Triphenylmethane Dye Ethynologues with Absorption Bands in the Near Infrared[1]

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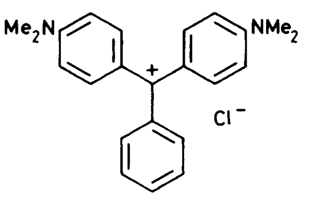
The first examples of triphenylmethane dye ethynologues (**9**) [4-(dimethylamino)phenylethynylxanthenylium, -thioxanthenylium, and -selenoxanthenylium perchlorates] absorbing in the near i.r. (up to 802 nm in CH_2Cl_2) have been synthesized by treatment of the corresponding alcohols (**8**) with acids, and their absorption spectral properties and chemical structures have been investigated and compared with the results of Pariser–Parr–Pople MO calculations. It has been shown that contribution of positive-charge-delocalized structures [resonance hybrids (**9**), (**9'**), and (**9''**)] is effective and independent of the counter ions.

Triphenylmethane dyes are a well known and important class of synthetic colouring materials. The acetylenic anlogues [*i.e.*, ethynologues (**1**) and (**2**)] of Malachite Green (**3**), Crystal Violet (**4**), and related compounds have been synthesized to investigate the effect of an acetylenic bond in such a dye system.



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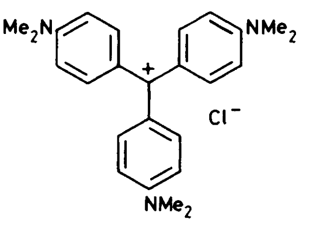

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It has been preliminarily reported that the introduction of an acetylenic bond into the resonating system of triphenylmethane dyes makes the cation moiety coplanar by releasing steric congestion between *ortho* hydrogen atoms of phenyl groups in the dyes and induces a strong bathochromic effect on the peak in the visible region of the spectra.[2] Here, the existence of a dimethylamino group on the benzene ring of a phenylethynyl moiety is very important. An enormous red shift (*ca.* 200 nm) observed in compound (**2a**) as compared with (diphenyl)(phenylethynyl)carbenium ion appears to be evidence for the contribution of the allene-quinoid and quinoid structures [(**2'**) and (**2''**)]. Moreover, it was anticipated that for the dye ethynologues a larger delocalization of the positive charge would be caused by replacement of the diphenyl part with a xanthene, thioxanthene, or selenoxanthene nucleus. These dyes can be expected to absorb in the near-i.r. region. Recently, near i.r. dyes showing absorption maxima beyond *ca.* 700 nm have been of interest for applications in such areas as optical and laser data storage technology.[3] In this paper, we report the synthesis of the first examples of triphenylmethane dye ethynologues (**9a**—**l**) absorbing in the near-i.r. region, and compare their light-absorption properties and chemical structures with Pariser–Parr–Pople MO (PPP-MO) calculations.

Results and Discussion

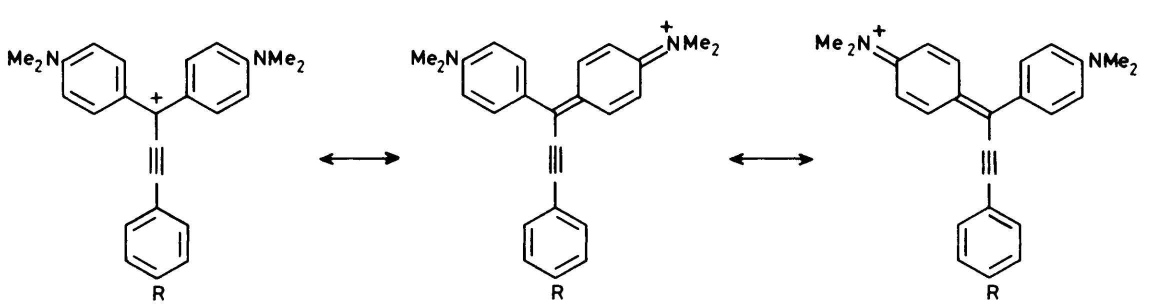
Synthesis of Dyes.—Triphenylmethane dye ethynologues (4-dimethylaminophenyl-xanthenylium, -thioxanthenylium, and -selenoxanthenylium compounds) have been synthesized according to the Scheme. Precursors (**8**) were prepared by the reaction of xanthones (**7**) with the metallated (4-dimethylamino)phenylacetylides (**6**) derived from β-chloro-4-dimethylaminostyrene (**5**).[4] Alcohols (**8**) were treated with the acids (perchloric acids, fluoroboric acid, or picric acid) to give dyes (**9**) as green or violet crystals bearing generally $\frac{1}{2}$—2 molecules of water (Table 1).

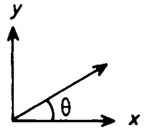
A solution of a dye (**9**) having low solubility in common organic solvents was stable in CH_2Cl_2 or benzene; however, in acetone, MeOH, or EtOH the colour faded gradually and the dye decomposed at room temperature under air. In connection with our studies on compounds (**9**), 9-(phenylethynyl)thioxanthen-9-ylium perchlorate (**10**), derivatives (**9b'**) and (**11**), and the leuco dye (**12**) were prepared and studied (Scheme). Fluoroborate (**9c**) is reduced by $NaBH_4$ in MeOH, giving the corresponding leuco dye (**11**) [$\lambda_{max.}$ 292 nm (CH_2Cl_2)], which regenerates dyes (**9**) under acidic conditions on aerial oxidation.

