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New Dye Systems Containing a C≡C Bond

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ABSTRACT

Preparation of the acetylenic analogues of triphenylmethane dyes (triphenylmethane dye ethynylogues. TPMDE) and studies on their colour and constitution are described. Derivatives of pyrylium dyes and merocyanine dyes have been obtained in the preparative studies of TPMDE. The absorption and emission spectral properties of bis(phenylethynyl) benzenes and the related anthracene derivatives are summarized, together with some donor–acceptor tolan derivatives; for the preparation of these, a novel one-stage conversion of the C=C bond to the C≡C acetylenic bond was found to be useful.

INTRODUCTION

We have previously studied the synthetic and structural chemistry of conjugated π-electron systems containing one or more C≡C bonds, e.g. cyclic acetylenes,[1] aryl-substituted poly-ynes[2] and dehydroannulenes.[3–5] The results of these studies have shown that conjugated triple bond systems turn out to be of an increasingly cumulenic nature, together with

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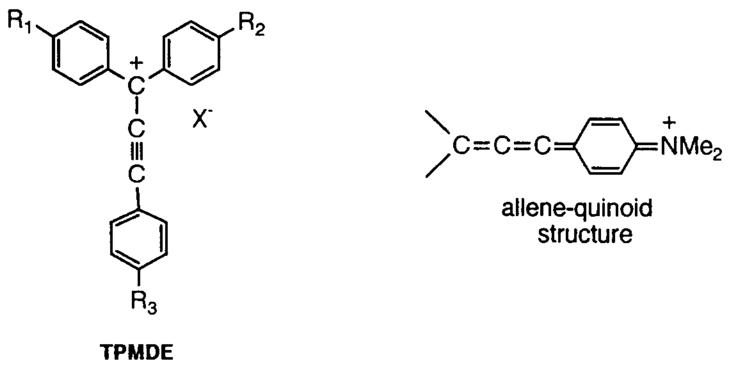


Fig. 1. Triphenylmethane dye ethynylogues (TPMDE) and allene–quinoid structure.

extended conjugation, and that full delocalization of the π-electrons is realized in the symmetric dehydroannulenes. Subsequently, as shown in Fig. 1, we were interested in the development of new dye systems incorporating the C≡C bond.

The unique properties of the C≡C bond introduced into a conjugated π-electron system is thought to be due to the allene–quinoid structure being incorporated into the system, and the advantages of the resulting chromophoric systems can be summarized as follows:

(1) an enhancement of the rigidity of the chromophoric system;
(2) an enhancement of the planarity of the chromophoric system;
(3) an extension of the π-conjugation.

On the other hand, some disadvantages must also be considered, i.e.

(1) a decrease in the stability, related to the increased unsaturation;
(2) a decrease of solubility in conventional organic solvents.

As described in the following, the disadvantage (1) proved to be advantageous from another point of view, i.e. it indicated the development of new dye systems. This review is concerned with:

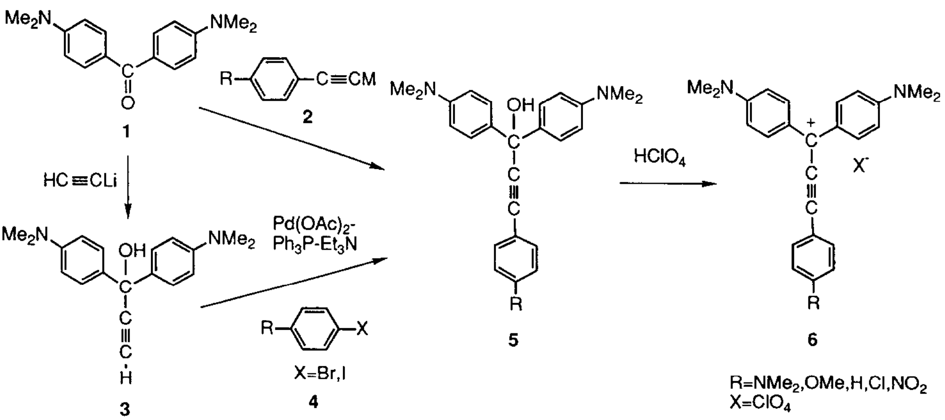
(1) the synthesis and absorption spectral properties of the triphenylmethane dye ethynylogues (TPMDE);
(2) the synthesis of pyrylium dyes from the 1,4-pentadiyn-3-ol system;
(3) near-infrared (NIR) absorbing TPMDE;
(4) the synthesis of new merocyanine dyes from the 1,1-diaryl-2 propyn-1-ol system;
(5) the synthesis and absorption/emission spectral properties of bis-(phenylethynyl)benzenes and the related anthracene derivatives:
(6) the synthesis of donor–acceptor tolan derivatives.

RESULTS AND DISCUSSION

Synthesis and absorption spectral properties of TPMDE[6–11]

Triphenylmethane dyes (TPMD) are a well-known class of dyes having a carbenium ion structure, and colour and constitution relationships within them have been widely investigated.[12–15] Griffiths and Pender[16] and Griffiths[17] showed that the observed absorption spectra of TPMD conform well with those calculated by the Pariser–Parr–Pople self-consistent filed configuration interaction molecular orbital (PPP–SCF–CI–MO) method. The TPMD system has a non-planar configuration, the steric hindrance of the *o,o*'-hydrogen atoms in the phenyl rings preventing conjugation over the whole system. We therefore initially prepared more planar dyes by introduction of one or more C≡C bonds into Crystal Violet (CV) or Malachite Green (MG), and investigated the relationship between the colour and the structure of these acetylenic analogues (ethynylogues) of TPMD, namely, TPMDE.[9,11] The preparation of *p*-substituted phenylacetylenes **2** (M = H) was the first step in the synthesis of dyes TPDME, and was performed by several methods.[10] Dyes **6** were obtained by acid treatment of the aryl-substituted acetylenic alcohols **5** prepared by nucleophilic addition of compound **2** to benzophenone derivatives such as Michler ketone **1**, or, as an alternative method, the acetylenic alcohols **5** were prepared by the Pd(II)-catalysed reaction of the ethynylated benzophenones **3** with halobenzenes **4** (Scheme 1).

