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Effective Length of the Annelated End-Groups of Polymethine Dyes

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ABSTRACT

The influence of benz-annelation of end-groups on the long-wavelength absorption maximum of polymethine dyes is studied using the effective length as a topological parameter. Both alternant and non-alternant hydrocarbon end-groups are considered. In each case the dependence of the effective length upon the number of annelating benzene rings is determined for various possible types of annelation and some extreme annelation effects are demonstrated. The results predicted by means of the theory are shown to be in agreement with the experimental data.

1 INTRODUCTION

Annelation of the end-groups of polymethine dyes is a practical way of changing their electron properties. A previous paper[1] described the effect of end-group annelation on the topological parameter Φ_0 which quantitatively characterizes end-group basicity. This present study concerns the effect of end-group annelation on the energy of the first electron transition of dyes **I**: G denotes the end-groups

$$G^{+}\!\left(\!-CH{=}CH\!-\right)_{n}CH{=}G$$

I

The wavelength of the transition is linearly related to the length of a polymethine chain n:[2-5]

$$\lambda_n = V(n + L) \tag{1}$$

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where $V \simeq 100$ nm and L is the effective length of the end-group, expressed as the equivalent number of vinylene groups. The parameter L is a quantitative measure of the bathochromic shift of the long-wavelength absorption band and the value of L reflects correctly the end-group topology, including linear or branched structure, cyclizations, isomerizations, and the influence of the nature and the position of the heteroatoms and heterobonds.[5] Thus it is reasonable to utilize the effective length in theoretical studies of relationships between dye constitution and colour, and in the present case the parameter is used with particular respect for the analysis of annelation effects.

2 APPLICATION OF NON-BONDING MOLECULAR ORBITAL METHOD

Both the topological parameters L and Φ_0 of the end-groups can be calculated through the coefficients of the characteristic polynomials of the end-groups,[2-5] and also by application of the method of non-bonding molecular orbitals (NBMO).[6,7] It should be assumed that for relatively large values of n the energies of the frontier MOs approach those of the energy of a non-bound p-electron, i.e. to the Fermi level or to zero energy, if treated in terms of the Hückel MO method. Hence the parameter L can be determined using the relationship

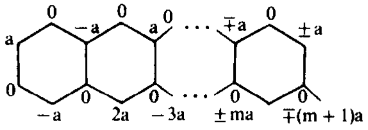
$$L = \frac{2\sum_{\mathrm{VEG}} C_v^2 + C_0^2}{C_1^2 + C_0^2} \tag{2}$$

where C_v are NBMO coefficients at the end-group atoms, C_1 is NBMO coefficient at the end-group atom connected to the polymethine chain, and C_0 that for the atom in the α-position of the chain. It is not necessary to normalize NBMO coefficients; they can be determined from the system of equations involving all the atoms of the end-group

$$C_\mu h_\mu + \sum_{v(\neq \mu)} C_v \eta_{\mu v} = 0 \qquad (\mu = 1, 2, \ldots, N) \tag{3}$$

where N is the total quantity of π-centres and h_μ and $\eta_{\mu v}$ are constant factors modifying the Coulomb (α_X) and the resonance (β_{CX}) integrals of heteroatoms and heterobonds in HMO approximation, so that $\alpha_X = \alpha + h_X\beta$ and $\beta_{CX} = \eta_{CX}\beta$, where α and β concern atom C and bond C—C. The summation is made in respect to all the neighbours of atom μ.

The solution of eqn (3) has a number of peculiarities in the case where an acene chain is taken as an end-group. For instance, NBMO coefficients of the annelated end-groups **II** are never equal to zero in some positions:



II

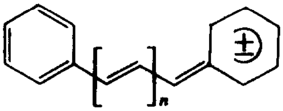
The signs of the coefficients within the acene cycle adjacent to the polymethine chain depend upon the parity of m. In the molecular graph **II** the vertices of degree 3 have their NBMO coefficients equal either to zero or to the constant value. In contrast, the coefficients at the vertices of degree 2 increase by a constant value 'a' on passing to the next cycle along the acene chain, nearer to the connection of the end-group and the polymethine chain. A recurrence relation holds good for them: $C_r = -C_{r-1} - a$. Therefore NBMO coefficients, and hence the effective length L, are influenced by the number of benzene rings involved in the annelation.

