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SYNTHESIS, ^{1}H-NMR AND ELECTRONIC ABSORPTION SPECTRA OF BIS-(1,2-DIMETHYL-3-INDOLYL)-HETARYLMETHANE DYES

R. Naef

Institut für Farbenchemie der Universität Basel, St. Johannsvorstadt 10,
CH-4056 Basel, Switzerland

SUMMARY

The synthesis of a series of bis-(1,2-dimethyl-3-indolyl)-hetarylmethane dyes is described where hetaryl is 2-benz-oxazolyl, 2-benzothiazolyl, 1-methyl-2-benzimidazolyl, 4-pyridyl and 2-pyridyl.

The ^{1}H-NMR data of these dyes are interpreted, and their electronic absorption spectra as well as those of their protonated forms are discussed. Good correlation of their longwave absorption band shifts relative to the 'unsubstituted' bis-(1,2-dimethyl-3-indolyl)monomethine cyanine with 'second order perturbation' based on HMO calculations could be found.

Protonation constants pK^* and hydroxylation constants $pK^*_{R^+}$ are measured.

1. INTRODUCTION

Cationic dyes such as triphenylmethane dyes are of wide theoretical and practical interest.[1] Comparatively little work has been done using diaryl-hetaryl-[1] and aryl-dihetarylmethane compounds.[2] Trihetarylmethanes are, with a few exceptions,[2,3] widely unknown. It is the purpose of this paper to describe the synthesis of a series of diindolylmethane dyes substituted at the central carbon atom with various heteroaromatic rings, forming trihetarylmethane dyes with two 'donor'—and one 'acceptor'—heterocycles and to discuss their ^{1}H-NMR data and their electronic absorption spectra as well as the pH dependence of the latter.

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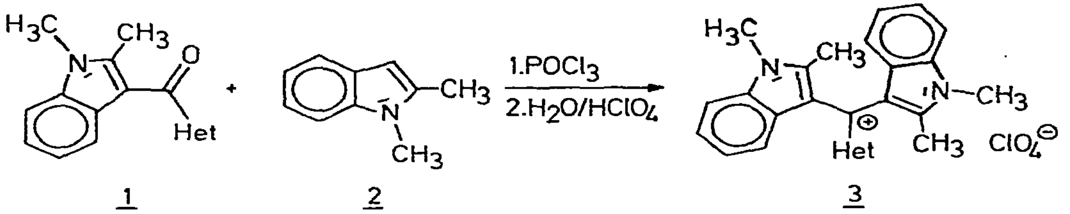
2. SYNTHESES

Compounds **3A–3E** have been synthesised by a method analogous to the preparation of many triphenylmethane dyes (Scheme 1).



A : Het = 2-benzoxazolyl
B : Het = 2-benzothiazolyl
C : Het = 1-methyl-2-benzimidazolyl
D : Het = 4-pyridyl
E : Het = 2-pyridyl

Scheme 1

Unsymmetrical dihetarylketones[4] were condensed with 1,2-dimethylindole **2** in phosphorus oxychloride under reflux conditions. While compounds **1A, 1B, 1D** and **1E** reacted fairly well within $\frac{1}{2}$–1 h to give **3A**, **3B**, **3D** and **3E** in yields of *c.* 20–85%, reaction of **1C** with **2** resulted in **3C** in low yields of *c.* 7%, together with mostly tarry byproducts. This can be well understood from the fact that in **1C**—as the most basic compound of the series—the nitrogen of the benzimidazole part competes most successfully with the carbonyl oxygen in complexation with phosphorus oxychloride and thus, by forming an unfavourable side-equilibrium, hampers the first catalytic step of the straightforward reaction.

After careful hydrolysis, compounds **3A** and **3B** precipitated on addition of 60% perchloric acid as perchlorates; **3C** as hydrodiperchlorate. The acidic aqueous solutions of **3D** and **3E** were neutralised with solid sodium acetate and the dyes precipitated with sodium perchlorate.

3. ^{1}H-NMR SPECTRA

3.1. *Method*

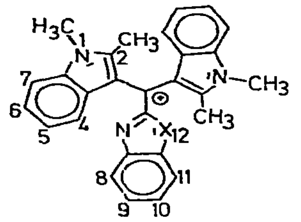
All ^{1}H-NMR spectra were recorded on a 90 MHz Fourier NMR spectrometer. Perdeuterated dimethylsulphoxide was used as solvent, tetramethylsilane as internal standard.