^1H *N.m.r. Spectra of Compounds* (**9**).—^1H N.m.r. data showed that the dimethylamino and aromatic protons shift to lower magnetic field than those of the corresponding alcohols (**8**) and that their shifts are almost independent of the cation species. These results seem important in a discussion of the structure of dyes (**9**).

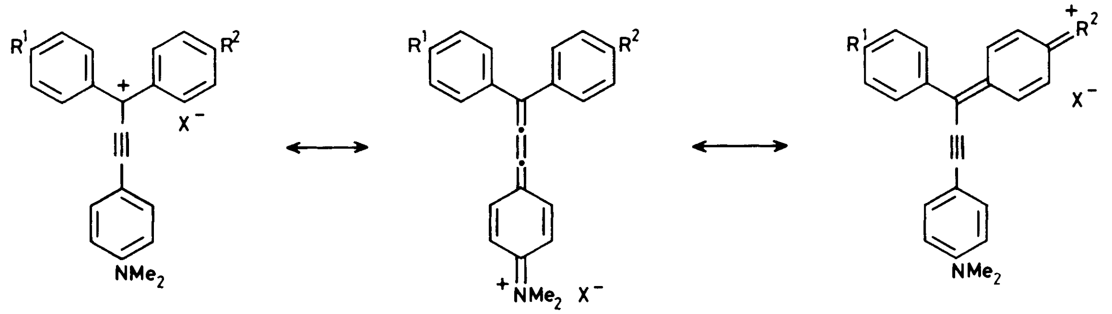
Visible Absorption Spectroscopic Properties.—Observations. Absorption spectra of the dyes [(**9**), (**10**, and (**11**)] were recorded in dichloromethane and the results are summarized in Table 2.

Remarkable shifts [Δλ (nm)] of the longest-wavelength absorption maxima between closely related dyes are exhibited in Table 3 and systematically illustrate the effects caused by the introduction of various substituents, an acetylenic bond, and/or a heteroatom (O, S, or Se) into the resonating system. First of all, large red shifts (70—80 nm) were observed by the insertion of an acetylenic bond into triphenylcarbenium ions (**13**), (**3**), and (**4**). The introduction of a dimethylamino group into ions (**13**), (**14**), and (**10**) yielded enormous bathochromic shifts





(1) **a**; R = H
b; R = OMe
c; R = NO_2
d; R = Cl
e; R = NMe_2



(2) **(2′)** **(2″)**

	R^1	R^2	X^-
(2a)	H	H	$CF_3CO_2^-$
(2b)	H	NMe_2	ClO_4^-

Table 1. Elemental analyses of new compounds

		Analysis (%)					
		Found			Requires		
Compound	Formula	C	H	N	C	H	N
(8a)	$C_{23}H_{19}NO_2$	80.7	5.5	4.1	80.9	5.6	4.1
(8b)	$C_{23}H_{19}NOS$	76.8	5.1	3.6	77.3	5.4	3.9
(8j)	$C_{23}H_{18}ClNOS$	70.3	4.9	4.1	70.5	4.6	3.6
(9a)	$C_{23}H_{18}ClNO_5\cdot\frac{1}{2}H_2O$	63.7	4.5	3.2	63.8	4.4	3.2
(9b)	$C_{23}H_{18}ClNO_4S\cdot\frac{1}{2}H_2O$	61.5	4.1	3.1	61.5	4.3	3.1
(9b′)	$C_{25}H_{22}ClNO_4S\cdot\frac{1}{2}H_2O$	63.1	4.8	3.15	62.9	4.7	2.9
(9c)	$C_{23}H_{18}BF_4NS\cdot\frac{1}{2}H_2O$	63.6	4.0	3.2	63.3	4.2	3.2
(9d)	$C_{23}H_{18}F_6NPS\cdot\frac{1}{2}H_2O$	55.9	3.8	2.8	55.7	3.9	2.8
(9f)	$C_{29}H_{20}N_4O_7S\cdot 2H_2O$	57.3	3.6	9.5	57.6	4.0	9.3
(9g)	$C_{30}H_{25}NO_3S_2\cdot 2H_2O$	66.2	5.6	3.0	65.8	5.3	2.6
(9i)	$C_{27}H_{26}ClNO_4S\cdot\frac{1}{2}H_2O$	63.8	5.1	2.8	64.4	5.4	2.8
(9j)	$C_{23}H_{17}Cl_2NO_4S\cdot 2H_2O$	54.0	3.7	2.7	54.1	4.1	2.8
(9k)	$C_{23}H_{18}ClNO_4Se\cdot\frac{1}{2}H_2O$	55.7	3.8	2.9	55.7	3.9	2.8
(9l)	$C_{24}H_{20}ClNO_5Se\cdot\frac{1}{2}H_2O$	55.2	4.0	2.7	54.8	4.0	2.7
(10)	$C_{21}H_{13}ClO_4S\cdot\frac{3}{2}H_2O$	59.6	3.5		59.5	3.8	
(11)	$C_{22}H_{15}ClO_5S\cdot H_2O$	59.3	3.6		59.4	3.85	
(12)	$C_{23}H_{19}NS$	81.2	5.7	3.8	80.9	5.6	4.1

