

Synthesis and Properties of 3,6-Bis(dimethylamino)fluorenylium Dye Ethynologues: New Highly Bathochromic π -Electron System¹

Shin'ichi Nakatsuji,^{a,*†} Hiroyuki Nakazumi,^b Hiroko Fukuma,^a Tomio Yahiro,^a Kenichiro Nakashima,^a Masahiko Iyoda^c and Shuzo Akiyama^{a,*}

^a School of Pharmaceutical Sciences, Nagasaki University, 1-14 Bunkyo-machi, Nagasaki 852, Japan

^b Department of Applied Chemistry, College of Engineering, University of Osaka Prefecture, 4-804 Mozu-Umemachi, Sakai 591, Japan

^c Department of Chemistry, Faculty of Science, Osaka University, Toyonaka, Osaka 560, Japan

A series of acetylenic analogues of 3,6-bis(dimethylamino)fluorenylium dye, which absorb near-IR light (up to 1096 nm in CH₂Cl₂), have been systematically prepared and their characteristic light-absorption spectroscopic properties, as well as their pK_a⁺-values, are discussed with the aid of PPP-SCF-MO calculations, and compared with data for the corresponding unbridged triphenylmethane dye ethynologues.

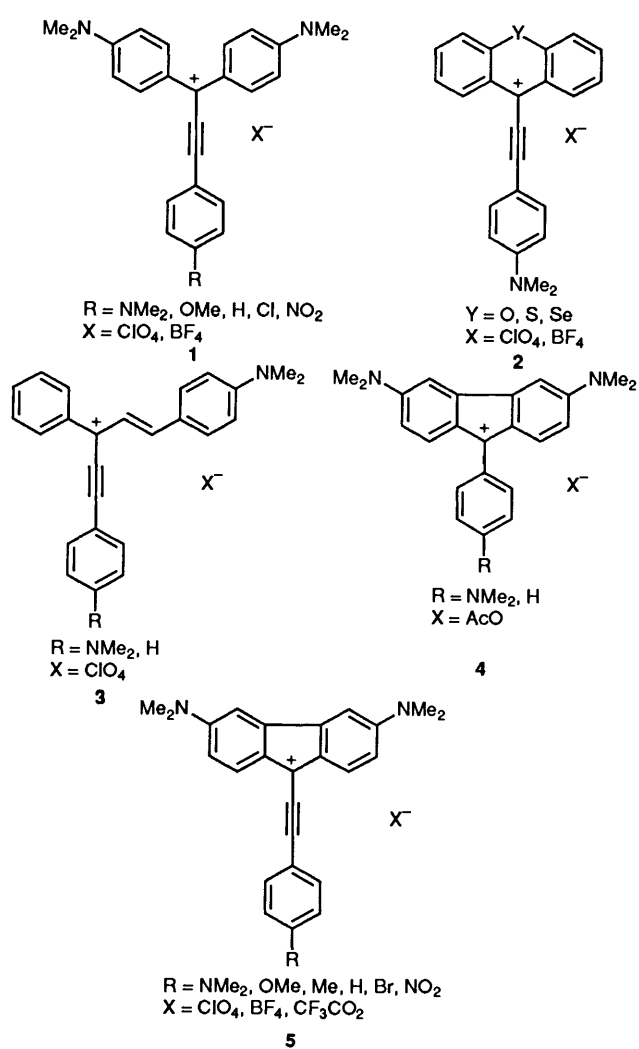
Recent progress in optical and laser data storage technology provides a new trend in chemistry towards the development of new dye systems as functional materials.² Although a number of new dye systems have been prepared along these lines and have been proposed as functional dyes in recent years, there are still only a limited number of compounds which absorb the light of the near-IR region.³ Consequently, it is of current interest to search for new near-IR-absorbing chromogenic systems.

During the course of our studies on acetylenic analogues of triphenylmethane dyes (triphenylmethane dye ethynologues) **1**,⁴ we have recently prepared and reported on the new near-IR-absorbing dye ethynologues **2**⁵ and ethynolovinologues **3**.⁶ In the reported systems, xanthenylium, thioxanthenylium, and selenoxanthenylium dye ethynologues⁵ have shown interesting absorption spectral features, *viz.* characteristic IR-absorbing properties due to the larger delocalization of the positive charge by replacement of the diphenyl part of the triphenylmethane dyes with a xanthene, thioxanthene, or selenoxanthene nucleus. We have been interested in such bridging effects and subsequently planned to develop fluorenylium dye ethynologues, in which the 2- and 2'-position of the diphenylmethane moiety are directly linked to form a five-membered central ring. In 1954, Barker and Barker reported the synthesis of the prototype compound **4**; R = NMe₂ and H in which the 2- and 2'-position of Crystal Violet (CV) or Malachite Green (MG) are bonded directly; CV and MG have their longest wavelength bands at 850 nm and 955 nm, respectively.⁷ Such a bridging effect in **4**; R = NMe₂ and H displaces the longest wavelength band of CV and MG some 260 nm and 267 nm to longer wavelength, respectively.⁸ Several theoretical treatments explained this interesting behaviour fairly satisfactorily but there still remain some controversies concerning this shift.⁹ Therefore we thought it quite interesting to synthesize fluorenylium dye ethynologues **5** and to investigate their absorption spectral properties. We report the synthesis of a series of the fluorenylium dye ethynologues **5a-f** absorbing in the near-IR region and compare their light-absorption properties and chemical structures with the results of Pariser-Parr-Pople MO (PPP-MO) calculations.

