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Dyes and Pigments 40 (1999) 151–156

DYES AND PIGMENTS

Extended conjugation in di- and tri- arylmethane dyes. Part 3. The effects of increased planarity in Victoria Blue dyes

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Received 30 March 1998; accepted 27 April 1998

Abstract

The synthesis of novel derivatives of the Victoria Blue series of dyes containing the 3,6-bis(dimethylamino)fluoren-9-yl moiety is reported. The consequent increased planarity of the system results in a large bathochromic shift of the *x*-band compared to the parent compound. © 1998 Elsevier Science Ltd. All rights reserved.

Keywords: Triarylmethane dyes; Fluorenes; Leuco compounds; Synthesis; Absorption spectra

1. Introduction

As part of a continuing study of triarylmethane (TPM) dyes **1** [1], we have reported the synthesis and spectral properties of a range of analogues of Victoria Blue **2** [2]. Extension of the π-system by the inclusion of a naphthalene unit causes a bathochromic shift of the long wavelength absorption compared to the parent triarylmethane dyes Crystal Violet (CV) **1a** and Malachite Green (MG) **1b**. However, the red shifts observed with these compounds are moderated by the ability of the triarylmethane cation to assume a lower energy, non-planar state by rotation about the bonds to the central carbon atom, and are only of the order of 30 nm.

Bridging the 2′- and 2″-positions of a triphenylmethane dye restricts rotation to the free phenyl ring and theory predicts [3] that a bridging mesomeric electron-donating heteroatom should produce a large hypsochromic shift of the first absorption band. Indeed, the oxygen-bridged analogues **3a** and **3b** of Crystal Violet and Malachite Green, respectively, exhibit blue-shifted *x*-bands [4]. At the same time, the very weak *y*-band of the latter dye is shifted into the ultraviolet. In the 2′,2″-isopropylene-bridged TPM dyes **4a** and **4b**, the electronic effect of the bridging group is rather small, and no marked shift of the *x*-band is observed [5]. As in the case of the oxygen analogue, the pronounced blue shift of the *y*-band of the Malachite Green derivative is attributed to the deconjugation of the unbridged phenyl ring. Accordingly, the introduction of even *ortho*-substituents into this ring does not modify the absorption spectrum.

Remarkable bathochromic shifts of ca 60 and 220 nm of the main absorption band are produced when the 2′- and 2″- positions of CV and MG, respectively, are directly linked to each other, forming the 9-fluorenyl TPM derivatives **5a** and **5b** (Table 1). A new band appears in both examples, a further 100–200 nm to the red. Again, the

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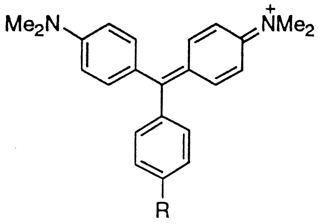
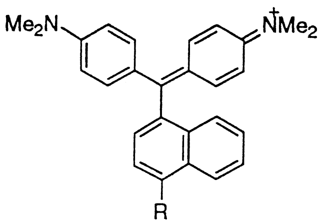
PII: S0143-7208(98)00041-2



1 (**a**) R = NMe$_2$
(**b**) R = H



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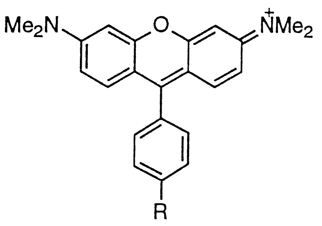

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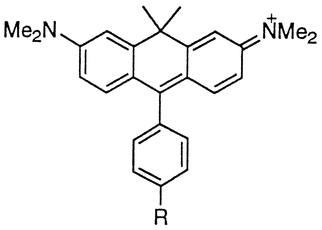

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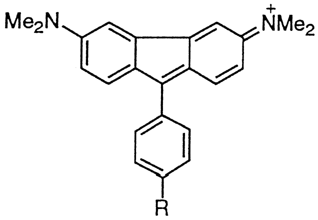

5 (**a**) R = NMe$_2$
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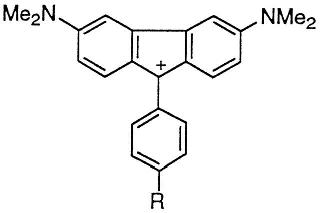
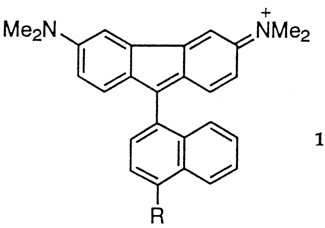


