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Synthesis, ^{1}H-NMR and Electronic Absorption Spectra, and Halochromic Properties of Bis(1,2-dimethyl-3-indolizinyl)hetarylmethane Dyes

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SUMMARY

A series of bis(1,2-dimethyl-3-indolizinyl)hetarylmethane dyes has been synthesised, where the hetaryl substituents are 2-benzoxazolyl, 2-benzothiazolyl, 1-methyl-2-benzimidazolyl, 4- and 2-pyridyl and 4-quinolyl.

The interpretations of the ^{1}H-NMR spectra supported the postulated structure of these dyes The dependence of the electronic absorption spectra on the variation of the hetaryl substituents as well as on the pH conditions of the water/methanol solvent mixture (halochromism) is discussed on the basis of PPP–CI and HMO calculations Analogously to trihetarylmethane dyes described earlier[1] a second-order perturbational effect could be shown to make the main contribution to the bathochromic shift on substituting the chromophoric di-indolizinylmonomethinecyanine fragment at the central carbon atom. This effect was superimposed on the general first-order perturbational shift induced by the increased out-of-plane rotation of the chromophore on substitution with the bulky hetarenes*

Lower dissociation constants K^* and $K^*_{R^+}$ in comparison with the di-indolylhetarylmethane series[1] confirmed the calculated better delocalisation of the positive charge on the central carbon in the present system

1. INTRODUCTION

Triphenylmethane dyes as a subgroup of the cationic dyes have found their heteroaromatic counterparts in diarylhetaryl-, aryldihetaryl- and

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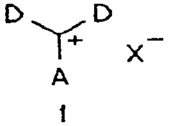
trihetaryl-methane dyes, examples of which are given in refs. 3–4. In an earlier paper[1] the synthesis and spectroscopic qualities of trihetaryl-methane systems **1** built with two 1,2-dimethylindole functions as 'donors' D and various 'acceptor'-heteroaromatic groups A joined to the common carbenium centre have been described.



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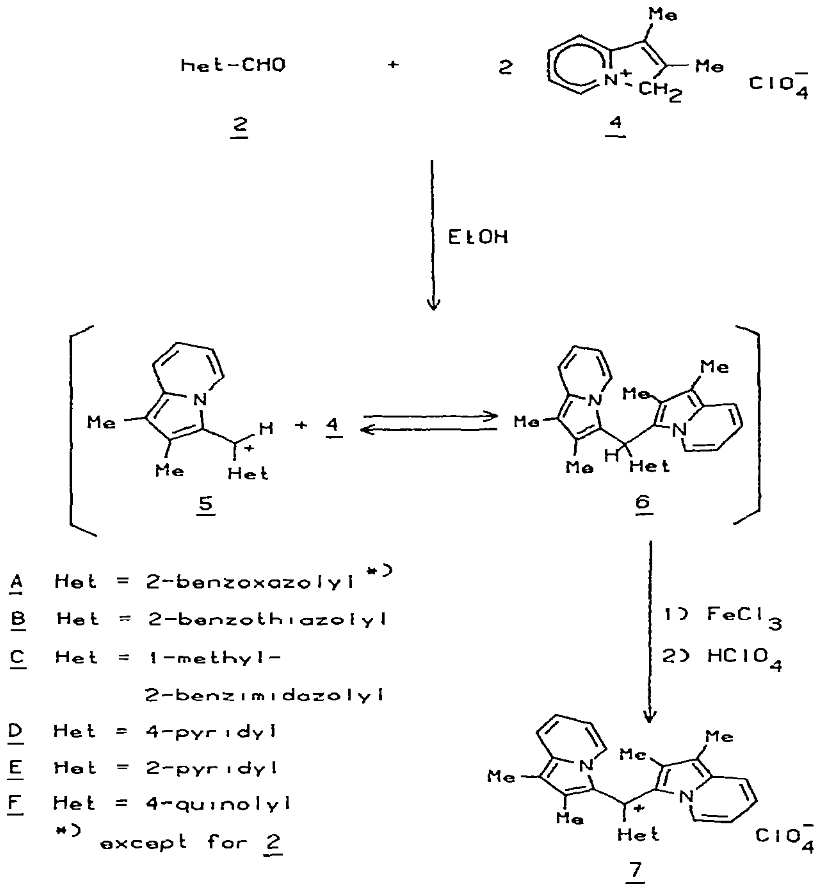
An interesting correlation has been found between the electronic absorption shift induced by the substitution of the di-indolylmethane chromophore by the varied acceptor hetarenes and the second-order perturbation of the LUMO of the chromophore with the LUMOs of the substituents.

The aim of the present paper is to demonstrate the synthesis of a series of trihetarylmethane dyes analogous to those previously described,[1] replacing the mentioned donor hetarene by 1,2-dimethylindolizine, and to investigate the influence of the various heteroaromatic substituents on the electronic absorption spectrum of the di-indolizinylmethane system as well as the spectral changes as a function of the pH (halochromism) It might be intriguing to examine whether the simple LCMO scheme applied in the interpretation of the spectral properties of the di-indolylmethane dye series can be extended to the present dye series

2 SYNTHESES

Indolizine is a very weak base, protonated preferentially at position C-3 Longuet-Higgins and Coulson[5] concluded from MO calculations that the same position is also favoured in an electrophilic attack. Hence the long-known synthetic principle[3f] of fusing 1 mol of a carbaldehyde with 2 mol of a nucleophilic (het)arene with subsequent oxidation of the intermediate was successfully applied [6]

