initially the molecular symmetry, the idealized molecule belongs to the point group C_{2v} . However, within the framework of the HMO approximation, non-neighbouring interactions are neglected, and consequently the symmetry of the molecular structure is higher. As the Hückel Hamiltonian is independent of the steric configuration, the molecular structure of dyes **I** can be assigned either to the D_{2h} point group or to the D_{2d} point group. The symmetry of the D_{2d} point group has one degenerate symmetry type E , correlating with the symmetry types A_u and B_{3g} of the D_{2h} point group. In this case some levels, such as ϕ_{m-1} and ϕ_{m+3} , are double-degenerate (Fig. 4(a)). These are mainly involved in the construction of the excited-state functions S_2 , S_3 , S_4 and S_5 . As a result the second transition is also double-degenerate. The next excited states can involve either ϕ_{m+2} or other non-degenerate MOs or degenerate MOs. The electron configuration interaction can be determined in the PPP approximation. It is apparent from Table 3 that the higher electron transitions have closely similar energies. It should be noted that the MO degeneracy is absent in this case, in so far as in the PPP approximation the electron interaction between non-neighbouring atoms is taken into consideration. Consequently, four energetically close electron transitions give rise to a broad absorption band in the spectral region around 400 nm. According to PPP calculations for the thiatricarbocyanine 4-S₃, the energies of the third and fourth electron transitions are closer than those of the second and third

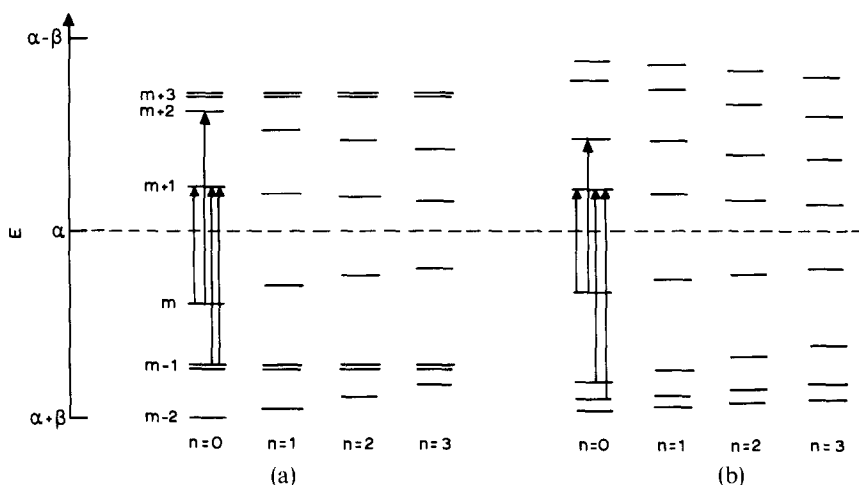


Fig. 4. Electron levels of 4- O_n (a) and 2- O_n (b) calculated by means of the Hückel MO method.

transitions. In contrast, the calculations indicate that the second and third transition energies are close in the case of $n = 2$.

This treatment of the electron transitions in dyes **I** can be extended to a study of the isomeric dyes **II**, which have a similar bond configuration.

3.2 α -Isomer dyes **II**

Dyes **II** differ from the isomeric series **I** only with respect to the position of the heteroatoms. Some typical spectra are shown in Fig. 5. The long-

TABLE 3
Electron Transition Characteristics of Dyes **I** and **II** Calculated by the PPP Approximation (λ^{theor} , nm)

n	4- N_n	2- N_n	4- O_n	2- O_n	4- S_n	2- S_n	4- Se_n	2- Se_n
0	490	496	504	527	519	551	531	566
	370	383	355	376	350	370	357	375
	368	336	352	328	347	333	356	339
	310	301	331	315	323	328	326	334
1	589	572	586	605	609	623	617	635
	391	419	369	411	350	400	356	404
	390	374	368	358	349	341	356	341
	344	300	342	319	344	330	347	336
2	683	652	696	684	677	703	694	716
	410	448	390	441	474	427	479	431
	408	404	387	386	421	366	429	366
	382	314	375	335	343	347	348	354