5c



10 (**a**) R = NMe$_2$
(**b**) R = H
(**c**) R = N$^+$HMe$_2$

non-bridged phenyl ring is largely twisted out of the molecular plane and the angle of torsion has been estimated at between 45 and 70° [6,7]. Although the Crystal Violet analogue **5a** was described at the turn of the century [8], the origins of the significant spectral shifts are still unclear [9]. A shift of the x-band towards the near infrared as a result of the increased planarity of the system can be predicted remarkably well by simple HMO calculations [10], or more elaborate PPP–MO calculations [11], and the two peaks observed above 800 nm for the Malachite Green analogue **5b** have been identified as the vibronic components of a unique transition [11]. However, calculations specifically taking into account the anti-aromatic nature of the fluorenyl cation are also successful [7] and in this case, the electronic structure of the fluorene dyes is better represented by **5c**. However, the anti-aromatic nature of the 9-arylfluorenyl cation is still a matter of controversy [6,7,12–14].

Table 1
Visible absorption spectra of some fluorenyl analogues of triarylmethane dyes in 98% acetic acid

Dye	λ (nm) ($10^{-4}\epsilon$ [l mol^{-1} cm^{-1}l])			
5a	850 (1.6)	647 (7.6)	470 (0.7)	445 (0.4)
5b	955 (2.0[a])	850 (1.5[a])	505 (2.2)	480 (2.1)
10a	835 (1.5)	701 (2.1)	485 (0.6)	450 (0.3)
10b	>900 (–)	858 (1.5)	535 (1.5)	495 (1.4)
10c	>900 (–)	860 (1.45)	525 (1.1)	490 (1.5)

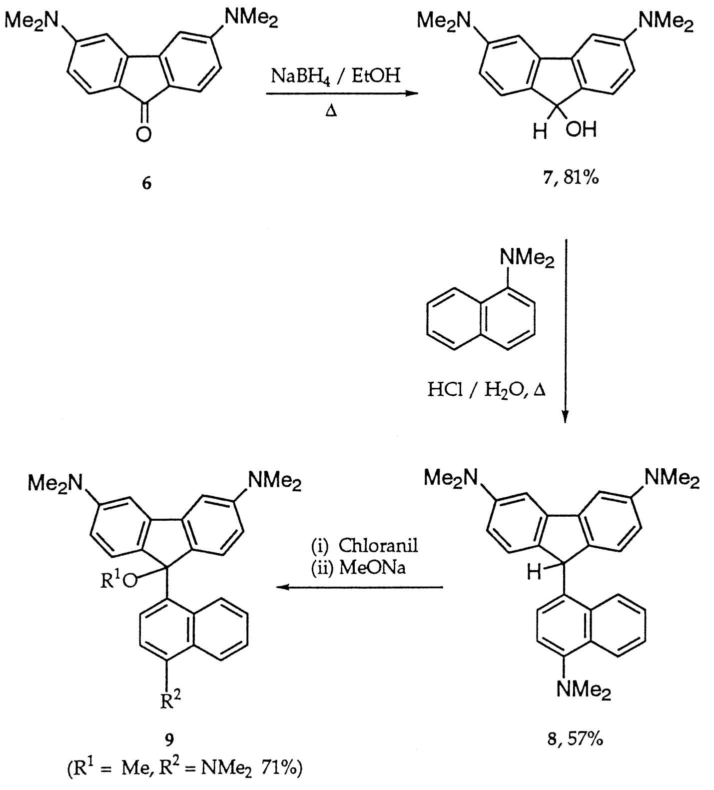
[a] Estimated from Ref. 6.

In spite of their interesting spectral parameters, which include useful infrared absorption characteristics, little is known about this series of modified triphenylmethane dyes presumably because of the difficulty in their synthesis [15,16]. We have recently reported a facile synthesis of 3,6-bisdimethylaminofluorenone [17] and now describe the incorporation of the fluorene moiety into the Victoria Blue dye system.

2. Results and discussion

The conversion of 3,6-bis(dimethylamino)fluoren-9-one **6** into the leuco base **8** was accomplished by the reduction of the ketone and reaction of the resulting 9-hydroxyfluorene derivative **7** with *N*,*N*-dimethyl-1-naphthylamine (Scheme 1). Subsequent oxidation with chloranil gave the dye cation which was converted into its methyl ether 9 (R^1 = Me, R^2 = NMe_2) using sodium methoxide. It was important to avoid crystallisation of the hydroxyfluorene in order to prevent its decomposition and reoxidation.