While carbaldehydes **2D**–**2F** are available commercially, **2C** was generated in excellent yield through addition of dimethylformamide[7] to 1-methyl-2-lithiobenzimidazole[8] and aqueous working up. Compound **2B** was readily prepared by the oxidation of 2-hydroxymethylbenzothiazole with selenium dioxide in dioxane containing little water,[9]

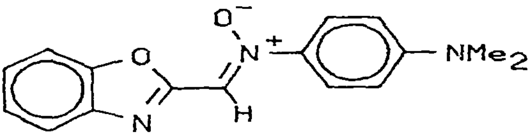


A Het = 2-benzoxazolyl *)
B Het = 2-benzothiazolyl
C Het = 1-methyl-2-benzimidazolyl
D Het = 4-pyridyl
E Het = 2-pyridyl
F Het = 4-quinolyl
*) except for 2

whereas attempts to oxidise 2-methylbenzoxazole with the same oxidant, which should afford benzoxazole-2-carbaldehyde according to ref 10, failed totally.

However, the oxidation of 2-methylbenzoxazole in two steps, firstly with iodine in pyridine to give an *N*-(2-benzoxazolylmethyl)pyridinium salt and secondly conversion of this salt with *p*-nitrosodimethylaniline in pyridine in the presence of dilute sodium hydroxide solution, resulted in the *p*-dimethylaminophenyl nitron **3**,[11] the disguised form of benzoxazole-2-carbaldehyde

The condensation reaction of the carbaldehydes **2B–2F** with 1,2-dimethylindolizinium perchlorate **4** required no further catalysis except raised temperature. As the chemical properties of the nitrons resemble



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those of ordinary carbaldehydes, compound **3** reacted quite analogously to **4**.

The intermediate compound always precipitated as an orange to red slurry which has been identified earlier[6 12] as the 1:1 condensation products **5** They undergo a slow and probably reversible[6] second condensation reaction with another mole of the solute **4**, providing the leuco bases **6** which then in an irreversible oxidation step give green dyes **7**

Oxidation of the leuco bases **6** was best performed with an equivalent amount of iron trichloride without previous isolation of the precipitated intermediate Compound **6D** is oxidised without addition of the oxidant, perhaps by an excess of the carbaldehyde (compare ref 6) It is worth mentioning that contrary to the observed noncatalysed oxidation of **6** with Het = 2-benzimidazolyl[6] the *N*-methylated analogue **6C** is stable even under atmospheric oxygen[6] and is converted only slowly to dye **7C** with iron trichloride

The green reaction solutions were generally evaporated to dryness prior to isolation of the product from the residue by column-chromatographic separation on silica gel

3 ^{1}H-NMR SPECTRA

3.1. Method

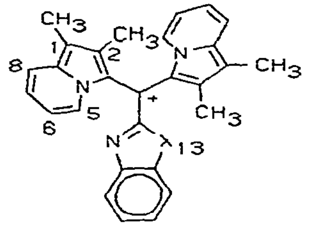
The ^{1}H-NMR spectra have been recorded on a 90 MHz Fourier NMR spectrometer for the purpose of structural identification of dyes **7**. Perdeuterated dimethylsulphoxide and acetonitrile served as solvents with tetramethylsilane as internal standard

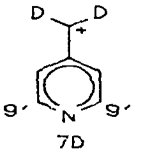
3.2. Results and discussion

In Table 1 the relevant peaks of the ^{1}H-NMR spectra of **7A**–**7F** are collected. Evidently with one exception the C(1)- and C(2)-methyl groups

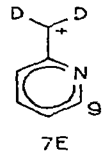
TABLE 1

Proton Signals of Dyes **7A–7F** from 90 MHz ^{1}H-NMR Measurements in Perdeuterated Dimethylsulphoxide and Acetonitrile

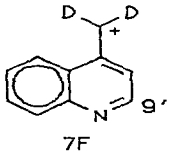




7D



7E



7F

7A X=O, 7B X=S, 7C X=NCH_3

Proton	*Chemical shift (ppm) (Multiplicity*[a]*)*					
	In acetonitrile			*In dimethylsulphoxide*		
	7A	**7B**	**7C**	**7D**	**7E**	**7F**
$H_3C—C(1)$	2 34(s)	2 31(s)	2 36(s)	2 30(s)	2 30(s)	2 24/ 2 30(2s)
$H_3C—C(2)$	2 15(s)	1 74(s)	1 62(s)	1 60(s)	1 54(s)	1 34/ 1 50(2s)
H—C(5)	7 08/ 7 15(d)	7 12/ 7 20(d)	7 00–7 29(m)	7 17/ 7 25(d)	7 21/ 7 28(d)	6 90-8 35(m)
H—C(6)	6 84/ 6 86/ 6 92/ 6 94/ 7 01(t)	6 79/ 6 81/ 6 86/ 6 88 6 96(t)	6 80-7 29(m)	6 94/ 7 01/ 7 08(t)	6 93/ 7 00/ 7 08(t)	6 90–8 35(m)
H—C(8)	7 47-8 04(m)	7 50–7 91/ 8 09-8 29(m)	7 71–8 16(m)	7 90/ 8 00(d)	7 89/ 7 98(d)	6 90–8 35(m)
$H_3C—N(13)$			3 88(s)			
H—C(9')				8 78/ 8 84(d)	8 80/ 8 83(d)	9 10/ 9 15(d)
H—C (rest)	7 47-8 04(m)	7 50–7 91/ 8 09-8 29(m)	7 71-8 16(m)	7 44–7 82(m)	7 50–8 20(m)	6 90–8 35(m)

[a] Multiplicities s singlet d, doublet t triplet m, multiplet

at the two indolizine moieties experience mutually identical shifts It is however doubtful whether the molecule takes up a rigid configuration with a symmetry which fulfils the conditions of a homotopic or enantiotopic neighbourhood for these methyl protons The magnetic equivalence of the two methyl pairs is more probably a result of the practically unhindered rotation of the three hetaryl functions about the central bonds at room temperature.