3.2. *Results and discussion*

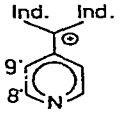
The results of the ^{1}H-NMR measurements are given in Table 1. It can be seen that the two *N*-methyl groups at the indole parts are identical in all dyes

TABLE 1

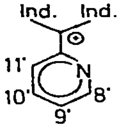
90 MHZ ^{1}H-NMR DATA OF DYES 3A–3E IN PERDEUTERODIMETHYLSULPHOXIDE



3A: X=O, 3B: X=S, 3C: X=N-CH$_3$



3D



3E

Proton	*Chemical Shift* (*Multiplicity*[a]) (ppm)				
	3A	**3B**	**3C**	**3D**	**3E**
H$_3$C—N (1)	4·00 (s)	3·99 (s)	4·00 (s)	3·96 (s)	3·96 (s)
H$_3$C—C (2)	2·22 (s)	2·18 (s)	2·01/ 2·19 (2·s)	2·18 (s)	2·08 (s)
H—C (4)	6·72/ 6·81 (d)	6·70/ 6·79 (d)	6·36/ 6·45 (d)	6·62/ 6·71 (d)	6·56/ 6·65 (d)
H—C (5)	7·11/ 7·12/ 7·20/ 7·28/ 7·29 (t)	7·09/ 7·17/ 7·25 (t)	6·84/ 6·94/ 7·04 (t)	7·05/ 7·07/ 7·13/ 7·15/ 7·22/ 7·24 (t)	7·05/ 7·07/ 7·14/ 7·21/ 7·22 (t)
H—C (6)	7·38/ 7·40/ 7·48/ 7·55/ 7·56 (t)	7·36/ 7·44/ 7·52 (t)	7·13/ 7·24/ 7·35 (t)	7·31/ 7·33/ 7·41/ 7·49–7·67 (m)	7·32/ 7·33/ 7·41/ 7·42/ 7·49/ 7·50 (t)
H—C (7)	7·84/ 7·92 (d)	7·7–8·0 (m)	7·7–8·0 (m)	7·77/ 7·79/ 7·85/ 7·87 (d)	7·78/ 7·86 (d)
H—C (8), H—C (9), H—C (10), H—C (11)	7·6–7·8 (m)	7·7–8·4 (m)	7·4–8·0 (m)		
H$_3$C—N (12)			3·51 (s)		
H—C (8′)				8·81/ 8·87 (d)	8·84/ 8·88 (d)
H—C (9′)				7·49–7·67 (m)	7·7–8·2 (m)
H—C (10′), H—C (11′)					7·7–8·2 (m)

[a] Multiplicities: s = singlet, d = doublet, t = triplet and m = multiplet.

and experience very little variation in their chemical shifts. Yet there is a significant unsteadiness in the signals of the C(2)-methyl groups in that in **3C** they are split into two distinct singlets. Assuming a propeller like structure where the two indole parts are turned 'head-to-tail' (see **3**)—which Stuart–Briegleb models suggest as the most stable conformation—the splitting may be ascribed to a greater distortion angle of the bulkier 1-methyl-benzimidazole function compared to the other heteroaromatics and, for the same reason, to obstruction of free rotation of the three heterocycles to a greater extent than in the other dyes. This in turn causes the closer C(2)-methyl group to get under a more effective diamagnetic influence of the ring current of the imidazole section of the benzimidazole function.

The benzene parts of the two indole groups are magnetically equivalent, their protons representing an ABCD system. Since the relation 'coupling constant/relative chemical shift' is greater than 0·1 (*c.* 0·15) and the resolution of the spectrum only *c.* 0·8 Hz, a first order interpretation of the NMR spectrum yields erroneous results, and therefore only the 10 main peaks out of the theoretical *c.* 40 are entered in Table 1. The four-spin system consists of two closely adjacent triplets—their peaks split by 0·9 Hz—framed by two doublets. A comparison of this feature with data from the unsubstituted indole[5] shows that, apart from a general downfield shift, the doublet which is strongly shifted upfield in relation to the other three protons must be ascribed to the proton at C(4). Obviously this proton lies in the shielding region of one of the neighbouring aromatic or heteroaromatic ring currents.

