Dyes and Pigments **6** (1985) 233–249

Synthesis, ^{1}H-NMR and Electronic Absorption Spectra, and Halochromic Properties of Bis(2-methyl-1-phenyl-3-isoindolyl)-(het)arylmethane Dyes

R. Naef

Research and Development Department, Dyestuffs and Chemicals Division,
Ciba–Geigy Ltd, Basle, Switzerland

(Received: 7 September, 1984)

SUMMARY

Several bis(2-methyl-1-phenyl-3-isoindolyl)-(het)arylmethane perchlorate dye salts have been synthesised, the (het)aryl substituent representing the acceptor systems 2-benzothiazolyl, 1-methyl-2-benzimidazolyl, 4-quinolyl, 4- and 2-pyridyl as well as phenyl.

The constitution of these green dye salts was supported by their ^{1}*H-NMR spectra. The variation of the electronic absorption maxima of this dye series was in accord with theoretical considerations based on SCF–CI and PMO calculations. They give rise to the statement that the bathochromic effect of the varied (het)aryl group is essentially due to a LUMO–LUMO interaction with the di-isoindolylmethane cyanine moiety, i.e. a second-order perturbation, enlarging the bathochromic shift caused by the increased twist angles inflicted on the central bonds by the bulkiness of the (het)aryl substituents (a first-order perturbation). The halochromic properties of these dyes are explicable on the same basis.*

The dissociation constants pK* *and* $pK^*_{R^+}$ *were measured and compared with analogous di-indolyl-* (**1**) *and di-indolizinyl-hetarylmethane dyes* (**4**), *showing little difference with regard to the former and the distinct sequence indolizinyl > indolyl > isoindolyl dye series for the latter.*

Dyes and Pigments 0143-7208/85/$03·30 © Elsevier Applied Science Publishers Ltd, England, 1985. Printed in Great Britain

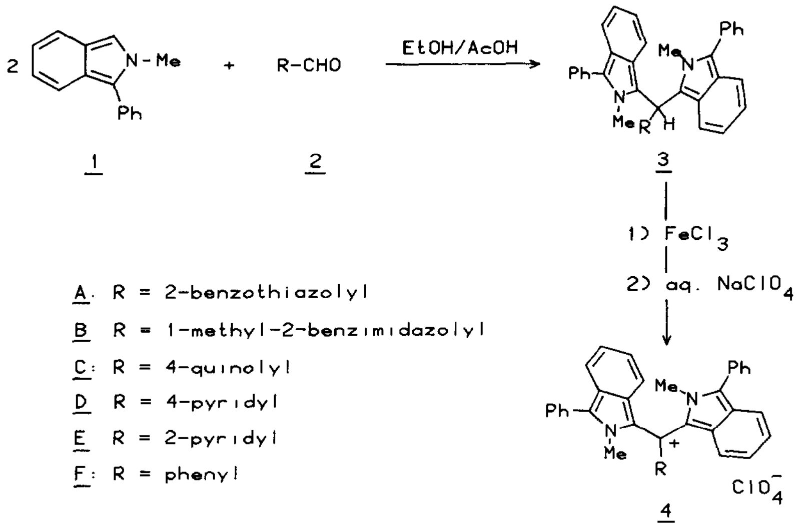
1. INTRODUCTION

In the field of cationic dyes the triphenylmethane representatives range among the most widely investigated dye systems, examples of which are given in Ref. 1, reference 1. Their heteroaromatic parents, however, only recently found theoretical and industrial interest in view of the colour-forming potential of their lactone[2] and ether derivatives.[3] However, a systematic approach to the spectroscopic qualities of these tri(het)arylmethane dyes has not been provided up till now. Two earlier papers,[1,4] dealing with (substituted) di-indolyl- and di-indolizinyl-hetarylmethane systems respectively, proved interesting correlations of their electronic absorption spectra with respect to various heteroaryl substituents. As the two mentioned hetarenes are both aza analogues of the indenyl anion, this raised the question as to whether these correlations could also be found in a third relatively easily available azaindenyl system, the isoindole derivative.

This paper demonstrates the synthesis of a series of trihetarylmethane dyes with two 2-methyl-1-phenylisoindoles as donor groups and various acceptor hetarenes. It then discusses the influence of the acceptor groups on the electronic absorption spectrum and its pH dependence (halochromism). An attempt to interpret these results on the simple LCMO basis will be made analogous to that in Ref. 1.

2. SYNTHESES

Unlike indolizine, 2-methyl-1-phenylisoindole **1**[5] can be handled as a free base, as it is less basic due to its smaller negative net charge on the potential protonation centres 1 or 3. (This is caused by a smaller π-electron density as well as a greater (positive) σ-core charge as these centres are direct neighbours of the more electronegative nitrogen, as signalled by SCF calculations including σ-polarisation.[6]) Nevertheless it undergoes acid-catalysed condensation very readily (Scheme 1) with various aromatic or heteroaromatic carbaldehydes **2** to give a corresponding tri(het)arylmethane **3** if a molar isoindole:carbaldehyde ratio of 2:1 is applied.[7] Subsequent oxidation of the intermediates **3** without isolation by means of iron trichloride gives the final products **4** in moderate yield. In the case of **4F** the oxidant seems to be unreacted



A. R = 2-benzothiazolyl
B R = 1-methyl-2-benzimidazolyl
C: R = 4-quinolyl
D R = 4-pyridyl
E R = 2-pyridyl
F: R = phenyl

Scheme 1.

benzaldehyde itself, since even in the absence of oxygen or iron trichloride a fairly high yield of the dye could be isolated.

