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Synthesis, ^{1}H-NMR, Mass and Electronic Absorption Spectra of 4-(1-Alkylbenz[cd]indol-2-ylidene)-2,5-cyclohexadien-1-ylidenepropanedinitriles

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ABSTRACT

A series of variously substituted 4-(1-alkylbenz[cd]indol-2-ylidene)-2,5-cyclohexadien-1-ylidenepropanedinitriles has been synthesised, yielding unexpected substitution products. The postulated structures of these dye systems are confirmed by ^{1}*H-NMR and mass spectroscopy. The substitution pattern as well as their influence on the electronic absorption spectra is discussed on the basis of variable-electronegativity PPP-CI calculations.*

1 INTRODUCTION

Dyes containing the benz[cd]indole moiety are well known to show generally long electronic absorption wavelengths. Thus systems such as substituted 2-(4-aminophenyl)-1-alkylbenz[cd]indolium cations **1** give violet to blue shades on acrylic fibres, examples of which have been referenced.[1-5] On the other hand, a recent paper[6] has described some near-IR dyes, among them **2** and **3**, which are closely related to Bindschedler's Green and Neutral Red, respectively, but absorb at much longer wavelengths. In a straightforward analogy, one could assume that replacement of the dialkylamino group by the dicyanomethylene group in **1** would yield similar bathochromic shifts. The subsequently neutral dye might then be suitable for hydrophobic fibres such as polyester, possibly giving green shades.

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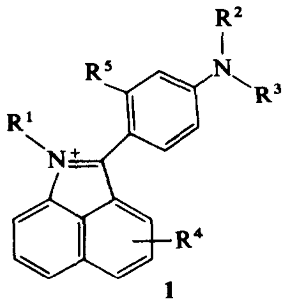
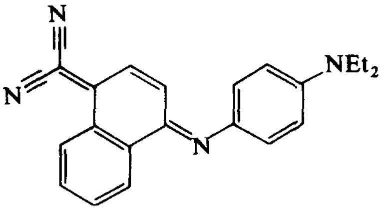


1



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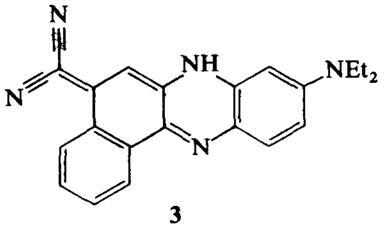


3

This present paper reports on the synthesis of a series of the title compounds, exhibiting unexpected substitution reactions, which will be interpreted on the basis of frontier MO arguments. The confirmation of their substitution pattern is based on ^{1}H-NMR and mass spectroscopy, discussion of their electronic absorption spectra derived from SCF-CI calculations and the perturbational MO method.

2 SYNTHESES

The reaction of 1-alkyl-2-(4-dialkylaminophenyl)-benz[cd]indolium cations **1** with malonodinitrile in the presence of triethylamine in ethanol exhibited some peculiarities, which are worth outlining. While addition of triethylamine to the ethanolic solution of **1** (in the absence of malonodinitrile) discoloured the blue solution only very slowly, the addition of malonodinitrile caused an immediate discolouration of the solution, whereas a reaction mixture of **1** and malonodinitrile in the absence of a base did not produce any colour change at all. Quick acidification of the above-mentioned discoloured solution with diluted hydrochloric acid led to recovery of the starting material **1**. However, heating the initially colourless reaction mixture mentioned first for several hours at reflux gave a recolouration of the solution, from which new dyes in low to moderate yields could be isolated.

The unusual behaviour of the reaction mixture gave reason to the assumption that the kinetically controlled first step in the reaction sequence

