3,6-Bis(dimethylamino)fluorenylium Dye Ethynologues: New Highly Coloured π-Electron Systems[1]

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Acetylenic analogues (**3**) of 3,6-bis(dimethylamino)fluorenylium dyes, which absorb near-IR light (up to 1056 nm in CH_2Cl_2), have been prepared; their characteristic absorption properties are discussed on the basis of PPP–CI–MO calculations.

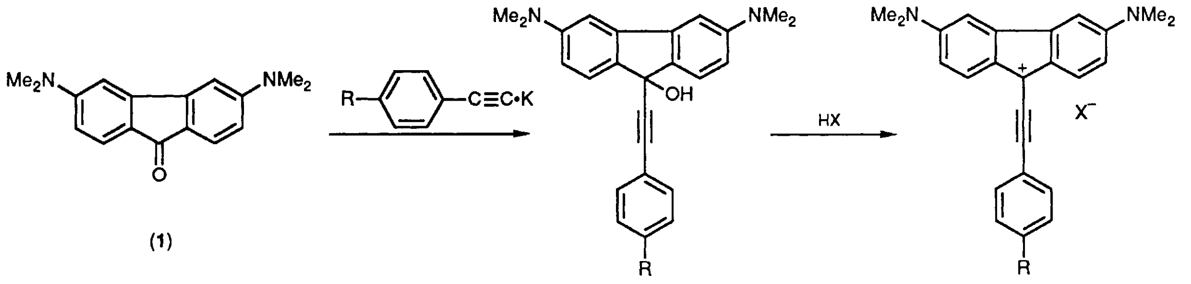
In 1954, Barker and Barker reported the synthesis of compound (**4**; R = NMe_2), in which the 2- and 2′-positions of Crystal Violet are bonded directly, *i.e.*, without a bridging atom; it has its longest absorption band at 850 nm.[2] This bridging effect in (**4**; R = NMe_2) shifts the longest absorption band of Crystal Violet bathochromically by up to 260 nm.[3] During the course of our studies on triphenylmethane dye ethynologues (acetylenic analogues), we became interested in the 'bridging effect' and reported recently a series of dye ethynologues (**6**)[4] and dyes without bridges (**7**)[5] of relevance to the production of functional near-IR dyes.[6]

We now report the synthesis and spectroscopic properties of the fluorenylium dye ethynologues (**3**) [acetylenic analogues of 2,6-bis(dimethylamino)fluorenylium dyes)], which show a marked bathochromic shift compared with the fluorenylium dyes (**4**). The fluorenylium dye ethynologues (**3**) were prepared as in Scheme 1. The precursors (**2**) of the cationic dyes were prepared by the reaction of 3,6-bis(dimethylamino)-fluorenone (**1**)[2] with potassium *para*-substituted phenylacetylides. The alcohols (**2**) were then treated with acid ($HClO_4$ or HBF_4) to give the dyes (**3**) as crystals [m.p. (°C), % yield based on (**1**): (**3a**), *ca.* 300 (decomp.), 54; (**3b**),

Table 1. Light absorption data of the dyes (**3**), (**4**), and (**5**).

		Exp.		Calc.[a]		Calc.[b]		
Dye	R	$\lambda_{max.}$/nm	($10^{-4}\,\varepsilon_{max.}$ /mol^{-1} cm^{-1})	$\lambda_{max.}$/nm	(f[d])	$\lambda_{max.}$/nm	(f[d])	Transition direction[e]
(**3a**)	NMe_2	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
(**3c**)	OMe	1025	(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
(**3e**)	H	1052	(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
(**4**)	NMe_2	850	(1.70)	780	(0.74)	848	(0.25)	0 (*x*) H → L
		646	(7.50)	678	(1.37)	574	(1.27)	90 (*y*) NH → L
(**5a**)[c]	NMe_2	663	(13.1)	657	(1.52)	624	(1.30)	0 (*x*) H → L
		—	—	538	(1.43)	505	(1.37)	90 (*y*) NH → L
(**5b**)[c]	OMe	680	(10.3)	665	(1.53)	632	(1.33)	0 (*x*) H → L
		530	(4.26)	484	(1.26)	468	(1.22)	−90 (*y*) NH → L
(**5c**)[c]	H	688	(10.1)	673	(1.55)	641	(1.35)	180 (*x*) H → L
		493	(3.62)	457	(1.14)	448	(1.10)	−90 (*y*) NH → L

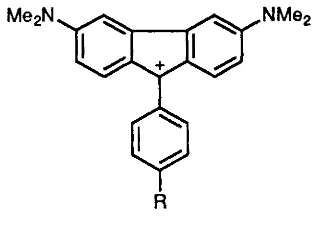
[a] E_i (ionization potential) 12.7 eV, γ_{rr} 6.08 eV, Z 2.0 eV for N atoms. *Cf.* J. Griffiths, *Dyes Pigm.*, 1982, **3**, 211. [b] E_i 25.3 eV, γ_{rr} 17.44 eV, Z 2.0 eV for N atoms. Central C: Z 0.6—0.8 eV [for (**3**) and (**4**)]. [c] Exp. and calc. values as reported in ref. 4(b). [d] f = oscillator strength. [e] H, HOMO; L, LUMO; NH, Next HOMO.



