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Polymethine Dyes Containing Condensed Isoindole Nuclei

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ABSTRACT

Using the approximation of the quasi-long polymethine chain, relationships between the chemical structure of azolo- and azino-isoindole residues in polymethine dyes and the dye spectral parameters are evaluated. Aza-substitution in the condensed isoindoles is shown to be the predominant factor influencing the effective length and the electron donor ability of the dye end-groups.

1 INTRODUCTION

Isoindole and its derivatives are heterocyclic compounds of great interest. Thus, the isoindole nucleus is a component of the stable and deeply coloured phthalocyanine pigments. However, cyanine dyes of relative simple structure, and including an isoindole nucleus as their end-group, have not yet been described. Such dyes could be of interest both in respect to their application properties and as compounds of value in theoretical studies. The synthesis of cyanines of this type involves new isoindole derivatives and derived condensed heterocycles; in this study, the synthesis and spectral properties of dyes containing azino- and azolo-indole residues (i.e. isoindole rings) annelated by an additional cyclic system at the [a]-bond are reported on.

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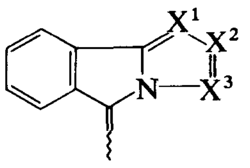
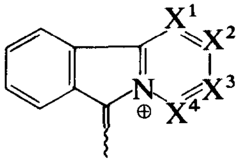
2 ANALYSIS OF DYE END-GROUP PARAMETERS

To estimate the effect of the structure of the end-group on the colour and stability of the dyes, the approximation of the quasi-long polymethine chain[1-3] was applied. Enumeration of the azolo- and azino-isoindole residues (**I** and **II**, respectively) was carried out initially:



I

$X^1, X^2, X^3 = CH$ or N or ^{+}NR



II

$X^1, X^2, X^3, X^4 = CH$ or N

In the synthesis of the series with end-groups of **I**, the position of a single $\geqslant{}^{+}NR$ group with a pyridinium nitrogen atom, the quantity (0 to 2) and the positions of pyridine nitrogen atoms (—N═) were varied, whereas the synthesis of the end-groups of **II** involved only varying the number (0 to 4) and the positions of the pyridine nitrogen atoms. For the pyridinium nitrogen, $h_{N^+} = 1{\cdot}5$ and $\eta_{N^+C} = 1$, and for the pyridine nitrogen, $h_N = 0{\cdot}5$ and $\eta_{NC} = 1$, according to the relationships

$$h_X = (\alpha_X - \alpha_C)/\beta_{CC}$$

$$\eta_{XC} = \beta_{XC}/\beta_{CC}$$

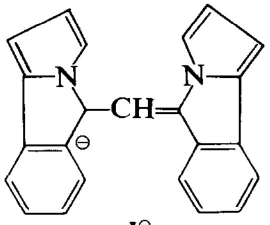
where h_X is the parameter of the heteroatom electronegativity, η_{XC} characterizes the strength of the bond X—C, and α_X and β_{XC} are the Coulomb and resonance integrals, respectively.

The effective length (L) and the electron donor ability (φ_0)[1,2] were considered for all the heterocyclic end-groups. The effective length can be used to estimate the wavelength of the first electron transition of the corresponding symmetric monomethinecyanine, and the electron donor ability can be used to characterize the relative disposition of the Fermi level and the energy gap of these dyes. The technique involving asymptotic non-bonding molecular orbitals (NBMO)[3] enables the determination of L and φ_0 values to be readily made, as well as their derivatives with respect to the parameters h_X and η_{XC}.[4] The derivative values reflect the sensitivity of the colour of the polymethine and its redox-stability to structural changes in the end-groups.

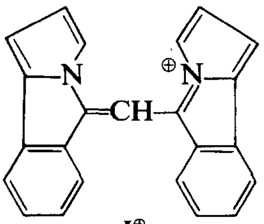
The estimated values of L and φ_0 for the condensed isoindole residues were compared with those for the 'parent' structures ($X^{1-3} = X^{1-4} = CH$). This approach proved to be useful, even in the case where the pertinent dye does not exist. Nevertheless, it does serve as a structure for comparison, and permits some qualitative conclusions to be made on the tendencies of changes in the effective length and the electron donor ability caused by aza-substitution.