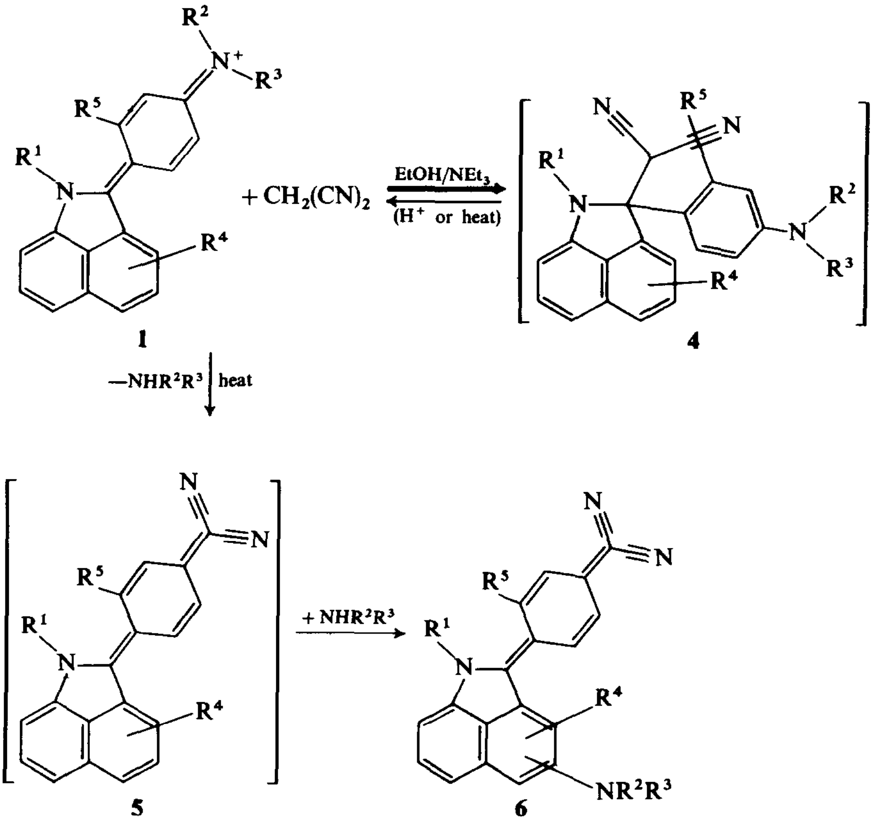


Fig. 1. Assumed reaction path for dyes **6**.

is the attack of the malononitrile anion at the 2-position of the benz[cd]indole moiety in **1** (Fig. 1), thus interrupting the chromophoric system at a crucial centre to give **4**. This reaction, however, can be reversed by acid or heat. This assumption is supported by frontier orbital considerations (Fig. 2): both charge and especially orbital control direct the nucleophilic malonodinitrile anion to the observed primary reaction centre.

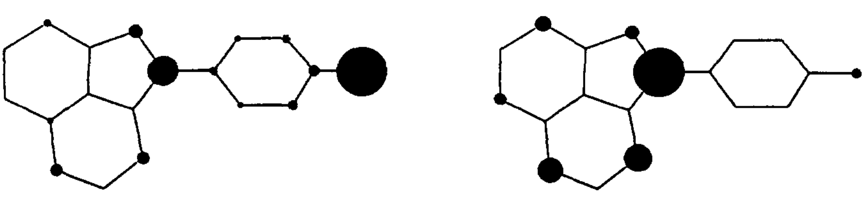
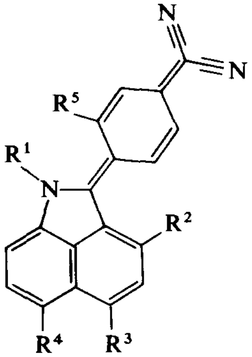


Fig. 2. Left: Net charges in ground state of **1** (R^{1-5} = H). (Full circles: positive charge, grey circles: negative charge.) Right: Virtual frontier-electron density of **1** (R^{1-5} = H).

Under thermodynamic control, however, the less probable attack of the anion at the desired dialkylamino-substituted position in **1** is followed by an irreversible loss of the dialkylamino group leading to **5**. Elemental analysis, ^{1}H-NMR and mass spectroscopic data of the purified products (discussed later) proved that the latter compound is not the final dye. The eliminated dialkylamino group always turned up elsewhere in the new dye system **6**, calling for an addition-oxidation mechanism not yet fully understood, except in the case of the 6-bromo derivative of **1**, where the bromo substituent was replaced by the dialkylamino group. The position of the dialkylamino groups in the dyes **6** is discussed in Section 3.2.