Results and Discussion

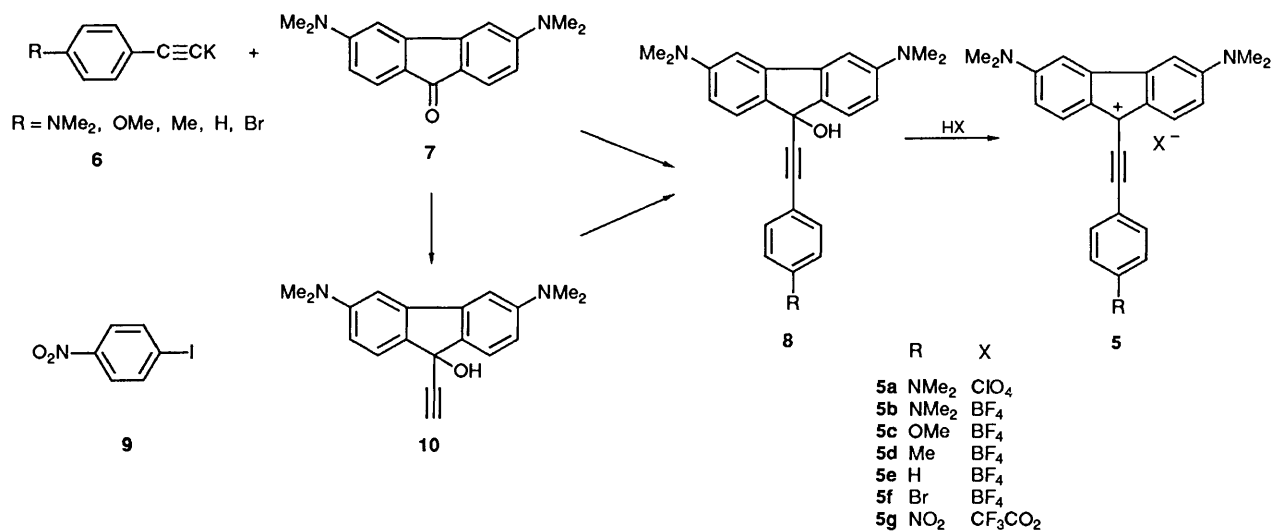
Synthesis of Dyes.—A series of fluorenylium dye ethynologues **5** have been prepared according to Scheme 1.

The reaction of metallated 4-substituted phenylacetylides **6** derived from the corresponding β -chlorostyrene derivatives¹⁰ or commercially available phenylacetylenes (for **5d** and **5e**) with



3,6-bis(dimethylamino)fluoren-9-one¹¹ **7** afforded the acetylenic alcohols **8**, which after treatment with acids (perchloric acid, fluoroboric acid) gave the desired cationic dyes **5a-f** as

[†] Present address: Department of Materials Science, Faculty of Science, Himeji Institute of Technology, Shosha 2167, Himeji, Hyogo 671-22, Japan



Scheme 1

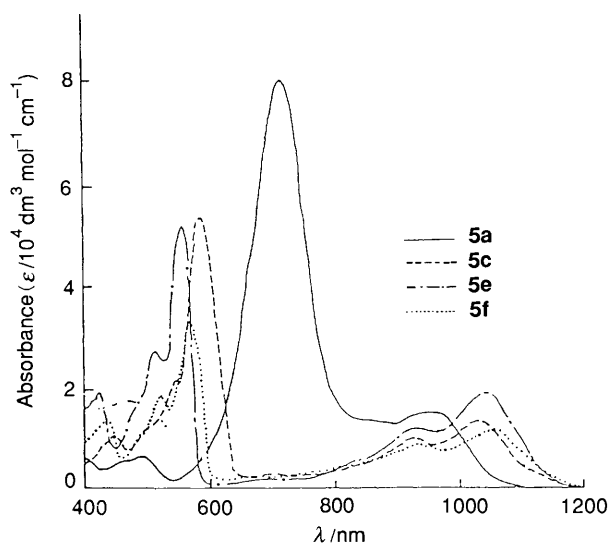


Fig. 1 Absorption spectra of fluorenylium dye ethynologues **5a**, **5c**, **5e** and **5f** in dichloromethane

deeply coloured crystals with high decomposition points (see Experimental section). The nitro derivative of the dye ethynologue **5g** could be prepared by another synthetic method. The ethynylated alcohol **10** gave the acetylenic alcohol **8g** by the Pd⁰-catalysed coupling reaction with *p*-iodonitrobenzene **9**.¹² The cationic salt **5g** was too labile to be isolated as crystals by the usual acid treatment; however, the absorption spectrum of the cation could be measured by addition of CF₃CO₂H in a CH₂Cl₂ solution of the alcohol **8g**. The compounds **5a–5f** are fairly stable in the solid state, but are so hygroscopic, as is commonly found in such salts, that they take up usually 0.5–2.5 moles of water per molecule of dye salt. These dye solutions are also fairly stable in aprotic solvents (*e.g.*, CH₂Cl₂), but the colour of their solution faded gradually in protic solvents (*e.g.*, EtOH).

