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Electron Donor Ability of the Annelated End-Groups of Polymethine Dyes

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ABSTRACT

The influence of benzannelation on the electron donor ability of polymethine dye end-groups is studied in terms of the recently proposed quasi-long dye approximation combined with a graphical–theoretical approach. The Sachs–Coulson graph theorem enables the electron donor ability to be expressed in an analytical form and related to the number of annelating rings and to the type of annelation. Both alternant and non-alternant hydrocarbon end-groups are considered, including anti-Hückel ones, as well as nuclei containing heteroatoms. In each case the dependence of the electron donor ability on the number of annelating benzene rings is determined for all possible types of annelation. The results predicted by means of the theory are shown to be in agreement with the literature and experimental data.

1 INTRODUCTION

The basicity of annelated end-groups of cyanine dyes has been analysed by Brooker,[1] who found that annelation considerably influenced the basic properties. Thus, 2-benzothiazolyl has lower basicity than thiazolyl, whereas 2-benzo[*h*]quinolyl is more basic compared with 2-quinolyl.

Brooker used a concept of additional double bond stabilization (ADBS) for interpretation of these results. The basicity of a nucleus rises if annelation causes an increase in the Kekulé structure number (KS) of its acceptor form, and vice versa. Increase of the KS value of the donor form on annelation results in a decrease in the basicity.

End-group annelation is often used and we discuss it in detail, using a more correct parameter, referred to as the electron donor ability, Φ_0.[2,3] This parameter was recently introduced as an approximation in 'dyes with a quasi-long polymethine chain (PC)'.[2,3] It depends directly on the chemical nature of the end-group. The value of Φ_0 for dyes of formula **I** has been shown[2,3] to be constant within the vinylene series and it is determined by the disposition of the frontier MOs in respect to the Fermi level of a π-electron.[2,3]

$$[E^+\text{—}(CH{=}CH)_n\text{—}CH{=}E] \longleftrightarrow [E{=}CH\text{—}(CH{=}CH)_n\text{—}E^+]$$

I

The definition enables the parameter to be related to dye redox potentials:[4] Φ_0 can be readily computed according to eqn (1)

$$\tan\Phi_0 = -q_0/r_0 \tag{1}$$

through the free characteristic polynomial terms q_0 and r_0 for acceptor (polynomial Q) and donor (polynomial R) forms of an end-group. It is necessary to bear in mind that nuclei should be represented in a form which ensures that the LUMO is antisymmetrical when $n = 0$, in order to ensure that the dye belongs to Class A and that the Φ_0 value is positive.[2,3]

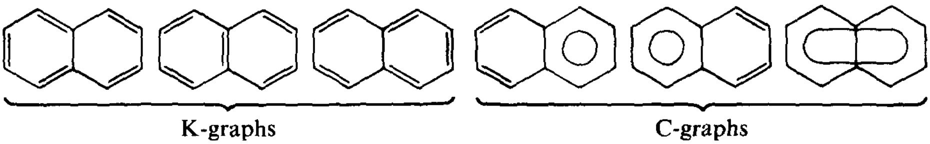
We assume the PC to be rather long and frontier levels to be delocalized within a dye molecule.

2 APPLICATION OF GRAPH THEORY

Polynomial coefficients q_0 and r_0 can be calculated in numerous ways, e.g. by expanding the characteristic determinant in a polynomial series, through the Sachs–Coulson theorem, NBMO theory, etc.[2,3] However, we prefer graph theory as the most convenient method, since it resembles the traditional method for estimating basicity through KS, and it has a simple graphic expression, readily apparent to practical chemists.

Coefficients of the characteristic polynomial are related to molecular graph topology in accord with the Sachs–Coulson theorem.[5] The π-conjugated system **I** considered in this present paper will be represented as a molecular graph. The discussion should involve the so-called Sachs graphs, i.e. graphs including only complete graphs of degree 1 ($\sigma_1 = 1$) and cycles as subgraphs. Subgraphs of degree 1 correspond to the π-bonds in KS (if any), and cycles represent the π-electron delocalization along cyclic perimeters.[3] The set of Sachs graphs must therefore be divided into two parts, viz.