Although the yields by the latter method were not always superior to those by the former, the nitro derivatives could be obtained only by the latter method. Dyes **6** (*X* = ClO_4) were isolated as stable deeply coloured crystals and their absorption spectral properties are listed in Table 1. It is



Scheme 1

evident that the first absorption bands show a red shift related to the increase in the electron-withdrawing nature of the *p*- substituents, and that the second bands show a red shift related to the increase in the electron-donating nature of the *p*-substituents. A good linearity was observed between the frequency of the bands and the McDaniel–Brown substituent coefficients; a similar tendency was found with the TPMD series.

The first absorption bands correspond to a one-electron transition from the HOMO to the LUMO level having a transition moment along the *x*-axis, whereas the second absorption bands, from NHOMO (next HOMO) to the LUMO level, have a transition moment along the *y*-axis. The observed tendency, e.g. electron-withdrawing substituents in the *p*-position which bring about bathochromic shifts, can then be rationalized. The results also suggest that the dyes belong to a typical non-alternant hydrocarbon system having efficiency charge distribution and an allene–quinoid structure.[8]

TABLE 1

Absorption spectra of monoethylogues **6**

R	*Experimental*[a]		*Calculated*[b] λ_{max} *(nm)* *(f)*[c]	*Transition direction* *(θ)*
	λ_{max} *(nm)*	$10^{-4}\varepsilon$ $(dm^3\,mol^{-1}\,cm^{-1})$		
NO_2	713	8·18	659 (1·37)	180 (*x*)
	494	3·01	450 (1·24)	−90 (*y*)
Cl	695	9·00	— —	—
	498	3·36	— —	—
H	688	10·10	641 (1·35)	180 (*x*)
	493	3·62	448 (1·10)	−90 (*y*)
OMe	680	10·30	632 (1·33)	0 (*x*)
	530	4·26	468 (1·22)	−90 (*y*)
NMe_2	663	13·10	624 (1·30)[d]	0 (*x*)
			505 (1·37)	90 (*y*)
			666 (1·64)[e]	180 (*x*)
			611 (1·22)	90 (*y*)

[a] Solvent CH_2Cl_2.

[b] Calculated by PPP–CI method with variable β approximation. Griffiths standard parameter sets (see Refs 16 and 17) were used.

[c] Oscillator strength.

[d] Values of Z 2·0, ionization potential (IP) 25·3 eV, and γ_{rr} 17·44 eV for nitrogen atom in the 4'-position were used.

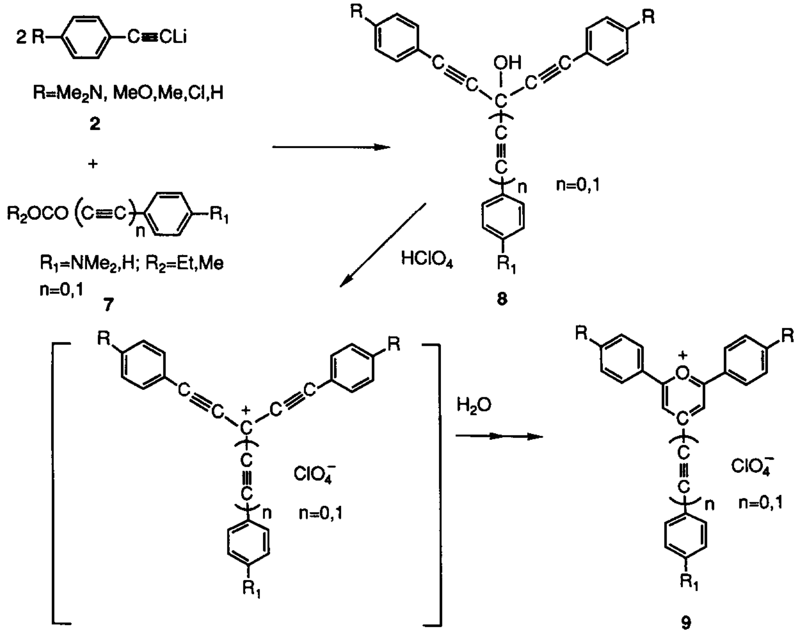
[e] Values of Z 1·66, IP 12·70, and γ_{rr} 17·44 eV for all nitrogen atoms were used.

Synthesis of pyrylium dyes from the 1,4-pentadiyn-3-ol system[18,19]

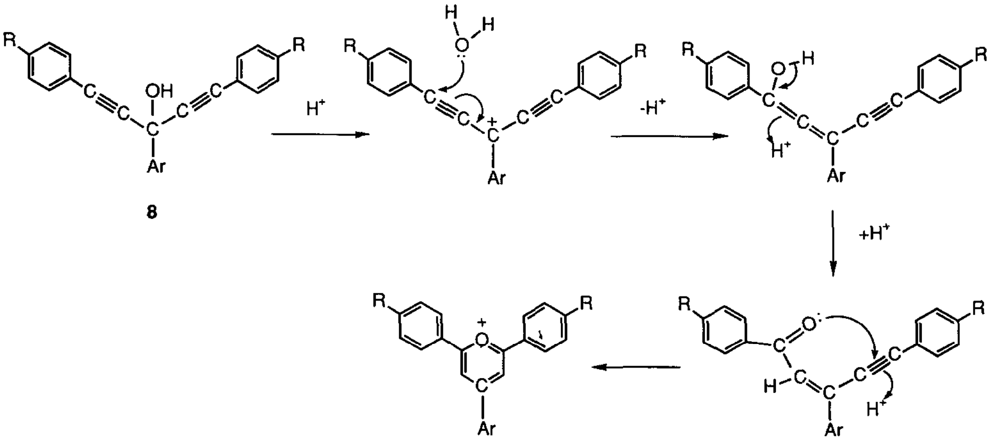
As a further extension of the work on TPMDE, we attempted to synthesize bis- and/or tris-ethynylogues to obtain further insight into the introduction of the acetylenic bond into the TPMD system. As shown in Scheme 2, the acetylenic alcohols **8** obtained by the reaction of the *p*-substituted phenyl acetylides **2** with the ester derivatives **7** were treated with perchloric acid to give deeply coloured compounds. Structural elucidation of the dyes by ^{1}H NMR, MS, IR and elemental analyses indicated that the dyes obtained were pyrylium salts (**9**). Scheme 3 shows a feasible reaction mechanisms involving ring closure after (rapid) Meyer–Schuster rearrangement of the labile cation yielded from **8** by the acid. Interestingly, the reaction proceeded more easily when the electron-donating nature of the *p*- substituent increased (Me_2N > MeO > Me > H > Cl). More recently, unsubstituted bis- and tris-ethynylogues were prepared *in situ* by the super acid treatment of the corresponding acetylenic alcohols.[20]