This equivalence is lifted in the case of **7F** due to the greater bulk of the 4-quinolyl fragment which raises the energy barrier for rotation and consequently forces the methyl groups into differently strong diamagnetic ring currents of the respective neighbouring hetarenes.

It must be noted, however, that unlike those in the ^{1}H-NMR spectrum of the analogous di-indolylmethane system[1] the methyl signals of **7C** are not split, hence indicating a smaller rotational activation-energy barrier.

Another conspicuous feature is the increasing upfield shift of the C(2)-methyl protons with decreasing acceptor strength of the varied hetarene, while the methyl group at C(1) is hardly influenced One might be tempted to explain this by an increased electron density at C(2) on changing from strong to weak acceptor substituents. Yet quantum-theoretical calculations on the simple HMO basis—regarding the atom–atom polarisability[13] of the adjacent π centre C(2) by the (variously substituted) carbenium centre—lead to the opposing result that this methyl group should not be affected by different substitution

However, a comparison with the ^{1}H-NMR spectra of 1- and 2-methylindolizine (in carbon tetrachloride)[14] reveals a drastic diamagnetic shift acting on the C(2)-methyl group and hardly any effect on the C(1)-methyl protons of the 1,2-dimethylindolizine components in dyes **7** The protons at C(5) suffer a similarly strong upfield shift (from *ca* 7 7 ppm[14]) due to the neighbouring ring currents, over-compensating the deshielding effect emerging from the positively charged carbenium substituent. The latter nevertheless evidently operates on the C(6) proton which is shifted paramagnetically in relation to the unsubstituted indolizine (*ca* 6 3 ppm[14]).

Except for the protons at the vicinal position to the pyridine and quinoline nitrogen (i e H—C(9')) which suffer the strongest downfield shift, the remaining protons form a complex multiplet in the typical aromatic range.

4 ELECTRONIC ABSORPTION SPECTRA (HALOCHROMISM)

4.1. Method

Recordings of the electronic absorption spectra have been executed in an equimolar water/methanol mixture. The fixing of pH* and H_0^* values is described elsewhere.[1] Beer–Lambert's law was valid in all cases in the concentration range 10^{-4}–10^{-5}M

4.2. Results and discussion

The electronic absorption spectra of **7A–7F**, depicted in Figs. 1–4, in media ranging from neutral to weakly basic and strongly acidic, show great mutual similarity. The two long-wave absorption bands in the visible spectral range resemble those of the di-indolylhetarylmethane dyes[1] in shape and extinction. However, the absorption maxima are shifted towards longer wavelengths (Table 3). High acidity of the solvent causes a bathochromic shift of the longest wavelength bands, revealing halochromic properties (compare Fig. 1 with Fig 2, and Fig. 3 with Fig. 4).

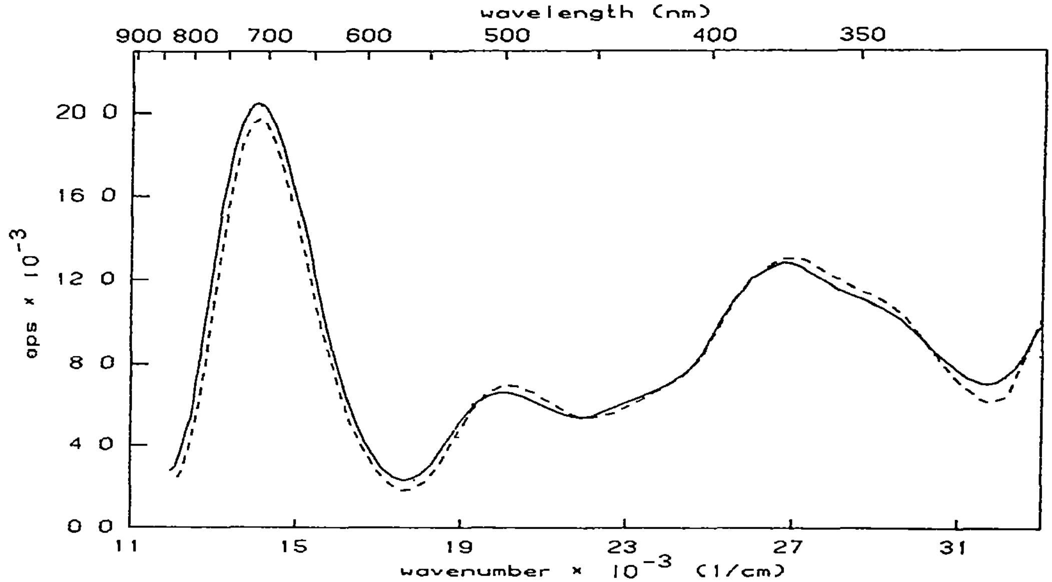


Fig. 1. Electronic absorption spectra of **7A–7C** at 298 K in equimolar methanol/water ———, **7A**, pH* 8 96, – – –, **7B**, pH* 8 57, , **7C**, pH* 5 2