The phenyl group in position 1 was chosen instead of the methyl group, as in the indole and indolizine parents, to prevent possible formation of a methylene base from the corresponding trihetarylmethane dye which might undergo unfavourable side reactions.

Purification of **4** was accomplished by evaporation of the reaction mass to dryness and preparative thin-layer-chromatographic separation on silica gel.

3. ^{1}H-NMR SPECTRA

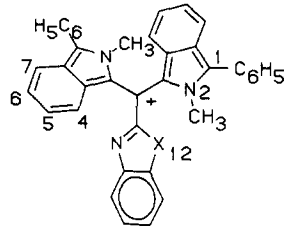
3.1. Method

In order to ascertain the structures of dyes **4** their ^{1}H-NMR spectra have been recorded on a 90-MHz Fourier NMR spectrometer. Perdeuterated acetonitrile served as solvent, tetramethylsilane as internal standard.

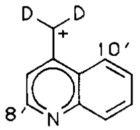
3.2. Results and discussion

As a result of the fairly poor solubility of dyes **4**, the NMR spectra are not very well resolved. However, from Table 1, collecting the most

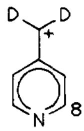
TABLE 1
Proton Signals of Dyes **4A–4F** from 90 MHz ^{1}H-NMR Measurements in Perdeuterated Acetonitrile



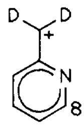
4A X = S, 4B: X = NCH_3



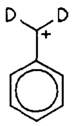
4C



4D



4E



4F

Proton	*Chemical shift (ppm) (Multiplicity^a)*					
	4A	**4B**	**4C**	**4D**	**4E**	**4F**
H_5C_6—C(1)	7·75(m)	7·74(m)	7·70(s)	7·74(m)	7·73(m)	7·72(m)
H_3C—N(2)	3·50(s)	3·40/ 3·58(2s)	3·35(s)	3·42(s)	3·40(s)	3·41(s)
H—C(4^b)	6·80/ 6·83/ 6·89(t)	6·7–7·0(m)	6·65–6·9(m)	6·7–6·9(m)	6·6–6·9(m)	6·6–6·8(m)
H—C(5), H—C(6), H—C(7^b)	7·42/ 7·45/ 7·46/ 7·50/ 7·52(m)	7·4–7·6(m)	7·3–7·6(m)	7·39/ 7·43/ 7·46/ 7·50(m)	7·39/ 7·42/ 7·46/ 7·49(m)	7·36/ 7·39/ 7·43/ 7·46/ 7·50(m)
H_3C—N(12)		3·44(s)				
H—C(8′)			9·15/ 9·20(d)	8·88/ 8·94(d)	8·92/ 8·96(d)	
H—C(rest)	7·6–8·4(m)	7·6–8·0(m)	7·8–8·4(m)	7·6–8·0(m)	7·6–8·2(m)	7·7–8·1(m)

[a] Multiplicities: s, singlet; d, doublet; t, triplet; m, multiplet.
[b] Assignment uncertain.

prominent peaks, it can be seen that the protons common to all systems suffer only minor shifts on varying the acceptor (het)arene. A comparison with the NMR spectrum of 2-methyl-1-phenylisoindole (in the same medium) reveals that the protons of the phenyl substituent in **4** are shifted downfield (from 7·47 ppm) as expected, whereas the N(2)-methyl signals are moved in the opposite direction (from 3·88 ppm); this can only be ascribed to the diamagnetic field effect of the neighbouring ring currents (compare Ref. 4). The fact that these two methyl signals appear as one singlet (except for **4B**) reflects the free rotation of the hetaryl groups about the central bonds rather than an enantiotopic neighbourhood in a rigid molecule.[1,4]

In **4B** the rotation seems to be hampered by the bulkier 1-methylbenzimidazole moiety causing a split of the two N-methyl signals, analogous to the parent di-indolylmethane dyes.[1] However, it is not fully understood why in the case of the indolizine parents the split of the corresponding C(2)-methyl groups is found in the 4-quinolyl and not in the 1-methylbenzimidazole derivative,[4] contrary to the present results for **4B** and **4C**. The assignment of the multiplet in the range 6·7–6·9 ppm is open to question since both protons at C-4 and C-7 may be affected by a diamagnetic shift of neighbouring aromatic ring currents. The NMR data of the corresponding isoindole itself show a multiplet for two protons in the same region (6·8–7·0 ppm) which might be ascribed to the corresponding protons at C-5 and C-6, whereas there is no single proton signal found significantly shifted upfield. (The remaining protons absorb in the region 7·1–7·8 ppm as an unresolved multiplet.) As the multiplet between 6·6 and 6·9 ppm undoubtedly stands for only two protons in the dyes **4** (according to the integration curve) we tend to favour the assignment given in Table 1, in particular since similar upfield shifts are observed in the indole and indolizine parents.[1,4]

4. ELECTRONIC ABSORPTION SPECTRA

4.1. Method

Owing to the limited solubility of dyes **4** in water, the electronic absorption spectra were recorded in an equimolar water/methanol mixture with fixed pH* and H_0^* values described earlier.[1] The spectra obeyed Beer–Lambert's law in the observation range 10^{-4}–10^{-5} M.