The remaining protons at the varied heterocycles are unresolved except for those adjacent to the nitrogen in the pyridine ring.

Addition of trifluoroacetic acid to the sample solutions had no effect whatsoever on the NMR spectra, although the colours of the solutions changed drastically (see following section).

4. ELECTRONIC ABSORPTION SPECTRA

4.1. *Method*

The electronic absorption (EA) spectra were recorded in an equimolar mixture of methanol and water. The pH* range 1–11[6] was scanned by Merck Titrisol buffers; H_0^* values[7] in the range from −8 to +1 were achieved by means of pure sulphuric acid in the mentioned solvent mixture. The validity of Beer–Lambert's law was observed in all cases.

4.2. *Results and discussion*

Electronic absorption spectra in weakly acidic solution are given in Fig. 1. A pH well below 7 (except for **3C**) had to be chosen to prevent hydroxylation described below. Figure 2 shows the EA spectra of the dyes at high acid concentrations.

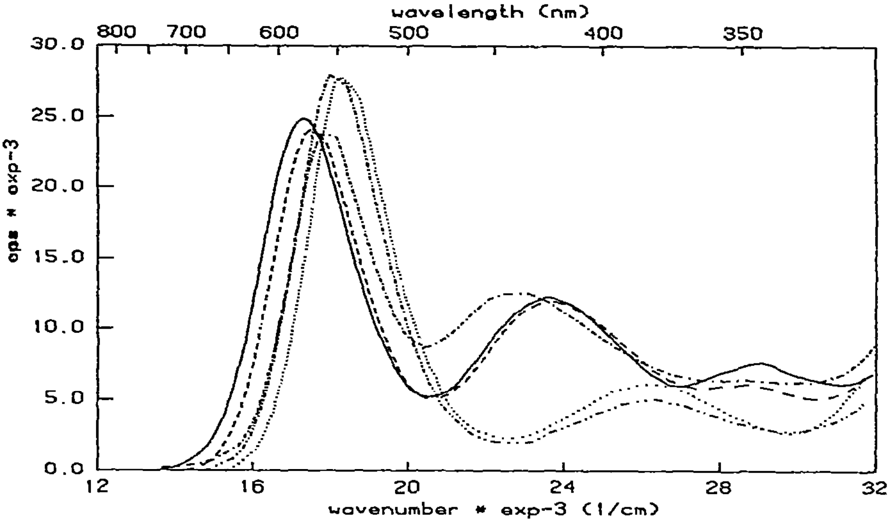


Fig. 1. Electronic absorption spectra of **3A–3E** at 298 K in equimolar methanol/water. ———: **3A**, pH* 2·60; – – –:**3B**, pH* 1·28; –·–·–:**3C**, pH* 6·49; –··–··–:**3D**, pH* 4·30; ·····:**3E**, pH* 4·34.