Visible Absorption Spectroscopic Properties.—In Fig. 1 are shown the absorption spectra of the dye ethynologues **5a**, **5c**, **5e** and **5f** in CH₂Cl₂. Remarkable bathochromic shifts of the dye systems, which absorb light in the near-IR region, compared with the spectra of bis-(4-substituted phenyl)(4-dimethylaminophenylethynyl)carbenium ions⁴ have been observed. To our knowledge the near-IR absorptions of species **5** up to

1025–1096 nm are the first examples among the triphenylmethane dyes. Table 1 summarizes the absorption spectral data of compounds **5** together with the calculated results from the PPP-CI-MO method.

The first and second bands for **5a** are superimposed and cannot be distinguished, but are well separated for other derivatives. Both of the bands show a hypsochromic shift, the magnitude of which follows the sequence NO₂ > Br > H > Me > MeO > NMe₂, and in turn the third bands shift bathochromically (NMe₂ > MeO > Me > H > Br > NO₂) depending on the electron-donating nature of the substituents on the *para*-position of phenylethynyl group. These effects are well predicted by the PPP-MO method. It was suggested from PPP-MO calculations for the parent dye **4** that the first and second bands, which may be vibronic components of the first excitation, are assigned to the *x*-band and the third band to the *y*-band.¹⁴ The spectral features of the dyes resemble those of the fluorenylium dyes **4**, except for the remarkable bathochromic shifts in the former compounds caused by the triple bond, and are quite different to those of the bis-(*p*-dimethylaminophenyl)-(*para*-substituted phenylethynyl)carbenium ions,⁴ showing the significant change derived not only from the increase of planarity but also from the electronic state of the dyes by cyclisation. Their spectral features are so remarkable that they show absorption maxima in the very long wavelength region in spite of their rather short chromophoric system.

pK_R⁺-Values of Dyes.—To estimate the relative (thermodynamic) stabilities, we then measured pK_R⁺-values for some of the derivatives. Fig. 2 shows the absorption spectral change of compound **5d** as a function of pH in 10% MeCN–water. From this spectrophotometric titration the pK_R⁺-value of the methyl derivative was found to be 7.8. In a similar manner, the pK_R⁺-values of the dyes are obtained as shown in Table 2, together with those of compounds **1a** and **1c** as well as of CV and MG.^{15,*} The relative stability could be estimated from those pK_R⁺-values.¹⁶ The stability of the cation **5** is shown to be reduced with a decrease in the electron-donating nature of R. This behaviour is well demonstrated by the decrease of the pK_R⁺-value by *ca.* one unit, *e.g.* in the cases of R = NMe₂ and H, compared with the corresponding compounds **1a** and **1c**, which are even more unstable compared with CV and MG. The results suggest that some antiaromatic nature of the fluorenylium or a

* The differences between the cited data¹⁵ and our experimental results are mainly due to the difference in solvent system used.