4.2. Results and discussion

In Figs 1 and 2 the complete electronic absorption spectra of **4A–4F** are depicted. Solvent conditions were variously acidic in order to suppress hydroxylation. Apart from the close mutual similarity, the spectra display the same features in the visible range as their parent dyes mentioned earlier.[1,4] Their absorption maxima are distinctly shifted to longer

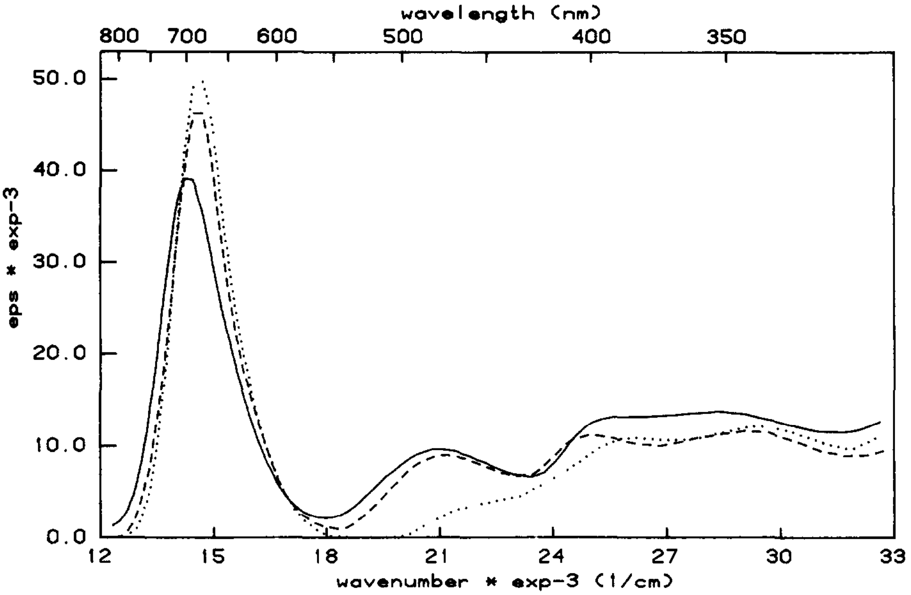


Fig. 1. Electronic absorption spectra of **4A**–**4C** at 298 K in equimolar methanol/water. ——, **4A**, H_0^* 0·0; – – –, **4B**, pH* 1·40; ·····, **4C**, pH* 3·85.

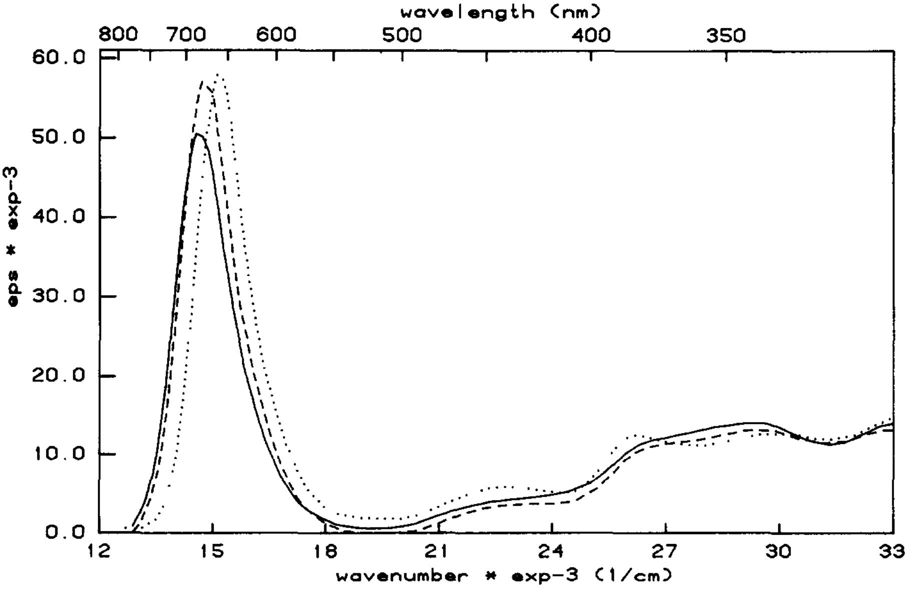


Fig. 2. Electronic absorption spectra of **4D**–**4F** at 298 K in equimolar methanol/water. ——, **4D**, pH* 3·82; – – –, **4E**, pH* 2·34; ·····, **4F**, H_0^* −2·0.