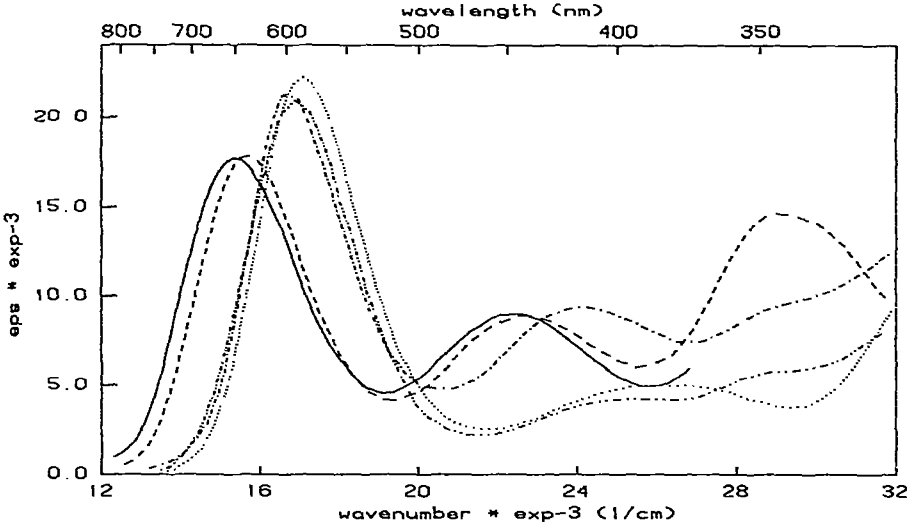


Fig. 2. Electronic absorption spectra of **3A**(H^+)–**3E**(H^+) at 298 K in equimolar methanol/water. ———:**3A**(H^+), H_0^* −6·0; – – –:**3B**(H^+), H_0^* −6·0; –·–·–:**3C**(H^+), H_0^* −2·0; –··–··–:**3D**(H^+), H_0^* −0·1; ·····:**3E**(H^+), H_0^* −1·0.

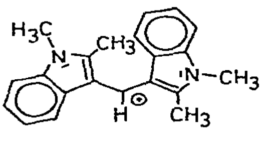
TABLE 2
MAXIMA OF THE ELECTRONIC ABSORPTION SPECTRA OF 3A–3E AND THEIR PROTONATED FORMS 3A(H$^+$)–3E(H$^+$)

Compound	$\lambda_{max\,1}$ (nm)	$\lambda_{max\,2}$ (nm)	$\lambda_{max\,3}$ (nm)	log ε
3A	579			4·396
		423		4·088
			345	3·881
3B	571			4·383
		424		4·078
			348	3·785
3C	557			4·382
		439		4·100
			351	3·807
3D	551			4·452
		381		3·700
3E	545			4·449
		382		3·789
3A(H$^+$)	651			4·248
		444		3·954
3B(H$^+$)	640			4·253
		443		3·949
3C(H$^+$)	598			4·331
		415		3·975
3D(H$^+$)	593			4·319
		393		3·630
3E(H$^+$)	585			4·347
		378		3·703
4	490[a]			

[a] in nitromethane[16]

All dyes under investigation show two well separated absorption bands in the visible or near-visible wavelength range (see Table 2). These features resemble those of the well known triphenylmethane dyes,[8] where these two bands have been calculated[9] to be polarised perpendicularly to one another, confirming experimental results.[10] SCF–CI calculations based on the Pariser–Parr–Pople (PPP) method[11] have been carried out on dyes **3A–3E**.

The PPP program was used in Zahradnik's version.[12] The two-centre integrals were computed according to the equation of Mataga and Nishimoto.[13] Zahradnik's parameter set[14] was used, based on idealised geometry with bond lengths of 140 pm, regular rings and standard angles. Distortions affecting the



4[16]

corresponding β-values were considered by applying $\beta = \beta_0 . \cos \omega$, ω being the twist angle.

Due to the inadequacy of the parameters and the uncertainty of the conformation of the dyes, the calculated electronic absorption bands did not correspond very well with the experimental results. For example, for **3A**: $\lambda_1 = 536$ nm, log $\varepsilon = 4{\cdot}428$, $\lambda_2 = 478$ nm, log $\varepsilon = 4{\cdot}524$, including σ-polarisation by the method of Nishimoto[15] and a twist angle of the central bonds of 40° each. However, the computations under all variations of parameters and conformations unambiguously stated that the first transition $S_0 \rightarrow S_1$ is polarised along the diindolyl–methane long axis, being a *c*. 98% pure HOMO–LUMO transition, whereas the second transition ($S_0 \rightarrow S_2$) is polarised nearly perpendicularly to the first and represents a *c*. 90% pure NHOMO–LUMO transition.

The high absorption coefficient of the second band indicates still too low a twist angle of the bond between the central carbon and the varied heterocycle.

Considering these results on a LCMO basis one can say that with respect to the first transition these systems correspond to a diindolylmonomethine cyanine dye perturbed by the π-systems of the heterocycles joined to the central carbon. It should therefore be possible to find a correlation between the shift of the longwave absorption band in relation to the unperturbed system **4**[16] and the 'second order perturbation', defined by eqn (1).[17]

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

The use of this simplified equation instead of the accurate formula seems justified in view of the high (but unknown) twist angle of the bond being considered as suggested by the SCF–CI calculations, which ensures that the interaction between the partial systems R and S is just a perturbation of the π-system of **4** and not a full π-bond.