Table 2. Visible absorption spectral data of dyes (**9**) and related compounds [in CH_2Cl_2; $\lambda_{max.}$/nm ($\varepsilon_{max.}$/l mol^{-1} cm^{-1})]

(**9a**)	249 (27 700), 313 (9 050), 371 (25 100), 737 (72 100)
(**9b**)	273 (52 700), 315 (13 500), 378 (23 000), 775 (86 500)
(**9b′**)	273 (53 600), 318 (11 600), 380 (21 400), 786 (94 100)
(**9c**)	274 (47 700), 316 (10 200), 381 (20 700), 775 (84 400)
(**9d**)	273 (50 900), 315 (11 800), 380 (21 800), 775 (88 800)
(**9e**)[a]	273 (86 100), 315 (21 600), 380 (30 800), 775 (105 000)
(**9f**)	273 (43 100), 315 (12 500), 380 (30 300), 775 (65 600)
(**9g**)	314 (22 500), 380 (6 370), 775 (22 400)
(**9h**)	285 (45 800), 322 (18 100), 370 (15 900), 427 (24 600), 745 (54 400)
(**9i**)	293 (13 200), 315 (13 300), 392 (18 900), 762 (81 700)
(**9j**)	278 (42 000), 322 (9 800), 385 (14 000), 802 (62 000)
(**9k**)	276 (33 100), 317 (10 600), 387 (18 400), 802 (84 300)
(**9l**)	280 (34 000), 315 (10 800), 427 (24 700), 755 (71 600)
(**10**)	289 (47 300), 396 (19 100), 445 (17 700), 510 (8 560), 543 (13 600), 586 (11 900)
(**11**)	275 (35 000), 292 (24 600), 392 (21 000), 492 (12 300), 572 (30 600), 609 (49 700)
(**12**)	292 (33 800)

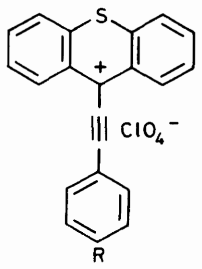
[a] In CH_2Cl_2-DMSO (50:1 v/v).

Table 3. Shifts of absorption spectra of dyes[a]

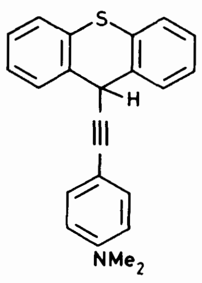
		Shifts[e] in nm from									
Dye	$\lambda_{max.}$/nm	(**13**)	(**14**)	(**4**)	(**10**)	(**3**)	(**1a**)	(**2a**)	(**2b**)	(**9a**)	(**9b**)
(**13**)[b]	429										
(**14**)	504	75									
(**4**)	584					−37					
(**10**)	586		82								
(**11**)	609		105		23						
(**3**)[c]	621	192									
(**1e**)	663			79			−25		−64		
(**1a**)	688		84			67					
(**2a**)	705		201								
(**2b**)	727							22			
(**9a**)	737							32			
(**9b**)	775				189			70		38	
(**9b′**)	786				200			81		49	11
(**9k**)	802							97			27
(**15**)[d]	814								87		

[a] In CH_2Cl_2. [b] In FSO_3H-SbF_5; G. A. Olah, C. U. Pittman, Jr., R. Waack, and M. Doran, *J. Am. Chem. Soc.*, 1966, **88**, 1488. [c] In 98% acetic acid; C. C. Barker and G. Hallas, *J. Chem. Soc.*, 1961, 1529. [d] Ref. 5. [e] Red shifts are given positive values, blue shifts negative ones.

(190—200 nm) in the corresponding products (**3**), (**2a**), and (**9b**). Meanwhile, it was found that the insertion of an ethylenic bond into (**2b**), *e.g.* compound (**15**),[5] gave an enormous red shift of 87 nm. Shifts of 25 nm in (**1a**) and 64 nm in (**2b**) relative to (**1e**) can be easily explained by stabilization due to the degeneracy of the HOMO in (**1e**) as well as in (**4**) relative to (**3**). The presence of the heteroatom induced marked red shifts relative to compounds (**14**) and (**2a**), particularly in the cases of S [(**10**), 82 and (**9b**), 70 nm] and Se [(**9k**), 97 nm], which are probably due to both an increase of coplanarity and the extended conjugation of the dye system. In the series (**9a**), (**9b**), and (**9k**), the pronounced red shifts were clearly observed with a decrease in electronegativity [O (3.5), S (2.5), and Se (2.4)]. As shown in Table 2, it is noted that the dyes have large molar absorption coefficients, the absorption wavelengths of (**9b**—**g**) are independent of the counter ion, and there are obviously substituent effects on the thio- and seleno-xanthenyl nuclei. The chloro dye (**9j**) shows a shift to longer wavelength (802 nm), while the dyes (**9h**), (**9i**), and (**9l**) give blue shifts based on the corresponding parent compounds. Replacement of the Me_2N group by Et_2N brings about a colour change, corresponding to a bathochromic shift of *ca.* 10 nm [see (**9b′**)].