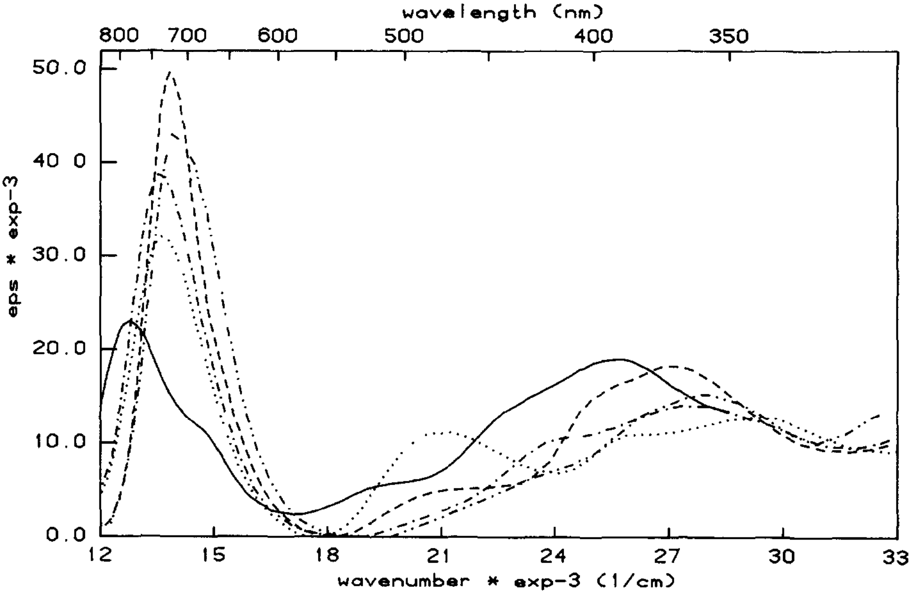


Fig. 3. Electronic absorption spectra of the protonated forms of **4A**–**4E** at 298 K in equimolar methanol/water. ——, **4A**(H^+), H_0^* −4·0; – – –, **4B**(H^+), H_0^* −2·0; · · · ·, **4C**(H^+), H_0^* 0·0; – · –, **4D**(H^+), H_0^* 0·0; – · · – · ·, **4E**(H^+), H_0^* 0·0.

wavelengths than those of the di-indolylhetarylmethane dyes[1] and lie in the range of the indolizinyl derivatives.[4]

Protonation of the dyes with a basic centre causes a bathochromic shift of the first two absorption bands in analogy to their parent dyes,[1,4] revealing halochromic properties (Fig. 3).

In order to explain the spectral variations on the donor and acceptor hetarenes, quantum-theoretical calculations have been carried out. SCF–CI computations, the method and parameterisation mentioned elsewhere,[4] including the same twist angle of 45° for the central bonds, proved that the first two electronic excitations are nearly pure HOMO–LUMO and NHOMO–LUMO transitions, the first being x- and the second y-polarised, analogous to ordinary triphenylmethane dyes.[9] Table 2 compares the calculated absorption maxima with the experimental results, showing that except for the 'unsubstituted' dye **4** (R = H) the experimental maxima are higher by 30–70 nm. As discussed earlier,[4] this may be caused by an additional bathochromic shift due to an increase of the twist angles of the central bonds inflicted on **4** by the bulky substituents R which was not considered in the calculations. (Consider

TABLE 2
Experimental and Calculated Visible Absorption Maxima of Dyes **4** and Their Protonated Forms **4**(H^+)

Compound	*Calculated (nm)*		*Experimental (nm)*		*log ε*
	$\lambda_{max\ 1}$	$\lambda_{max\ 2}$	$\lambda_{max\ 1}$	$\lambda_{max\ 2}$	
4A	651		697		4·61
		537		477	4·00
4A(H^+)	666		777		4·37
		539		500	3·81
4B	645		685		4·67
		535		475	3·94
4B(H^+)	661		721		4·64
		521		476	3·76
4C	643		684		4·71
		523		450	(sh.)
4C(H^+)	654		730		4·51
		510		465	4·02
4D	636		682		4·39
		427		425, 375	(sh.)
4D(H^+)	645		732		4·28
		422		406	(sh.)
4E	638		675		4·76
		445		425, 375	(sh.)
4E(H^+)	646		722		4·68
		449		425	(sh.)
4F	626		658		4·76
		443		445	3·81
4(R = H)[8]	629		614		

especially the phenyl-substituted derivative **4F**, for which the PPP model predicts no shift at all in relation to **4** (R = H).)

The purity of the first two transitions does however allow a discussion of the spectral influence of the nitrogen position in the three di-azaindenylmethane dyes, i.e. the indole,[1] indolizine[4] and isoindole derivatives, as well as the effect of the substituents R on the simple PMO basis.

Implying therefore that the total trihetarylmethane systems may be broken up into the di-donorhetarylmethane fraction and the varied (hetero)aromatic substituents R, and further idealising the former π-system by applying the isoelectronic di-indenylmethane anion in a planar

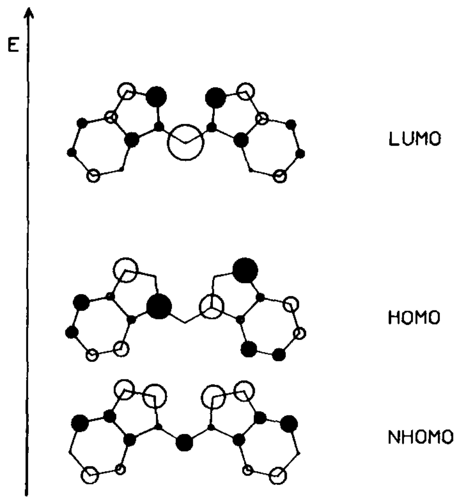


Fig. 4. Expansion coefficients of the frontier orbitals of the di-indenyl anion.

form, the HMO calculation yields the frontier orbital functions shown in Fig. 4.

The above-mentioned foundation for the additional bathochromic shift (relative to the PPP calculations) is now easily explicable: while the HOMO is insensitive to twisting, since it is non-bonding in the central bonds, the LUMO energy is decreased because of its fairly strong antibonding character in them, resulting in the observed bathochromic effect.