This equation implies the following simplifications:

1. To form the LUMO (HOMO) of the combined system R–S, only the LUMO's (HOMO's) of the partial system R and S interact to an essential extent, assuming that the energy differences (i.e. the numerator in eqn (1)) between the HOMO's (LUMO's) of the one part and the LUMO's (HOMO's) of the other are much greater than for LUMO–LUMO (HOMO–HOMO) interaction, and $c_{\mathrm{HOMO,s}}$ is much smaller than $c_{\mathrm{LUMO,s}}$, which in all but two cases (**3E** and **3E**(H$^+$)) was true.
2. Identifying R as the diindolylmethine cyanine part, $c_{\mathrm{HOMO,r}}$ must be zero from symmetry considerations, thus the HOMO–HOMO interaction is zero in all cases.

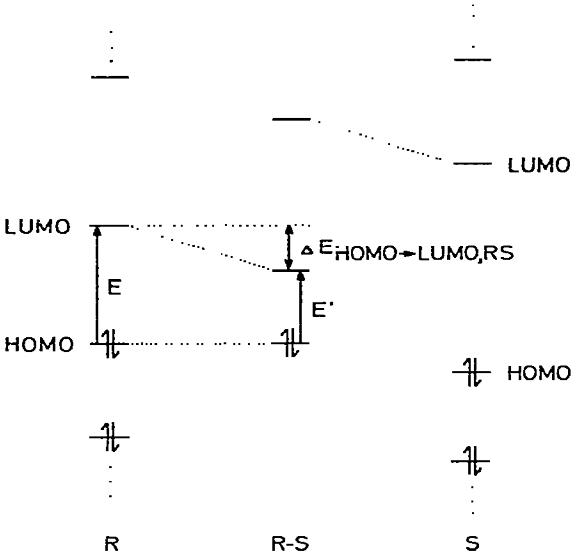


Fig. 3. LCMO-scheme of two systems R and S, where $c_{HOMO,r} = 0{\cdot}0$, $c_{LUMO,r}$ and $c_{LUMO,s} \neq 0{\cdot}0$ and neglecting all but frontier orbital interactions.

As a result, the electronic absorption shift only depends on the LUMO–LUMO interaction of the two partial systems R and S (see Fig. 3). The greater this interaction, the smaller the transition energy *E'* and thus the more bathochromic the shift will be.

Figure 4 correlates the shift of the longwave absorption band of dyes **3A–3E** and of **3A**(H^+)–**3E**(H^+) with their second order perturbation factor obtained from HMO calculations leaving $\beta_{r,s}$ unspecified.

Both partial systems were taken as planar for the HMO calculations and Streitwieser's parameters[18] were used. Indole nitrogens of the diindolylmethane cation were assumed to bear $+\frac{1}{2}$ charge each and therefore their parameters were averaged between those of neutral N of aniline and the fully charged N^+ of pyridinium.

The high correlation coefficient of 0·986 is surprising, since several disturbing factors might contribute to deviations apart from those originating from the simplifications mentioned above.

The different steric shapes of the varied heterocycles lead to various distortion angles of the r–s bond (affecting $\beta_{r,s}$) and also cause different distortions within the diindolylmethane cyanine part (influencing $c_{LUMO,r}$), thus affecting electronic absorption also through first order perturbation.