Near-IR absorbing TPMDE[8]

It is of current interest to develop new dye systems with absorption beyond λ_{max} > 700 nm as photo-recording materials or functional dyes, subsequent to the development of diode laser systems (especially

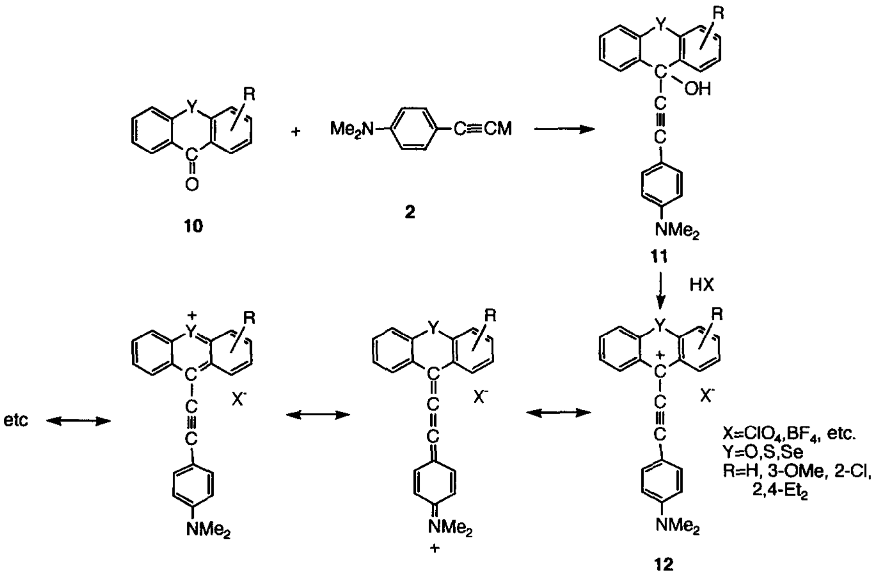


Scheme 2



Scheme 3

Al–Ga–As) which emit light from 780 to 830 nm. Many dye systems have been proposed, such as NIR absorbing dyes including polymethine, phthalocyanine, donor–acceptor substituted azo, naphthoquinone, anthraquinone, bridged polymethine, indophenol and charge transfer (CT) dyes.[20–26] On the basis of these trends, we have attempted to develop new NIR dyes by molecular design, resulting in compounds showing a bathochromic shift as a result of enhancement of planarity, by ring closure or bridging, or by extension of the π-conjugation. As a conse-



Scheme 4

quence, the following systems were the target dyes and we briefly discuss the results below.

Xanthenylium, thio- and selenoxanthenylium dye ethynylogues[8,27,28]

To elucidate more clearly the bridging effect in relation to increase in the planarity of the dye system, and the influence of the hetero atoms on the absorption spectral properties, we initiated investigations into such dye systems. As outlined in Scheme 4, the synthesis of the dyes **12** was performed as follows: the metal acetylides **2** derived from ω-chloro- or ω-bromostyrene derivatives were added to xanthone, thio- and selenoxanthone or their derivatives **10** to afford acetylenic alcohols **11**, which yielded the corresponding dye ethynylogues **12** by treatment with acids.

As shown in Table 2, dyes **12** have their longest absorption maxima in the NIR (*ca.* 740–800 nm). With respect to the effect of the hetero atoms, bathochromic shifts of 30–40 nm were observed, related to the decrease in the electronegativity of the atoms. The dyes showed their first absorption bands in the NIR region, although they have relatively small π- conjugation. The results calculated by the PPP–MO methods using standard parameter sets[16,17] correlated well with the experimental data, as shown in Table 3.

It is apparent from the data that the first absorption bands of the dyes are based on a one-electron transition from the HOMO to the LUMO

TABLE 2
Colour and Absorption Spectral Data of Dyes **12**

Y	*X*	*R*	*Colour of crystals*	*CH_2Cl_2* λ_{max} *(nm) (log ε)*
O	ClO_4	H	Deep green	737 (4·86)
S	ClO_4	H	Brownish green	775 (4·94)
S	BF_4	H	Deep green	775 (4·92)
S	PF_6	H	Green	775 (4·95)
S	$PtCl_6/2$	H	Deep violet	775 (5·02)[a]
S	Pc[b]	H	Deep violet	775 (4·82)
S	TS[c]	H	Deep blue	775 (4·35)
S	ClO_4	3-MeO	Deep violet	745 (4·74)
S	ClO_4	2,4-Et_2	Deep violet	762 (4·91)
S	ClO_4	2-Cl	Deep violet	802 (4·89)
Se	ClO_4	H	Brownish green	802 (4·93)
Se	ClO_4	3-MeO	Green	755 (4·85)

[a] Solvent 2% DMSO–CH_2Cl_2.
[b] Picrate
[c] Tosylate.