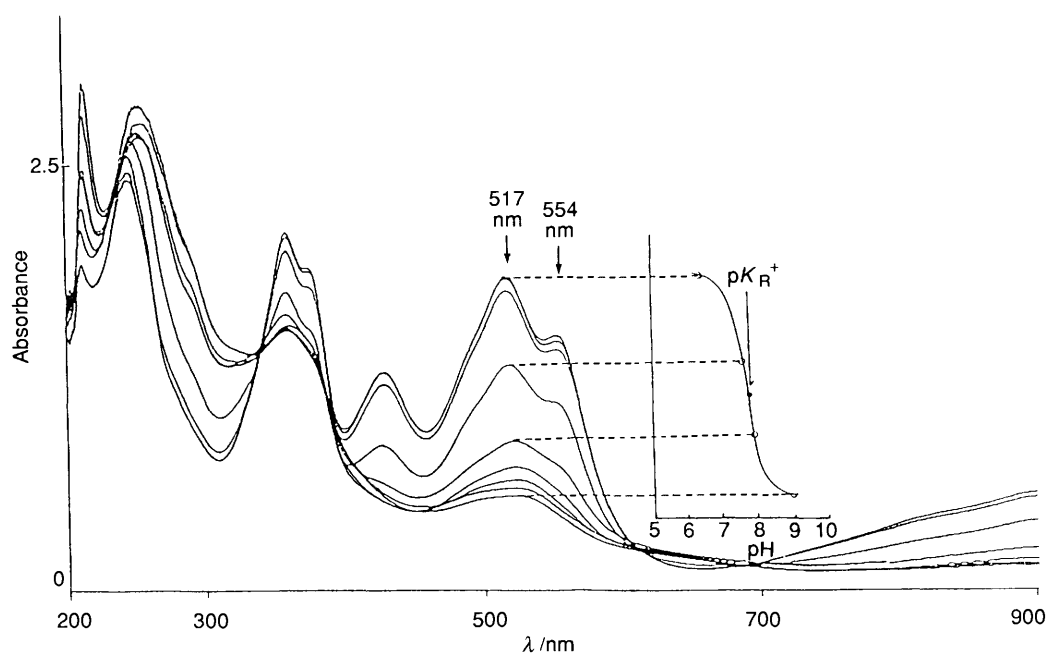


Fig. 2 Absorption spectral changes of compound **5d** as a function of pH

Table 1 Light-absorption data for dyes **5**, **4** and **1**

Dye	R	X	Exp.		Calc. ^a		Calc. ^b		Transition direction ^d
			λ_{\max}/nm	$(10^{-4} \epsilon_{\max}/\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1})$	λ_{\max}/nm	(f) ^c	λ_{\max}/nm	(f) ^c	
5a	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
5b	NMe ₂	BF ₄	956	(1.70)					
			718	(9.37)					
5c	OMe	BF ₄	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
5d	Me	BF ₄	1040	(0.88)					
			920	(0.61)					
			559	(3.39)					
5e	H	BF ₄	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
5f	Br	BF ₄	1056	(1.19)					
			931	(0.89)					
			558	(3.42)					
5g	NO ₂	CF ₃ CO ₂	1096		868	(0.97)	1002	(0.29)	0 (x) H → L
			961						
4a	NMe ₂	AcO	560		492	(1.04)	544	(1.18)	90 (y) NH → L
			850	(1.70)	780	(0.74)	848	(0.25)	0 (x) H → L
1a ^e	NMe ₂	ClO ₄	646	(7.50)	678	(1.37)	574	(1.27)	90 (y) NH → L
			663	(13.1)	657	(1.52)	624	(1.30)	0 (x) H → L
1b ^e	OMe	ClO ₄			538	(1.43)	505	(1.37)	90 (y) NH → L
			680	(10.3)	665	(1.53)	632	(1.33)	0 (x) H → L
1c ^e	H	ClO ₄	530	(4.26)	484	(1.26)	468	(1.22)	-90 (y) NH → L
			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 IP = 12.7 eV, γ_{rr} = 608 eV, Z = 2.0 eV for N atoms. Cf. ref. 13. ^b IP = 25.3 eV, γ_{rr} = 17.44 eV, Z = 2.0 eV for N atoms. Central C: 0.6–0.8 eV (for compounds **4** and **5**). ^c f = Oscillator strength. ^d H = HOMO, L = LUMO, NH = Next HOMO. ^e Experimental and calculated values were reported in ref. 5b.

central cyclopentadienyl cation moiety¹⁷ would contribute to the instability of compounds **5**, which might also affect, at least in part, the electronic state of compounds **5**.

PPP-MO Calculations.—The reasonable agreements between experimental and calculated absorption maxima of near-IR dyes are generally found by the PPP method using the modified

ionization potential (VSIP) and one-centre repulsion integral (γ_{rr}) only for heteroatoms.^{5b}

Though some calculations using modified VSIP and γ_{rr} for nitrogen atoms in dyes **4** and **5** were carried out, the correction from the calculated values using standard parameters [cf. ref. 13] was small.

The calculated near-IR absorption maxima of fluorenylium

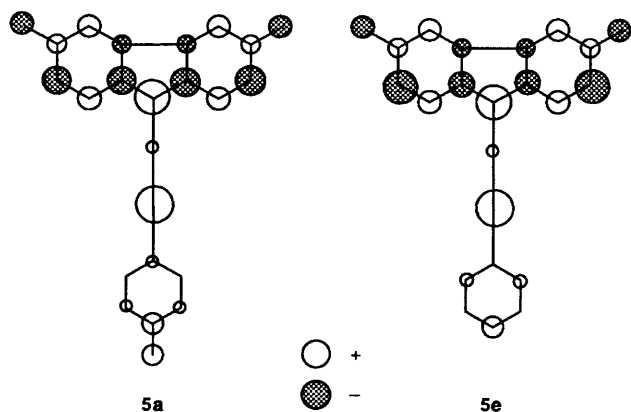


Fig. 3 Change of electron density of one-electron transitions responsible for the first absorption maxima of dyes **5a** and **5e**

Table 2 pK_R^+ -Data of dyes in 10% MeCN-water

Dye	R	pK_R^+ -Value	Dye	R	pK_R^+ -Value
5a	NMe ₂	8.8	1a	NMe ₂	9.5
5c	MeO	8.4	1c	H	8.9
5d	Me	7.8	CV	NMe ₂	12.0
5e	H	8.1	MG	H	9.4
5f	Br	7.8			