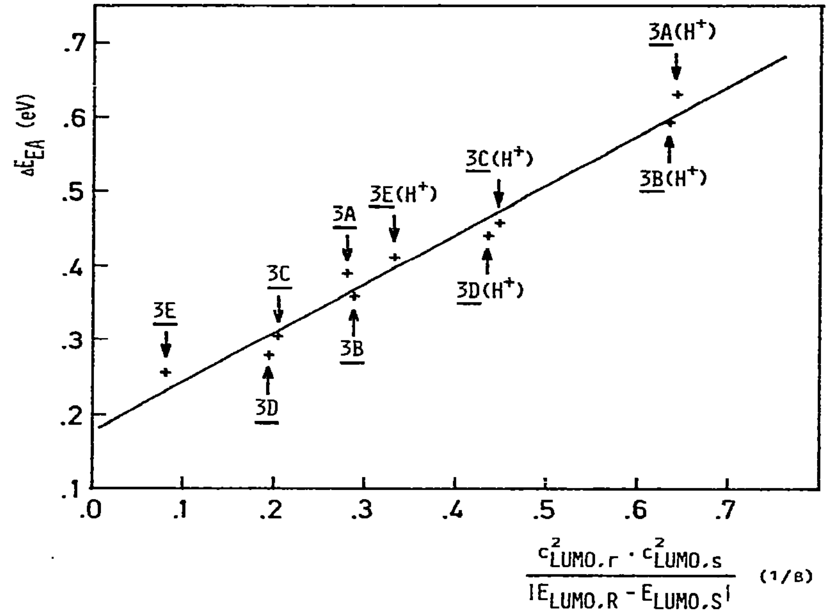


Fig. 4. Correlation of second order perturbation vs. electronic absorption shift of dyes **3A–3E** and **3A(H⁺)–3E(H⁺)**.

On the other hand, there are some advantages:

1. The HOMO–HOMO interaction is zero whatever distortion the bond r–s may suffer.
2. The Hueckel coefficient of the LUMO of R, $|c_{\mathrm{LUMO},r}|$ is exceptionally high: 0·608, thus the LUMO–LUMO interaction is very sensitive to variations of $c_{\mathrm{LUMO},s}$.
3. The LUMO energy of R (−0·236[β]) is low enough to guarantee that all the LUMO energies of S lie above. This and the fact that the HOMO of R is identical with that of the combined system R–S (see Fig. 3) confirms that the transition in R–S remains essentially located on R.

The evaluated regression line in Fig. 4 is given in eqn (2).

$$\Delta E_{\mathrm{EA}} = 0{\cdot}176 + 0{\cdot}658\ \Delta E_{\mathrm{HOMO \rightarrow LUMO,RS}} \qquad (2)$$

It can be seen that the absorption shift ΔE_{EA} keeps a finite value if the second order perturbation $\Delta E_{\mathrm{HOMO \rightarrow LUMO,RS}}$ is zero. This is explained if first order perturbation is included: The centre s of the various heterocycles S bears a positive charge in all cases, which attracts electrons through σ bond r–s, thus causing a slight increase of the Coulomb potential α_r of $\delta\alpha_r$. This in turn lowers

TABLE 3

pK^* AND $pK^*_{R^+}$ VALUES AND SLOPES N OF 3A–3E IN METHANOL/WATER (EQUIMOLAR) AT 298 K

Compound	pK^*	n^a	$pK^*_{R^+}$	n^a
3A	−4·09±0·05[b]	0·88±0·07	7·04±0·02	0·97±0·04
3B	−2·53±0·03[b]	1·04±0·06	7·76±0·02	1·01±0·04
3C	0·60±0·01	1·58±0·06	9·35±0·06	0·80±0·08
3D	1·20±0·03	1·22±0·07	8·82±0·02	0·95±0·05
3E	0·35±0·02	2·07±0·10	9·80±0·04	0·96±0·06

[a] see eqn (4)
[b] from H_0^* function[7]

the LUMO energy while the HOMO remains unaffected because of $c_{HOMO,r} = 0$. The result of this first order perturbation (3) is a bathochromic shift.

$$\Delta E'_{EA} = c^2_{LUMO,r}\;\delta\alpha_r \tag{3}$$

These results in some respects contradict Brooker's series of different basicities,[19] which however is formulated on an entirely different basis: in his series the varied heteroaromatics are an integral part of the first electronic transition, whereas in the case of the trihetarylmethanes, a 'preformed' dye (R) plays the role of a probe, the LUMO of which is only being perturbed by heterocycles (S).