3 CALCULATIONS AND DISCUSSION

3.1 Alternant Hückel end-groups

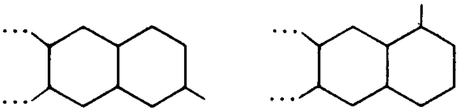
We consider here some of the most stable monocyclic end-groups. It should be noted that the basic calculation can be restricted to carbocyclic residues only, since the energy gap of a dye is determined predominantly by the molecular topology rather than by the effects of heteroatoms.[5]

α,ω-Diphenylpolymethines **III** in their cationic or anionic forms can be regarded as the simplest polymethine dyes with alternant end-groups:



III

There are two possible ways of annelating their end-groups, viz.



(a) (b)

(The first atom of the polymethine chain is represented by the exocyclic atom of the end-group.)

TABLE 1
Effective Length of the Annelated End-Groups of Polymethine Dyes

m	III				XII				XVI			
	III*a*		III*b*		XII*a*		XII*b*		XVI*a*		XVI*b*	
	L	Δ*L*	*L*	Δ*L*	*L*	Δ*L*	*L*	Δ*L*	*L*	Δ*L*	*L*	Δ*L*
1	2·50	—	2·50	—	2·80	—	2·80	—	5·44	—	5·44	—
2	2·78	0·28	3·44	0·94	4·25	1·45	2·71	−0·09	8·00	2·56	6·25	0·81
3	3·25	0·47	4·25	0·81	5·69	1·44	2·87	0·16	10·60	2·60	7·00	0·75
4	3·80	0·55	5·00	0·75	7·10	1·41	3·18	0·31	13·22	2·62	7·72	0·72
5	4·39	0·59	5·72	0·72	8·51	1·41	3·50	0·32	15·85	2·63	8·43	0·71
6	5·00	0·61	6·43	0·71	9·92	1·41	3·82	0·32	18·50	2·65	9·13	0·70
7	5·63	0·63	7·12	0·69	11·33	1·41	4·15	0·33	21·15	2·65	9·82	0·69
8	6·26	0·63	7·81	0·69	12·73	1·40	4·48	0·33	23·80	2·65	10·50	0·68

Note: $\Delta L = L_m - L_{m-1}$.

The NBMO coefficients for case (a) are the same as for the molecular graph **II**. It is therefore possible for the parameter *L* to be calculated by means of eqn (2):

$$L = \frac{1}{2}\left(2m + 2 + \frac{7}{m+1}\right) \tag{4}$$

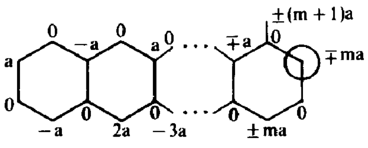
where *m* is the number of annelating rings. Table 1 gives the effective lengths of the end-groups with $m = 1$–8.

Where *m* is rather larger, eqn (4) can be simplified to

$$L = \tfrac{2}{3}(m+1)$$

With lengthening of the acene chain the shift of the long-wavelength absorption maximum of dyes **III** (per annelating ring) tends to its limiting value, approximately equal to $\Delta\lambda = V\Delta L = 2V/3$ or 60–70 nm. However, for small values of *m* the annelation effect is much less: 28 and 47 nm (see Table 1).

If the end-groups of dyes **III** are annelated according to type (b), the NBMO coefficients are as follows:



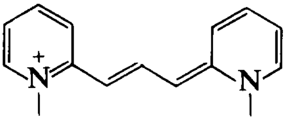
IV

Contrary to the above case (a), the molecular graph **IV** has its NBMO coefficient in the encircled position *m* times as great as that for molecular graph **II**. Hence the free term and the coefficient at $(m+1)^{-1}$ in eqn (5) for the effective length increases compared with eqn (4):

$$L = \frac{1}{3}\left(2m + 8 - \frac{5}{m+1}\right) \tag{5}$$

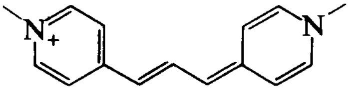
It is apparent from eqn (5) and Table 1 that the limiting value of the spectral annelation effect per benzene ring for large values of m is the same as that for the above case: $\Delta\lambda = 2V/3$. However, the first members of the acene chain exhibit a much more pronounced bathochromic shift: $\Delta\lambda \simeq (0{\cdot}8 - 0{\cdot}9)V$ per benzene ring. Additionally, unlike annelation type (a), the annelation effect grows weaker with lengthening of the polymethine chain (see Table 1).