Table 3 The net π -electronic charge Q of the cyclopentadienyl moiety of compounds **4** and **5** calculated by the PPP-MO method

Dye	R	Antiaromaticity Q^a
5a	NMe ₂	+0.090
5c	MeO	+0.102
5e	H	+0.109
5g	NO ₂	+0.113
4a	NMe ₂	+0.111 (+0.098 ^b)

^aTotal net π -electronic charge of the cyclopentadienyl moiety: $Q = \sum_{i=0}^5 (1 - q_i)$, $q_i = \pi$ -electron density. ^b Ref. 9c.

dyes **4** and **5** were found to be sensitive to the core charge of central cyclopentadienyl moiety in PPP-MO calculations. The core charges for the central carbon of the cyclopentadienyl moiety were calculated to be 0.91 and 0.83, respectively, by the CNDO/2 method, for dyes **5a** and **5e** with the geometry optimized by the MNDO method.

In the PPP-MO calculations using standard parameters, the absorption maxima of compounds **5a** and **5e** were calculated to be 684 ($f = 0.27$), 595 nm ($f = 1.75$) and 722 ($f = 0.31$), 513 nm ($f = 1.31$), respectively, while they changed to 809 ($f = 0.28$), 624 nm ($f = 1.59$) and 841 ($f = 0.30$), 528 nm ($f = 1.28$) when the core charges for the carbon atoms in the 1-, 3- and 4-position of the five-membered cyclic ring of dyes **5a** and **5e** are taken to be 0.8, 0.9 and 0.9, respectively, and those for other carbons are taken to be 1.0. Thus, the calculated near-IR absorption band of fluorenylium dyes **5** is shifted to a remarkably longer wavelength by assuming a lower core charge for the carbon atoms, compared with the visible absorption band. These results mean that the core coulomb integrals for the central atoms are sensitive to the calculated absorption bands. The modification of the core coulomb integral is made by the change of VSIP or the core charge. The distribution of total integer core charges into non-integer core charges is carried out for heteroatoms and carbon atoms in compounds including any

substituent groups such as a nitro group in PPP-calculations.¹⁸

Optimum values (0.6 and 0.8) for carbon atoms of the cyclopentadienyl moiety and a carbon atom of the triple bond found empirically by the divided six core charges give the best fit between the predicted and experimental absorption bands for compounds **4a** and **5** (Table 1).

The electron-density migrations accompanying the first electron excitation for dyes **5a** and **5e** suggested as shown in Fig. 3 that the extended π -conjugation unit including acetylene bond plays an important role in the first excitation.

We have the following explanation for the significant bathochromic shift caused by the ring closure from dyes **1** to dyes **5**. Since the symmetric LUMO (C_{2v}) in species **1** which exhibits relatively high coefficients (0.223–0.225) in the *ortho,ortho'*-position is expected to be markedly lower in energy upon ring closure, and since the bond order of dyes **5** increases between the *ortho*- and *ortho'*-position upon the first excitation, then a significant bathochromic shift was observed in fluorenylium dyes **5**. The conjugated acetylene bond, not an ethylene bond, contributes to the C_{2v} symmetry of the LUMO in species **5**, as well as in diarylmethane dyes. Also, some contribution of a diradicaloid nature from the central cyclopentadienyl unit could be considered but its effects remain unclear. Fluorenylium dye **4a** has a little antiaromatic character, in which the calculated net π -electronic charge Q of the cyclopentadienyl moiety, taken as a measure of the antiaromatic character, is 0.098.^{9c} This value was also reproduced by the PPP-MO calculations using our new parameter set, and the same calculations for fluorenylium dyes **5** show slightly smaller values due to the extended π -conjugation, compared with the dye **4a** (Table 3) and show that the antiaromatic character of dyes **5** decreases with an electron-donating substituent.

Conclusions.—We have prepared a series of fluorenylium dye ethynologues **5** having absorptions at wavelengths up to 1095 nm (CH₂Cl₂) in the near-IR region. The anomalous bathochromic shift compared with triphenylmethane dye ethynologues is well expressed by PPP-MO calculations with a parameter set using a reduced core charge for some carbon atoms and is due to significantly lowering the LUMO energy level.

Experimental

All m.p.s were measured on a Yanako micro melting point apparatus and are uncorrected. UV-VIS spectra were obtained on a Shimadzu UV-265F, an Hitachi UV-210, or an Hitachi U-3400 spectrometer. IR spectra were measured on a JASCO 810 spectrophotometer. ¹H NMR spectra were taken using a JEOL JNM-FX-90Q or an JNM-GX 400 spectrometer, chemical shifts are given as δ -values with respect to SiMe₄ as internal standard, and J -values are given in Hz. Mass spectra were measured on a JEOL JMS-DX 303 mass spectrometer.