The dependence of the spectral variations on the acceptor hetarenes and solvent conditions are easily explicable quantum-theoretically.[4] MO calculations on the many-electron basis of Pariser, Parr and Pople (PPP–CI method)[15] with an improved set of parameters (Table 2) have been carried out in a program version devised by Zahradnik,[16] the two-centre integrals being computed by means of the Mataga-Nishimoto equation.[17]

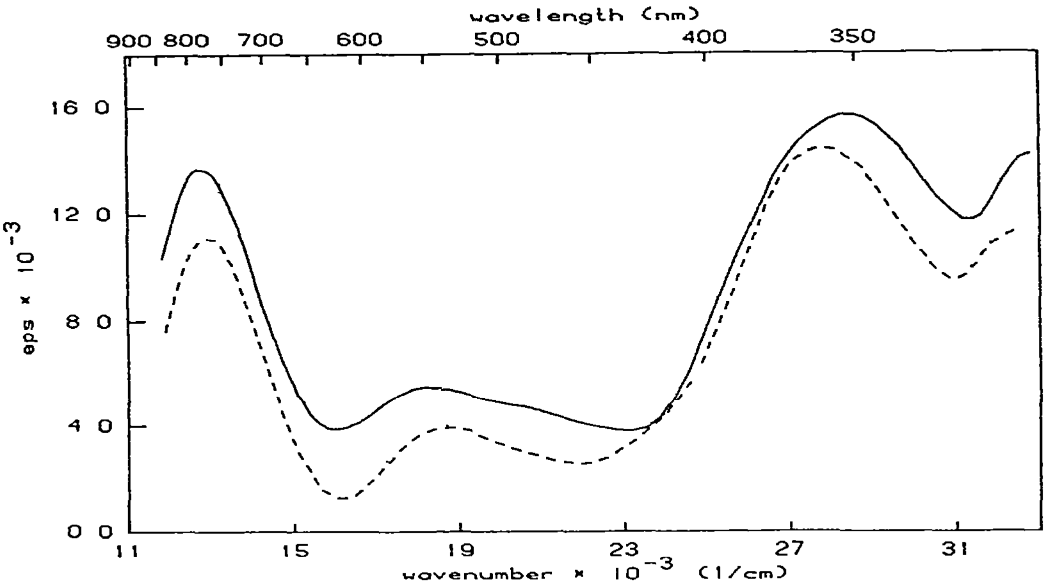


Fig. 2. Electronic absorption spectra of the protonated forms of 7A–7C at 298 K in equimolar methanol/water ———, 7A(H⁺), H_0^* −6.0, - - -, 7B(H⁺), H_0^* −3.0, 7C(H⁺), H_0^* 0.0

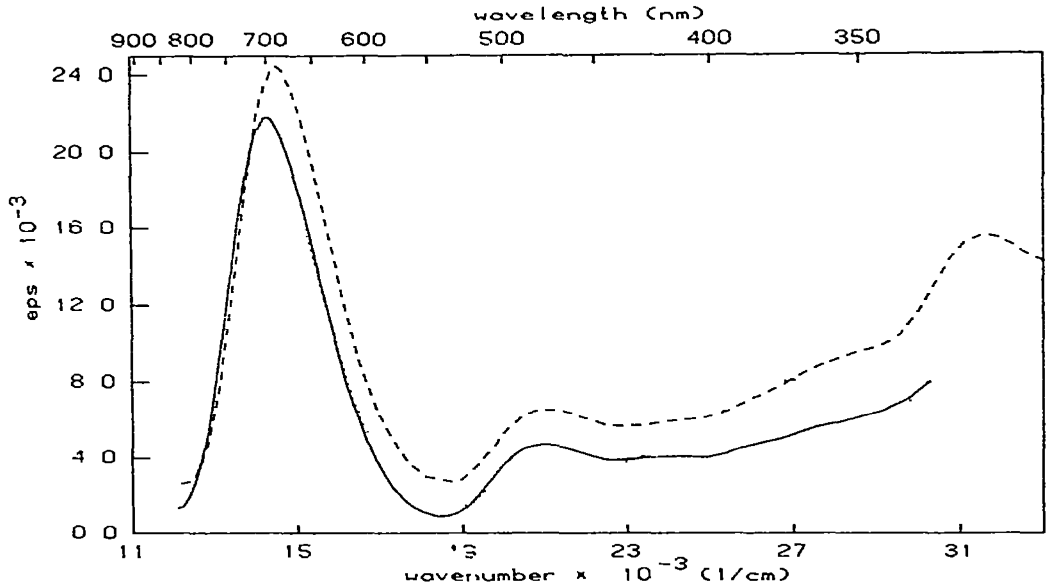


Fig. 3. Electronic absorption spectra of 7D–7F at 298 K in equimolar methanol/water ———, 7D, pH* 5.4, - - -, 7E, pH* 11.05 , 7F, pH* 10.9