2.1 Azoloisoindoles

Generally speaking, in the dye with end-groups of this type, pyrrolo-isoindole (**I.0**) ($X^1 = X^2 = X^3 = CH$) can exist both in donor and acceptor forms, i.e. the two dye types ($\mathbf{I}_M^{\oplus}$ and $\mathbf{I}_M^{\ominus}$) appear to be possible:



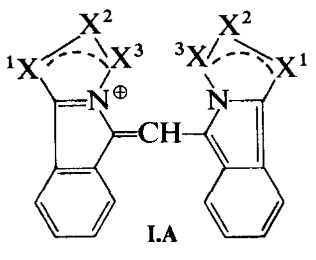
$\mathbf{I}_M^{\ominus}$



$\mathbf{I}_M^{\oplus}$

However, according to the criterion of stability,[5] the molecule of the corresponding monomethinecyanine should contain 26 π-electrons, i.e. existing preferably as monocation $\mathbf{I}_M^{\oplus}$.

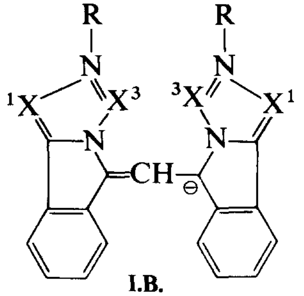
Heterocyclic residues of **I** derived from the above end-group belong to three series, depending on their principal structural differences and hence the electron density distribution in the dye molecules. For instance, the end-groups **Ia** ($X^2 \neq NR$) lead to the stable monocationic dye, **I.A**, in which the π-electron density is delocalized:



I.A

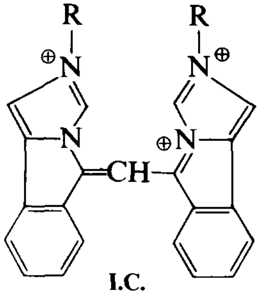
$X^1, X^3 = CH$ or N or NR
$X^2 = CH$ or N

In contrast, end-groups of series **Ib** ($X^2 = NR$) result in an unusual dye electronic structure; the monomethines containing imidazolo-[4,3-*a*]-isoindole residues, **Ib.1.1**, exists preferentially as the trication **I.C**, and triazolo- and tetrazolo-isoindole end-groups form the mesoionoic cations **I.B**:



I.B.

$X^1, X^3 = CH$ or N



I.C.

Calculated values of $\lambda_M = 100\,L$ (nm) and φ_0 (degrees) for azolo-isoindole end-groups are presented in Table 1. In order to clarify the description of the dyes, an additional parameter is also used: the reduced electron donor ability ($\varphi_0{}^*$). This value is always positive[1] and is related to $\varphi_0{}^2$ in a simple way, i.e. $\varphi_0^* = 90^\circ\,(1\text{-sine }\varphi_0)$.[2] The greater the value of $\varphi_0{}^*$ the higher is the reducing capacity of the dye.

Introduction of nitrogen atoms (of the pyridine type, and especially of the pyridinium type) results in considerable lowering of the π-electron levels, causing an increase in the number of bonding orbitals and π-electrons necessary for obtaining the closed shell (28 electrons as opposed to 26 within the 'parent' dye molecule $I_M^{\oplus}$). Moreover, a change of the dye class also occurs, and therefore φ_0 changes its sign.[1,2]

TABLE 1
Parameters of Azolo-isoindole Residue in Dyes

Compound	X^1	X^2	X^3	$\lambda_M = 100L$ (*nm*)	φ_0^* (φ_0) (*degrees*)	$\Delta\lambda$	$\Delta\varphi_0{}^*$ ($\Delta\varphi_0$)
I.0	CH	CH	CH	528	4 (4)	—	—
Ia.1.1	NR	CH	CH	514	70 (−20)	−14	66 (−24)
Ia.1.2	CH	CH	NR	583	70 (−20)	55	66 (−24)
Ia.2.3	NR	N	CH	517	70 (−20)	−11	66 (−24)
Ia.2.4	N	CH	NR	564	66 (−24)	36	62 (−28)
Ia.2.5.	NR	CH	N	521	66 (−24)	−7	62 (−28)
Ia.2.6	CH	N	NR	573	60 (−30)	45	56 (−34)
Ia.3.7	N	N	NR	558	58 (−32)	30	54 (−36)
Ia.3.8	NR	N	N	515	65 (−35)	−13	61 (−39)
Ib.1.1	CH	NR	CH	541	3 (3)	13	−1 (−1)
Ib.2.2	N	NR	CH	515	84 (−6)	−13	80 (−10)
Ib.2.3	CH	NR	N	551	75 (−15)	23	71 (−19)
Ib.3.4	N	NR	N	524	71 (−19)	−4	67 (−23)