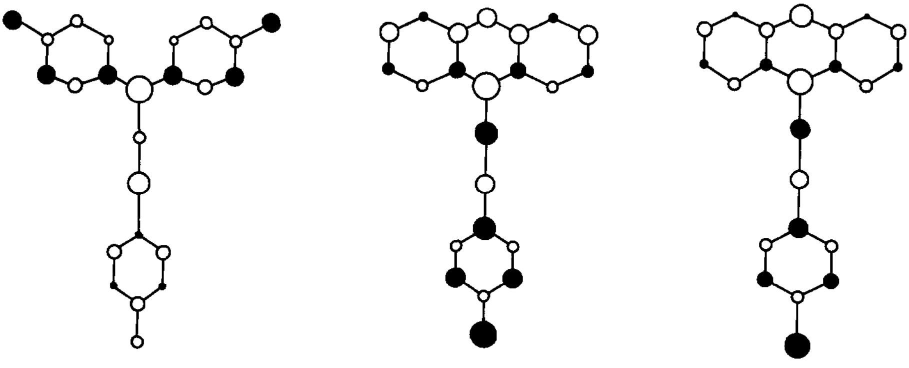
TABLE 3
Observed and Calculated Absorption Spectral Data of **12**

X	*R*	*Experimental* λ_{max} *(nm)* ($\varepsilon \times 10^{-4}$)	*Calculated* λ_{max} *(nm)* (f^{a})	*Transition direction (θ)*
O	H	737 (7·21)	705 (1·64)	90(*y*)
		371 (2·51)	415 (0·11)	180(*x*)
			382 (0·13)	−90(*y*)
S	H	775 (8·65)	731 (2·05)	−90(*y*)
		378 (2·30)	448 (0·15)	180(*x*)
			463 (0·006)	−90(*y*)
S	3-MeO	745 (5·44)	730 (2·05)	−91(*y*)
		427 (2·46)	434 (0·16)	−169(*x*)
			463 (0·03)	115(*y*)
S	2,4-Et$_2$	762 (4·62)	729 (2·04)	−90(*y*)
		390 (1·15)	447 (0·15)	179(*x*)
			464 (0·007)	−87(*y*)

[a] Oscillator strength.

level, the direction of the transition being along the *y*-axis and the red shift observed by the replacement of the oxygen atom by sulphur being adequately explained as a result of the destabilization of the HOMO energy level and the stabilization of the LUMO level.

Figure 2 shows the π-electron transition of the xanthenylium and thioxanthenylium dye ethynylogues (a closed circle represents decrease of π-electron density and an open circle represents increase of the density). The first absorption bands are based on the transition along the *y*-axis, showing a distinct difference from TPMDE (Fig. 2). Additionally, the



R = NMe$_2$ X = O X = S

Fig. 2. π-Electron density changes for the first electron transition. ○, Positive charge; ●, negative charge.

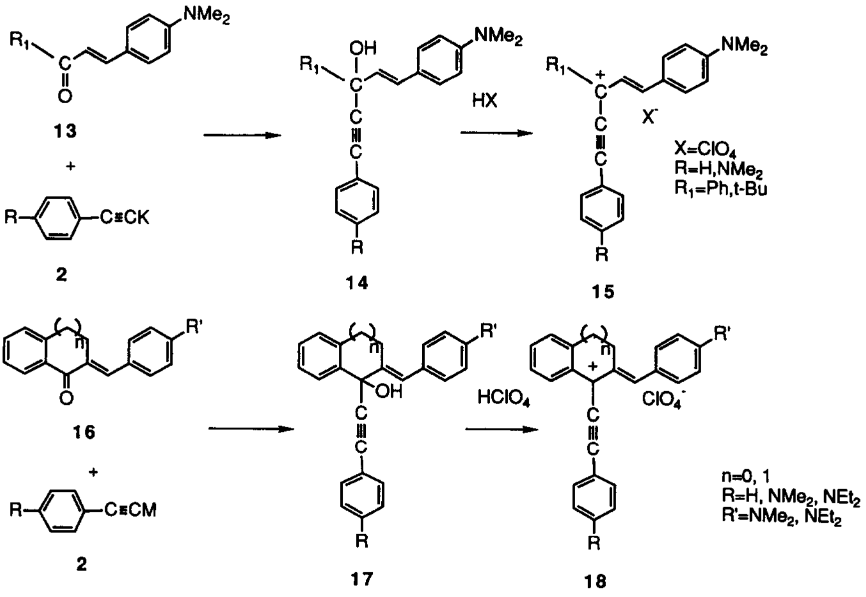
appreciable decrease of π-electron density on the nitrogen atoms, and increase on the oxygen or sulphur atoms indicates an intramolecular CT type absorption. X-Ray photoelectron spectroscopic results have suggested some differences of charge distribution in the ground state between xanthenylium and thioxanthenylium dye ethynylogues.[28]

MG ethynylvinylogues[29,30]

To obtain the bathochromic shift by extension of conjugation, we attempted to synthesize the MG ethynylvinylogues (**15** and **18**). Dyes **15** were prepared as shown in Scheme 5 from potassium phenylacetylides **2** and the derivatives **13** in a similar manner to that described above; the properties of **15** and **18** are shown in Table 4. As expected, the first absorption bands of dyes **15** appeared in the NIR region, as a result of the vinylene shift[31] by extension of conjugation; this result is in accord with values calculated using the PPP–MO method. Some bridged ethynylvinylogues **18** were also prepared, to obtain further bathochromic shifts in this class of dyes; the shifts were realized where R = H. Unfortunately, the preparation of the derivatives in which R is NMe_2 or NEt_2 has not yet been attained.