K-graphs, corresponding to KS, and C-graphs, resembling structures with delocalized π-electrons. Thus three K-graphs and three C-graphs are possible for naphthalene:

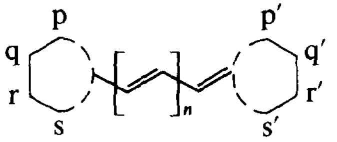


According to this approach, heteroatoms are represented with loops.[3,5] Let us characterize heteroatoms and heterobonds with the parameters h and η, the former determining the Coulomb integral ($\alpha_x = \alpha + h_x\beta$), and the latter determining the resonance integral ($\beta_{cx} = \eta_{cx}\beta$) in terms of the HMO method. In graph theory, the parameters h and η are used to estimate the weight of the Sachs graph. Thereby a free characteristic polynomial term p_0 can be obtained in a general form:[3,6]

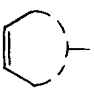
$$p_0 = \sum_S \left\{ (-1)^{c(S)} 2^{q(S)} \prod_x h_x f(\eta_{cx}) \prod_i (-1)^{v_i} \right\} \tag{2}$$

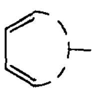
Summation is carried out over all the Sachs graphs. The first multiplication concerns all the heteroatoms and the second multiplication all the cycle, containing v_i vertices in each Sachs graph. Constants $c(S)$ and $q(S)$ are the numbers of components and cycles respectively in a graph S. The function $f(\eta_{cx})$ equals η_{cx}^2 if the heterobond belongs to a K-graph and η if it belongs to a cycle in a C-graph.

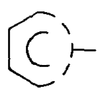
Let us represent a polymethine dye formula with arbitrary end-groups as follows:



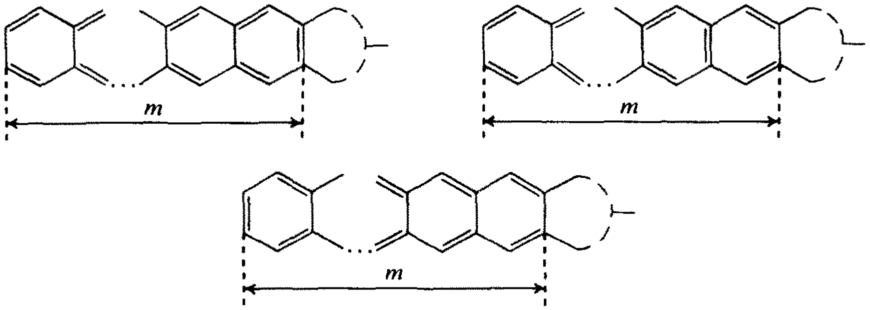
A linear section formed by the atoms p, q, r, s is marked out to designate the bond qr assumed to be annelated. In the general case two K-graphs and one C-graph are possible for the section pqrs:


(a)

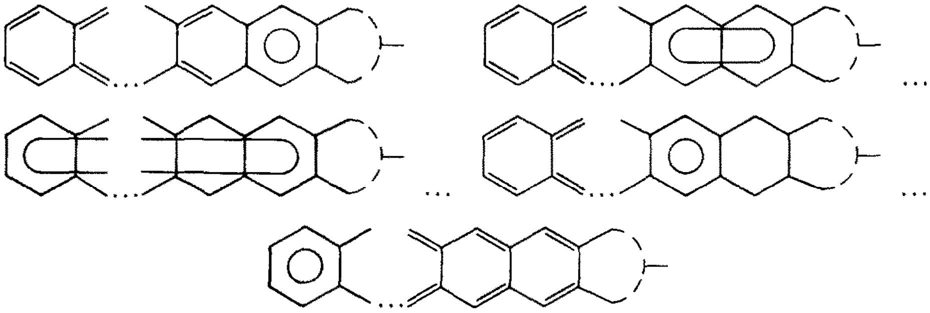

(b)


(c)