	R^1	R^2	R^3	R^4	R^5
6A	C_2H_5	H	$N(CH_3)_2$	H	H
6B	CH_3	H	H	$N(C_2H_5)C_2H_4OH$	H
6C	CH_3	$N(CH_3)_2$	$COOCH_3$	H	H
6D	CH_3	$N(C_2H_5)_2$	$COOCH_3$	H	H
6E	CH_3	$N(C_2H_5)_2$	CN	H	H
6F	CH_3	$N(C_2H_5)C_2H_4OH$	CN	H	H
6G	CH_3	$N(C_2H_5)_2$	CN	H	OCH_3

3 ^{1}H-NMR SPECTRA

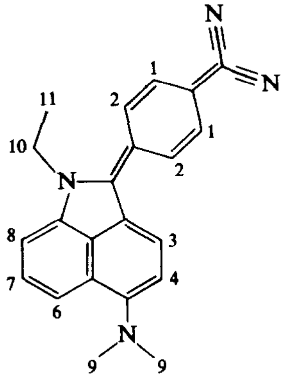
3.1 Method

In order to identify the correct structure of the dyes **6**, ^{1}H-NMR spectra were recorded on a Bruker-AM 360-MHz Fourier NMR spectrometer with perdeuterated dimethylsulfoxide as solvent and tetramethylsilane as internal standard.

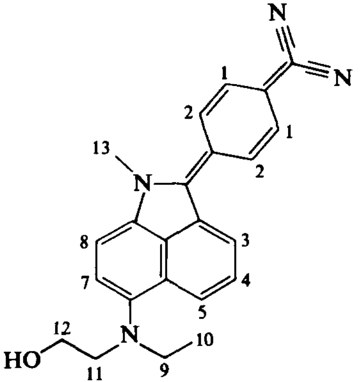
3.2 Results and discussion

The NMR signals of the protons are collated in Tables 1 and 2. A detailed comparison of the data of **6A** and **6B** (Table 1) does not provide a direct proof of the actual positions of the respective dialkylamino groups, since the peak pattern of the protons at positions 1 to 8 for both systems is very similar with respect to both shift and coupling. Therefore the correct substitution

TABLE 1
Proton Signals of Dyes **6A** and **6B** from 360 MHz–NMR Measurements in Perdeuterated Dimethylsulfoxide



6A



6B

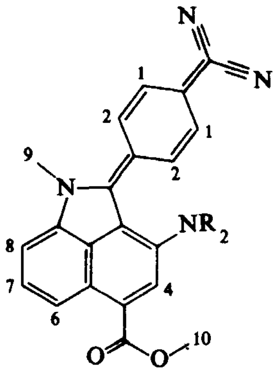
Proton	*Chemical shift (ppm) (Multiplicity*[a]*, Number)*	
	6A	**6B**
H–C (1)	6·96/6·98 (d, 2)	6·87/6·89 (d, 2)
H–C (2)	7·60/7·62 (d, 2)	7·73/7·75 (d, 2)
H–C (3)	7·71/7·74 (d, 1)	8·37/8·39 (d, 1)
H–C (4)	7·17/7·20 (d, 1)	7·73/7·75/7·77 (t, 1)
H–C (5)	—	9·11/9·13 (d, 1)
H–C (6)	8·76/8·78 (d, 1)	—
H–C (7)	7·67/7·69/7·71 (t, 1)	6·97/6·99 (d, 1)
H–C (8)	8·09/8·11 (d, 1)	7·85/7·87 (d, 1)
H–C (9)	3·08 (s, 6)	3·53 (m, 4[b])
H–C (10)	4·42/4·44/4·46/4·48 (q, 2)	1·16/1·18/1·20 (t, 3)
H–C (11)	1·39/1·41/1·43 (t, 3)	3·53 (m, 4[b])
H–C (12)	—	3·62/3·64/3·66 (t, 2)
H–C (13)	—	4·14 (s, 3)

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

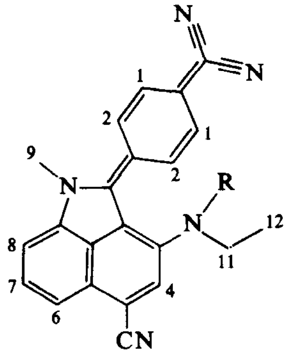
[b] H–C (9) and H–C (11) unresolved.