(10) R = H
(11) R = OMe



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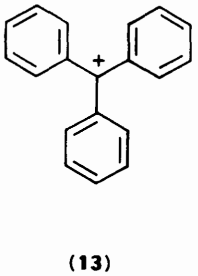

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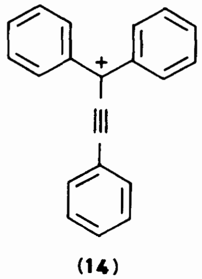

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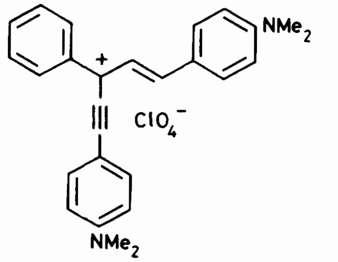

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*MO Calculations.**—The structural conversion of compound (**3**) into dye (**1a**) results in a bathochromic shift of the two visible bands from 621 and 428 nm to 688 and 493 nm, respectively. These bathochromic shifts are well predicted by the PPP calculations ($\Delta\lambda$: 67 and 65 nm). Though the electron-density migration accompanying the first electronic excitation

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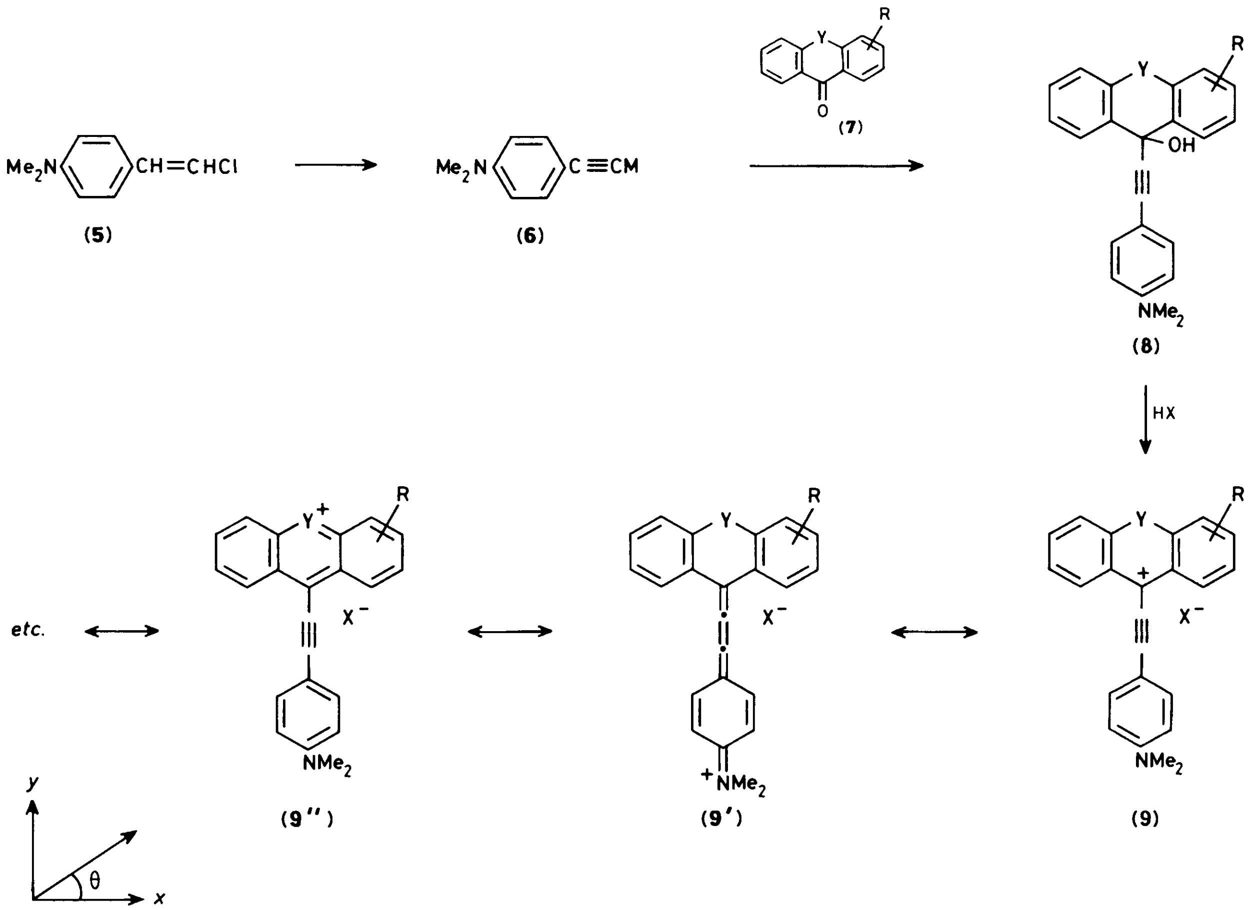
* The PPP method was used with variable β approximation. Electronic excitation energies were similarly refined by a configuration interaction (C.I.) treatment as described in previous papers.[6,7] The ionization potential (I.P.) and one-centre electron repulsion integral (γ_{rr}) for carbon atoms were as used elsewhere.[8-10] Values for the carbon atom affected by the ethyl group were 10.00 (I.P.) and 9.80 (γ_{rr}) eV. All input data for the two nitrogen atoms along the x axis in (**1**) were the same as those used in the calculations of triarylmethane dyes (I.P. 12.70 eV, γ_{rr} 6.80 eV, Z 1.5).[8,9] The values of I.P. 11.0 eV, γ_{rr} 6.08, and Z 1.5 for the nitrogen atom in dyes (**9**) were used. The simplest possible geometries and planar structures were assumed for the various molecules studied. The bond length of a triple bond is taken as 1.20 Å.