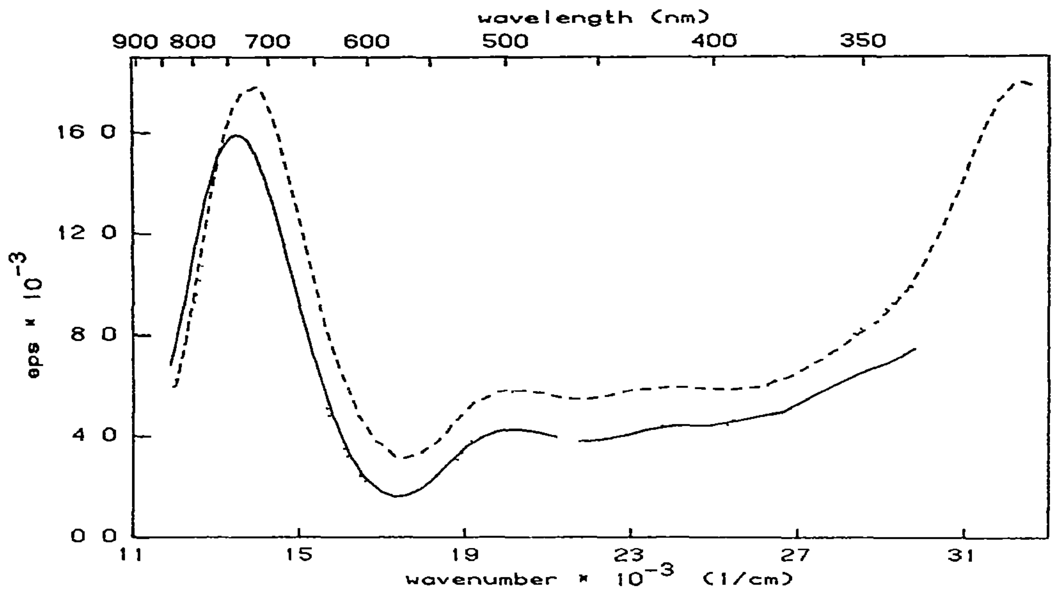


Fig. 4. Electronic absorption spectra of the protonated forms of 7D–7F at 298 K in equimolar methanol/water ———, 7D(H$^+$), pH* 1 2, - - -, 7E(H$^+$), H_0^* −1 0, . . . , 7F(H$^+$), pH* 0 9

For this purpose idealised geometry with bond lengths of 140 pm, regular rings and standard angles has been assumed. The configuration interaction (CI) procedure included the 25 lowest singly excited states emerging from transitions of an electron from one of the highest five occupied into one of the five lowest unoccupied orbitals. In order to

TABLE 2
PPP–CI Parameters Used for Calculations of the Electronic Absorption Spectra of Dyes 7–11

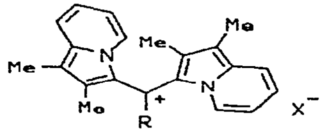
Proton	$-\beta_{C-X}$ (*eV*)	$-VSIP_X$[a] (*eV*)	γ_{XX}[b] (*eV*)	$Z_{core\,X}$[c]	*Ref*
C	2 39	11 16	11·13	1	19
N(I)	2 40	14·10	12 30	1	20
N(II)	2 40	27 30	18 00	2	20
O(II)	2 60	32 90	11 43	2	19
S(II)	1 623	20 40	10 84	2	20

[a] Valence state ionisation potential of atom X
[b] One-centre electron repulsion integral for atom X.
[c] Core charge of atom X

TABLE 3
Experimental and Calculated Visible Absorption Maxima of Dyes 7–11 and Their Protonated Forms $7(H^+)$–$11(H^+)$

Compound	*Calculated (nm)*		*Experimental (nm)*		*log ε*
	λ_{max1}	λ_{max2}	λ_{max1}	λ_{max2}	
7A	662		714		4 31
		537		499	3 84
7A(H^+)	688		783		4 13
		553		550	3 74
7B	648		712		4 28
		534		498	3 79
7B(H^+)	666		780		4 08
		538		547	3 69
7C	642		697		4 39
		532		497	4 03
7C(H^+)	659		710		4 23
		522		507	3 73
7D	638		700		4 33
		443		475	3 67
7D(H^+)	648		753		4 18
		445		505	3 63
7E	636		688		4 35
		453		476	3 66
7E(H^+)	646		725		4 20
		462		505	3 61
7F	643		698		4 35
		522		477	3 60
7F(H^+)	656		746		4 14
		512		483	3 82
8[18]	627		629		4 61
9[6]	624		682		4 40
		451		471	3 81
10[6]	630		683		4 41
		500		495	3 97
10(H^+)[6]	645		705		4 30
		507		495	3 72
11[6]	642		697		4 39
		532		497	4 03
11(H^+)[6]	659		724		4 27
		522		511	3 82

obtain fair agreement with the experimental spectrum of the 'unsubstituted' basic system **8**,[18] measured in ethanol, the central bonds have been assumed to be twisted equally by angles ω of 45° each, the corresponding β values being altered according to the equation $\beta = \beta_0 \cos \omega$. The experimentally determined absorption maxima are compared with the calculated values in Table 3.



8 R = H [18]
9 R = phenyl [6]
10 R = 2-imidazolyl [6]
11 R = 2-benzimidazolyl [6]

It is obvious that except for the 'calibrating dye' **8** the measured absorption wavelengths are distinctly higher. A comparison of the calculated spectrum of **8** assuming different twist angles about the central bonds shows the strong dependence of the long-wave absorption shift on rotation: presuming a twist angle of 30° for each central bond an absorption is expected at 580 nm, in contrast to the resultant 627 nm (Table 3), obtained for corresponding angles of 45°!

It cannot therefore quite be rejected to suppose that a good deal of the bathochromic shift on substituting the carbenium centre of the chromophore is caused by increased twist angles due to steric crowding.