TABLE 2

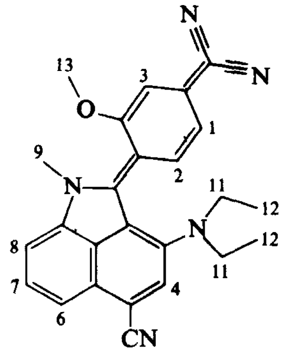
Proton Signals of Dyes **6C–6G** from 360 MHz–NMR Measurements in Perdeuterated Dimelthylsulfoxide



6C: R=$C^{11}H_3$
6D: R=$C^{11}H_2C^{12}H_3$



6E: R=$C^{11}H_2C^{12}H_3$
6F: R=$C^{13}H_2C^{14}H_2OH$



6G

Proton	*Chemical shift (ppm) (Multiplicity[a], Number)*				
	6C	**6D**	**6E**	**6F**	**6G**
H–C (1)	6·92/6·95 (d, 2)	6·88/6·91 (d, 2)	6·88/6·91 (d, 2)	6·90/6·93 (d, 2)	6·46/6·48 (d, 1)
H–C (2)	7·53/7·56 (d, 2)	7·51/7·54 (d, 2)	7·52/7·55 (d, 2)	7·50/7·53 (d, 2)	7·20/7·22 (d, 1)
H–C (3)	—	—	—	—	6·43 (s, 1)
H–C (4)	7·97 (s, 1)	8·01 (s, 1)	7·76 (s, 1)	7·78 (s, 1)	7·77 (s, 1)
H–C (6)	8·28/8·30 (d, 1)	8·29/8·31 (d, 1)	7·99/8·01 (d, 1)	7·98/8·00 (d, 1)	7·96/7·98 (d, 1)
H–C (7)	7·53/7·55/7·57 (t, 1)	7·55/7·57/7·59 (t, 1)	7·60/7·62/7·64 (t, 1)	7·60/7·62/7·64 (t, 1)	7·61/7·63/7·65 (t, 1)
H–C (8)	7·91/7·93 (d, 1)	7·92/7·94 (d, 1)	7·70/7·72 (d, 1)	7·72/7·74 (d, 1)	7·73/7·75 (d, 1)
H–C (9)	3·99 (s, 3)	3·99 (s, 3)	3·88 (s, 3)	3·88 (s, 3)	3·86 (s, 3)
H–C (10)	3·85 (s, 3)	3·89 (s, 3)	—	—	—
H–C (11)	3·06 (s, 6)	3·43/3·45/3·47/3·49 (q, 4)	3·45/3·47/3·49/3·51 (q, 4)	3·45/3·47/3·49/3·51 (q, 4[b])	3·43/3·45/3·47/3·49 (q, 4)
H–C (12)		1·13/1·15/1·17 (t, 6)	1·13/1·15/1·17 (t, 6)	1·13/1·15/1·17 (t, 3)	1·16/1·18/1·20 (t, 6)
H–C (13)		—	—	3·45/3·47/3·49/3·51 (q, 4[b])	3·76 (s, 3)
H–C (14)		—	—	3·58/3·60/3·62 (t, 2)	

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

[b] H–C (11) and H–C (13) unresolved.

pattern for **6A** could only be ascertained indirectly by comparing its UV-VIS spectral data with those of **6B** (see Section 5.2), which was prepared from the 6-bromo derivative of **1** (R^1 = Me, R^2 = Et, $R^3 = C_2H_4OH$, R^4 = 6-bromo). Further evidence for the suggested substitution position is given by the virtual frontier-electron density distribution in the intermediate **5** ($R^1 = R^4 = R^5$ = H) (Fig. 3), a measure for the selectivity of a nucleophilic attack, calculated analogously to the usual frontier-electron density, but based on the lowest unoccupied orbitals. It shows that attack of the dialkylamino group should mainly occur, apart from the (possibly yield-lowering) 2-position, at positions 3 and 5. However, position 3 can be excluded for reasons of the NMR shifts of the neighbouring protons (compare position 3 in **6A** with position 5 in **6B**, considering the upfield shift effect of the dialkylamino group on the further distant proton, exemplified by the shift difference of the protons at positions 3 or 8, respectively, in both **6A** and **6B**).