In the series with azolo-isoindole residues, the electron donor ability is much more sensitive to aza-substitution by the NR-group in positions 1 and 3 ($\Delta\varphi_0 = -24°$) than in position 2 ($\Delta\varphi_0 = -1°$). Indeed, the function $\partial\varphi_0/\partial h_i$, calculated through NBMO coefficients and reflecting the φ_0 sensitivity to changes of atomic electronegativity,[3,4] is more than 20 times greater in positions 1 and 3 than in position 2 (about −0·41 and −0·02, respectively).

Due to the influence of the nitrogen atom in position 1, the highest occupied molecular orbital (HOMO) is lowered more than the lowest unoccupied level, so that a hypsochromic shift in the absorption occurs. The function $\partial L/\partial h_1$, characterizing the sensitivity of L to the change of atom electronegativity in this position[4] has a negative value ($\approx -0{\cdot}44$). At the same time, the presence of a nitrogen atom in position 2 causes bathochromic shifts ($\partial L/\partial h_2 \approx 0{\cdot}08$). Aza-substitution in position 3 leads to a strong bathochromic shift, being more pronounced for the more electronegative pyridinium nitrogen atom (although $\partial L/\partial h_3 \approx -0{\cdot}07$ about $h = 0$, the value becomes more positive with h in the range 0·5–1·5).

When influenced by two nitrogen atoms present in the end-group, the effective length changes in a rather additive manner. For instance, passing from pyrrolo-isoindole to triazolo-indoles, **Ia.2.3** and **Ib.2.2**, a hypsochromic shift can be observed, since aza-substitution in position 2 (slightly increasing the effective length) does not compensate the strong opposing effect of the nitrogen atoms in position 1. In contrast, the isomeric triazolo-isoindole end-group, **Ia.2.4**, has a greater effective length as compared to the initial residue (**I.0**) or the isomeric one (**Ia.2.5**), since the pronounced bathochromic shift due to the pyridinium nitrogen atom in position 3 is significantly greater than the hypsochromic effect of aza-substitution in position 1.

The additivity of such effects in tetrazolo-isoindole end-groups is less pronounced than that in triazolo-isoindole ones. Nevertheless, the maximum bathochromic shift can be expected for the 3-substituted isomer of end-group **Ia.3.7**, because of the maximum electronegativity increase in position 3 ($\Delta h = 1{\cdot}5$) and the minimum in position 1 ($\Delta h = 0{\cdot}5$).

2.2 Azinoisoindoles

The pyridoisoindole end-group is characterized by a relatively high electron donor ability. The presence of the nitrogen atom results in a lowering of the π-electron level system, though not as extensive as in the case of azolo-isoindoles. Hence, pyrido-isoindole and its aza-substituted analogues belong to the same dye class.

It is notable (see Table 2) that the electron donor ability undergoes the maximum decrease if methine groups are substituted by nitrogen atoms in positions 2 and 4 ($\partial\varphi_0/\partial h_2 = \partial\varphi_0/\partial h_4 \approx -0{\cdot}35$, i.e. markedly greater than