Analogously to those of ordinary triphenylmethane dyes[21] the SCF computations confirm that the first two excited states of dyes **7** descend from nearly pure HOMO–LUMO and NHOMO–LUMO transitions respectively which are polarised mutually perpendicularly The intense long-wave absorption band is always polarised along the long axis of the di-indolizinylmethane moiety, defined as the x-band.

Hence the requirements for a study of the first transitions of these trihetarylmethane dyes on the HMO basis are fulfilled comparably to those described for di-indolylhetarylmethane systems.[1] Considering therefore dyes **7** as being composed of dye fragment **8** and the various hetarenes, a similar correlation of the absorption shifts ΔE_{EA} of the longest wavelength band with the second-order perturbation $\Delta E_{\mathrm{LUMO,RS}}$, defined by eqn (1),[22] should be obtained, where $C_{\mathrm{LUMO\ r(s)}}$ is the expansion coefficient at the joining position r(s) and $E_{\mathrm{LUMO,R(S)}}$ the eigen-value of the LUMO of the partial π system R(S).

$$\Delta E_{\mathrm{LUMO,RS}} = \frac{C^2_{\mathrm{LUMO,r}} \cdot C^2_{\mathrm{LUMO,s}}}{E_{\mathrm{LUMO,R}} - E_{\mathrm{LUMO,S}}} \cdot \beta^2_{\mathrm{rs}} \tag{1}$$

A Hueckel parameter set which was extracted from a comparison with PPP calculations[23] has been chosen for the HMO computation of the π system fragments The resulting correlation is depicted in Fig. 5. (The value for the quinolinium derivative **7F**(H$^+$) has been omitted because its LUMO eigen-value lies too close to the LUMO of the chromophoric partial system **8**, leading to an abnormally high perturbation, i.e. the concept of the perturbation theory is violated.[22])

The regression line is represented by eqn (2), leaving β_{rs} undetermined. The correlation coefficient is smaller ($r = 0{\cdot}894$) than for the di-indolylmethane dye series. However, it has to be taken into account that the experimental shift range of the present systems is only about half that of the indole parents. Correspondingly the 'sensitivity' of the chromophoric system **8** towards substituents at the carbenium centre only amounts to half that of the di-indolylmethane series which is expressed in the smaller slope in eqn (2).

$$\Delta E_{EA} = -0{\cdot}119 + 0{\cdot}323 \Delta E_{LUMO\,RS} \tag{2}$$

Nevertheless the fact that the shifts of the protonated forms fit quite well in the same regression indicates that the variable influence of the substituents is essentially carried by the LUMO–LUMO interactions

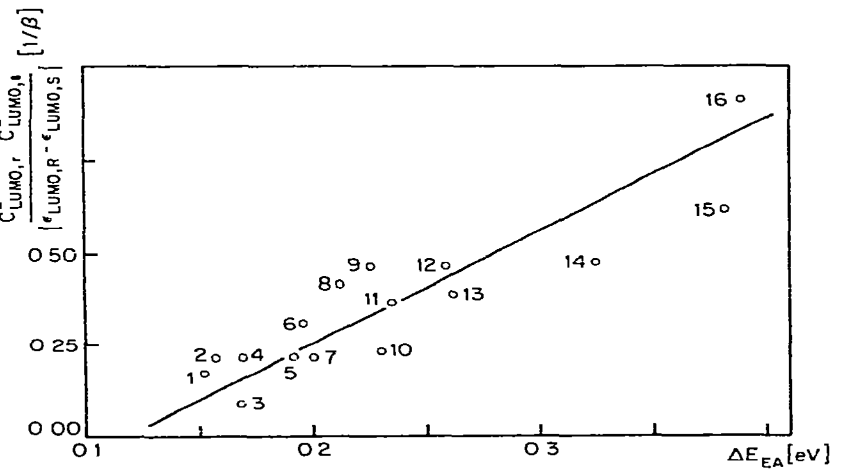


Fig. 5. Correlation of the electronic absorption shifts ΔE_{EA} versus the second-order perturbations of (het)arene-substituted bis(1,2-dimethyl-3-indolizinyl)methane dyes and their protonated forms (1, **9**,[6] 2, **10**,[6] 3, **7E**, 4, **7C**, 5, **11**,[6] 6, **7F**, 7, **7D**, 8, **10**(H$^+$),[6] 9, **7C**(H$^+$), 10, **7B**, 11, **7A**, 12, **11**(H$^+$),[6] 13, **7E**(H$^+$), 14, **7D**(H$^+$), 15, **7B**(H$^+$), 16, **7A**(H$^+$))

since their protonation hardly affects their steric shapes. Consequently one may conclude that the additional bathochromic shift of the dyes **7**–**11** in relation to the PPP calculations is indeed caused by the first-order perturbational effect of an increased distortion of the chromophore due to the bulkiness of the substituents.

5. DETERMINATION OF PROTOLYSIS CONSTANTS

5.1. Method

Protolysis constants have been determined by observing the electronic absorption spectra of **7A**–**7F** in an equimolar water/methanol mixture at various pH* and H_0^* values respectively. The pH* values measured by means of a glass electrode have been corrected for its surface potential difference between water and the applied solvent mixture with an additive term of +0·15.[24] The calculation of the pK^* values was based on a least-squares fitting of eqn (3) to the measured electronic absorption values at several fixed wavelengths.