If position 5 in the starting material **1** is occupied by an acceptor function (i.e. R^4 = 5-COOMe or 5-CN), irreversible reaction of the dialkylamino group takes place at the next best position suggested by the virtual frontier-electron density distribution of the corresponding intermediate **5** (highly resembling the one in Fig. 3), which is position 3, resulting in the dye systems **6C**–**6G**. The NMR shift and coupling pattern of these systems given in Table 2 unambiguously prove the suggested substitution position: the proton at C(4) appears as a singlet, whereas the ABC system representing positions 6–8 as well as the AB system characterising positions 1 and 2 indicate no substitution in this area. An interesting detail is the distinct upfield shift of the proton at position 6 on going from **6A** to **6C**–**6G**, a peri-effect, which is in clear contrast to observations in 1-substituted naphthalenes compared to naphthalene itself.[7] Another factor of interest is the spectral identity of the two pairs of protons at C(1) and C(2) in **6C**–**6F** in spite of their different neighbourhood. Force-field calculations show that the twist angle between the benz[cd]indole and the dihydrophenylene moiety is only *c.* 10°, whereas the torsion angle between the dialkylamino group in the 3-position and the aromatic system amounts to about 40°, thus effectively minimising any neighbour-group anisotropy.

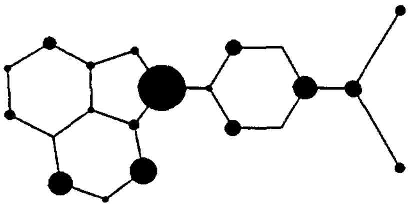


Fig. 3. Virtual frontier-electron density of **5** ($R^1 = R^4 = R^5$ = H).

4 MASS SPECTRA

The largest fragment peaks of the dyes **6A**–**6G** from mass spectroscopic measurements are presented in Table 3. Apart from the mass peaks of the molecular ions confirming their elemental analysis, the spectra show fragments, which are ascribed to the loss of substituents (or parts of them), including the dialkylamino group. The leaving group causing a mass difference of M-26, found in **6C**, **6E** and **6F**, is most probably C_2H_2, a well-known cleavage product from the paraquinone moiety, probably leading to the corresponding four-ring molecule ion. No peaks among the larger fragment ions could be found in any of the dyes indicating a loss of cyano groups (as HCN), contrary to the fragmentation pattern of the similar TCNQ radical cation.[8]

5 ELECTRONIC ABSORPTION SPECTRA

5.1 Method

Electronic absorption spectra were recorded in ethylacetate throughout. In all cases Beer–Lambert's law was valid in the concentration range 10^{-3} to 10^{-4}M.

5.2 Results and discussion

UV-VIS spectral data, given in Table 4, confirm the longwave absorption common to the benz[cd]indole dye systems. However, the green shades hoped for could only be found for **6B**, whereas the remaining systems exhibit even a slightly hypsochromic shift compared to their respective starting materials. However, a direct comparison is not reasonable in view of the unequal substitution pattern.

Viewing the spectral data of Table 4 in detail, the larger difference between $\lambda_{\max 1}$ of **6A** and **6B** is striking, taking into account that they are essentially only distinguished by the peripheral position of the dialkylamino groups. A PMO consideration based on the calculation of the 'unsubstituted' dye system confirms a strong bathochromic shift effect of a donor substitution at position 6, whereas position 5 is supposed to be relatively insensitive. The higher donor effect of an ethyl group at N(1) (in **6A**) instead of a methyl group (in **6B**) is comparably negligible. These findings are reflected in the calculations of the complete π systems (Table 4). The weak second absorption band found experimentally in the spectrum of dye **6A**, however, cannot be ascribed to one of the calculated π-π^* transitions.