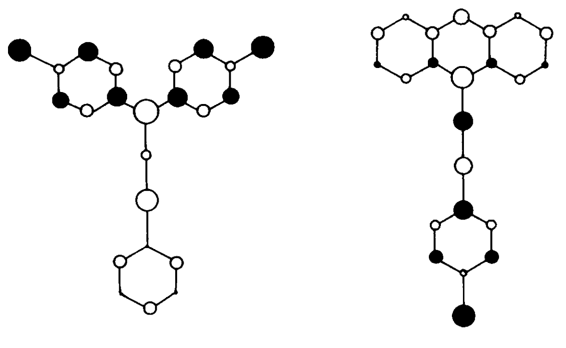
Scheme.

	Y	R	X$^-$
(9a)	O	H	ClO_4^-
(9b)	S	H	ClO_4^-
(9b')[a]	S	H	ClO_4^-
(9c)	S	H	BF_4^-
(9d)	S	H	PF_6^-
(9e)	S	H	$(PtCl_6^{2-})_{\frac{1}{2}}$
(9f)	S	H	picrate
(9g)	S	H	toluene-*p*-sulphonate
(9h)	S	3-OMe	ClO_4^-
(9i)	S	2,4-Et_2	ClO_4^-
(9j)	S	2-Cl	ClO_4^-
(9k)	Se	H	ClO_4^-
(9l)	Se	3-OMe	ClO_4^-

[a] Diethylamino derivative.

for dye (**1a**) indicated that this compound belongs to a typical alternate hydrocarbon system, there are pronounced increases in π-electron density at the bridging central carbon and the carbon of the acetylenic bond, as shown in the Figure. These positions play an important role in this chromophore, *i.e.* the expansion of the conjugated π-electron system was produced by contribution of the allene-quinoid structure (**2'**) and other resonance forms. The red shift produced by the acetylenic bond is similar to vinylene shifts (80—90 nm) observed for various dyes,[10] and is due to a decrease of transition energy between frontier orbitals by raising of the HOMO and lowering of the LUMO (Table 4).

According to the C.I. calculation on compound (**1**), the first and second absorption bands are calculated to correspond to one-electron excitation of HOMO $\longrightarrow$ LUMO (coefficients of C.I. 0.981—0.988) and NHOMO (next HOMO) $\longrightarrow$ LUMO (0.975—0.986), respectively. The direction of the first transition is along the *x* axis (*x*-band) and the second is along the *y* axis (*y*-band). The substituent effect on two absorption bands of dye (**1a**) is similar to that of compound (**3**),[8,9] *i.e.*



(**1a**) (**9b**)

Figure. Change of electron density of one-electron transitions responsible for the first absorption maxima of dyes (**1a**) and (**9b**). The magnitude of positive or negative charge is indicated by the open and filled circles, respectively

Table 4. Absorption spectra and PPP-MO calculations of compounds (**1a—d**) and (**2b**)

		Exp.					
Dye	R	$\lambda_{max.}$/nm	(10^{-4} $\varepsilon_{max.}$/ l mol^{-1} cm^{-1})	Calc. $\lambda_{max.}$/nm (f)^a	Transition direction (θ)	LUMO/eV	HOMO/eV
(**1a**)	H	688	(10.1)	641 (1.35)	180 (*x*)	−3.851	−7.808
		493	(3.62)	448 (1.10)	−90 (*y*)		
(**1b**)	OMe	680	(10.3)	632 (1.33)	0 (*x*)	−3.743	−7.748
		530	(4.26)	468 (1.22)	−90 (*y*)		
(**1c**)	NO_2	713	(8.18)	659 (1.37)	180 (*x*)	−4.119	−7.918
		494	(3.01)	450 (1.24)	−90 (*y*)		
(**1e**)	NMe_2	663	(13.1)	624 (1.30)^b	0 (*x*)	−3.645	−7.680
				505 (1.37)	90 (*y*)		
				666 (1.64)^c	180 (*y*)	−3.437	−7.328
				611 (1.22)	90 (*x*)		
(**2b**)		727	(8.51)	707 (1.88)	69 (*y*)	−3.985	−7.707
				437 (0.62)	−30 (*x*)		

[a] Oscillator strength. [b] Values of Z 2.0, I.P. 25.3 eV, and γ_{rr} 17.44 eV for nitrogen atom in the 4′-position of compound (**1e**) were used. [c] Values of Z 1.66, I.P. 12.70 eV, and γ_{rr} 17.44 eV for all nitrogen atoms were used.