Fluorenylium dye ethynylogues[32,33]

This class of dyes was expected to give a bathochromic shift because of the increase in planarity by ring closure and the antiaromatic nature of



Scheme 5

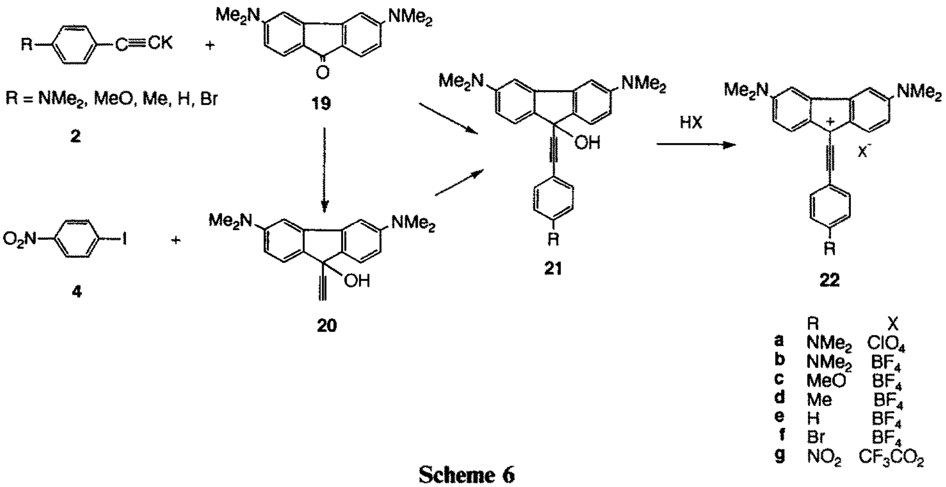
TABLE 4
Properties of **15** and **18**

R_1	*R*	*R'*	*n*	*Colour of crystals*	*CH_2Cl_2* *λ_{max} (nm) (log ε)*
15					
t-Bu	H	—	—	Violet	530 (4·68)
Ph	H	—	—	Dark violet	568 (4·47)
t-Bu	NMe_2	—	—	Dark violet	760 (4·42)
Ph	NMe_2	—	—	Dark violet	814 (4·67)
18					
—	H	NEt_2	0	Dark blue	615 (4·10)
—	H	NEt_2	1	Dark violet	603 (4·32)
—	H	NMe_2	1	Dark violet	605 (4·62)

the fluorenylium π-electron system. As shown in Scheme 6, dyes **22** were prepared from 3,6-bis(dimethylamino)fluorenone **19**[33] and compound **2**. In the case where R was NO_2, compound **21g** was prepared by a Pd(0)-catalysed coupling reaction between *p*-iodonitrobenzene **4** and ethynylalcohol **20**; dye **22g** was not stable enough to isolate in the solid state, but could be generated *in situ* from compound **21g**.

As indicated in Table 5, dyes **22** thus prepared showed their first absorption bands in the NIR region from 900 to 1100 nm, and the second bands above 700 nm; their spectral features were deduced from Barkers' fluorenylium dyes,[34] i.e. the non-ethynylogues of **22**, and were different from TPMDE **6**.

To our best knowledge, the NIR absorption up to 1096 nm is the first example of such long-wavelength absorption in TPMD. The batho-



Scheme 6

TABLE 5
Absorption Spectral Data of **22**

R	*X*	*Experimental*[a] λ_{max} *(nm)*	*Experimental*[a] *($\varepsilon \times 10^{-4}$)*	*Calculated*[b] λ_{max} *(nm)*	*Calculated*[b] *(f^c)*	*Calculated*[b] λ_{max} *(nm)*	*Calculated*[b] *(f^c)*	*Transition direction*[d]
NMe_2	ClO_4	956	(1·53)	841	(0·90)	975	(0·26)	0 (*x*) H → L
		718	(8·02)	585	(1·24)	674	(1·55)	90 (*y*) NH → L
NMe_2	BF_4	956	(1·70)	—	—	—	—	
		718	(9·37)	—	—	—	—	
MeO	BF_4	1 025	(1·40)	848	(0·93)	985	(0·27)	0 (*x*) H → L
		910	(0·99)	—	—	—	—	
		579	(5·41)	531	(1·12)	615	(1·39)	−90 (*y*) NH → L
Me	BF_4	1 040	(0·88)	—	—	—	—	
		920	(0·61)	—	—	—	—	
		559	(3·39)	—	—	—	—	
H	BF_4	1 052	(1·94)	856	(0·99)	996	(0·28)	0 (*x*) H → L
		927	(1·29)	—	—	—	—	
		551	(5·38)	501	(1·01)	570	(1·23)	90 (*y*) NH → L
Br	BF_4	1 056	(1·19)	—	—	—	—	
		931	(0·89)	—	—	—	—	
		558	(3·42)	—	—	—	—	
NO_2	CF_3CO_2	1 090	—	868	(0·97)	1 002	(0·29)	0 (*x*) H → L
		961	—	—	—	—	—	
		560	—	492	(1·04)	544	(1·18)	90 (*y*) NH → L

[a] IP = 12·7 eV, γ_{rr} = 6·08 eV, Z = 2·0 eV for N atoms. (See Refs 16 and 17).
[b] IP = 25·3 eV, γ_{rr} = 17·44 eV, Z = 2·0 eV for N atoms. Central C: 0·6–0·8 eV.
[c] Oscillator strength.
[d] H, HOMO; L, LUMO; NH, next HOMO.

chromic shifts of the first and the second absorption bands were increased as the electron-withdrawing nature of *p*- substituents increased, and in turn, hyposochromic shifts were observed for the third bands. The results calculated by the PPP–MO method support these observations (Table 5). A shown in Table 5, the calculated results using the modified parameters gave better results than those using standard parameters.[16,17] The first and second band sets are the vibronic components, and their average values correspond to the calculated values whose direction of transition is along the *x*-axis, whereas the direction of transition of the third bands is along the *y*-axis. The different nature of the change of π-electron density for the first electron transition from the xanthenylium dye ethynylogues series 12 is well represented in Fig. 3, e.g. it is large for diarylmethane units (R = H, NMe_2).