TABLE 3

Largest Fragments of Dyes **6A–6G** from Mass Spectroscopic Measurements

Dye	*m/z*	*Relative abundance*	*Fragment*
6A	364	100	$[M]^+$
	349	5	$[M\text{-}CH_3]^+$
	335	16	$[M\text{-}C_2H_5]^+$
	320	6	$[M\text{-}N(CH_3)_2]^+$
	305	6	$[M\text{-}N(CH_3)_2-CH_3]^+$
	291	9	$[M\text{-}N(CH_3)_2-C_2H_5]^+$
6B	394	100	$[M]^+$
	365	17	$[M\text{-}C_2H_5]^+$
	363	20	$[M\text{-}CH_2OH]^+$
	348	4	$[M\text{-}CH_3-CH_2OH]^+$
	334	78	$[M\text{-}C_2H_5-CH_2OH]^+$
	319	10	$[M\text{-}CH_3-C_2H_5-CH_2OH]^+$
	291	9	$[M\text{-}CH_3-N(C_2H_5)C_2H_4OH]^+$
6C	408	100	$[M]^+$
	393	9	$[M\text{-}CH_3]^+$
	382	22	$[M\text{-}C_2H_2]^+$
	364	8	$[M\text{-}N(CH_3)_2]^+$
	349	5	$[M\text{-}N(CH_3)_2-CH_3]^+$
	338	6	$[M\text{-}N(CH_3)_2-C_2H_2]^+$
	305	8	$[M\text{-}N\ (CH_3)_2-COOCH_3]^+$
	279	7	$[M\text{-}N(CH_3)_2-COOCH_3-C_2H_2]^+$
6D	436	77	$[M]^+$
	421	100	$[M\text{-}CH_3]^+$
	410	6	$[M\text{-}C_2H_2]^+$
	407	16	$[M\text{-}C_2H_5]^+$
	364	7	$[M\text{-}N(C_2H_5)_2]^+$
	305	12	$[M\text{-}N(C_2H_5)_2-COOCH_3]^+$
6E	403	51	$[M]^+$
	388	100	$[M\text{-}CH_3]^+$
	377	4	$[M\text{-}C_2H_2]^+$
	374	7	$[M\text{-}C_2H_5]^+$
	331	13	$[M\text{-}N(C_2H_5)_2]^+$
	316	13	$[M\text{-}N(C_2H_5)_2-CH_3]^+$
	305	16	$[M\text{-}N(C_2H_5)_2-C_2H_2]^+$
	290	7	$[M\text{-}N(C_2H_5)_2-C_2H_2-CH_3]^+$
6F	419	28	$[M]^+$
	388	100	$[M\text{-}CH_2OH]^+$
	374	3	$[M\text{-}C_2H_5OH]^+$
	331	10	$[M\text{-}N(C_2H_5)C_2H_4OH]^+$
	316	6	$[M\text{-}N(C_2H_5)C_2H_4OH-CH_3]^+$
	305	12	$[M\text{-}N(C_2H_5)C_2H_4OH-C_2H_2]^+$
	290	5	$[M\text{-}N(C_2H_5)C_2H_4OH-C_2H_2-CH_3]^+$
6G	433	57	$[M]^+$
	418	100	$[M\text{-}CH_3]^+$
	402	35	$[M\text{-}OCH_3]^+$
	361	4	$[M\text{-}N(C_2H_5)_2]^+$
	330	6	$[M\text{-}N(C_2H_5)_2-OCH_3]^+$

TABLE 4
Experimental and Calculated Visible Absorption Maxima of Dyes **6A–6G**

Dye	*Experimental*			*Calculated*		
	$\lambda_{\max 1}$ *(nm)*	$\lambda_{\max 2}$ *(nm)*	*log* ε	$\lambda_{\max 1}$ *(nm)*	$\lambda_{\max 2}$ *(nm)*	f_{osc}
6A	577 (544[a])		4·66	604		2·04
		456	3·93		378	0·01
6B	751 (695[a])		4·02	742		1·54
		450	2·85		461	0·35
6C[b]	577[c]		3·94	607		1·63
		468	4·25		459	0·47
6D[b]	584[c]		3·84	607		1·63
		477	4·18		459	0·47
6E[b]	610[c]		3·90	617		1·60
		484	4·28		468	0·53
6F[b]	615[c]		3·89	617		1·60
		483	4·21		468	0·53
6G[b]	605[c]		3·89	614		1·61
		488	4·26		471	0·42

[a] Shoulder.
[b] Calculated values assuming a twist angle between diethylamino group and π system of 60°.
[c] Broad band.