From the depicted wave functions of the di-indenylcarbeniate anion (Fig. 4) it can be derived that this anion, if available, would absorb at longer wavelengths than its heteroanalogue indole.[1] Even further bathochromism can be expected if nitrogen is placed at the 2-position to give the isoindole derivatives. A similar but less pronounced effect is expected for the indolizine parent. Thus the order of the absorption maxima should be indole $\ll$ indolizine $<$ isoindole dye. However, the experimental results gave the following order: indole $\ll$ isoindole $<$ indolizine. This discrepancy is not surprising in view of the simplifications of the model; it might be removed simply on inclusion of a σ-frame polarisation.[10]

Earlier papers[1,4] described correlations of the absorption shifts ΔE_{EA} of the longest wavelength band of the variously hetaryl-substituted di-indolyl- and di-indolizinylmethane dyes with the second-order perturbation $\Delta E_{\mathrm{LUMO,RS}}$, defined by eqn (1), where c_{LUMO} is the Hückel coefficient at

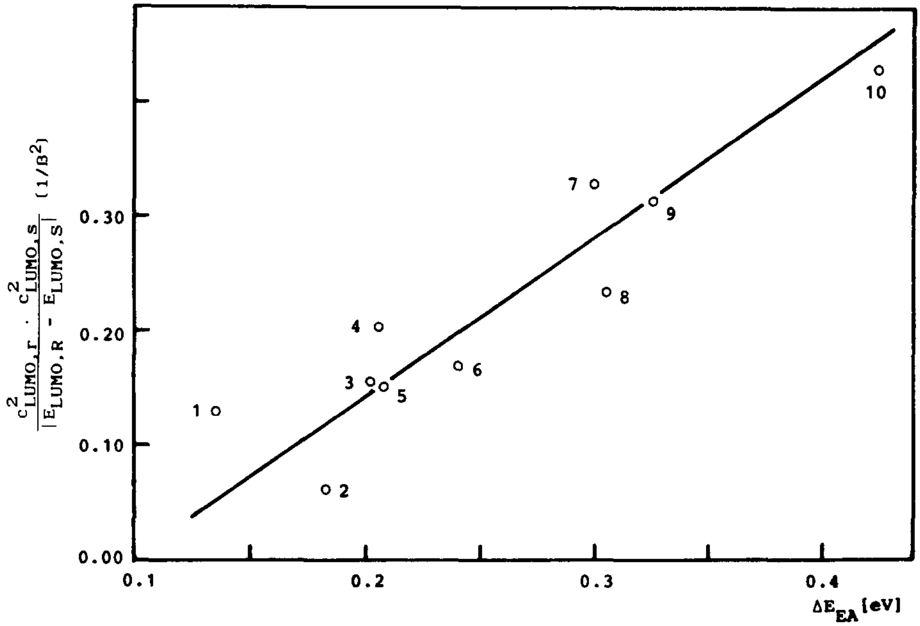


Fig. 5. Correlation of electronic absorption shifts E_{EA} versus second-order perturbations of (het)arene-substituted dyes **4** and their protonated forms: 1, **4F**; 2, **4E**; 3, **4D**; 4, **4C**; 5, **4B**; 6, **4A**; 7, **4B**(H$^+$); 8, **4E**(H$^+$); 9, **4D**(H$^+$); 10, **4A**(H$^+$).

the connecting centres r and s, E_{LUMO} the LUMO energy of the partial π-systems R and S and β the resonance integral.

$$\Delta E_{LUMO,RS} = \frac{c^2_{LUMO,r} \cdot c^2_{LUMO,s}}{|E_{LUMO,R} - E_{LUMO,S}|} \cdot \beta^2_{rs} \qquad (1)$$

Quite an analogous correlation could be found in the present dye series as is shown in Fig. 5. The c_{LUMO} and E_{LUMO} values were obtained by introduction of a PPP-based Hückel-parameter set[11] into the HMO calculations of the fragments R and S. The dye fragment R was assumed to be symmetrically rotated about the central bonds by 45° each, the effect of which was taken into account by applying $\beta = \beta_0 \cos \omega$, ω being the rotational angle.

The value for the quinolinium system 4C(H$^+$) has been omitted because the LUMO eigenvalues of the partial π-systems R and S lie too close together, thus violating the perturbation concept.[12] Excluding

4C(H$^+$) a correlation coefficient r of 0·926 results for the regression line (Fig. 5) which is represented by eqn (2), leaving β undetermined.

$$\Delta E_{\mathrm{EA}} = 0{\cdot}098 + 0{\cdot}721\, \Delta E_{\mathrm{LUMO,RS}} \tag{2}$$

The correlation is slightly less satisfactory than for the di-indolylmethane series[1] which at least is partly due to the narrower shift range. In view of all the inherent uncertainties of this model (variation of the twist angles of the central bonds, neglect of the first-order perturbation, i.e. σ-core polarisation, varying solvent effects) apart from those arising from the simplifications in deriving eqn (1) the correlation is still acceptable. This indicates that the influence of the substituents on the absorption spectra of **4** is indeed mainly carried by the LUMO–LUMO interaction of the partial π-systems, a conclusion which cannot be extended to di- and triphenylmethane dye systems however.[6]

5. DETERMINATION OF PROTOLYSIS CONSTANTS

5.1. Method

The method of measuring the protolysis constants of dyes **4A**–**4F** in an equimolar water/methanol mixture has been described elsewhere.[1,4] The resulting pK^* and H_0^* values respectively have been obtained from a least-squares fitting of eqn (3) to the measured spectral data at several protic concentrations and for several wavelengths.

$$E(\mathrm{pH}^*) = \frac{E_0 + E_\infty \cdot 10^{n(\mathrm{pH}^* - \mathrm{p}K^*)}}{1 + 10^{n(\mathrm{pH}^* - \mathrm{p}K^*)}} \tag{3}$$

5.2. Results and discussion

Analogously to the indolyl[1] and indolizinyl parents[4] the present systems suffer marked spectral changes under various protic conditions, reflecting their amphoteric character. While protonation of the basic centre of the acceptor-hetarene parts of **4** causes a bathochromic shift of the two absorption bands in the visible spectral range (Table 2) the hydroxylation at high pH values bleaches the dyes, a feature common to most triphenylmethane dyes. In extremely highly acidic solution even the phenyl derivative **4F** is protonated, but the drastic reduction of the intensity of the long-wave absorption band indicates that the proton attacks the di-isoindolylmethane chromophore rather than the phenyl residue.