The pk_{R^+} values of the dyes were measured by spectrophotometric titration to estimate the relative stability of the dyes: pk_{R^+} value (10% CH_3CN–H_2O): **22** (R = Me_2N), 8·8; **22** (MeO), 8·4; **22** (Me), 7·8; **22** (H), 8·1; **22** (Br) 7·8; **6** (Me_2N) 9·5; **6** (H), 8·9; CV, 12·0; MG, 9·4. It is apparent that the fluorenylium dye ethynylogues are less stable than the corresponding TPMDE **6**, by about 1 pk_{R^+} unit, showing the largest value when R = NMe_2; the pk_{R^+} values of CV and MG ethynylogues were found to be less stable than those of CV and MG. It is possible that the antiaromatic nature of the fluorenylium ion or central cyclopentadienyl cation part has some influence on the absorption spectral parameter of the fluorenylium dye ethynylogues, affording such anomalous shifts. We therefore estimated the antiaromatic nature of the dyes by an antiaromatic index (*Q*), which is calculated from the total net π-electron charge of the cyclopentadienyl moiety as proposed by Tyutyulkov and

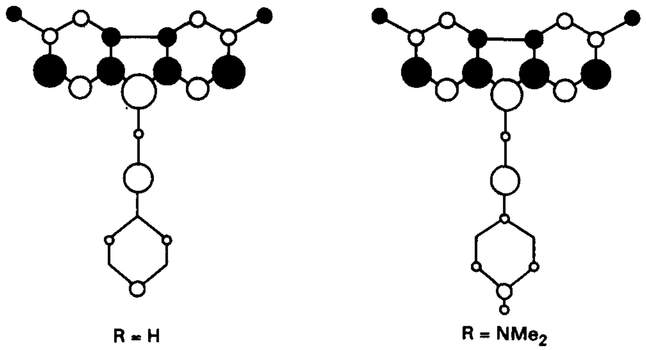


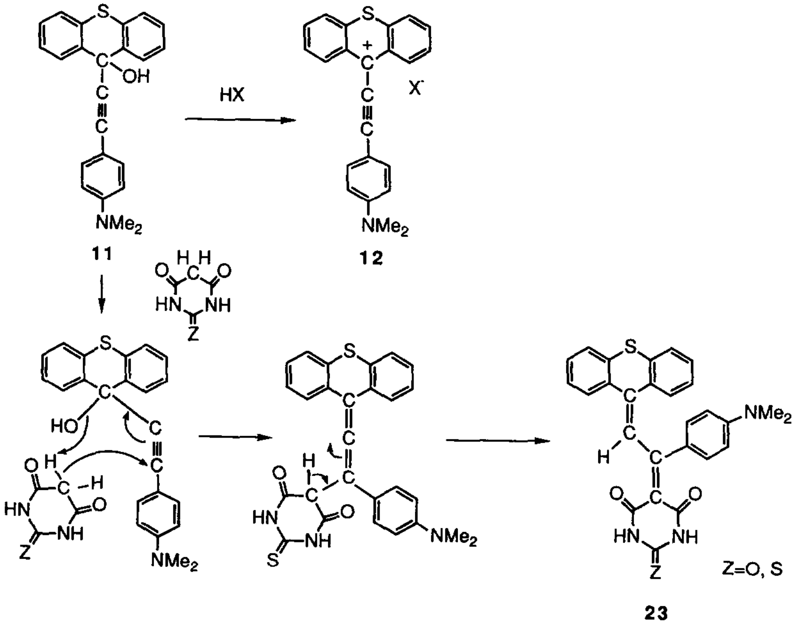
Fig. 3. π-Electron density changes for the first electron transition of **22**. ○, Positive charge; ●, negative charge.

Tasseva:[35] Q value ($Q = \sum(1 - q_i)$, q_i = π-electron density): R = Me_2N, +0·090; MeO, +0·102; H, +0·109; NO_2, +0·113.

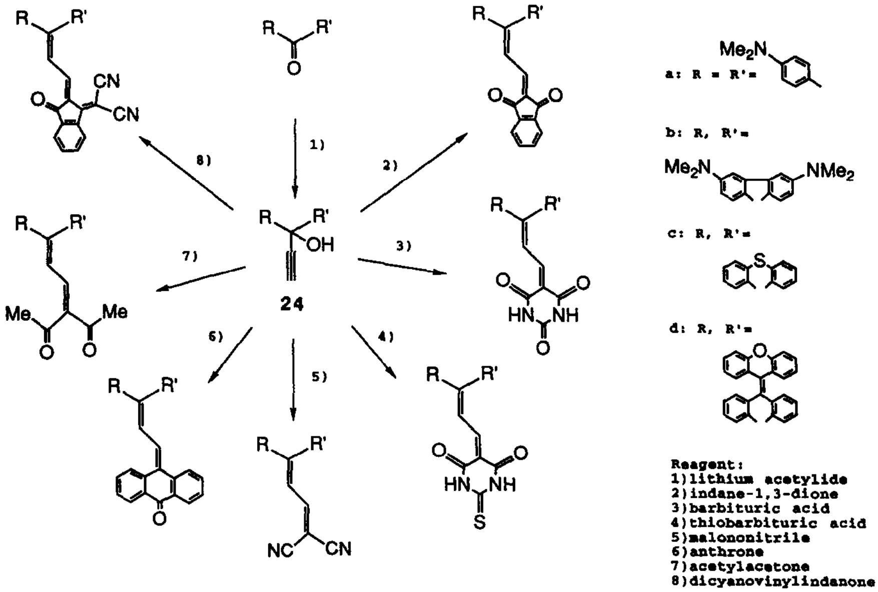
Accordingly, the bathochromic shift of the first absorption band caused by electron-withdrawing substituents was qualitatively estimated from the data. The results calculated by PPP–MO explain the anomalous shifts of the dyes as follows: a significant bathochromic shift was observed in fluorenylium dye ethynologues for two reasons: (1) both the symmetric LUMO (C_{2v}) of TPMDE, exhibiting relatively high coefficients (0·223–0·225) in the *o,o'*-position, is expected to be markedly lower in energy upon ring closure; (2) the bond order of fluorenylium dye ethynylogues increases between the *o*- and *o'*-position up the first excitation.