The most surprising feature of the spectra of the remaining dyes is the fact that the longest wavelength band is extremely broad, extending to well over 700 nm in all cases, and consequently has an extinction coefficient about half the size of that of the second band, which in contrast shows a more normal bandwidth. This is not confirmed by the theoretical calculations. Force-field calculations on these systems, however, indicate that the dialkylamino group in the 3-position suffers a strong interaction with the phenylene moiety, leading to a twist angle between the benz[cd]indole plane and the dialkylamino group of well over 40°, and between the former and the phenylene plane of up to 10°. SCF-CI calculations, taking into account various twist angles for the corresponding bonds, revealed a strong dependence of the absorption maxima of the first two electronic absorptions, i.e. the larger the twist angle of the bond between the benz[cd]indole plane and the dialkylamino group, the shorter the wavelength of the first and the longer the one of the second absorption band. On the other hand, the oscillator strength f_{osc} of the first absorption is hardly affected, whereas f_{osc} of the second is highly sensitive to twisting of the dialkylamino group, increasing distinctly with a growing twist angle up to a maximum around 60°. These observations lead to the conclusion that the peculiarity of the absorption spectra of **6C–6G** may originate from a wide range of the twist-angle distribution in the dye solutions.

6 EXPERIMENTAL

6.1 General

Corrected melting points were measured on melting-point measuring equipment (by Dr Tottoli) from W. Büchi Glasapparatefabrik. The elemental and microanalytical department of Ciba-Geigy AG carried out the microelemental analyses. ^{1}H-NMR spectra were recorded on a Bruker AM-360, mass spectra on a Varian CH7, IR spectra on a Perkin-Elmer 983 spectrometer and electronic absorption spectra on a Perkin-Elmer Lambda 9 spectrophotometer at the physical department of Ciba-Geigy AG.

Calculations were performed on a Compac Deskpro 386/20e computer with a Brother HL-8e laser printer. For quantumchemical calculations a VEPPPM (Variable-Electronegativity Pariser Parr Pople Mataga) software package[9] was used, consisting of a graphical input program with an integrated 2D-geometry optimiser, the actual VEPPPM-CI calculation program and an output-interpretation program including an output-data bank. Laser printout of some results was performed by a Pizzazz Plus program from Application Techniques, force-field calculations were carried out by means of an ALCHEMY Molecular Modeling software package from Tripos Associates.

6.2 Syntheses

General procedure: 1 g (*c.* 2·5 mmol) of starting material (as zinc tetrachloride salt) was heated for 3–14 h with 0·4 g (6 mmol) malonodinitrile in 100 ml ethanol and 0·8 ml triethylamine as catalyst. After cooling, the precipitate was filtered and purified column-chromatographically on silica gel with hexane/ethylacetate (1:1).

4-(5-Dimethylamino-1-ethylbenz[cd]indol-2-ylidene)-2,5-cyclohexadien-1-ylidenepropanedinitrile (**6A**): From **1** (R^1 = ethyl, $R^2 = R^3$ = methyl, $R^4 = R^5$ = H), yield 50 mg (6%), m.p. 232–3°C. IR (KBr) (cm^{-1}): 3430(w), 2195/2185(s), 1600(s), 1520(s), 1427(s), 1393(s), 1376(s), 1305(s), 1267(s), 1191(s), 1045(s), 817(s), 749(s). Anal. calcd for $C_{24}H_{20}N_4 . 0{\cdot}1H_2O$ (366·3) C 78·71, H 5·56, N 15·30, O 0·44%. Found: C 78·74, H 5·67, N 14·95, O 0·3%.

4-(6-(Ethyl-2-hydroxyethylamino)-1-methylbenz[cd]indol-2-ylidene)-2,5-cyclohexadien-1-ylidenepropanedinitrile (**6B**): From **1** (R^1 = methyl, R^2 = ethyl, R^3 = 2-hydroxyethyl, R^4 = 6-chloro/6-bromo, R^5 = H), yield 450 mg (*c.* 54%), m.p. 276–8°C. IR (KBr) (cm^{-1}): 3440(w), 2185/2160(s), 1600(s), 1445(s), 1267(s), 1195(s), 1168(s), 1062(s). Anal. calcd for $C_{25}H_{22}N_4O.0{\cdot}1H_2O$ (396·3): C 75·77, H 5·65, N 14·14, O 4·44%. Found: C 75·82, H 5·88, N 13·95, O 4·35%.