TABLE 3

Dissociation Constants $pK^*_{R^+}$ and pK^* and n Values[a] of **4A–4F** in Equimolar Methanol/Water at 298 K (Ionic Strength = 0·1 M)

Compound	$pK^*_{R^+}$	n	pK^*	n
4A	6·27 ± 0·28	0·47 ± 0·14	−2·30 ± 0·05	1·29 ± 0·06
4B	6·93 ± 0·02	1·10 ± 0·05	1·32 ± 0·02	2·16 ± 0·43
4C	7·35 ± 0·05	1·40 ± 0·20	1·60 ± 0·05	1·81 ± 0·31
4D	7·44 ± 0·05	0·90 ± 0·12	1·97 ± 0·06	1·15 ± 0·14
4E	8·27 ± 0·02	1·15 ± 0·04	1·12 ± 0·01	2·58 ± 0·11
4F	9·37 ± 0·02	1·26 ± 0·02	−6·03 ± 0·20[b]	0·93 ± 0·11

[a] For definition see eqn (3).

[b] Protonation at the isoindolyl fragment, value defined by H_0^* function.[15]

Consequently the spectra of all the other systems **4A–4E** suffer the same hypochromic effect under these extreme conditions. Yet pK_2^* values for this second protonation equilibrium could not be obtained due to solvatochromic effects superimposed on the protolytic equilibrium.[13]

In Table 3 the pK^* values and the hydroxylation constants $pK^*_{R^+}$,[14] including the quantity n, defined by eqn (3), are given. From the n values, which should normally be 1·0, it can be deduced that the constants should be interpreted '*cum grano salis*'. The reason is that in the case of the determination of $pK^*_{R^+}$ the solutions had to stand overnight in order to achieve hydrolytic equilibrium leading to partial degradation of the carbinols. The measurements of the pH* in the range 0–2, on the other hand, are uncertain due to the unknown acid error of the glass electrode in the water/methanol mixture. Nevertheless a comparison with the respective indole[1] and indolizine[4] parents reveal an unambiguous sequence indolizinyl > indolyl > isoindolyl dye with respect to the $pK^*_{R^+}$ values. This contrasts with the basicity of these systems lying within a range of less than 1 pK^* unit, reflecting the unpredictable influence of the solvation energy and entropy differences of the respective reaction partners.

6. EXPERIMENTAL

6.1. General

A heating table equipped with a monocular from Leitz (Wetzlar) was used for measuring melting points (m.p.), which are corrected. The analytical departments of Ciba–Geigy AG and Sandoz AG carried out the microelemental analyses. Electronic absorption spectra of the dyes in Merck Uvasol solvents were recorded on a Beckman Acta M IV spectrophotometer. Control of pH* and of H_0^* was maintained by means of Merck Titrisol buffers and pure sulphuric acid respectively. Column-chromatographic purification of product **4A** was achieved on silica gel 60 from Merck with grain size 0·063–0·2 mm. Preparative thin-layer chromatography was carried out on Merck TLC plates with silica gel 60 F_{254} of 2 mm thickness.

PPP–CI calculations were carried out on the Univac 1100/81 TSO-system computer from Sandoz AG; the remaining computations including HMO calculations, least-squares optimisations, and drawings of EA spectra and molecular formulae, were executed on a MINC 11-BD computer from Digital Equipment Corp. fitted with a 4662 Tektronix plotter and an LA 120 printer (DEC).

6.2. Syntheses

Bis(2-methyl-1-phenyl-3-isoindolyl)-2-benzothiazolylcarbenium perchlorate (**4A**)

Condensation of 395 mg (2·41 mmol) benzothiazole-2-carbaldehyde **2A** and 1 g (4·82 mmol) 2-methyl-1-phenylisoindole **1** was carried out under catalysis by a few drops of acetic acid by refluxing for 2 h in 10 ml ethanol. At room temperature the precipitated intermediate was redissolved with a little chloroform and oxidised with 1·3 g (4·82 mmol) iron trichloride (hexahydrate); the deep green solution was washed after 2 h with saturated aqueous sodium perchlorate, then with water and finally evaporated to dryness.

The crude product was purified by column chromatography on silica gel with methylene chloride containing an increasing amount of acetonitrile and finally with acetonitrile plus one drop 70% perchloric acid/100 ml solvent. The solution was evaporated and the residue recrystallised from ether/petrol ether to yield 242 mg (15%) pure green product, m.p. 190 °C (contraction).

$C_{38}H_{28}N_3O_4SCl . 0{\cdot}6\,H_2O$ (669·0)

	C	H	N	O	Cl	H_2O
Calc.	68·23	4·40	6·28	11·00	5·30	1·61%
Found	67·94	4·61	6·30	10·73	5·37	0·84%

Bis(2-methyl-1-phenyl-3-isoindolyl)-(1-methyl-2-benzimidazolyl) carbenium perchlorate (**4B**)

A solution of 386 mg (2·41 mmol) 1-methylbenzimidazole-2-carbaldehyde **2B** and 1 g (4·82 mmol) 2-methyl-1-phenylisoindole **1** in 10 ml ethanol and a few drops acetic acid was refluxed for 3·5 h in a nitrogen atmosphere. Addition of 652 mg (2·41 mmol) iron trichloride turned the green colour of the solution temporarily brown; the precipitate was dissolved by 6 ml chloroform and the reaction mixture washed with saturated aqueous sodium perchlorate and water, and the organic phase evaporated. The residue was purified by preparative thin-layer chromatography on silica gel with methylene chloride/acetonitrile (3:1) to give 126 mg (8 %) green dye salt, melting at 199 °C (contraction).