Synthesis of new merocyanine dyes from 1,1-diaryl-2-propyn-ol systems[36–40]

From reaction of compound **11** and barbituric acid or thiobarbituric acid red or reddish violet crystals were obtained. These were found not to be the expected cationic dyes, but new merocyanine dyes **23** consisting of an aryl-substituted donor acceptor butadiene system, whose structures were determined by instrumental analyses. As shown in Scheme 7, a plausible process for the reaction involves reaction of barbituric and thiobarbituric acids as a nucleophile.



Scheme 7

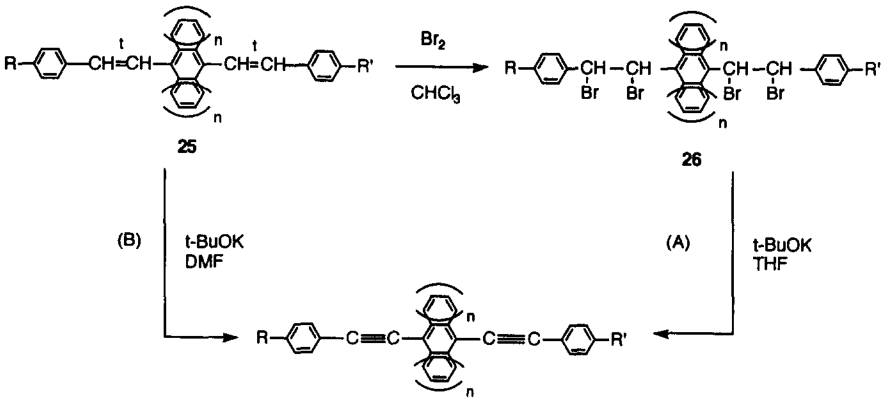


Scheme 8

We have explored and found the reactions of the acetylenic alcohols **24** with various kinds of nucleophiles, and have found that they yield new merocyanine dyes, as shown in Scheme 8.

Synthesis and absorption/emission spectral properties of bis(phenylethynyl)benzenes and anthracenes[41,42]

In the course of our studies on the development of new fluorescent and/or chemiluminescent probes for analytical and/or biological studies, we have prepared some heterocyclic fluorescent compounds, i.e. benzofuran, benzothiazole, pyrylium, and pyrimidopyrimidine derivatives, and investigated their analytical applications.[43–45] Moreover, we have studied the fluorescence characteristics of α, ω-di(1- and 9-anthryl)poly-ynes, and have found that both the excitation and emission maxima have regular relationships with the number of triple bonds.[46] We have further been interested in the synthesis of a series of bis(phenylethynyl)benzenes and bis(phenylethynyl)anthracenes, to examine systematically their absorption and emission spectral properties.[41] Compounds **25** (n = 0, 1) were synthesized by the Wittig and Arbusov–Horner reaction a a key step, and compounds **27** (n = 0; R = R' = MeO, Me, H and Br) and **27** (n = 1; R = R' = MeO, Me, H and Cl) could be prepared by an orthodox method, i.e. a bromination–dehydrobromination reaction (Scheme 9).



(A) n = o : R = R' = MeO, Me, H, Br
n = 1 . R = R' = MeO, Me, H, Cl

(B) n = 1 : R = R' = NEt$_2$, CN
n = 1 · R = MeO, R' = NO$_2$

Scheme 9

During the course of the preparative studies, we observed that compounds **27** ($n = 1$; R = R' = NEt$_2$ and CN; R = MeO, R' = NO$_2$) were unexpectedly obtained from the corresponding olefinic compounds **25** by treatment with an excess of *t*-BuOK in DMF at pressure; details of the reaction are given in the next section. Absorption and fluorescence spectral data in the longest-wavelength region are summarized in Table 6.

It is apparent that both electron-donating and electron-withdrawing groups in the *p*- position affect the absorption bathochromically, and a linear relationship between wavenumber and Hammett σ_p value was observed in the series **25** and **27**. Agreement between the transition energies calculated by the PPP–MO method and the experimental absorption maxima was satisfactory. A large bathochromic shift and appreciable substituent effect were observed in the emission spectra of a series of **27** ($n = 1$) compared with those of **27** ($n = 0$).

Examination of the chemiluminescence properties of **26** and **27** as a fluorescent enhancer was carried out to evaluate the peroxyoxalate chemiluminescence reaction system with a flow injection method previously developed by us,[47] and the results are given in Table 7.

A relative chemiluminescence intensity (RCI) value could hardly be detected in **25** ($n = 1$) and **27** ($n = 0$), whereas it was clearly observed in **25** ($n = 0$) and **27** ($n = 1$). It was apparent that the high RCI value (for the representative electron-donating substituent, NEt$_2$) in the anthracene series would reflect a high efficiency of the chemiluminescence reaction.

TABLE 6

Adsorption and Fluorescence Spectral Data of **25** and **27**[a]

R, R'	*Absorption spectra* λ_{max} *(nm) (ε/10⁴ dm³ mol⁻¹ cm⁻¹)*					*Fluorescence spectra* λ_{em} *(nm) (RFI[b])*			
	25 *(n = 0)*	**25** *(n = 1)*	**27** *(n = 0)*	**27** *(n = 1)*		**25** *(n = 0)*	**25** *(n = 1)*	**27** *(n = 0)*	**27** *(n = 1)*
NEt_2	407 (7·68)	437 (2·81)	— —	486 (5·28)	505 (5·19)	458 (0·92)	562 (0·03)	— —	545 (0·36)
NH_2	386 (6·92)	— —	— —	— —	— —	439 (0·58)	— —	— —	— —
MeO	367 (5·71)	415 (2·05)	331 (8·71)	450 (4·13)	471 (4·17)	454 (0·78)	564 (0·20)	364 (1·00)[c]	488 (0·80)
Me	360 (6·81)	411 (2·08)	324 (6·79)	441 (3·83)	466 (4·04)	418 (0·08)	560 (0·89)	354 (0·67)	479 (0·90)
H	355 (6·39)	410 (1·76)	320 (6·19)	438 (3·46)	461 (3·68)	410 (0·97)	550 (0·85)	366 (0·63)	474 (0·90)
Cl	— —	411 (2·05)	— —	441 (3·77)	466 (3·64)	— —	558 (0·91)	— —	479 (0·85)
Br	362 (7·45)	— —	326 (7·72)	— —	— —	421 (1·00^A)	— —	357 (0·71)	— —
CO_2Et	373 (6·18)	— —	— —	— —	— —	436 (0·82)	— —	— —	— —
CN	371 (6·81)	418 (2·28)	— —	450 (4·32)	477 (4·49)	433 (0·63)	560 (1·00^B)	— —	487 (0·93)
NO_2	395 (5·28)	431 (2·17)	— —	— —	— —	415 (0·03)	568 (0·78)	— —	— —
NO_2, MeO	— —	424 (2·05)	— —	455 (3·17)	— —	— —	570 (0·02)	— —	538 (0·09)
NO_2, Me	— —	431 (2·32)	— —	— —	— —	— —	565 (0·05)	— —	— —