The theoretical conclusions obtained agree with the experimental data. To illustrate this, spectral parameters are shown for the carbocyanines **V–IX**, in which the end-groups are aza-substituted derivatives of alternant hydrocarbon residues:[8,9]



$\lambda_{max} = 560$ nm

V

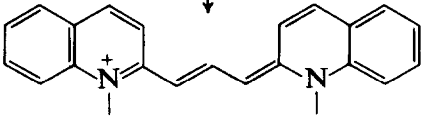


$\lambda_{max} = 602$ nm

VIII

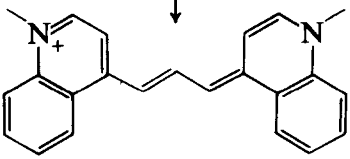
45 nm

109 nm



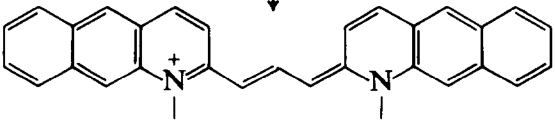
$\lambda_{max} = 605$ nm

VI



IX $\lambda_{max} = 711$ nm

42 nm

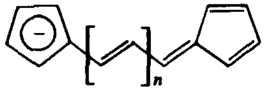


VII $\lambda_{max} = 647$ nm

Comparing series **V–VII** and **VIII–IX** shows that the annelation of pyrido-4-carbocyanines results in a much more significant bathochromic effect than that of pyrido-2-carbocyanines, which is in good accord with eqns (4) and (5), as well as with the calculated data (see Table 1).

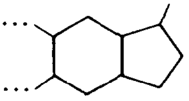
3.2 Non-alternant end-groups

We discuss here dyes **X** as examples of dyes having end-groups involving only five-membered ring systems, since other ring systems having an odd number of ring atoms are rather rare in dye molecules of practical importance:

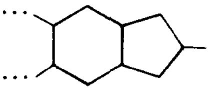


X

It is possible for such end-groups to be annelated in two ways:

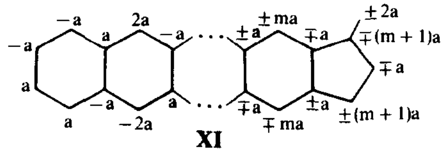


(a)



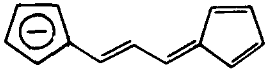
(b)

Asymptotic NBMO of a dye has no nodes within a non-alternant end-group. The NBMO coefficients for case (a) are shown below:

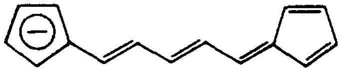


XI

Substituting them into eqn (2) and ignoring the term of the same order of magnitude as m^{-1}, it is found that the limiting value of the effective length increase on annelation per benzene ring is $\lim_{m\to\infty} \Delta L = 4/3$. A pronounced bathochromic shift should be expected on the basis of such a large increase in the effective length L, the value ΔL being slightly sensitive to the number of annelating benzene rings (see Table 1). In fact the observed absorption maxima of annelated α,ω-di(cyclopentadienyl)polymethines show that large bathochromic shifts accompany the annelation, although the shifts are somewhat lower than the calculated ones:[10]



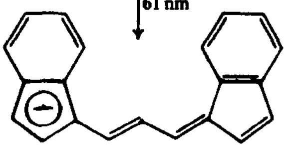
$\lambda_{max} = 564$ nm
XII



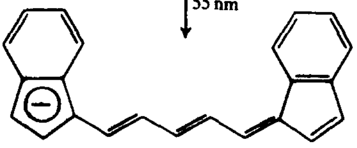
$\lambda_{max} = 665$ nm
XIV

↓ 61 nm

↓ 55 nm



$\lambda_{max} = 625$ nm
XIII

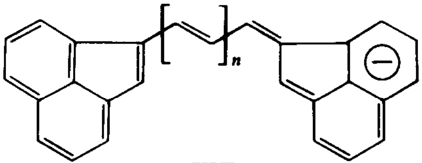


$\lambda_{max} = 720$ nm
XV

The coefficients $C_1 = a$ and $C_0 = -2(m+1)a$ for annelation type (b), with m growing infinitely, make the sum $C_0^2 + C_1^2$ nearly four times as great as that for type (a). Therefore, on lengthening the acene chain, the value of ΔL tends to its limit 1/3, which is smaller by a factor of four (see Table 1). It is of interest to note that annelation by the first benzene ring causes a negative effect: $\Delta L = -0{\cdot}09$. Further building up of the acene chain results in an increase of the effective length, although less pronounced in comparison to case (a).