$C_{39}H_{31}N_4O_4Cl.0{\cdot}65\,H_2O$ (666·9)
Calc. C 70·24 H 4·88 N 8·40 O 11·16 Cl 5·32 H_2O 1·75 %
Found C 70·00 H 5·04 N 8·53 O 10·80 Cl 5·37 H_2O 1·26 %

Bis(2-methyl-1-phenyl-3-isoindolyl)-4-quinolylcarbenium perchlorate (**4C**)

Under a nitrogen atmosphere, a mixture of 300 mg (1·91 mmol) quinoline-4-carbaldehyde **2C** and 800 mg (3·86 mmol) 2-methyl-1-phenylisoindole **1** was stirred in 5 ml ethanol and three drops acetic acid at room temperature for 2 h. To the resulting greenish slurry a solution of 1·04 g (3·86 mmol) iron trichloride in 5 ml ethanol was added, changing the colour of the precipitate immediately to brown. After addition of chloroform and washing with a saturated aqueous sodium perchlorate solution, the organic phase was evaporated and the residue worked up analogously to **4B**. The yield of pure green crystals, melting at 193 °C (contraction), was 130 mg (10 %).

$C_{40}H_{30}N_3O_4Cl.0{\cdot}4\,H_2O$ (659·4)
Calc. C 72·87 H 4·71 N 6·37 O 10·68 Cl 5·38 H_2O 1·09 %
Found C 72·92 H 4·58 N 6·46 O 10·97 Cl 5·43 H_2O 1·05 %

Bis(2-methyl-1-phenyl-3-isoindolyl)-4-pyridylcarbenium perchlorate (**4D**)

In a solution of 10 ml ethanol and three drops acetic acid a mixture of 260 mg (2·43 mmol) pyridine-4-carbaldehyde **2D** and 1 g (4·82 mmol) 2-methyl-1-phenylisoindole **1** was brought to reaction at room temperature for 1 h under a nitrogen atmosphere. To the resultant slurry 1·3 mg (4·82 mmol) iron trichloride was added and stirring continued for another 3 h. After addition of chloroform and an aqueous sodium perchlorate solution, the organic phase was separated and worked up according to the procedure outlined for **4B**, yielding 330 mg (23 %) green dye salt, m.p. 312–14 °C (decomposition).

$C_{36}H_{28}N_3O_4Cl.0{\cdot}5\,H_2O$ (611·1)
Calc. C 70·76 H 4·78 N 6·88 O 11·78 Cl 5·80 H_2O 1·47 %
Found C 70·71 H 4·83 N 6·83 O 11·53 Cl 5·98 H_2O 0·3 %

Bis(2-methyl-1-phenyl-3-isoindolyl)-2-pyridylcarbenium perchlorate (**4E**)
In 10 ml ethanol 130 mg (1·21 mmol) pyridine-2-carbaldehyde **2E** was condensed with 500 mg (2·41 mmol) 2-methyl-1-phenylisoindole **1** at room temperature, in the absence of oxygen and catalysed by three drops acetic acid. After 3 h stirring, 650 mg (2·41 mmol) iron trichloride was added to the strongly fluorescent solution, causing an immediate dark green colouration. A further 20 min stirring, after working up as described for **4B**, gave 200 mg (27 %) pure green crystals, melting at 195 °C (contraction).

$C_{36}H_{28}N_3O_4Cl.0{\cdot}5\,H_2O.0{\cdot}07\,HClO_4$ (618·1).
Calc. C 69·95 H 4·74 N 6·80 O 12·37 Cl 6·14 H_2O 1·46 %
Found C 70·09 H 4·64 N 6·66 O 12·35 Cl 6·16 H_2O 1·13 %

Bis(2-methyl-1-phenyl-3-isoindolyl)-phenylcarbenium perchlorate (**4F**)
A solution of 26 mg (0·24 mmol) benzaldehyde **2F** and 100 mg (0·48 mmol) 2-methyl-1-phenylisoindole **1** in 5 ml ethanol was stirred at room temperature under a nitrogen atmosphere in the presence of three drops acetic acid. After 30 min the fluorescent, whitish slurry was heated for 3 h, during which time the colour turned a deep blue-green. After cooling, 130 mg (0·48 mmol) iron trichloride was added to complete the oxidation. The reaction mixture was then diluted with chloroform, washed twice with 10 % perchloric acid, then with water and the organic phase evaporated. Twofold recrystallisation from methylene chloride/ether/petrol ether gave 44 mg (30 %) pure green salt, m.p. 172 °C (contraction).

$C_{37}H_{29}N_2O_4Cl.0{\cdot}25\,H_2O$ (605·6)
Calc. C 73·38 H 4·91 N 4·63 O 11·23 Cl 5·85 H_2O 0·74 %
Found C 73·48 H 4·95 N 4·66 O 11·25 Cl 5·77 H_2O 0·78 %

ACKNOWLEDGEMENT

The author is indebted to the companies Ciba–Geigy AG and Sandoz AG for their financial support of the present work.