Additional Sachs graphs can be constructed due to the acene chain of the annelated end-group. If the initial nucleus is annelated with *m* benzene rings, $(m+1)$ K-graphs turn out to exist in the case (a):

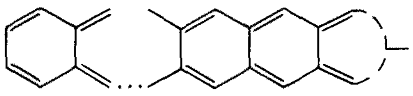


In addition, C-graphs with a single cyclic subgraph (C_1) are possible in the case of (a). We can write $m(m+1)/2$ such graphs:

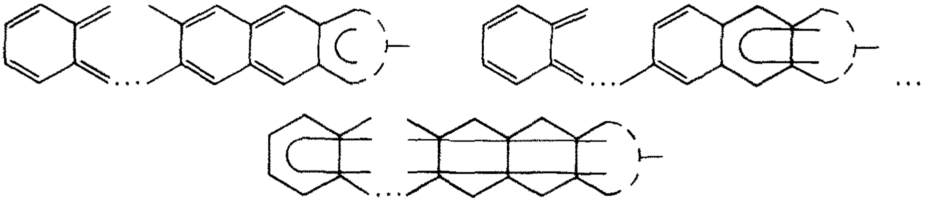


No other C-graph exists.

For case (b), a single K-graph is possible:



For case (c), one K-graph and *m* C-graphs can be constructed:

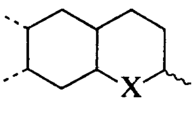


Let us now consider the most typical variants of end-group annelation in polymethine dyes.

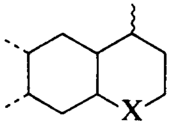
3 RESULTS AND DISCUSSION

3.1 Heteroanalogues of alternant end-groups

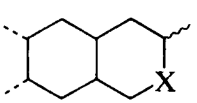
Taking monocyclic end-groups initially, insofar as alternant hydrocarbon end-groups always have $\Phi_0 = 0°$ (or $90°$) irrespective of annelation, we study their heteroanalogues. The case to consider deals with the end-groups containing a single heteroatom conjugated with a polymethine chain. The possible annelation variants for Hückel end-groups are as follows (X = NR, O, S, Se):



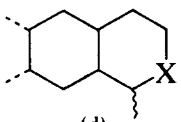
(a)



(b)

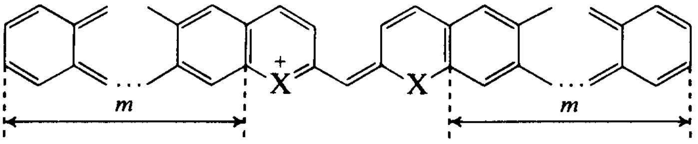


(c)



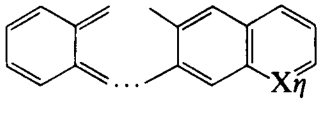
(d)

For the case (a), monomethine dyes of class A with annelated end-groups are depicted in a form such as to meet the condition that Φ_0 is positive:[2,6]



II

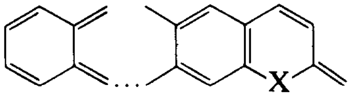
Counting up the Sachs graphs for dyes **II** in the acceptor form



gives $(m + 2)$ K-graphs and $(m + 1)(m + 2)/2$ C_1-graphs with the same weight η^2. Hence it follows from eqn (2) that:

$$q_0 = -(m + 2)^2\eta^2$$

The Sachs graphs obtained for dyes **II** in the donor form



can be counted up in a similar way, their weights being equal to h. The polynomial R free term also depends upon the number of annelating rings:

$$r_0 = (m + 1)^2 h$$

If q_0 and r_0 are substituted in eqn (1), eqn (3) is obtained:

$$\tan\Phi_0 = \frac{\eta^2}{h}\left(1 + \frac{1}{m+2}\right)^2 \tag{3}$$

For some numerical examples the reader is referred to Table 1. Like eqn (3), the table clearly indicates that linear annelation causes the basicity to decrease with increase in the number of benzene rings. This regularity is proved by experimental investigation of annelated nuclei, deviations of unsymmetrical dyes being taken as measure of nucleus basicity.[1,7] Deviation increases if one of the end-groups becomes more basic with respect to the other. According to Ref. 8, the deviation is 123 nm for pyrido-2-styryls and 80 nm for quino-2-styryls, thus indicating the lower basicity of the quinolyl nucleus and confirming the above results.