TABLE 2
Parameters of Azino-isoindole Residues in Dyes

Compound	X^1	X^2	X^3	X^4	$\lambda_M = 100L$ (*nm*)	$\varphi_0{}^*$ (φ_0) (*degrees*)	$\Delta\lambda$	$\Delta\varphi_0{}^* = \Delta\varphi_0$
II.0	CH	CH	CH	CH	575	59 (−31)	—	—
II.1.1	N	CH	CH	CH	561	58 (−32)	−14	−1
II.1.2	CH	N	CH	CH	589	48 (−42)	14	−11
II.1.3	CH	CH	N	CH	585	58 (−32)	10	−1
II.1.4	CH	CH	CH	N	566	48 (−42)	−9	−11
II.2.5	N	N	CH	CH	586	48 (−42)	11	−11
II.2.6	N	CH	N	CH	573	57 (−33)	−2	−2
II.2.7	N	CH	CH	N	563	48 (−42)	−12	−11
II.2.8	CH	N	N	CH	606	45 (−45)	31	−14
II.2.9	CH	N	CH	N	566	37 (−53)	−9	−22
II.2.10	CH	CH	N	N	567	48 (−42)	−8	−11
II.3.11	CH	N	N	N	572	36 (−54)	−3	−23
II.3.12	N	CH	N	N	564	48 (−42)	−11	−11
II.3.13	N	N	CH	N	592	35 (−55)	17	−24
II.3.14	N	N	N	CH	606	45 (−45)	31	−14
II.4	N	N	N	N	595	35 (−55)	20	−24

$\partial\varphi_0/\partial h_1 = \partial\varphi_0/\partial h_3 \approx -0{\cdot}05$). The additivity of the aza-substitution effects is apparent. Thus, the presence of a nitrogen atom in positions 2 or 3 results in an electron donor ability change ($\Delta\varphi_0$) equal to $-11°$ and $-1°$, respectively, and the total parameter change ($\Delta\varphi_0 = -14°$) in triazino-isoindole **II.2.8** is almost the same as the sum of the above independent effects.

A nitrogen atom in positions 1 or 4 of the pyridoisoindole residue causes a hypsochromic shift ($\partial L/\partial h_1 \approx \partial L/\partial h_4 \approx -0{\cdot}30$), in contrast to positions 2 or 3 ($\partial L/\partial h_2 \approx \partial L/\partial h_3 \approx +0{\cdot}20$). Changes of effective length are less additive than those of electron donor ability. However, additivity can account for some spectral features of dyes with polyaza-substituted end-groups. For instance, the end-group with nitrogen atoms in positions 2 and 3 gives the maximum bathochromic shift if compared with other triazino-isoindoles (**II.2**), and a hypsochromic shift is the most pronounced provided aza-substitution is in positions 1 and 4.

In conclusion, some regularities concerning the effects of aza-substitution on the redox properties and the spectral absorption region of dyes with pyrrolo- and pyrido-isoindole end-groups can be made. These are given in Table 3.

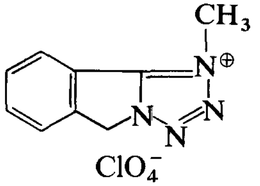
TABLE 3
Aza-substitution Effect on Parameters of Condensed Isoindole Residues in Dyes

Position	I				II	
	N		*NR*		*N*	
	L	φ_0	*L*	φ_0	*L*	φ_0
1	−[a]	−	− −	− −	−	≈0[c]
2	≈0	≈0	≈0	≈0	+[b]	−
3	+	−	+ +	− −	+	≈0
4					−	−

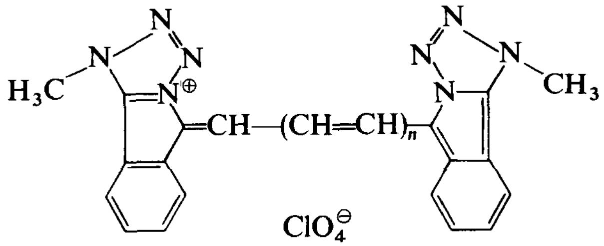
[a] Hypsochromic effect or decrease of electron donor ability.
[b] Bathochromic effect or increase of electron donor ability.
[c] Negligible charges.

3 GENERAL EXPERIMENTAL AND DISCUSSION

5*H*-Tetrazolo-[5,1-a]-isoindole was obtained[6] from *o*-chloromethylbenzonitrile and sodium azide, as well as by diazotization of 1-hydrazinoisoindolenine.[7] On treating tetrazolo-isoindole with the excess of dimethylsulphate, the quarternary salt, **III**, was formed. Reaction of the perchlorate, **III**, with ethyl-*ortho*formate and its vinylogue, β-ethoxyacroleindiethylacetal, led to mono- and trimethinecyanines (**IVa** and **IVb**, respectively).