MO Calculations.—The CNDO/2 core charges for the five carbon atoms of the cyclopentadienyl moiety in dyes **5a** and **5e**, calculated using the geometry optimized by the MNDO method, are as follows; **5a**: $Z = 0.976, 1.071, 0.987, 0.987, 1.066$. **5e**: $Z = 0.891, 1.076, 0.986, 0.999, 1.072$. Relative values of the core charge for each atom of the five-membered cyclic ring are as follows; **5a**: $Z = 0.91, 1.00, 0.92, 0.92, 1.00$. **5e**: $Z = 0.83, 1.00, 0.92, 0.93, 1.00$. In PPP-MO calculations, the core charges for the five carbon atoms of the cyclopentadienyl moiety and the two carbon atoms of the triple bond are taken to be 0.6, 1.0, 0.8, 0.8 and 1.0; and 1.0 and 0.8, respectively. Hence, total six-core charges for the central carbon atoms having a six- π -electron system are presumed. PPP calculations using such core charges

rapidly converged (iteration counts 6–9). The standard ionization potential, and one-centre electron repulsion integral for nitrogen, carbon and oxygen atoms were used. The PPP-MO method was used with a valuable β approximation described in a previous paper.^{5b} The simplest possible geometries and planar structures were assumed for the molecules studied in the PPP-MO calculations.

Synthesis of Compound 5a.—To a stirred solution of β -chloro-4-dimethylaminostyrene (0.50 g, 2.75 mmol) in THF (50 cm³) was added Bu^tOK (2.8 g, 10 mol equiv.) at room temperature under nitrogen and then after 5 min 3,6-bis(dimethylamino)-fluoren-9-one (0.50 g, 1.9 mmol) was added. The mixture was stirred for 1 h at room temperature and the resulting orange-yellow solution was poured onto water. The organic layer was extracted with benzene, and the extract was washed and dried (MgSO₄). The orange solid (0.44 g, 56%) obtained by evaporation of the extract was recrystallized from CH₂Cl₂-diethyl ether to give compound **8a**, m.p. 214–216 °C (decomp.) (Found: C, 78.7; H, 7.1; N, 10.0. C₂₇H₂₉N₃O requires C, 78.8; H, 7.1; N, 10.2%); ν_{\max} (KBr)/cm⁻¹ 3370 (OH), 2210 (C≡C) and 1605 (C=C); EI-MS (*m/z*) 411 (M⁺).

To a solution of compound **8a** (80 mg, 0.19 mmol) in CH₂Cl₂-MeOH (40 cm³) was added perchloric acid (60%; 2 drops). The mixture was stirred for 10 min and the resulting precipitate was filtered off, washed with diethyl ether, and dried (MgSO₄) to give compound **5a** as greenish black solid (90 mg, 96%). An analytically pure sample was obtained by recrystallization from acetone and had m.p. >270 °C (decomp.) (Found: C, 63.0; H, 5.5; N, 8.1. C₂₇H₂₈ClN₃O₄·H₂O requires C, 63.3; H, 5.9; N, 8.6%); ν_{\max} (KBr)/cm⁻¹ 2130 (C≡C) and 1595 (C=C); δ_{H} ([²H₅]acetone) 3.22 (6 H, s, NMe₂), 3.39 (12 H, s, NMe₂), 6.54 (2 H, dd, *J* 2 and 9, ArH), 6.92 (2 H, d, *J* 9, ArH), 7.41 (2 H, d, *J* 2, ArH), 7.45 (2 H, d, *J* 9, ArH) and 7.72 (2 H, d, *J* 9, ArH); FAB-MS (*m/z*) 394 (M - ClO₄).

The salt **5b** was prepared from compound **8a** by addition of fluoroboric acid instead of perchloric acid and was isolated as dark violet crystals (78%); m.p. ~265 °C (decomp.) (Found: C, 66.2; H, 5.9; N, 8.6. C₂₇H₂₈BF₄N₃·0.5H₂O requires C, 66.1; H, 6.0; N, 8.6%); ν_{\max} (KBr)/cm⁻¹ 2140 (C≡C) and 1600 (C=C); FAB-MS (*m/z*) 394 (M - BF₄).

Compounds **5c**, **5d**, **5e** and **5f** were prepared according to the above method. The acetylenic alcohols **4b–4f** were used without further purification.

Compound 5c: dark violet crystals, 35% (2 steps); m.p. >270 °C (decomp.) (Found: C, 62.9; H, 5.5; N, 5.7. C₂₆H₂₅BF₄N₂O·H₂O requires C, 63.1; H, 5.6; N, 5.8%); ν_{\max} (KBr)/cm⁻¹ 2160 (C≡C) and 1600 (C=C); δ_{H} (CD₂Cl₂) 3.37 (12 H, s, NMe₂), 3.89 (3 H, s, OMe), 6.27 (2 H, d, *J* 9, ArH), 6.98 (2 H, d, *J* 9, ArH), 7.12 (2 H, s, ArH), 7.22 (2 H, d, *J* 9, ArH) and 7.63 (2 H, d, *J* 9, ArH); FAB-MS (*m/z*) 381 (M - BF₄).