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

5.2. Results and discussion

The trihetarylmethane dyes **7** exhibit marked halochromic properties (as mentioned earlier) which are a result of two consecutive protolytic equilibria: (1) protonation of the basic acceptor-hetaryl function at high acidity of the solvent and (2) hydroxylation of the carbenium centre of the dye in highly basic media The former causes a bathochromic shift of the two long-wave absorption bands whereas the latter bleaches the dye through interruption of the π system

Under extremely acidic conditions a distinct change of the absorption spectra of the protonated species of the most basic systems **7D**–**7F** could be observed for which a second protonation must be assumed.

The pK^* values and the hydroxylation constants $\mathrm{p}K^*_{\mathrm{R}^+}$[25] of dyes **7** are collected in Table 4, together with the slopes n, defined by eqn (3). These slopes deviate considerably from 1·0 for several reasons: in strongly acidic solutions the dye spectra suffered a general shift, superimposed on the

TABLE 4
Dissociation Constants pK^* and $pK^*_{R^+}$ and Slopes n^a of 7A–7F in Methanol/Water (Equimolar, 298 K, Ionic Strength = 0 1 M)

Compound	pK^*	n	$pK^*_{R^+}$	n
7A	−3 37 ± 0 03[b]	0 75		
7B	−2 02 ± 0 03[b]	1 22		
7C	1 51 ± 0 02	1 68	12 26 ± 0 15	0 69
7D	2 12 ± 0 06	0 98	12 68 ± 0 19	1 61
7E	0 99 ± 0 13	1 01		
7F	1 68 ± 0 05	1 48	12 50 ± 0 04	1 52

[a] See eqn (3)
[b] From H_0^* function [1]

protolytic equilibrium;[26] the unknown acid error of the glass electrode in the pH* range 0–2 leaves some uncertainty about the exact pH* in the water/methanol mixture;[27] before measuring, strongly basic solutions of the dyes had to stand overnight to achieve hydrolytic equilibrium and this was accompanied by a degradative side reaction.

The values in Table 4 are thus only to be taken as estimates. Nevertheless a comparison with the analogous constants of the di-indolylmethane systems[1] reveals that the present dyes are generally more basic by one pK^* unit, manifesting the increased delocalisation of the positive charge at the carbenium centre over the donor hetarenes as found in the quantum-theoretical calculations Consequently hydroxylation at this centre only occurs at high base concentrations, the $pK^*_{R^+}$ values therefore lying well above those of Crystal Violet ($pK^*_{R^+} = 10\ 72 \pm 0\ 01$, $n = 1{\cdot}30$) or Malachite Green ($pK^*_{R^+} = 7{\cdot}50 \pm 0{\cdot}04$, $n = 1{\cdot}14$) in the same solvent mixture (The stability of dyes **7A**, **7B** and **7E** at high basicity of the solvent was too low to afford reasonable values.)

A third dissociation constant, pK^*_2, at extremely high acid concentration could be evaluated in the case of dye 7F, lying at $H_0^* = -5{\cdot}83$ ($n = 0\ 98$) which probably corresponds to a protonation of one of the indolizine components at C-1 or C-3

6. EXPERIMENTAL

6.1. General

Corrected melting points (m p.) were measured on a heating table with a monocular from Leitz (Wetzlar). Microelemental analyses were carried out by the analytical departments of Ciba–Geigy AG and Sandoz AG. The electronic absorption spectra of the dyes were recorded on a Beckman Acta M IV spectrophotometer in Merck Uvasol solvents; Merck Titrisol buffers and pure sulphuric acid were employed to maintain defined pH* and H_0^* conditions. Silica gel 60 from Merck with grain size 0·063–0·2 mm was used for column chromatography

Calculations have been carried out on a Minc 11-BD computer from Digital Equipment Corp. with a 4662 Tektronix plotter for least-squares optimisation, HMO calculations, drawings of EA spectra and molecular formulae The Univac 1100/81 TSO system computer from Sandoz AG performed the PPP–CI calculations.

6.2. Syntheses

Bis(1,2-dimethyl-3-indolizinyl)-2-benzoxazolylcarbenium perchlorate (**7A**)· In 3 ml ethanol, a mixture of 176 mg (0·71 mmol) 1,2-dimethylindolizinium perchlorate (**4**) and 100 mg (0·36 mmol) *N*-(2-benzoxazolylidene)-4-dimethylaminophenylamine-*N*-oxide (**3**) was stirred at a slightly raised temperature. After 15 min, 120 mg (0·44 mmol) iron trichloride (hexahydrate) was added and the solution heated under reflux for 20 min. The deep green solution was then evaporated to dryness and the crude product separated from the residue by twofold column-chromatographic purification on silica gel with methylene chloride containing 25 % acetone and 2–3 drops of 60 % perchloric acid per 100 ml solvent. Recrystallisation from acetonitrile/water/(a little) perchloric acid yielded 47 mg (25 %) dark green crystals, m.p. 243 °C.