4-(3-Dimethylamino-5-methoxycarbonyl-1-methylbenz[cd]indol-2-ylidene)-2,5-cyclohexadien-1-ylidenepropanedinitrile (**6C**): From **1** ($R^1 = R^2 = R^3 =$ methyl, $R^4 =$ 5-methoxycarbonyl, $R^5 =$ H), yield 90 mg (10%), m.p. 205–6°C. IR (KBr) (cm^{-1}): 3440(w), 2200(s), 1715(m), 1606(s), 1545(s), 1488(s), 1435(m), 1366(m), 1280(s), 1191(m), 1125(m), 1081(m), 810(m). Anal. calcd for $C_{25}H_{20}N_4O_2.0{\cdot}4H_2O$ (415·7): C 72·24, H 5·04, N 13·48, O 9·24%. Found: C 72·22, H 5·25, N 13·33, O 8·80%.

4-(3-Diethylamino-5-methoxycarbonyl-1-methylbenz[cd]indol-2-ylidene)-2,5-cyclohexadien-1-ylidenepropanedinitrile (**6D**): From **1** ($R^1 =$ methyl, $R^2 = R^3 =$ ethyl, $R^4 =$ 5-methoxycarbonyl, $R^5 =$ H), yield 120 mg (13%), m.p. 211–13°C. IR (KBr) (cm^{-1}): 3460(w), 2190/2178(s), 1717(m), 1605(s), 1543(s), 1486(s), 1452(m), 1358/1345(m), 1266(s), 1199(m), 1081(m), 867(m), 811(m), 772(m). Anal. calcd for $C_{27}H_{24}N_4O_2$ (436·5): C 74·29, H 5·54, N 12·83, O 7·33%. Found: C 74·49, H 5·90, N 12·71, O 7·24%.

4-(5-Cyano-3-diethylamino-1-methylbenz[cd]indol-2-ylidene)-2,5-cyclohexadien-1-ylidenepropanedinitrile (**6E**): From **1** ($R^1 =$ methyl, $R^2 = R^3 =$ ethyl, $R^4 =$ 5-cyano, $R^5 =$ H), yield 107 mg (12%), m.p. 261–2°C. IR (KBr) (cm^{-1}): 3440(w), 2200(s), 1600(s), 1549(m), 1488(s), 1454(m), 1286(s), 1196(s), 860(m), 803(m), 767(m). Anal. calcd for $C_{26}H_{21}N_5.0{\cdot}1H_2O$ (405·3): C 77·05, H 5·27, N 17·28%. Found: C 77·24, H 5·44, N 16·98%.

4-(5-Cyano-3-(ethyl-2-hydroxyethylamino)-1-methylbenz[cd]indol-2-ylidene)-2,5-cyclohexadien-1-ylidenepropanedinitrile (**6F**): From **1** ($R^1 =$ methyl, $R^2 =$ ethyl, $R^3 =$ 2-hydroxyethyl, $R^4 =$ 5-cyano, $R^5 =$ H), yield 70 mg (8%), m.p. 270–1°C. IR (KBr) (cm^{-1}): 3480(w), 2100(s), 1601(s), 1543(m), 1486(s), 1451(m), 1280(s), 1196(m), 1125(m), 869(m), 805(m), 765(m). Anal. calcd for $C_{26}H_{21}N_5O.0{\cdot}2H_2O$ (423·1): C 73·81, H 5·10, N 16·55, O 4·54%. Found: C 73·95, H 5·33, N 16·22, O 4·06%.

4-(5-Cyano-3-diethylamino-1-methylbenz[cd]indol-2-ylidene)-2-methoxy-2,5-cyclohexadien-1-ylidenepropanedinitrile (**6G**): From **1** ($R^1 =$ methyl, $R^2 = R^3 =$ ethyl, $R^4 =$ 5-cyano, $R^5 =$ methoxy), yield 60 mg (7%), m.p. 265–6°C. IR (KBr) (cm^{-1}): 3440(w), 2200(s), 1610(s), 1548(m), 1488(s), 1451(m), 1283/1264(s), 1230(m), 1144(m), 1123(m), 1026(m), 861(m), 764(m). Anal. calcd for $C_{27}H_{23}N_5O$ (433·5): C 74·81, H 5·35, N 16·15, O 3·69%. Found: C 75·03, H 5·46, N 15·78, O 3·54%.

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