Compound 5d: dark violet crystals, 52% (2 steps); m.p. >300 °C (Found: C, 62.7; H, 5.6; N, 5.5. C₂₆H₂₅BF₄N₂·2.5H₂O requires C, 62.8; H, 6.0; N, 5.6%); ν_{\max} (Nujol)/cm⁻¹ 2200 (C≡C) and 1600 (C=C); δ_{H} (CD₂Cl₂) 2.34 (3 H, s, Me), 3.34 (12 H, NMe₂), 6.27 (2 H, dd, *J* 2 and 9, ArH), 7.15 (2 H, d, *J* 2, ArH), 7.21 (2 H, d, *J* 9, ArH), 7.28 (2 H, d, *J* 8, ArH) and 7.56 (2 H, d, *J* 8, ArH); FAB-MS (*m/z*) 366 (M - BF₄).

Compound 5e: dark violet crystals, 35% (2 steps); m.p. >300 °C (Found: C, 65.7; H, 5.5; N, 6.2. C₂₅H₂₃BF₄N₂·H₂O requires C, 65.8; H, 5.5; N, 6.1%); ν_{\max} (KBr)/cm⁻¹ 2150 (C≡C) and 1600 (C=C); δ_{H} (CD₂Cl₂) 3.35 (12 H, s, NMe₂), 6.28 (2 H, dd, *J* 2 and 9, ArH), 7.19 (2 H, d, *J* 2, ArH), 7.21 (2 H, d, *J* 9, ArH) and 7.46–7.68 (5 H, m, ArH); FAB-MS (*m/z*) 351 (M - BF₄).

Compound 5f: dark violet crystals, 39% (2 steps); m.p. >300 °C (Found: C, 56.7; H, 4.5; N, 5.4. C₂₅H₂₂BBF₄N₂·0.5 H₂O requires C, 57.1; H, 4.4; N, 5.3%); ν_{\max} (Nujol)/cm⁻¹ 2200

(C≡C); δ_{H} (CD₂Cl₂) 3.36 (12 H, s, NMe₂), 6.32 (2 H, dd, *J* 2 and 8, ArH), 7.21 (2 H, d, *J* 8, ArH), 7.12 (2 H, d, *J* 2, ArH), 7.28 (2 H, d, *J* 8, ArH) and 7.68 (2 H, d, *J* 8, ArH).

Preparation of Compound 8g.—To a stirred solution of acetylenic alcohol **10** (37 mg, 0.13 mmol), *p*-iodonitrobenzene **9** (40 mg, 0.16 mmol) and triphenylphosphine (84 mg, 0.32 mmol) in triethylamine (30 cm³) was added palladium acetate (36 mg, 0.16 mmol) and the reaction mixture was warmed to reflux. After 0.5 h, the mixture was filtered, the residue was washed by dichloromethane and the combined filtrate and washings were concentrated under reduced pressure. Aq. sodium hydrogen-carbonate was added to the mixture which was then extracted by dichloromethane; the extract was dried (MgSO₄), and then evaporated under reduced pressure to yield a brownish solid, which was recrystallized from benzene-hexane and then from dichloromethane to give compound **8g** as brown crystals (10 mg, 19%), m.p. >300 °C (Found: C, 67.2; H, 5.3; N, 8.9. C₂₅H₂₃N₃O₃·0.5CH₂Cl₂ requires C, 67.2; H, 5.3; N, 9.3%); δ_{H} (CDCl₃) 3.05 (12 H, s, NMe₂), 3.12 (1 H, s, OH), 6.68 (2 H, dd, *J* 2 and 9, ArH), 6.94 (2 H, d, *J* 2, ArH), 7.52 (2 H, d, *J* 9, ArH), 8.11 (2 H, d, *J* 9, ArH) and 7.57 (2 H, *J* 9, ArH); EI-MS (*m/z*) 413 (M⁺).

Spectroscopic Measurement of Compound 5g.—Owing to the instability of compound **5g** in the solid state, the light-absorption spectral measurement was speedily carried out (*in situ*) by treatment of the precursor **8g** with a solution of trichloroacetic acid (1% v/v) in CH₂Cl₂ at room temperature. The NMR spectrum was measured for compound **8g** in CD₂Cl₂ in a sample tube by addition of a trace amount of CF₃CO₂D; δ_{H} (CD₂Cl₂) 3.39 (12 H, s, NMe₂), 6.45 (2 H, d, *J* 8, ArH), 8.01 (2 H, d, *J* 8, ArH), 8.10 (2 H, s, ArH), 8.37 (2 H, d, *J* 9, ArH) and 8.20 (2 H, d, *J* 9, ArH).