The parameter Φ_0 is thus shown to depend greatly upon the nature of the heteroatom (see eqn (3) as well as experimental data[4]). With the increase of the acene chain Φ_0 tends to its limiting value:

$$\lim_{n\to\infty} \tan\Phi_0 = \arctan(\eta^2/h)$$

This type of annelation results in a decrease of the electron donor ability, since the acceptor and donor forms become almost equivalent in respect of their stability as the number of benzene rings increases. The fact is that Sachs graphs derived from the linear acene chain are much the same for both extreme forms, with the exception of m additional C_1-graphs involving the initial nucleus for the acceptor form. It is also necessary to bear in mind the

TABLE 1

Electron Donor Ability Φ_0 of the Annelated End-Groups of Polymethine Dyes (in degrees)

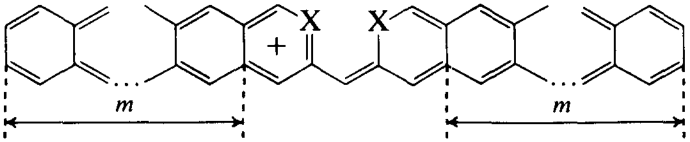
	X	*Y*	*Number of annelating rings*							
			0	*1*	*2*	*3*	*4*	*5*	*20*	
II	NR	—	66	61	57	55	54	53	48	45
II	0	—	48	42	38	36	34	33	29	27
III	NR	—	84	86	87·7	88·4	88·8	89·1	89·9	90
III	0	—	77	83	85·4	86·8	87·7	88·2	89·9	90
X	NR	—	45	45	45	45	45	45	45	45
X	0	—	27	27	27	27	27	27	27	27
XII	NR	NR	79	72	69·5	68·2	67·4	66·8	64·5	63·4
XII	NR	0	68	63	61·0	60·2	59·4	58·9	57·1	56·3
XIII	NR	NR	78	81	83·1	84·4	85·3	86·0	88·7	90
XIII	NR	0	72	66	72·7	73·8	74·5	75·5	77·5	78·7

Note: $\alpha_N = \alpha + \beta$; $\alpha_O = \alpha + 2\beta$; $\beta_{CN} = \beta_{CO} = \beta_{CC}$.

different weights of the Sachs graphs contributing to q_0 and r_0. It is the relation of graph weights that determines the limiting Φ_0 value.

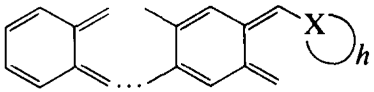
Annelation types (b) and (d) prove to be analogous to the one above. The numbers of Sachs graphs for acceptor and donor forms are equal in both cases, and so are the Φ_0 values. Therefore, the longer the acene chain, the lower are the basicities of the nuclei and the deviations of the styryl dyes, e.g. those for pyrido-4-styryl (127 nm) and quino-4-styryl (109·5 nm).

Annelation type (c) displays quite different changes of parameter Φ_0 on annelation. The general dye formula is as follows:



III

Only one K-graph with a weight h is possible for the donor form of compound **III**, viz.

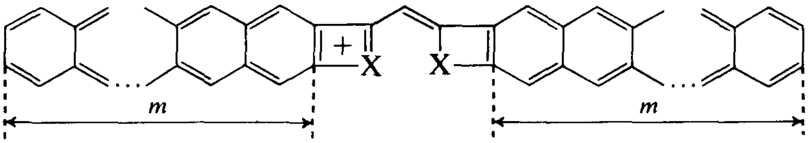


The free polynomial term r_0, consequently, is constant irrespective of the acene chain length: $r_0 = -h$. The coefficient q_0 is the same as in the previous case. Both q_0 and r_0 when substituted into eqn (1) give:

$$\tan \Phi_0 = (\eta^2/h)(m+2)^2 \tag{4}$$

It can be derived from eqn (4) that an increase in the acene chain also causes the electron donor ability to increase, tending to 90° (see Table 1). This result is proved experimentally, viz. dyes with isoquinolyl nuclei are more basic than those with pyridyl nuclei.