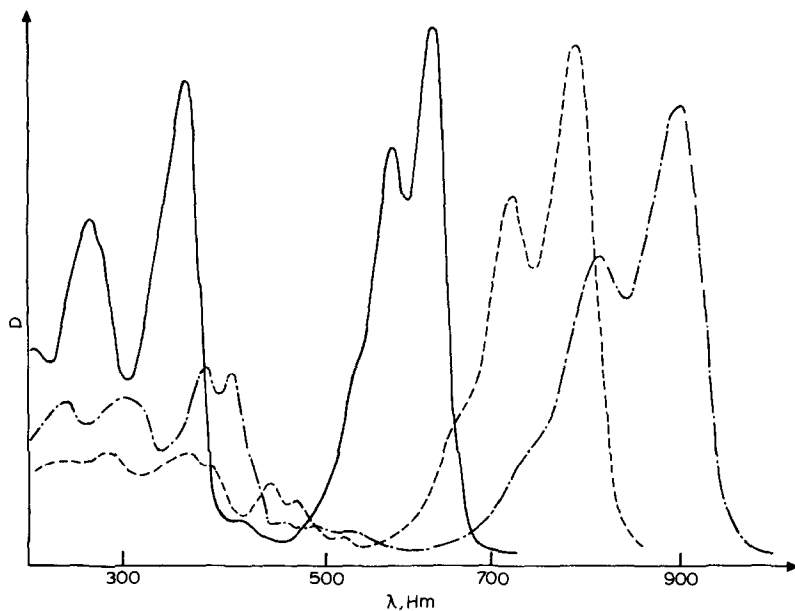


Fig. 5. Absorption spectra of α -pyrylocyanines 2-O_n. —, $n=1$; ---, $n=2$; - · -, $n=3$.

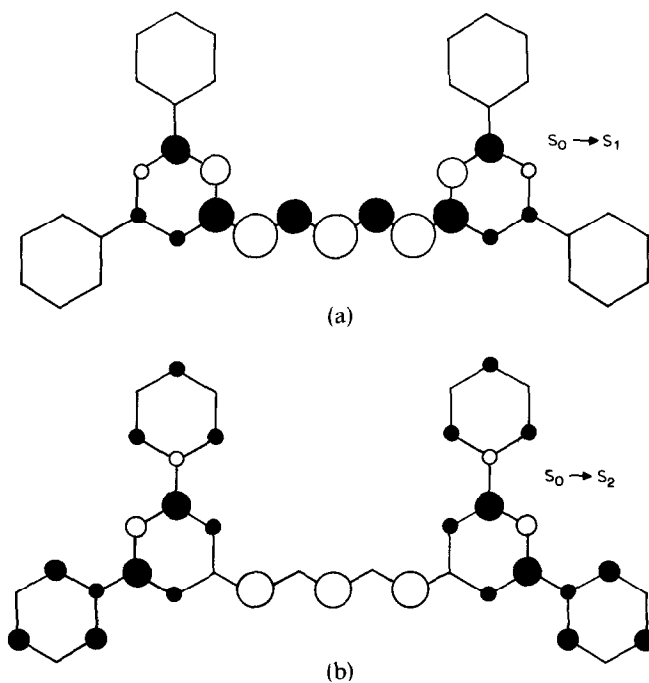


Fig. 6. Electron density redistribution on excitation of dyes 2-O₂. (a) First excited state; (b) second excited state.

wavelength bands of dyes **II** are seen to be typical polymethine bands, as in the corresponding compounds **I**, whilst the short-wavelength absorption is more complex, with a number of separate pronounced maxima.

The electron density redistribution diagram (Fig. 6) shows that the first transition is a polymethine one, as in dyes **I**. The experimental data are shown in Table 2. In general, the long-wavelength absorption maxima of dyes **II** are shifted to longer wavelength compared with the γ -isomers **I**, where X is O, S or Se, but are shifted to shorter wavelength if X is NMe and n is 1 or 2.

However, according to the quasi-long dye approximation, the effective lengths of the end-groups of dyes **II** are equal to those of dyes **I**, and the same resonance integrals can be used for the carbon-carbon bonds in the heterocycles. For a more correct treatment of the difference between the long-wavelength absorption positions of dyes **I** and the isomeric dyes **II**, the bond order alternation within the end-groups must also be taken into account. The molecular diagrams of the fragments, calculated by the HMO method, are shown in Fig. 7. Dyes **I** and **II** with comparatively long PC ($n = 5$) were used as model compounds; these correspond to the quasi-long approximation. The C-C bond alternation is seen to be greater in the γ -isomers.