III



IVa,b
a: $n = 0$
b: $n = 1$

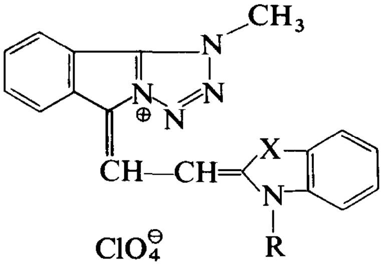
IVa is likely to be free of substantial steric crowding effects, and is slightly soluble and relatively stable. On lengthening the polymethine chain the normal vinylene shift in absorption maximum (94 nm) is observed.

The symmetric cyanines (**IV**) are relatively deeply coloured; the

TABLE 4
Spectral Parameters of Dyes V–VIII

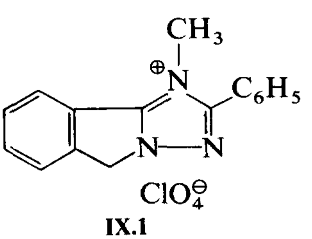
N	*X*	λ_{max} (*nm*)	$\Delta\lambda$
V	$C(CH_3)_2$	539	12·0
VI	O	516	3·0
VII	S	558	2·0
VIII	CH=CH	580	0·5

absorption maximum of **IVa** (557 nm)[8] is similar to that of thiatrimethinecyanine, in accord with theoretical estimates. On the basis of the deviation values for the unsymmetric dimethinecyanines (V–VIII), the electron donor ability of the 1-methyltetrazolo-isoindole end-group is close to that of the quinoline nuclei (Table 4).

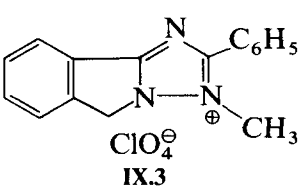


V–VIII

To study the influence of the chemical nature of the azolo-isoindole nucleus on the spectral parameters of these dyes, the relevant derivatives of 5*H*-*S*-triazolo-[5,1-*a*]-isoindole were synthesized. *o*-Chloromethylbenzonitrile was condensed with acid hydrazides.[9-11] The amino-isoindolines thus formed were found to convert readily into the isomeric salts of 5*H*-*S*-triazolo-[5,1-*a*]-isoindolium (**IX.1** and **IX,3**).



IX.1

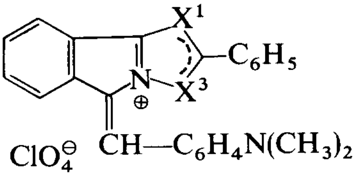


IX.3

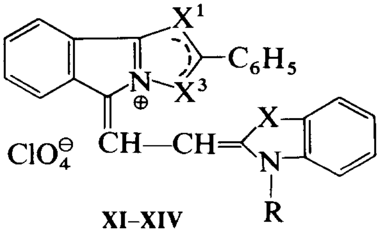
The perchlorates, **IX**, contain an active methylene group and yield cyanine dyes when they are treated with the suitable electrophilic reactants. The benzylidene derivatives, **X**, and the unsymmetric dimethinecyanines, **XI–XIV**, were obtained in this way (Table 5).

TABLE 5
Spectral Parameters of Triazolo-isoindole Dyes

Compound	X^1	X^3	X	λ_{max} (*nm*)	$\Delta\lambda$
X.1	NR	N		505	81
X.3	N	NR		514	
XI.1	NR	N	$C(CH_3)_2$	526	30
XI.3	N	NR	$C(CH_3)_2$	534	
XII.1	NR	N	O	512	13
XII.3	N	NR	O	517	
XIII.1	NR	N	S	550	13
XIII.3	N	NR	S	552	
XIV.1	NR	N	CH=CH	585	0
XVa				568	
XVb				672	