Table 5. Absorption spectra and PPP-MO calculations for dyes (**9**)

			Exp.					
Dye	Y	R	$\lambda_{max.}$/nm	(10^{-4} $\varepsilon_{max.}$/ l mol^{-1} cm^{-1})	Calc. $\lambda_{max.}$/nm (f)^a	Transition direction (θ)	LUMO/eV	HOMO/eV
(**9a**)	O	H	737	(7.21)	705 (1.64)	90 (*y*)	−3.107	−6.785
			371	(2.51)	415 (0.11)	180 (*x*)		
					382 (0.13)	−90 (*y*)		
(**9b**)	S	H	775	(8.65)	731 (2.05)	−90 (*y*)	−3.306	−6.589
			378	(2.30)	463 (0.006)	90 (*y*)		
					448 (0.15)	180 (*x*)		
(**9h**)	S	3-OMe	745	(5.44)	730 (2.05)	−91 (*y*)	−3.258	−6.520
			427	(2.46)	463 (0.03)	115 (*y*)		
					434 (0.16)	−169 (*x*)		
(**9i**)	S	2,4-Et_2	762	(8.17)	725 (2.02)	−90 (*y*)	−3.257	−6.575
			392	(1.89)	464 (0.01)	94 (*y*)		
					444 (0.16)	177 (*x*)		

[a] Oscillator strength.

substitution with a donor group in the 4′-position causes a bathochromic shift of the *y*-band and a hypsochromic shift of the *x*-band. The substituent in the 4′-position of dye (**1a**), as well as (**3**), affects the LUMO more predominantly than the HOMO, due to the nodal properties of the HOMO in structure (**1a**). In calculation of the electron distribution in compound (**1e**), a different parameter set for one nitrogen atom on the 4′-position was used, as dye (**1e**) was no longer symmetrical relative to (**4**). Calculation using this parameter predicts hypsochromic shift of the first absorption band of (**1e**), relative to (**1a**), whereas calculation using identical parameters for the three nitrogen atoms, predicts a bathochromic shift. PPP-MO Calculations were then carried out on dyes (**9a**), (**9b**), (**9h**), and (**9i**) using general parameters (Table 5).[6,7]

The calculated bands for the longest wavelengths are reasonable for the experimental values, except for (**9h**). The first and second absorption bands (Table 4) are determined to be due to one-electron excitation of HOMO ⟶ LUMO (coefficients of C.I. 0.967—0.973) and HOMO ⟶ NLUMO (next LUMO) (0.756—0.908), respectively. The direction of first calculated bands of dyes (**9**) is along the long axis (the *y* axis), as expected. The second band of dyes (**9b**), (**9h**), and (**9i**) is regarded as the *x*-band of the third calculated band, since the oscillator strengths of the second calculated band are very small. However, the direction of the second band of the dye (**9a**) is along the *x* axis. The bathochromic shift produced by replacement of the oxygen atom of dye (**9a**) by a sulphur atom is well predicted by the PPP calculations (exp. 28 nm; calc. 26 nm). This replacement gives rise to a decrease in transition energy between frontier orbitals, and consequently the absorption of compound (**9b**) may shift to longer wavelength. The electron-density migration of dye (**9b**) accompanying the first electronic excitation indicates that this compound is a typical cyanine dye and that an effective expanse of conjugated π-electrons of dyes (**9**) occurs through an acetylenic bond (Figure).

It has been shown through this investigation that dyes (**9**) absorb in the near-i.r. and the contribution of positive-charge-delocalized structures [resonance hybrids (**9**), (**9′**), and (**9″**)] is effective and independent of the counter ions. These results compare well with the closely related dyes (**1**) and (**2**) and with MO calculations.

Experimental

All m.p.s. are uncorrected and measured on a Yanako micro melting point apparatus. I.r. spectra were obtained on Shimadzu IR 408 and JASCO IRA 810 spectrophotometers. N.m.r. spectra were measured on a JEOL JNM-FX 90Q instrument and chemical shifts are given as δ values with respect to TMS used as an internal standard. U.v. and visible spectra were obtained on Hitachi 200-10 and U3400 spectrophotometers.

Mass spectra were taken using a JEOL JMS-DX 303 mass spectrometers.