REFERENCES

1. R. Naef, *Dyes and Pigments*, **2**, 57 (1981).
2. (a) Ch.-H. Lin (National Cash Register Co.), S. African Patents 68 00,132 and 68 00,170 (1968).
   (b) F. Okumura, Sh. Maeda, Sh. Inove and H. Honda (Mitsubishi Chemical Industries Co. Ltd), Japan Kokai 75 119,026.
   (c) Sh. Farber (National Cash Register Co.), Ger. Offen. 2 313 679 (1973).
   (d) H. P. Kuhltau and R. Raue (Bayer AG), British Patent 1 195 004 (1970); US Patent 3 886 152 (1975).
   (e) M. Kozutsumi, Y. Miyazawa, K. Motohashi and S. Ogawa (Hodogaya Chemical Co. Ltd), Japan Patents 73 21,329, 73 21,330, 73 00,853, 73 00,523 and 73 00,524.
   (f) M. Kozutsumi, Y. Miyazawa, K. Motohashi and M. Kiritani (Hodogaya Chemical Co. Ltd), Ger. Offen. 2 163 658 (1972).
   (g) R. Garner and J. C. Petitpierre (Ciba–Geigy AG), US Patent 4 186 134 (1980); Ger. Offen. 2 423 534 (1974).
   (h) N. N. Crounse and P. J. Schmidt (Sterling Drug, Inc.), Ger. Offen. 2 808 798 (1978).
   (i) M. Kondo, K. Yasui, M. Miyake, H. Iwasaki and T. Shiraishi (Kanzaki Paper Mfg Co. Ltd), *Nippon Kagaku Kaishi*, **1978** (2) 276; Ger. Offen. 2 629 937 (1977).
   (j) T. Akamatsu, K. Koga and M. Miyake (Sumitomo Chemical Co. Ltd), Japan Patents 73 08,728, 73 08,730, 73 08,729, 73 03,204 and 73 03,205.
   (k) Y. Miyazawa, M. Ozutsumi and S. Ogawa (Hodogaya Chemical Co. Ltd), Japan Kokai, 74 74,223 and 74 71,201; Ger. Offen. 2 435 408 (1975).
   (l) R. Gardner and M. Duennenberger (Ciba–Geigy AG), Ger. Offen. 2 265 233 (1977).
   (m) Sh. Farber and A. J. Wright (National Cash Register Co.), Ger. Offen. 2 322 497 (1973); US Patent 3 812 146 (1974).
   (n) Ch.-H. Lin (National Cash Register Co.), S. African Patent 68 00,323.
   (o) R. Garner and J. C. Petitpierre (Ciba–Geigy AG), S. African Patent 75 07,588.
   (p) J. C. Petitpierre (Ciba–Geigy AG), Ger. Offen. 2 550 483 (1976).
   (q) T. E. Hoover, Sh. Farber and W. J. Becker (Appleton Papers Inc.), Ger. Offen. 3 008 475 and 3 008 494 (1980).
   (r) R. Garner, J. B. Henshall and J. C. Petitpierre (Ciba–Geigy AG), Ger. Offen. 2 503 349 (1975).
3. (a) S. Gunzenhauser and H. Balli, *Helv. Chim. Acta*, **63**(5), 1264 (1980).
   (b) H. Balli, S. Gunzenhauser and J. C. Petitpierre (Ciba–Geigy AG), Ger. Offen. 2 724 682 (1976).
   (c) J. C. Petitpierre (Ciba–Geigy AG), Ger. Offen. 2 724 611 (1978).
4. R. Naef, *Dyes and Pigments*, **4**, 101 (1983).
5. (a) W. Theilacker and H. Kalenda, *Ann.*, **584**, 87 (1953); (b) W. Theilacker and W. Schmitt, *Ann.*, **597**, 95 (1955).
6. R. Naef, unpublished results.

7. E. Fischer, *Ann.*, **242**, 372 (1887).
8. S. Nanya and E. Maekawa, *Nippon Kagaku Kaishi*, **1975**(9), 1535.
9. (a) K. N. Paskins, Ph.D. Thesis, University of Leeds, 1975; (b) M. J. S. Dewar, *J. Chem. Soc.*, 2329 (1950).
10. R. D. Brown and M. L. Heffernan, *Aust. J. Chem.*, **12**, 319 (1959).
11. F. A. Van-Catledge, *J. Org. Chem.*, **45**, 4801 (1980).
12. M. J. S. Dewar and R. C. Dougherty, *The PMO theory of organic chemistry*. New York, London, Plenum Press, 1975.
13. (a) R. I. Zalewski and G. E. Dunn, *Can. J. Chem.*, **47**, 2263 (1963).
    (b) R. L. Reeves, *J. Am. Chem. Soc.*, **88**, 2240 (1960).
    (c) Ch. T. Davis and T. A. Geissman, *J. Amer. Chem. Soc.*, **76**, 3507 (1954).
14. (a) N. C. Deno, J. J. Jaruzelski and A. Schriesheim, *J. Amer. Chem. Soc.*, **77**, 3044 (1955).
    (b) N. C. Deno, H. E. Berkheimer, W. L. Evans and H. J. Peterson, *J. Amer. Chem. Soc.*, **81**, 2344 (1959).
15. (a) P. Letellier, R. Gaboriaud and R. Schaal, *C.R. Acad. Sci., Ser. C*, **271**, 1208 (1970).
    (b) K. Unverferth, D. Zschiesche and K. Schwetlick, *Z. phys. Chem., Leipzig*, **247** (5/6) 302 (1971).