The spectrophotometric investigation of the pK*s of dyes **3A–3E** presented difficulties in that for the least basic systems **3A** and **3B**, which had to be measured at high concentrations of sulphuric acid in methanol/water, the protonation equilibrium was accompanied by a general shift of the electronic absorption spectrum.[20] The pK*s of the remaining three dyes lie in a pH* region which is not very well defined due to the unknown acid error of the glass electrode used for pH* measurements in the water/methanol mixture.[21] The deviations of the slopes *n* (see eqn (4)) for pK* of **3C–3E** from 1·0 in Table 3 must therefore be ascribed at least in part to the uncertainties of the pH* measurements. The listed values of the pK*s, calculated by a least-square-fitting of eqn (4) to the measured values and for **3C–3E** corrected for the surface potential difference of the glass electrode between pure water and the methanol/water mixture and the medium effect with +0·15,[22] should therefore only be taken as estimates and in the case of **3C–3E** are certainly higher than the true values.

$$E(\mathrm{pH}^*) = \frac{E_0 + E_\infty \,.\, 10^{n(\mathrm{pH}^* - \mathrm{pK}^*)}}{1 + 10^{n(\mathrm{pH}^* - \mathrm{pK}^*)}} \tag{4}$$

Considering these reservations it can still be noted that the basicity of the dyes not only depends on the heterocycle involved but also on the position of the protonation centre relative to the partial charge of the central carbon (compare **3D** and **3E**). It is clearly unfavourable to build up another positive charge in the immediate neighbourhood of an existing one, which makes the 4-pyridyl-compound **3D** the most basic of the series.

In basic media the trihetarylmethane dyes show the same bleaching effect as has been found with ordinary triphenylmethane dyes (see, for example, ref. 23). Analogous to the latter ones, hydroxylation of the central carbon atom is assumed, causing an interruption of the π-system. In order to measure their $pK^*_{R^+}$ values, defined by Deno,[24] solutions of the dyes at various pH* were allowed to stand overnight to achieve total equilibrium. It could be noted that the equilibrium reaction was followed by a very slow degradation process which nevertheless prevented the system from being completely reversible. The $pK^*_{R^+}$ values summarised in Table 3 might therefore differ a little from the true values.

The $pK^*_{R^+}$ values computed by eqn (4) lie in the region of Malachite Green ($pK_{R^+} = 6{\cdot}90$[23e]) and Crystal Violet ($pK_{R^+} = 9{\cdot}36$[23e]), both measured in water. The expected increase from **3A** to **3C** should not be overemphasised in view of the pair **3D** and **3E** where one would predict the opposite sequence to that found. The difference of *c.* 1 pK unit (corresponding to 5·7 kJ mol^{-1} at room temperature) might easily be attributed to a slight difference in solvation entropy (19 J K^* mol^{-1}).

5. EXPERIMENTAL

5.1. *General*

Melting points (m.p.) were observed on a heating table with a monocular from Leitz (Wetzlar) and were corrected. Micro-elemental analyses were carried out at Ciba-Geigy AG and Sandoz AG. Electronic absorption spectra were recorded on a Beckman Acta C III spectrophotometer. Computer calculations were carried out on a MINC 11-BD computer from Digital Equipment Corp. with a 4662 Tektronix plotter for least-square-optimisations and electronic absorption spectra drawings. HMO computations were executed on a Hewlett-Packard 9830A table computer with 9862A plotter, and a UNIVAC-1100/81 TSO system served for SCF–CI calculations.

5.2. *Syntheses*

Bis-(1,2-dimethyl-3-indolyl)-2-benzoxazolylcarbenium perchlorate **3A**: A mixture of 200 mg (0·69 mmol) 2-(1,2-dimethyl-3-indoloyl)-benzoxazole **1A** and 100 mg (0·69 mmol) 1,2-dimethylindole **2** was heated under reflux in 2 ml phosphorus oxychloride for ½ h. After cooling and careful addition of water the blue solution was boiled for 5 min., filtered, and the product precipitated by addition of 60% perchloric acid. Filtration and washing of the raw product with water containing perchloric acid and drying at 120°C overnight, followed by column chromatographic purification on silica with chloroform/ethanol (9:1) plus 2–3 drops of 60% perchloric acid per 100 ml solvent mixture yielded 70 mg (20%) dark blue crystals melting at 195°C.