Bond order alternation can be quantitatively characterized by means of the parameter

$$\Delta = \sum_{r,s} |p_{rs} - p^{\circ}|$$

where p_{rs} is the bond order between atoms r and s , and p° is a standard bond order for a long conjugated chain ($p^{\circ} \approx 0.62$). The calculations show that the parameter Δ for γ -pyrylocyanine is more than double that of the α -isomer. If we assume that the resonance integral η_{rs} is equal to 1.1 if $p_{rs} > 0.70$ and is equal to 0.9 if $p_{rs} < 0.50$, we then obtain values of $L = 4.90$ for γ -pyrylocyanine and 6.01 for the α -isomer. It should be noted that the electron donor ability Φ_0 is greater for the α -isomer. This is due to the fact that in the α -isomer only one C-C bond differs significantly from the standard bond ($p_{rs} = 0.74$, Fig. 7). It is apparent that, whilst these results are rather approximate, they nevertheless explain the longer-wavelength absorption of the α -pyrylo- (2-O $_n$) and α -thiapyrylocyanines (2-S $_n$) compared with the γ -isomers.

For the pyridocyanines (X = NMe) the difference between the α - and γ -isomers is somewhat less. In fact the first dye in the vinylogous series 2-N $_0$ does absorb at longer wavelength, in agreement with the above conclusions (Table 2). However, the higher α -isomer vinylogues 2-N $_1$ and 2-N $_2$ absorb at

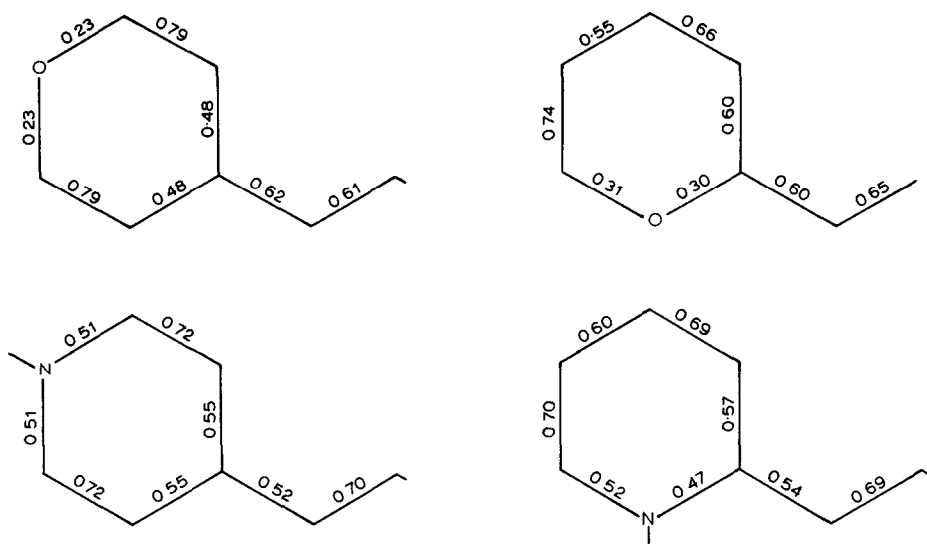


Fig. 7. Bond orders within end-groups calculated by means of the HMO method ($n=5$).

lower wavelength than the corresponding γ -isomer dyes, and this cannot solely be attributed to the C–C bond alternation within the end-groups.

On the other hand, PPP calculations taking into account the electron interactions give transition energies which agree with the experimental data (Table 3). Thus if $n=0$ then the α -isomer has lower energy, but if $n=2$ then the γ -isomer energy has the lower energy. Hence electron interactions seem to have a considerable influence on the transition energies. This results in the vinylenic shift being dependent on the electron donor ability of the end-groups Φ_0 .⁵ It is apparent from Table 2 that the vinylenic shifts of the α -pyridocyanines 2- N_n are lower than those of γ -isomers 4- N_n . This can be related to the greater electron donor ability (Φ_0) of the α -isomer end-groups, whilst the γ -isomer end-groups have a lower parameter Φ_0 , provided that the bond alternation is taken into consideration. When the PC of the pyridocyanine is short ($n=0$), then the absorption maximum depends mainly on the effective length ($L_\alpha > L_\gamma$), but in the case of higher vinylogues the influence of the parameter L decreases as the electron interaction increases. This appears to be the reason for the lower-wavelength absorption of α -pyridocarbocyanines and α -pyridodicarbocyanines compared with the γ -isomers.