$C_{28}H_{24}ClN_3O_5.0\ 3\ H_2O$ (523·4)
Calc. C 64·26 H 4·74 Cl 6 77 N 8 03 O 16·20 %
Found C 63·99 H 4·78 Cl 6·73 N 8·18 O 15·61 %

Bis(1,2-dimethyl-3-indolizinyl)-2-benzothiazolylcarbenium perchlorate (**7B**): A solution of 100 mg (0·61 mmol) benzothiazole-2-carbaldehyde (**2B**) and 300 mg (1·23 mmol) 1,2-dimethylindolizinium perchlorate (**4**) in 5 ml ethanol was heated to boiling point, at which, within a few minutes, a red intermediate precipitated; 0·73 mmol iron trichloride, dissolved in 3 ml ethanol, was then added and the solution maintained under reflux for 2 h, while the precipitate redissolved gradually and the solution turned green. A black precipitate was filtered off after chilling the solution and repurified by recrystallisation from acetone/water/60 % perchloric acid. Pure green crystalline product (89 mg; 27 %; m.p. 163 °C) was obtained by column-chromatographic purification on silica gel with acetone/methylene chloride (1:4) and precipitation from acetone with ether.

$C_{28}H_{24}ClN_3O_4S \cdot 0{\cdot}25\,H_2O$ (538·5)
Calc. C 62·45 H 4·95 Cl 6·58 N 7·80 O 12·63 S 5·95 %
Found C 62·68 H 4·56 Cl 6·66 N 7·94 O 12·67 S 5·89 %

Bis(1,2-dimethyl-3-indolizinyl)-(1-methyl-2-benzimidazolio)carbenium diperchlorate (**7C**(H$^+$)). In 10 ml ethanol, 200 mg (1·25 mmol) 1-methylbenzimidazole-2-carbaldehyde (**2C**) was brought to reaction with 613 mg (2·50 mmol) 1,2-dimethylindolizinium perchlorate (**4**) under reflux conditions. At *ca* 60 °C fast formation could be observed of a red precipitate which slowly disappeared on addition of 0·25 mmol iron trichloride at boiling point. After 8 h of stirring the green solution was evaporated to dryness and the crude product separated column-chromatographically from the residue on silica gel with methylene chloride containing an increasing amount of acetone (up to 25 %). Recrystallisation from a little ethanol with addition of a few drops 60 % perchloric acid yielded 358 mg (45 %) fine green crystals melting at 185 °C (contraction).

$C_{29}H_{28}Cl_2N_4O_8 \cdot 0{\cdot}65\,H_2O$ (643·2)
Calc. C 54·16 H 4·59 Cl 11·02 N 8·71 O 21·52 %
Found C 54·20 H 4·59 Cl 11·11 N 8·85 O 21·59 %

Bis(1,2-dimethyl-3-indolizinyl)-4-pyridylcarbenium perchlorate (**7D**). Pyridine-4-carbaldehyde (**2D**, 300 mg, 2·80 mmol) reacted readily with 690 mg (2·80 mmol) 1,2-dimethylindolizinium perchlorate (**4**) in 5 ml ethanol at room temperature to give a dark green oily precipitate. After 4 h of stirring the green emulsion was evaporated and the crude product purified column-chromatographically with methylene chloride/acetone (3:1). Subsequent threefold recrystallisation from ethanol/ether gave 300 mg (45 %) pure green crystals, m.p. 188–190 °C.

$C_{26}H_{24}ClN_3O_4$ (478·0)
Calc. C 65·34 H 5·06 Cl 7·42 N 8·79 O 13·39 %
Found C 65·24 H 5·18 Cl 7·32 N 8·84 O 13·54 %

Bis(1,2-dimethyl-3-indolizinyl)-2-pyridylcarbenium perchlorate (**7E**): A solution of 200 mg (1·87 mmol) pyridine-2-carbaldehyde (**2E**) and 917 mg (3·73 mmol) 1,2-dimethylindolizinium perchlorate (**4**) in 10 ml ethanol was kept at 50 °C, at which temperature an oily orange suspension formed Addition of 1·9 mmol iron trichloride and 10 ml acetonitrile and heating to reflux for 3 h provided a dark green crude product after distilling off the solvent Isolation and purification was achieved by twofold column-chromatographic separation on silica gel, firstly with methylene chloride with an increasing quantity of acetone, secondly with acetone containing a few drops 60 % perchloric acid per 250 ml solvent. Recrystallisation from diluted perchloric acid yielded 157 mg (18 %) pure green dye salt melting at 218–220 °C (contraction)

$C_{26}H_{24}ClN_3O_4.0\,95\,HClO_4.0\,6\,H_2O$ (584·2)
Calc C 53·46 H 4·51 Cl 11·83 N 7·19 O 32·01 %
Found C 53·29 H 4·30 Cl 11·66 N 7 23 O 32·33 %

Bis(1,2-dimethyl-3-indolizinyl)-4-quinolylcarbenium perchlorate (**7F**). In 10 ml ethanol, 200 mg (1·27 mmol) quinoline-4-carbaldehyde (**2F**) and 625 mg (2·54 mmol) 1,2-dimethylindolizinium perchlorate (**4**) were condensed at 50 °C, forming an orange suspension within minutes. Addition of 0 25 mmol iron trichloride after 15 min rapidly changed the colour of the solution to green. After boiling the solution for 2 h under reflux and subsequent evaporation to dryness the crude product was extracted column-chromatographically from the residue on silica gel with an increasing concentration of acetone in methylene chloride, and finally with acetone containing 1–2 drops 60 % perchloric acid per 100 ml eluant Recrystallisation from acetonitrile/water, adding a little sodium perchlorate, gave 362 mg (54 %) pure green crystals melting at 250 °C (contraction).

$C_{30}H_{26}ClN_3O_4\ 0\,05\,H_2O$ (528·9)
Calc. C 68·13 H 4·97 Cl 6·70 N 7·94 O 12·25 %
Found C 68 27 H 5 05 Cl 6·74 N 8 05 O 12·51 %

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