The dyes with anti-Hückel heterocycles are now considered, e.g. the annelated cyclobutadienyl cyanines of general formula **IV**:



IV

The initial nucleus has two K-graphs and one C_1-graph, so Sachs graphs for the acceptor form can be counted with ease:

(a)

(b)

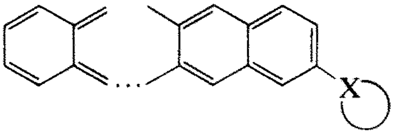
(c)

Annelation gives $(m+1)$ K-graphs and $m(m+1)/2$ C_1-graphs for case (a) and only one K-graph for (b), all of them contributing positively to q_0. From case (*c*) can be constructed $(m+1)$ C_1-graphs with negative contributions to q_0. Combination of these positive and negative contributions causes the frontier MOs to degenerate if X = CH (anti-Hückel carbocyclic nuclei).

The polynomial Q free term can be represented in the form:

$$q_0 = -\eta^2 m^2$$

A number of Sachs graphs [$(m+1)$ K-graphs and $m(m+1)/2$ C_1-graphs] with the identical weights h is possible for the donor form of **IV**:



Therefore, we obtain:

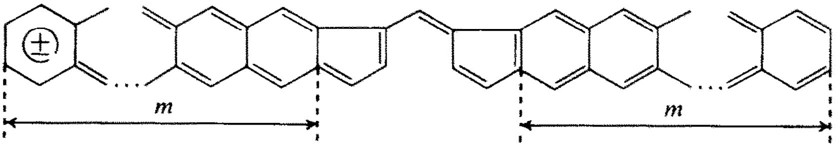
$$r_0 = -(m+1)^2 h$$

$$\tan \Phi_0 = \frac{\eta^2}{h}\left(1 - \frac{1}{m+1}\right)^2 \tag{5}$$

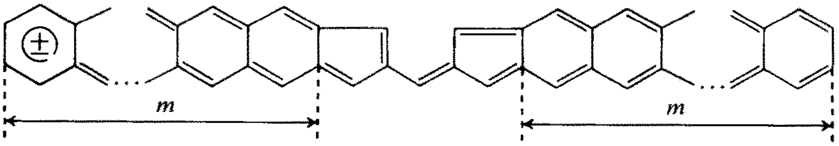
If m is zero, the parameter Φ_0 will have zero value, i.e. the LUMO will become a nonbonding MO. However, it increases on annelation, and electron donor ability increases. The limit of the Φ_0 value is determined by the nature of the heteroatom.

3.2 Non-alternant end-groups

The discussion is restricted to systems containing five- and seven-membered rings. Two variants of annelation are possible for five-membered rings and the dyes are presented so that Φ_0 is positive.

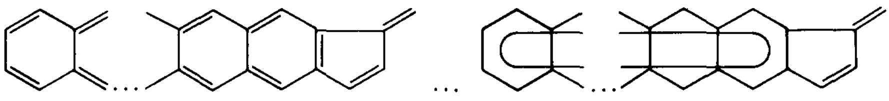


V



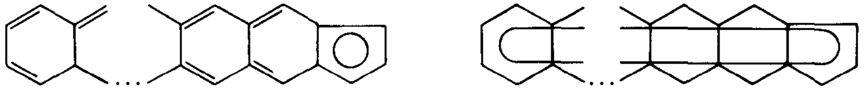
VI

The polynomial Q free term is contributed to by $(m+1)$ K-graphs and $m(m+1)/2$ C_1-graphs:



and it equals $q_0 = -(m+1)^2$.

The R-polynomial enables only $(m+1)$ C_1-graphs to be constructed:



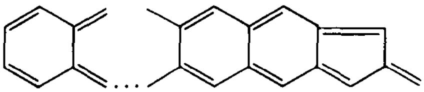
Thereby, $r_0 = 2(m+1)$.