Synthesis of Compound (**8b**) [(**8**; R = H, Y = S)].—A mixture of β-chloro-4-dimethylaminostyrene (**5**) (2.5 g, 14 mmol) and Bu^{t}OK (14 g) in tetrahydrofuran (THF) (100 ml) was stirred at room temperature for 5 min under nitrogen and a solution of the ketone (**7**; R = H, Y = S) (2.40 g, 11 mmol) in THF (100 ml) was then added. The mixture was stirred for 30 min at room temperature and was poured into water (300 ml). The organic layer was extracted with benzene (150 ml × 2), and the extract was washed with water, and dried. Evaporation of the extract resulted in pale yellow crystals (3.11 g, 79%) and these were recrystallized from ether to give pure *compound* (**8b**), m.p. 133—135 °C (decomp.); $\nu_{max.}$(KBr) 3 410 (OH), 2 200 (C≡C), and 1 605 cm^{-1} (C=C); δ_H(90 MHz; $CDCl_3$; Me_4Si) 2.96 (6 H, s, NMe_2), 3.04 (1 H, s, OH), 6.62 (2 H, d, *J* 9 Hz, ArH), 7.23—7.55 (8 H, m, ArH), and 8.17—8.56 (2 H, m, ArH); e.i.-m.s. (*m/z*) 357 (M^+) for analytical data see Table 1. The following compounds were similarly prepared.

The *xanthene* (**8a**; R = H, Y = O), pale yellow crystals (77%), m.p. 59—161 °C (decomp.); $\nu_{max.}$(KBr) 3 545 (OH), 2 210 (C≡C), and 1 610 cm^{-1} (C=C); δ_H($CDCl_3$) 2.74 (1 H, s, OH), 2.96 (6 H, s, NMe_2), 6.60 (2 H, d, *J* 9 Hz, ArH), 7.12—7.52 (8 H, m, ArH), and 7.99—8.10 (2 H, m, ArH); e.i.-m.s. *m/z* 341 (M^+).

The *thioxanthene* (**8j**; R = Cl, Y = S), pale yellow crystals (23%), m.p. 110 °C (decomp.); $\nu_{max.}$(Nujol) 3 600 (OH), 2 210 (C≡C), and 1 610 cm^{-1} (C=C); δ_H($CDCl_3$) 2.92 (6 H, s, NMe_2), 3.08 (1 H, s, OH), 6.58 (2 H, d, *J* 9 Hz, ArH), 7.26—7.48 (7 H, m, ArH), and 8.07—8.25 (2 H, m, ArH); e.i.-m.s. (*m/z*) 391 (M^+).

The xanthene (**8b′**; R = H, Y = S; NEt_2 instead of NMe_2), thioxanthenes (**8h**; R = 3-OMe, Y = S), and (**8i**; R = 2,4-Et_2, Y = S), and selenoxanthenes (**8k**; R = H, Y = Se), and (**8l**; R = 3-OMe, Y = Se) were prepared according to the above method and used in the following reaction without purification.

Synthesis of the Thioxanthenylium Salt (**9b**).—Perchloric acid (60%; 1 drop) was added to a solution of compound (**8b**) (0.40 g, 1.1 mmol) in benzene (80 ml). The mixture was mixed for 1 h and the resulting precipitates were filtered off, washed with ether, and dried to give the *salt* (**9b**) as deep green crystals (0.43 g, 90%). An analytically pure sample (analytical data are in Table 1) was obtained by recrystallization from CH_2Cl_2–ether and had m.p. > 195 °C (decomp.); $\nu_{max.}$(KBr) 2 100 (C≡C) and 1 590 cm^{-1} (C=C); δ_H(CD_2Cl_2) 3.34 (6 H, s, NMe_2), 6.97 (2 H, d, *J* 9.5 Hz, ArH), 7.84—8.12 (8 H, m, ArH), and 8.82—8.93 (2 H, m, ArH); δ_C(CD_2Cl_2; Me_4Si) 41.4 (NMe_2), 107.8, 114.5, 127.4, 129.8, 130.4, 134.0, 135.4, 139.2, 141.0, 146.7, 147.0, and 156.4; f.a.b.-m.s. (*m/z*) 340 [($M - ClO_4$)$^+$]. The following salts were similarly prepared.

Salt (**9b′**), 30%; m.p. 201—203 °C (decomp.); δ_H(CD_2Cl_2) 2.35 (6 H, t, *J* 7 Hz, CH_2*Me*), 3.68 (4 H, q, *J* 7 Hz, C*H*$_2$Me), 7.02 (2 H, d, *J* 9.5 Hz, ArH), 7.90 (4 H, m, ArH), 7.95 (2 H, d, *J* 9.5 Hz, ArH), and 8.76 (4 H, m, ArH).

Salt (**9a**), 91%; m.p. 184—185 °C (decomp.); $\nu_{max.}$(KBr) 2 100 (C≡C) and 1 595 cm^{-1} (C=C); δ_H(CD_2Cl_2) 3.37 (6 H, s, NMe_2), 6.99 (2 H, d, *J* 9.5 Hz, ArH), 7.66—8.19 (8 H, m, ArH), and 8.38—8.49 (2 H, m, ArH); δ_C(CD_2Cl_2) 41.5 (NMe_2), 106.8, 107.6, 114.9, 119.3, 122.5, 127.9, 130.1, 139.5, 140.0, 145.4, 150.7, 155.1, and 157.0; f.a.b.-m.s. (*m/z*) 324 [($M - ClO_4$)$^+$].