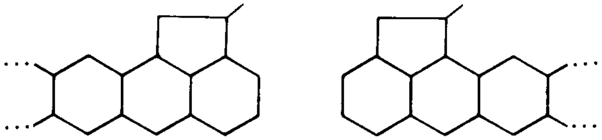
3.3 Extreme annelation effects

So far no annelation examples have been discussed which involve an extremely strong influence on the effective length. Nevertheless, drastic effects can occur in some special cases. To exemplify we consider the annelation of end-groups in the dye series **XVI**:



XVI

We limit ourselves to two possible ways of linear annelation:



(a) (b)

Calculating the NBMO coefficients and substituting them into eqn (2) give

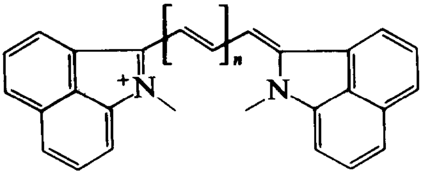
Type (a) $$L = \frac{1}{3}\left(8m + 7 + \frac{4}{m+2}\right) \tag{6}$$

Type (b) $$L = \frac{1}{3}\left(2m + 16 - \frac{5}{m+2}\right) \tag{7}$$

The effective lengths of the first members of the annelated end-group series are presented in Table 1.

It follows from eqn (6) that the limiting value of the bathochromic shift per benzene ring amounts to $8V/3$ or 250–300 nm. Thus annelation involving only one or two benzene rings should lead to a large bathochromic shift.

In the case of dyes **XVII** with benz[c,d]indole end-groups, i.e. the aza-analogues of dyes **XVI**, the annelation effect is even more pronounced:

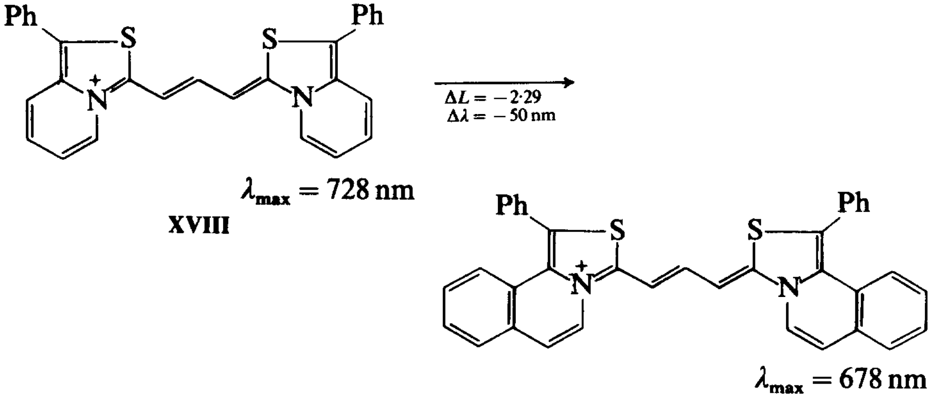


XVII

The effective length of the benz[c,d]indole end-group is equal to 6·50 and hence dyes **XVII** are of rather deep colour ($\lambda_{max} = 750$ nm if $n = 1$; $\lambda_{max} = 850$ nm if $n = 2$).[11] Monoannelation of type (a) causes the value L to increase to 9·62. Thus dyes with naphth[c,d]indole end-groups are likely to absorb light of wavelength of about 1000 nm even at $n = 0$.

Equation (7) and Table 1 show that annelation of a different type results in a much slighter effect. As the acene chain lengthens, the limiting value of the effective length increase per benzene ring tends to $\Delta L = 2/3$, which is the same value as for α,ω-diphenylpolymethines **III**. At the same time the free term in eqn (2) is notably greater than in eqns (4) or (5), thus accounting for the greater effective length of the end-groups of dyes **XVI**, if m is finite.

Moreover, in some particular cases annelation can cause a strong decrease of the effective length. Thus the isoquinothiazole end-group of dyes **XIX** has a lower effective length (7·07) compared to the pyridothiazole residues of dyes **XVIII** (9·36), and therefore the former dyes absorb light at shorter wavelengths:[12]



XVIII

XIX

To summarize, annelation can be regarded as the essential modifying factor of end-group topology, greatly influencing the energy of the electron transitions in polymethine dyes. As a rule notable bathochromic shifts of the first absorption maximum are observed, although hypsochromic effects can also occur.

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