Additional influence on the position of the long-wavelength maximum is caused by the interaction between the polymethine chromophore and localized ones.

The short-wavelength absorption of the α -isomer dyes **II** differs significantly from that of the γ -isomers **I**. To exemplify this, the spectra of the

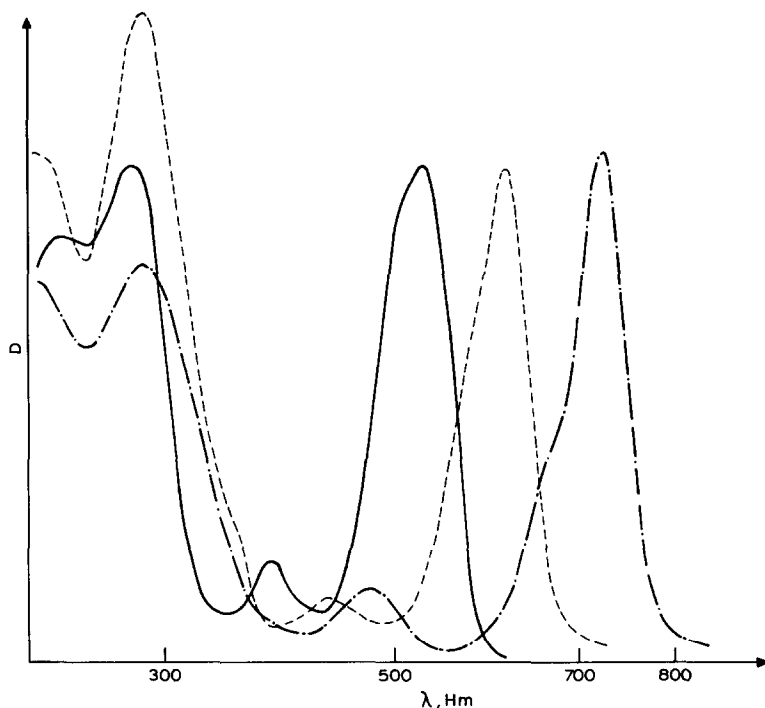


Fig. 8. Absorption spectra of α -pyridocyanines $2-N_n$. —, $n=0$; ---, $n=1$; - · -, $n=2$.

vinyllogous series $2-O_n$ and $2-N_n$ are shown in Figs 5 and 8. These dyes have more absorption maxima than the γ -isomers. Thus $2-O_0$ has two comparatively intense maxima at 340 and 285 nm, as well as a maximum at 415 nm of lower intensity. With lengthening of the PC ($n=1, 2$) of dyes $2-O_n$ each band is split twice. This phenomena can be treated by means of a molecular level diagram (Fig. 4). Whilst dyes **II** have a lower symmetry C_{2v} (unlike the γ -isomer dyes **I**), their Hückel MOs are not degenerate. It follows, therefore, that the high electron transition energies also differ. The distance between the molecular levels ϕ_{m-1} and ϕ_{m-2} , as well as ϕ_{m+3} and ϕ_{m+4} , corresponding to degenerate levels in dyes **I**, increases with PC lengthening. This also results in an increase in the energy difference between the states S_2 and S_3 , and S_4 and S_5 . As a result the short-wavelength bands are split. The PPP calculation also shows the large difference between the higher transition energies, in good agreement both with the above conclusions and with the experimental data (Table 3). The thia-analogues $2-S_n$ have similar spectra, although splitting of the absorption maxima is more pronounced. In the case of the α -pyridocyanines $2-N_n$ the short-wavelength band splitting does not appear and these dyes show only two broad absorption bands in the short-wavelength region.

Like dyes **I**, the higher electron transitions are mainly localized at the end-group atoms as well as at the even atoms within the PC. Figure 6 shows that the electron density passes from the PC on to the end-groups on excitation. The diagrams for the electron density redistribution (Fig. 6) are similar to those of the γ -isomers **I**. However, these diagrams are asymmetrical when the local chromophores of dyes **II** are also asymmetrical.

Thus investigation of the isomeric dyes **I** and **II** using Hückel and PPP calculations permits a meaningful treatment of the nature of their absorption spectra to be made.

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