The synthesis of the bridged Malachite Green dye base **9** ($R^1 = R^2 = H$) was achieved by boiling 3,6-bis(dimethylamino)fluoren-9-one **6** [17] with a



Scheme 1. Synthesis of 9-fluorenyl derivatives of Victoria Blue.

large excess of 1-naphthyl lithium in ether for 2 days. Even then, the reaction did not go to completion and ca 30% of the ketone was recovered unchanged, probably because of adverse steric and electronic factors. Given that phenyllithium reacts readily with Michler's ketone, it seems that here the more bulky naphthyllithium has restricted access to the carbonyl function. Competition studies have shown that Michler's ketone is less reactive towards organolithium reagents than benzophenone because of the reduced electrophilic character of its carbonyl group [18] and similar electronic considerations are against a complete, fast reaction in the present work.

The ^{1}H NMR spectrum of the carbinol **9** ($R^1 = R^2 = H$) and the leuco base **8** are of very different appearance. The carbinol showed broad signals for all the aromatic protons at 293 K. This is attributable to sterically restricted rotation about the C9-naphthyl bond caused by the clash of the naphthyl moiety with the protons at the 1- and 8- positions of the fluorene ring. This clash leads to rotamer formation and to the interconversion of the naphthyl ring between two energetically similar *syn* and *anti* conformers. This phenomenon has been described for several fluorene and 9-hydroxyfluorene compounds bearing bulky 9-aryl substituents [19–22]. It is also noteworthy that the signal for the dimethylamino group of the naphthalene ring is upfield (δ 2.81) and clearly separated from the resonance of the two dimethylaminophenyl moieties (δ 8 3.01). The methine proton resonates at δ 5.84.

Replacement of the 9-hydroxyl group by hydrogen lowers the energy of the ground state, thus increasing the barrier to rotation [20]. In some cases, enrichment of one rotamer has been achieved [23]. The ^{1}H NMR spectrum of the leuco base **8** is very complex, but the aromatic signals are sharp and well defined at 293 K, so that it may be assumed that the rotation about the C9-naphthyl bond is frozen with respect to the NMR timescale.

The spectral parameters for the new TPM dyes are presented in Table 1 together with the data for a number of related dyes.

The pronounced red shift noted previously for the fluorene analogues of CV and MG are not only manifest in the Victoria Blue derivatives but are further enhanced. Thus, a bathochromic shift of 54 nm is observed between the naphthyl derivative **10a** and the dimethylaminophenyl compound **5a**. However, this shift is accompanied by a marked reduction in intensity, suggesting a much reduced involvement of the naphthyl unit in the charge delocalisation process. Partial deconjugation of the dimethylamino group in the 9-naphthyl ring because of *peri* interaction with H-5 of the naphthyl unit surely plays a part, but deconjugation of the whole unit as a result of a steric clash between the *peri* (H-8) proton and H-1 and H-8 of the fluorenyl moiety is probably more important. A similar observation has been made for other bridged triphenylmethane cations [4,6]. This overall reduction in intensity of the main band does not appear to be accompanied by any increase in the extinction coefficients of the other bands and the naphthyl dye **10a** therefore appears to be less stable than its phenyl analogue **5a**. The red shift of the main absorption is in accord with the extension of the chromophoric system provided by the naphthyl ring, and a significant contribution probably arises from the enhanced twisting about the naphthyl-fluorenyl bond.

The poor conjugation of the naphthyl ring is confirmed when the acidity of the solvent is increased. The blue solution in 98% acetic acid rapidly turns pale red on addition of water and the spectrum of **10a** in 10% acetic acid is very similar to that of the corresponding Green dye **10b**, (Table 1), implying the formation of the dication **10c**. It is noteworthy that all the absorption bands of **10a** are shifted to the red in 10% acetic acid, none more so than the major band which shows a shift of 159 nm. The bands normally associated with polarisation along the *y*-axis in TPM dyes and attributed here to the involvement of the 9-naphthyl moiety also show increased intensifies.

The most noticeable difference between the phenyl **5b** and the naphthyl **10b** Green dyes is the red shift of 30 nm of the band in the 500 nm region. It is assumed that this band is associated with the 9-aryl substituent and that the shift results from an extension of the chromophore. The other bands show red shifts in the range 8–15 nm, but all the bands are reduced in intensity.

3. Experimental

Visible spectra were measured on a Hewlett–Packard 8452A diode array spectrophotometer using 10^{-5} M solutions of the carbinols or methyl ethers in glacial acetic acid containing 2% of water. This solvent system was chosen to allow comparison with earlier work [1] and because its acidity is sufficient to promote the complete formation of the dye cation while minimising the possibility of forming other species such as dications [24]. The use of acetic acid also has the advantage of giving easy access to a wide range of solutions of different acid strengths as the addition of water promotes the ionisation of the acid. The dyes were found to obey Beer's law in the concentration range $1–2.5\times10^{-5}$ M, a range in which the maximum absorbance was kept between 0.5 and 0.9. The visible spectra were measured immediately and redetermined after 1 h and 48 h to ensure constant values of $\epsilon_{\max}$.