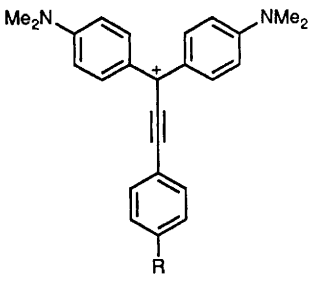
(1)

(2)

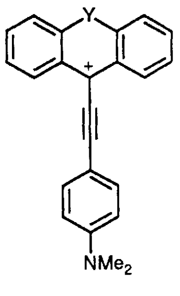
(**3**)**a**; R = NMe_2, X = ClO_4
b; R = NMe_2, X = BF_4
c; R = OMe, X = BF_4
d; R = Me, X = BF_4
e; R = H, X = BF_4
f; R = Br, X = BF_4



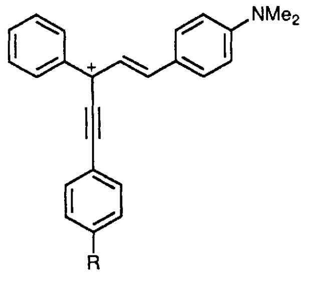
(**4**) R = NMe_2, H



(**5**) R = NMe_2, MeO, H, Cl, NO_2



(**6**) Y = O, S, Se



(**7**) R = NMe_2, H

ca. 265 (decomp.), 54; (**3c**), *ca.* 270 (decomp.), 35; (**3d**), >300, 52; (**3e**), >300, 30; (**3f**), >300, 39].†

Absorption spectral data of representative examples (**3a**), (**3c**), and (**3e**), and the related dyes (**4**) and (**5a—c**) are summarized in Table 1,† together with results calculated using the PPP–CI–MO method. The general tendency that the first and the second bands [they are the same for (**3a**)] shift hypsochromically (Br > H > Me > MeO > NMe$_2$) and in turn the third bands shift bathochromically depending on the electron-donating nature (NMe$_2$ > MeO > Me > H > Br) of the substituents on the *para*-position of phenylethynyl group was well explained by the calculated results using the general parameter sets as well as other sets cited in Table 1, better results being obtained with the latter. The spectral features of the bridged dyes are similar except for the marked bathochromic shifts with the fluorenylium dyes (**4**)[2] reported by Barker and Barker and are quite different from results for the unbridged bis(*p*-dimethylaminophenyl)(*p*-substituted phenylethynyl)carbenium ions (**5**).[7] Although the chromophore systems of these dyes are not large, their spectral features are remarkable. The characteristically large bathochromic shifts of the first and the second absorption bands of (**3**) into the near-IR region (*ca.* 1000 nm) by ring closure of the *o*- and *o*′-positions of the diphenylmethane units could hardly be ascribed to increase of planarity. Recently, as pointed out by Tyutyulkov,[8a,b] Fabian,[6a,8b,c] and Zahradnik,[6a] the contribution of antiaromatic or/and diradicaloid nature of the central cyclopentadienyl unit plays a significant role in conjugation leading to a lowering of the HOMO–LUMO energy gaps and hence contributes to the characteristic bathochromic shifts observed with (**3**). The results of our PPP–CI–MO calculations seem to elucidate fairly well the above fact.‡ To our knowledge, the near-IR absorptions of (**3c—f**) of up to 1025—1056 nm are the first examples among triphenylmethane dyes.

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† All the isolated salts (**3**) gave satisfactory spectroscopic and elemental analyses: $\lambda_{max.}$/nm ($10^{-4}\,\varepsilon_{max.}$/mol^{-1} cm^{-1}) (CH$_2Cl_2$): (**3b**), 956 (1.70) and 719 (9.37); (**3d**), 1040 (0.88), 920 (0.61), and 559 (3.39); (**3f**), 1056 (1.19), 931 (0.89), and 558 (3.42).

‡ Based on our closed shell-type PPP–MO calculations, the lowering of the LUMO and raising of the NHOMO energy levels resulting from the cyclization are suggested. The double peaks found at longest wavelengths of the dyes (**3c**)—(**3f**) could be assigned to the vibronic components of a single electron transition: *cf.* J. Griffiths and K. J. Pender, *Dyes Pigm.*, 1981, **2**, 37.