$C_{28}H_{24}ClN_3O_5.0{\cdot}5\,H_2O$ (527·0)

calc. C 63·82 H 4·78 Cl 6·73 N 7·97 O 16·70%
found C 63·55 H 4·78 Cl 6·79 N 7·51 O 16·60%

Bis-(1,2-dimethyl-3-indolyl)-2-benzothiazolylcarbenium perchlorate **3B**: In 2 ml phosphorus oxychloride, 200 mg (0·653 mmol) 2-(1,2-dimethyl-3-indoloyl)-benzothiazole **1B** were condensed with 95 mg (0·653 mmol) 1,2-dimethylindole **2** for $\frac{1}{2}$ h under reflux. Careful hydrolysis in 100 ml water, boiling for 5 min., filtration from insoluble tar and precipitation with 60% perchloric acid yielded 260 mg (75%) of a violet raw product. Recrystallisation from water containing some perchloric acid gave 180 mg (52%) pure product melting at 200°C (contraction from 186°C).

$C_{28}H_{24}ClN_3O_4S\,.\,H_2O$ (543·1)

calc. C 61·93 H 4·64 Cl 6·53 N 7·74 S 5·90 H_2O 1·66%
found C 61·91 H 4·55 Cl 6·72 N 8·01 S 5·69 H_2O 1·41%

Bis-(1,2-dimethyl-3-indolyl)-(1-methyl-2-benzimidazolio)-carbenium diperchlorate **3C**(H^+): 500 mg (1·65 mmol) 1-methyl-2-(1,2-dimethyl-3-indoloyl)-benzimidazole **1C** reacted with 276 mg (1·9 mmol) 1,2-dimethyl-indole **2** in 2 ml phosphorus oxychloride under reflux conditions for 2 h. The tarry mass was then dissolved in little ethanol, hydrolysed in an ice/water mixture and heated to boiling temperature for a few minutes. After cooling, the deep blue solution was neutralised with solid sodium acetate, filtered from insoluble byproduct and the raw product precipitated by addition of a concentrated aqueous solution of sodium perchlorate. Filtration and washing of the dark blue precipitate with water containing some sodium perchlorate and vacuum-drying at 120°C was followed by column chromatographic purification on silica with chloroform and an increasing amount of acetone plus a few drops of 60% perchloric acid per 200 ml solvent. Recrystallisation from ethanol/water/60% perchloric acid yielded 72 mg (7%) product, m.p. 192°C (contraction).

$C_{29}H_{28}Cl_2N_4O_8\,.\,0{\cdot}36\ HClO_4$ (667·6)

calc. C 52·17 H 4·28 Cl 12·53 N 8·39%
found C 52·44 H 4·07 Cl 12·83 N 8·57%

Bis-(1,2-dimethyl-3-indolyl)-4-pyridylcarbenium perchlorate **3D**: In 2 ml phosphorus oxychloride, a mixture of 200 mg (0·799 mmol) 4-(1,2-dimethyl-3-

indoloyl)-pyridine **1D** and 116 mg (0·799 mmol) 1,2-dimethylindole **2** was kept at boiling temperature for 40 min. After c. 20 min. the deep blue reaction slurry solidified. The cake was stirred in ice-cold water to dissolution, the blue solution filtered and neutralised with solid sodium acetate. The product was precipitated with a concentrated aqueous solution of sodium perchlorate, filtered and washed with little water to give 330 mg (86%) bluish red crystals. Recrystallisation from acetone/ether gave a pure product of m.p. 261–264°C.

$C_{26}H_{24}ClN_3O_4 . 0·25\ H_2O$ (482·5)

calc.	C 64·73	H 5·12	Cl 7·35	N 8·71%
found	C 64·76	H 4·97	Cl 7·16	N 8·66%

Bis-(1,2-dimethyl-3-indolyl)-2-pyridylcarbenium perchlorate **3E**: Using the same procedure as for **3D**, 100 mg (0·4 mmol) 2-(1,2-dimethyl-3-indoloyl)-pyridine **1E** reacted with 58 mg (0·4 mmol) 1,2-dimethylindole **2** in 1 ml phosphorus oxychloride for 1 h under reflux. Preparing the reaction mixture analogously to **3D** gave 111 mg (58%) bluish red crystals melting at 160°C (contraction).

$C_{26}H_{24}ClN_3O_4 . 0·25\ H_2O$ (482·5)

calc.	C 64·73	H 5·12	Cl 7·35	N 8·71	O 14·09%
found	C 64·59	H 5·13	Cl 7·29	N 8·83	O 13·96%

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