When substituting these values for q_0 and r_0 in eqn (1), Φ_0 is readily obtained:

$$\tan \Phi_0 = (m+1)/2 \tag{6}$$

It should therefore increase with extension of the acene chain.

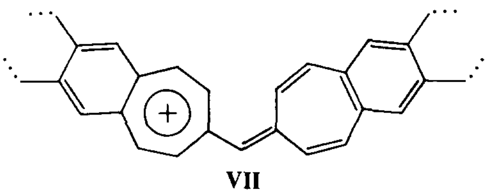
The end-groups of dyes **VI** make only one K-graph possible for polynomial Q:



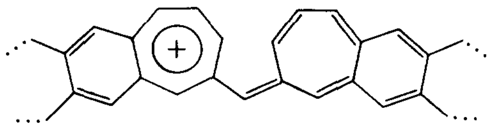
The polynomial R is the same as that in the above case. In contrast to dyes **V**, Φ_0 decreases with an increase in the acene chain:

$$\tan \Phi_0 = \frac{1}{2(m+1)} \tag{7}$$

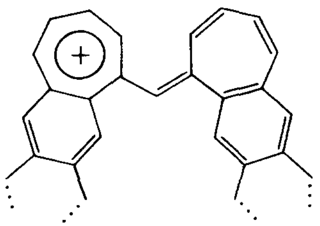
Three ways of annelating tropylium dyes are possible, viz. **VII–IX**:



VII

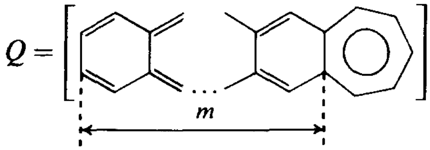


VIII



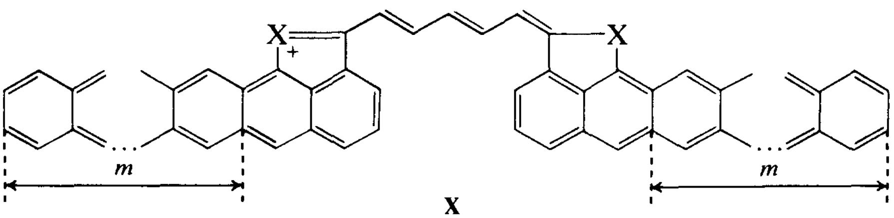
IX

Polynomial Q is identical in all three cases:



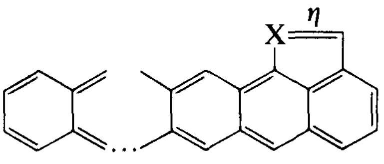
One can construct only $(m+1)$ C_1-graphs for it, and thus $q_0 = 2(m+1)$. Since a double bond is annelated in both cases, the donor form permits equal numbers of K- and C_1-graphs $[(m+1)$ and $m(m+1)/2$ respectively$]$ for dyes **VII** and **IX**. Therefore, $r_0 = -(m+1)^2$. In contrast to **VII** and **IX**, an ordinary bond is annelated in the donor form of dye **VIII**, so only the K-graph is possible, and $r_0 = -1$. Annelation of end-groups in dyes **VII** and **IX** results in a decrease of Φ_0 and vice versa. Annelation of dyes **VIII** results in $\Phi_0$increasing.

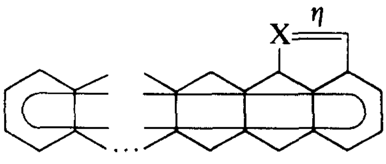
It is of interest to note, however, that in some special cases annelation does not affect the electron donor ability; for example, consider the benz[*c*,*d*]indole dyes (**X**):



X

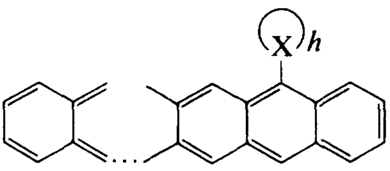
We can construct K- and C-graphs only for the acceptor form with a heterobond fixed, i.e.