Melting points are uncorrected. NMR spectra were recorded on a Bruker WM250 instrument for $CDCl_3$ solutions. Flash chromatography was performed on silica gel (Sorbsil C60, MPD 60 Å, 40–60 microns) according to the published procedure [25]. 3,6-Bis(dimethylamino)fluoren-9-one was synthesised from 2-amino-4′,4″-bisdimethylaminobenzophenone [17].

3.1. *3,6-Bis(dimethylamino)-9-hydroxyfluorene 7*

Sodium borohydride (13.2 mmol) was added to a solution of 3,6-bis (dimethylamino)fluoren-9-one (1.9 mmol) in ethanol (30 cm^3) and the mixture was refluxed for 3 h. The colourless precipitate which formed upon dilution with water (200 cm^3) was collected, washed with water and dried to give the hydroxyfluorene **7** (81%), m.p. 189°C, lit. [9] 190–191°C.

3.2. *3,6-Bis(dimethylamino)-9-(4-dimethylamino-l-naphthyl)fluorene **8***

A solution of 3,6-bis(dimethylamino)-9-hydroxyfluorene (1.1 mmol) and *N*,*N*-dimethyl-l-naphthylamine (1.2 mmol) in aqueous hydrochloric acid (20 cm^3; 2M) was refluxed overnight. The cooled solution was basified with ice-cold aqueous sodium hydroxide solution (30 cm^3; 2M) and the precipitate was collected, washed with water, dried and eluted from silica with 35% ethyl acetate in hexane. Recrystallisation from ethyl acetate and hexane gave colourless crystals of the leuco compound **8** (57%), m.p. 161–165°C (decomp.) (Found: C, 82.7; H, 7.3; N, 9.9. $C_{29}H_{31}N_3O$ requires C, 82.6; H, 7.4; N, 10.0%).

3.3. *3,6-Bis(dimethylamino)-9-(4-dimethylamino-1-naphthyl)fluorenyl Methyl Ether **9** ($R^1 = Me$, $R^2 = NMe_2$)*

A mixture of chloranil (1.5 mmol), the leuco compound **8** (1.35 mmol) and methanol (30 cm^3) was refluxed for 6 h, whereupon it was filtered into brine (300 cm^3). The salt which precipitated was collected, washed with water and diethyl ether and dried. A solution of sodium methoxide in methanol (1M) was added dropwise to a solution of this dye salt in methanol (15 cm^3) until the greenish colour of the mixture disappeared. Addition of water (100 cm^3) was followed by extraction with ethyl acetate (3×100 cm^3). The combined extracts were washed with water (2×100 cm^3) and brine (50 cm^3), dried (K_2CO_3) and the solvent was removed. The crude solid was eluted from silica with triethylamine/ethyl acetate/hexane (10/25/65) to afford the methyl ether (71%), m.p. 128–130°C (decomp.) as colourless granules (Found: C, 79.6; H, 7.5; N, 9.1. $C_{30}H_{33}N_3O$ requires C, 79.8; H, 7.4; N, 9.3%).

3.4. *3,6-Bis(dimethylamino)-9-hydroxy-9-(1-naphthyl)fluorene **9** ($R^1 = R^2 = H$)*

A slurry of 3,6-bis(dimethylamino)fluoren-9-one (1.12 mmol) in ether (10 cm^3) was added to a solution of l-naphthllithium prepared at 0°C from 1-bromonaphthalene (9.5 mmol) and *n*-butyllithium (2.5 M in hexane; 9.2 mmol) in dry diethyl ether (80 cm^3) and the mixture was refluxed for two days. After cooling and quenching with water (100 cm^3), the crude product was isolated in the usual manner. Elution from silica with triethylamine/ethyl acetate/hexane (10/25/65) afforded two fractions.

Fraction 1 yielded the dye base (45%), m.p. 161–170°C (decomp.) as colourless crystals from ethyl acetate and hexane (Found: C, 82.0; H, 6.5, N, 7.0. $C_{27}H_{26}N_2O$ requires C, 82.2; H, 6.7; N, 7.1 %).

Fraction 2 contained the starting ketone (33%), m.p. 247°C from ethanol, lit. [17] m.p. 245–247°C.

4. Conclusions

Joining the 2′- and 2″-positions of the Michler's hydrol moiety of the Victoria Blue dye system produces species which absorb well into the infra-red. However, the new fluorenyl cations are less stable than simpler TPM dyes, since the 9-aryl ring is denied effective conjugation with the rest of the molecule by its own steric bulk.

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