Acknowledgements

We express our gratitude to Professor Jurgen Fabian of Dresden Technical University for the optimization of the geometry of compounds **5a** and **5c** by the MNDO method. We are grateful to Professor (Emeritus) Masazumi Nakagawa (Osaka University) and to Professor Teijiro Kitao (University of Osaka Prefecture) for valuable discussions. The work in Nagasaki was partially supported by Grants-in-Aid for Scientific Research Nos. 62470035 and 63540406 from the Ministry of Education, Science and Culture of Japan.

References

- Part of this work has been published as a preliminary communication: S. Nakatsuji, H. Nakazumi, H. Fukuma, T. Yahiro, K. Nakashima, M. Iyoda and S. Akiyama, *J. Chem. Soc., Chem. Commun.*, 1990, 489. For Part 10 in the series of 'Ethnologies of Triphenylmethane Dyes,' see S. Nakatsuji, T. Yahiro, K. Nakashima, S. Akiyama and H. Nakazumi, *Bull. Chem. Soc. Jpn.*, in the press.
- M. Umehara, M. Abe and H. Oba, *J. Synth. Org. Chem. Jpn.*, 1985, **43**, 334; J. Fabian and R. Zahradnik, *Angew. Chem., Int. Ed. Engl.*, 1989, **28**, 677; H. Nakazumi, *J. Soc. Dyers Colour*, 1988, **104**, 121; J. Griffiths, *J. Soc. Dyers Colour*, 1988, **104**, 416; M. Matsuoka, *J. Soc. Dyers Colour*, 1989, **105**, 167.
- M. Matsuoka, *Absorption Spectra of Dyes for Diode Laser*, Bunshin Publishing Co., Tokyo, 1990; M. Matsuoka, *Infrared Absorbing Dyes*, Plenum, New York, 1990.
- S. Nakatsuji, N. Okamoto, K. Nakashima and S. Akiyama, *Chem. Lett.*, 1986, 329 and earlier paper.
- (a) S. Akiyama, S. Nakatsuji, K. Nakashima and M. Watanabe, *J. Chem. Soc., Chem. Commun.*, 1987, 710, 1420; (b) S. Akiyama, S. Nakatsuji, K. Nakashima, M. Watanabe and H. Nakazumi, *J. Chem. Soc., Perkin Trans. 1*, 1988, 3155.

- 6 S. Akiyama, S. Nakatsuji, K. Nakashima and S. Yamasaki, *Dyes Pigm.*, 1988, **9**, 459.
- 7 A. Barker and C. C. Barker, *J. Chem. Soc.*, 1954, 1307.
- 8 H. Zollinger, *Color Chemistry*, VCH Verlagsgesellschaft, Weinheim, 1987, p. 72.
- 9 (a) D. A. Brown and M. J. S. Dewar, *J. Chem. Soc.*, 1954, 2134; (b) J. Michl, R. Zahradnik and P. Hochmann, *J. Phys. Chem.*, 1966, **70**, 1732; (c) N. N. Tyutyulkov and M. Y. Tasseva, *C.R. Acad. Bulg. Sci.*, 1985, **38**, 871; (d) A. Mehlhorn, J. Fabian, N. N. Tyutyulkov, G. Olbrich and F. Dietz, *J. Prakt. Chem.*, 1986, **328**, 603; (e) J. Fabian, *Z. Chem.*, 1987, **27**, 28.
- 10 S. Akiyama, S. Nakatsuji, K. Yoshida, K. Nakashima, T. Hagiwara, H. Tsuruta and T. Yoshida, *Bull. Chem. Soc. Jpn.*, 1983, **56**, 361.
- 11 A. Barker and C. C. Barker, *J. Chem. Soc.*, 1954, 870.
- 12 S. Takahashi, T. Kuroyama, K. Sonogashira and N. Hagihara, *Synthesis*, 1980, 627; W. B. Austin, N. Bilow, W. J. Kelleghan and K. S. Y. Lau, *J. Org. Chem.*, 1981, **46**, 2280.
- 13 J. Griffiths, *Dyes Pigm.*, 1982, **3**, 211.
- 14 Cf. J. Griffiths and K. J. Pender, *Dyes Pigm.*, 1981, **2**, 37.
- 15 R. J. Goldacre and J. N. Phillips, *J. Chem. Soc.*, 1949, 1724.
- 16 N. C. Deno, J. J. Jaruzelski and A. Schriesheim, *J. Am. Chem. Soc.*, 1955, **77**, 3044; R. Breslow and H. W. Chang, *J. Am. Chem. Soc.*, 1961, **83**, 2367 and their related papers.
- 17 R. Breslow, *Topics in Nonbenzenoid Aromatic Chemistry*, eds. T. Nozoe, R. Breslow, K. Hafner, S. Ito and I. Murata, Hirokawa, Tokyo, 1974, pp. 81-94.
- 18 M. D. Gordon and J. F. Neumer, *J. Phys. Chem.*, 1974, **78**, 1868.

Paper 0/05225F

Received 20th November 1990

Accepted 12th March 1991