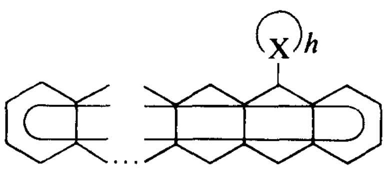




Otherwise the vertex of degree 3 (a common one for three cycles) will not be included into the Sachs graph. This vertex also prevents the construction of C-graphs with the five-membered ring.

Polynomial R permits Sachs graphs involving the acene chain and the heteroatom with a loop on it:





Other K- and C-graphs with a non-zero weight are impossible.

Therefore polynomials Q and R are determined by the same graph sets, differing however by their weight factors. Their free terms can be represented as follows:

$$q_0 = \eta^2(m+3)^2$$

$$r_0 = -h(m+3)^2$$

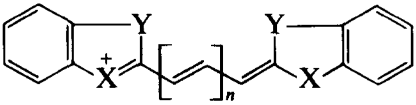
Coefficients q_0 and r_0 are substituted in eqn (1) to give:

$$\tan \Phi_0 = -\eta^2/h$$

Hence, the parameter Φ_0 does not depend upon the number of benzene rings and is only affected by the nature of the heteroatom. Some examples concerning nuclei with N- and O-atoms are shown in Table 1.

3.3 Annelation of cyanine dye end-groups

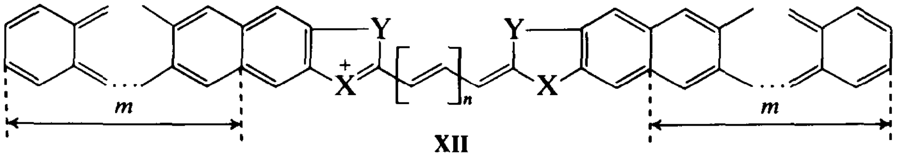
Finally, we shall consider the end-groups of traditional cyanine dyes, the typical form of which is:



XI

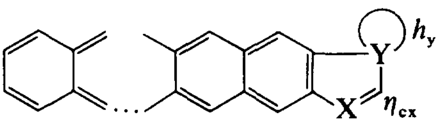
($Y = NR$, O, S, Se and $X = NR$, as a rule). However, we should pay attention to a general case. Heteroatom parameters are taken equal to h_x, h_y, η_{cx}, η_{cy}.

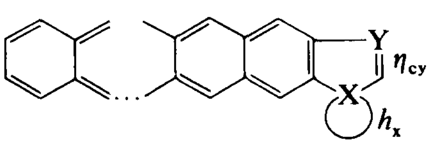
The general formula for monomethine dyes of class A with end-groups linearly annelated can be represented as:

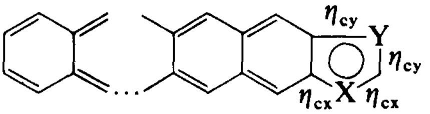


XII

If the double bond in the acene fragment is fixed, then three Sachs graphs are possible:







In addition, we can construct further graphs if we involve the π-bond and the cycle 'rearrangements' in the acene chain, viz. $(m+2)$ K-graphs and $(m+2)(m+3)/2$ C_1-graphs for each of two first structures shown above, and $(m+1)$ C_1-graphs involving heterocycles for the third structure. Hence:

$$q_0 = (h_x\eta_{cy}^2 + h_y\eta_{cx}^2)(m+1)^2 + 2\eta_{cx}^2\eta_{cy}^2(m+1)$$

The donor form enables $(m+2)$ K-graphs and $(m+1)(m+2)/2$ C_1-graphs with loops on the heteroatoms to be constructed. One K-graph including heterobonds is also possible. It should be pointed out that this graph contains one less component and gives an opposite (negative) contribution to eqn (2) compared with the K-graphs with loops on the heteroatoms.[9] As a result we obtain:

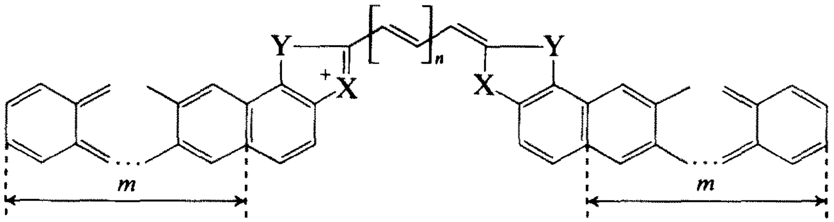
$$r_0 = -h_xh_y(m+1)^2 + \eta_{cx}^2\eta_{cy}^2$$

Parameter Φ_0 thus takes the value:

$$\tan\Phi_0 = \frac{(\delta_x+\delta_y) + 2\delta_x\delta_y/(m+2)}{1-\delta_x\delta_y/(m+2)^2} \qquad \lim_{m\to\infty} \tan\Phi_0 = \delta_x + \delta_y$$

where $\delta_x = \eta_{cx}^2/h_x$ and $\delta_y = \eta_{cy}^2/h_y$. Some examples concerning typical end-groups are shown in Table 1. It is apparent that linear annelation results in lowering of basicity, which is in agreement with the deviation values for annelated unsymmetrical dyes.[8] For instance, deviations of naphthothiazolo-(41 nm) and naphthimidazolo-styryls (118·5 nm) are lower than those of benzothiazolo- (58 nm) and benzimidazolo-styryls (134·5 nm), respectively.

The alternate change of Φ_0 was found for angular annelation of end-groups in dyes **XIII**:

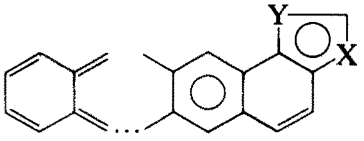


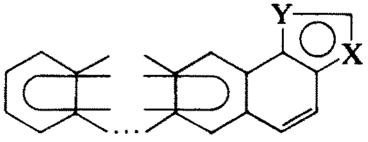
XIII

The corresponding donor form is presented by $(m+2)$ K-graphs and $(m+1)(m+2)/2$ C_1-graphs with loops on the heteroatoms, in addition to $(m+1)$ K-graphs and $m(m+1)/2$ C_1-graphs having localized heterobonds, the two latter sets contributing negatively to the polynomial free term r_0. Hence the value r_0 decreases in comparison with the above case:

$$r_0 = -h_xh_y(m+2)^2 + \eta_{cx}^2\eta_{cy}^2(m+1)^2$$

At the same time the value q_0 increases on account of $m(m+1)/2$ Sachs graphs with two cycles (C_2-graphs):





Additionally $(m+1)$ Sachs graphs are possible, including the heterocycle and involving π-bond 'rearrangements' in the acene chain. Thus, the polynomial free term q_0 is of the following form:

$$q_0 = (m+1)[2\eta_{cx}^2\eta_{cy}^2(m+1) + (\eta_{cx}^2 h_y + \eta_{cy}^2 h_x)(m+2)]$$

As a result, the electron donor ability of dyes **XIII** rises, tending to the limiting value:

$$\tan\Phi_0 = \frac{2\delta_x\delta_y(m+1/m+2) + \delta_x + \delta_y}{1 - \delta_x\delta_y(m+1/m+2)^2} \qquad \lim_{m\to\infty} \tan\Phi_0 = \frac{2\delta_x\delta_y + \delta_x + \delta_y}{1 - \delta_x\delta_y}$$

A number of examples are shown in Table 1 and these agree with the experimental data. Thus, on passing from benzothiazolo- to α- or β-naphthothiazolo-styryls, the deviations increase (58, 64 and 69·5 nm, respectively), as well as from 2-quinolino- to β-benzo-quinolino-styryls (80 and 100 nm, respectively). With angular bisannelation of the benzothiazolyl nucleus (two bonds are annelated at the same time), the dye deviation increases further (74·5 nm).

The above discussion shows that graphical applications to the theory of dye basicity are of great interest. Graph interpretation enables basicity changes to be ascertained in a simple and correct way. It is possible to characterize various types of annelation (both linear and angular), in respect of their effects on dye basicity.

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