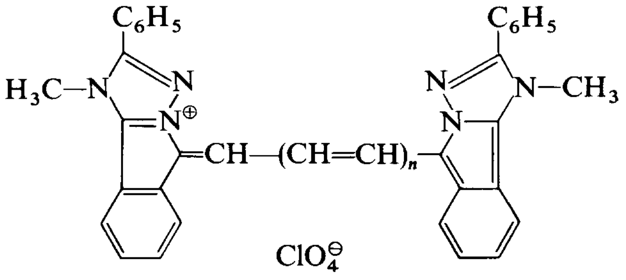
X
$X^1, X^3 = N$ or NR



XI-XIV

In accord with theoretical predictions, dyes obtained from the perchlorate salt, **IX.3**, absorbed at longer wavelength than the isomers derived from the salt, **IX.1**.

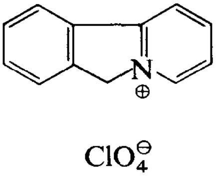
The perchlorate salt, **IX.1**, when reacted with ethyl-orthoformate or tetraethoxypropane, gave the mono- and trimethinecyanines (**XVa** and **XVb**, respectively).



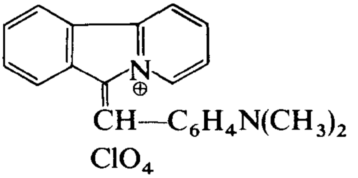
XVa,b
a: $n = 0$
b: $n = 1$

Comparison of the spectral parameters of the tetrazolo- and triazolo-isoindole nuclei showed that accumulation of nitrogen atoms in the azole cycle caused both the effective length and the electron donor ability of the end-group to decrease. Indeed, the deviation for dye **X.1** (81 nm) substantially exceeds that of the corresponding tetrazolo-isoindole derivative (60 nm). Thus, theoretical predictions and experimental data are in qualitative agreement.

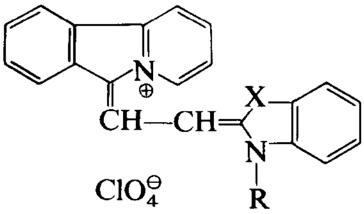
With respect to dyes containing the isoindole nucleus condensed with a six-membered heterocycle, the simplest system of this type is the pyrido-isoindole resulting from the photochemical cyclization of 2-bromo-1-benzylpyridinium bromide. Using the perchlorate **XVI**, the benzylidene derivative, **XVII**, was obtained, as well as a number of unsymmetric (**XVIII–XXI**) and symmetric (**XXIIa–c**) dyes[12] (Table 6).



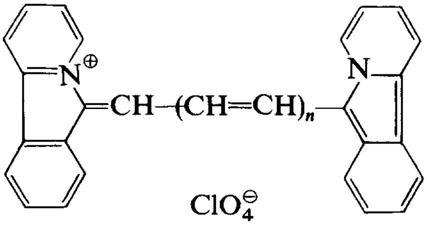
XVI



XVII



XVIII–XXI



XXIIa–c

	n	λ_{max} (*nm*)
a	0	630
b	1	716
c	2	826

It is of interest to note that the absorption maxima of the pyrido-isoindole dyes are shifted to longer wavelengths relative to those of the tetrazolo-isoindole or triazolo-isoindole cyanines. Bathochromic shifts for the mono- and trimethinecyanines, **XXIIa**, compared with dyes **IVa** and **IVb**, are 73 and 65 nm, respectively. This could be anticipated in view of the greater effective

TABLE 6
Spectral Parameters of Pyrido-isoindole Dyes

Compound	*X*	λ_{max} (*nm*)	$\Delta\lambda$
XVII		560	57
XVIII	$C(CH_3)_2$	572	15
XIX	O	550	6
XX	S	586	8
XXI	CH=CH	608	9

length of the pyrido-isoindole end-group compared with that of the tetrazolo-isoindole end group. At the same time, the latter group has a somewhat higher electron donor ability, as the deviation values for the styryl dyes suggest. For comparison, see parameters λ_M and $\varphi_0{}^*$ of dyes **Ib.3.4** (Table 1) abd **II.0** (Table 2).

To summarize, the design of new dyes having specific properties is possible, by utilizing the established relationships between the chemical nature of condensed isoindoles and the spectral features of the corresponding polymethines.

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