Salt (**9c**), 84%; m.p. 195 °C (decomp.); $\nu_{max.}$(KBr) 2 100 (C≡C) and 1 605 cm^{-1} (C=C); δ_H(CD_2Cl_2) 3.34 (6 H, s, NMe_2), 6.98 (2 H, d, *J* 9.5 Hz, ArH), 7.85—8.14 (8 H, m, ArH), and 8.84—8.96 (2 H, m, ArH); f.a.b.-m.s. (*m/z*) 340 [($M - BF_4$)$^+$].

Salt (**9d**), 60%; m.p. > 225 °C (decomp.); δ_H(CD_2Cl_2) 3.33 (6 H, s, NMe_2), 6.97 (2 H, d, *J* 9.5 Hz, ArH), 7.88—8.10 (8 H, m, ArH), and 8.82—8.97 (2 H, m, ArH).

Salt (**9e**), 66%; m.p. > 300 °C.

Salt (**9f**), 88%; m.p. 148—150 °C; $\nu_{max.}$(KBr) 2 110 (C≡C), and 1 615 and 1 600 cm^{-1} (C=C); δ_H(CD_2Cl_2) 3.33 (6 H, s, NMe_2), 6.95 (2 H, d, *J* 9 Hz, ArH), 6.90—8.10 (10 H, m, ArH), and 8.98 (2 H, s, ArH).

Salt (**9g**), 89%; m.p. 131 °C (decomp.); $\nu_{max.}$(Nujol) 2 110 (C≡C), and 1 610 and 1 595 cm^{-1} (C=C); δ_H(CD_2Cl_2) 2.36 (3 H, s, Me), 3.22 (6 H, s, NMe), and 6.92—8.06 (16 H, m, ArH).

Salt (**9h**),* 48%; m.p. > 230 °C; δ_H(CD_2Cl_2) 3.26 (6 H, s, NMe_2), 4.14 (3 H, s, OMe), 6.90 (2 H, d, *J* 9 Hz, ArH), 7.50—8.10 (7 H, m, ArH), and 8.84—8.96 (2 H, m, ArH).

Salt (**9i**), 25%; m.p. 170 °C (decomp.); $\nu_{max.}$(Nujol) 2 120 (C≡C) and 1 605 cm^{-1} (C=C); δ_H(CD_2Cl_2) 1.32—1.80 (6 H, m, CH_2*Me*), 2.80—3.20 (4 H, m, C*H*$_2$Me), 3.29 (6 H, s, NMe_2), 6.94 (2 H, d, *J* 9 Hz, ArH), 7.64—8.20 (7 H, m, ArH), and 8.72—8.92 (1 H, m, ArH).

Salt (**9j**), 43% m.p. 183—185 °C (decomp.); $\nu_{max.}$(Nujol) 2 100 (C≡C) and 1 605 cm^{-1} (C=C); δ_H(CD_2Cl_2) 3.38 (6 H, s, NMe_2), 7.02 (2 H, d, *J* 9 Hz, ArH), 7.84—8.10 (8 H, m, ArH), and 8.72—8.90 (1 H, m, ArH).

Salt (**9k**),* 53%; m.p. > 178 °C (decomp.); δ_H(CD_2Cl_2) 3.33 (6 H, s, NMe_2), 6.99 (2 H, d, *J* 9.5 Hz, ArH), 7.74—8.12 (8 H, m, ArH), and 8.90—9.02 (2 H, m, ArH).

Salt (**9l**),* 53%; m.p. 208—210 °C (decomp.); δ_H(CD_2Cl_2) 3.26 (6 H, s, NMe_2), 4.13 (3 H, s, OMe), 6.91 (2 H, d, *J* 9 Hz, ArH), 7.54—8.08 (7 H, m, ArH), and 8.90—9.02 1 H, m, ArH).

Salt (**10**), 43%; m.p. 118 °C; $\nu_{max.}$(Nujol) 2 200 cm^{-1} (C≡C).

Salt (**11**), 64%; m.p. 129 °C; $\nu_{max.}$(Nujol) 2 180 cm^{-1} (C≡C).

Synthesis of Leuco Dye (**12**).—A mixture of the salt (**9c**) (0.100 g, 0.24 mmol) and $NaBH_4$ (56 mg, 1.5 mmol) in MeOH (70 ml) was stirred under N_2 for 1 h in an ice–salt-bath and was then poured onto water (100 ml). The benzene extract (50 ml × 2) was washed with brine, dried ($MgSO_4$), and then evaporated under reduced pressure. The crude material was chromatographed over silica gel [10 g; hexane–benzene, 1:1 (v/v)] to give the *leuco dye* (**12**) as needles (0.044 g, 55%), m.p. 174 °C (decomp.) (Found: C, 81.2; H, 5.7; N, 3.8. $C_{23}H_{19}NS$ requires C, 80.9; H, 5.6; N, 4.1%); $\nu_{max.}$(Nujol) 2 230 (C≡C) and 1 605 cm^{-1} (C=C); δ_H($CDCl_3$) 2.97 (6 H, s, NMe_2), 4.68 (1 H, s, methine H), 6.68 (2 H, d, *J* 9 Hz, ArH), 7.18—7.57 (8 H, m, ArH), and 7.89—8.03 (2 H, m, ArH); e.i.-m.s. (*m/z*) 341 (M^+).

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