[a] Measured in dioxane.

[b] Relative fluorescence intensity; each sample concentration was 10^{-7} mol dm^{-3}. RFI vs A or B; RFI, A : B 50 : 1.

[c] Measured relative to this value in **27** (*n* = 1 and 2).

TABLE 7
Relative Chemiluminescence Intensities of **25** and **27**

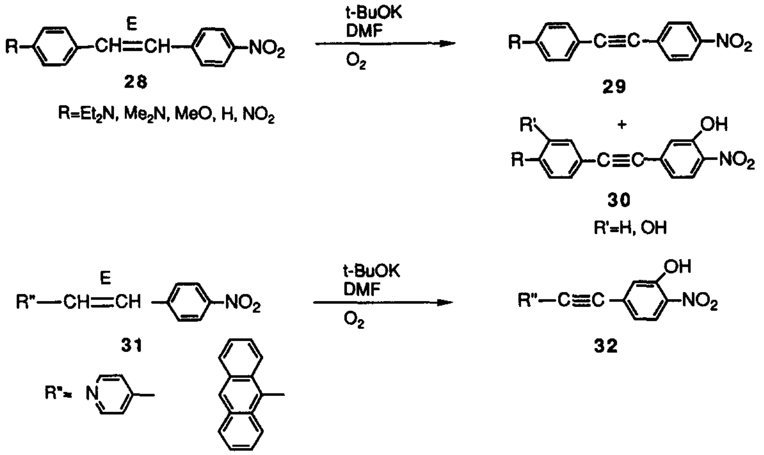
R, R'	*RCI*[a]			
	25 *(n = 0)*	**27** *(n = 0)*	**25** *(n = 1)*	**27** *(n = 1)*
NEt_2	111·38	—	nd	24·07
NH_2	10·69	—	—	—
MeO	1·24	nd	nd	7·15
Me	0·47	nd	nd	4·36
H	0·18	nd	0·09	3·19
Cl	—	—	nd	2·32
Br	0·16	nd	—	—
CO_2Et	0·10	—	—	—
CN	0·04	—	nd	1·32
NO_2	nd	—	nd	—
NO_2, MeO	—	—	nd	nd
NO_2, Me	—	nd	—	nd

[a] Relative chemiluminescence intensity; the RCI of 9, 10-diphenylanthracene was arbitrarily taken as 1·0.
nd: Non-detectable.

Synthesis of donor–acceptor tolan derivatives[48–50]

In view of the recent development of laser technology, the search for new functional materials with nonlinear optical properties provides a new field in dyestuff chemistry.[51,52] Non-centrosymmetric crystals or organic molecules with high polarizability are promising candidates for nonlinear optics. Diphenylacetylene derivatives bearing a donor group at one end and an acceptor group at the other end are likely to exhibit optical nonlinearity.[53,54] As described above we found that aromatic acetylenic compounds were directly obtained from the corresponding ethylenic compounds without proceeding through the usual halogenation–dehydrohalogenation process.[48,49] For examination of the novel one-stage direct conversion reaction of an ethylenic bond into an acetylenic bond, we chose a *p*-nitrostyryl system **28** and **31** and are now exploring the scope and the limitation of this process. As shown in Scheme 10, some donor–acceptor diphenylacetylene **29, 30** and **32** were obtained from the corresponding stilbenes by this procedure, in which combination of an excess of *t*-BuOK and DMF is essential, and the presence of molecular oxygen is necessary. Interestingly, compound **28** ($R = NO_2$) was converted into the bisphenol **30** ($R = NO_2$, $R' = OH$).

The presence of electronic withdrawing substituent(s) (e.g. a nitro



Scheme 10

group) on the benzene ring(s) is necessary to achieve the conversion and direct hydroxylation to the *o*-position of a nitro group. The results of the measurements of SHG activity on some nitro diphenylacetylene derivatives prepared have, in part, been reported.[50] We have recently found that 1-(substituted phenyl)-4-(3-hydroxy-4-nitrophenyl)butadiynes, being the higher ethynylogue of **30**, were readily synthesized from the corresponding butadienes in a one stage reaction.[55] The scope and limitation of this are now being explored (Akiyama, S. *et al.*, unpublished).

CONCLUSION

We have prepared a series of dye systems containing acetylenic bonds in TPMDE and investigated their spectroscopic properties. In attempts to synthesize the bis- and tris-ethynologues of TPMD, a new preparative method was found, which gives the derivatives of pyrylium salts. The reaction of acetylenic alcohols (i.e. the precursors of TPMD monoethynologues) with several nucleophiles afforded merocyanine dye systems having an aryl-substituted donor–acceptor butadiene moiety. Novel NIR-absorbing TPMDE were obtained by intramolecular bridging, or by extension of conjugation on TPMDE. The results of the investigation on the colour and constitution correlation, as calculated by the PPP–MO method, are briefly summarized. The absorption/emission spectral properties of bis(phenylethynyl)benzene and anthracene derivatives are summarized, together with the newly found C≡C bond forming reaction which led to the systematic preparation of donor–acceptor tolan derivatives.

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