Trivinylogs of Crystal Violet:† synthesis and absorption properties of new near-IR dyes

Saumitra Sengupta* and Subir Kumar Sadhukhan

Department of Chemistry, Jadavpur University, Calcutta 700 032, India

Received (in Cambridge, UK) 16th August 2000, Accepted 27th September 2000
First published as an Advance Article on the web 30th November 2000

Based on a Heck reaction protocol, trivinylogs of Crystal Violet have been prepared and show strong absorptions in the near-infrared region.

Near-infrared (NIR) absorbing dyes ($\lambda_{max} > 700$ nm) are of much current interest because of their potential applications in optical imaging systems, thermal writing displays, infrared photography, as filter elements for NIR emitting lasers, *etc.*[1] These dyes are usually prepared by end-capping of conjugated organic chromophores with strong donor and acceptor substituents. A wide variety of NIR dyes are known today, some of which *e.g.* the phthalocyanines, polymethines and squarylium dyes have found important uses in laser-based applications.[1,2] However, most of these dyes have large and complex architectures (long polyene chains with charged heterocyclic end-groups) which require multi-step synthetic procedures resulting in poor overall yields. Moreover, due to their large molecular weights, these dyes are often found to be insoluble in common organic solvents causing difficulties in their surface applications by spin-coating techniques. In view of these, there is a sustained interest in new NIR dyes that are easy to prepare, have improved solubility properties and yet show strong absorptions ($\log \varepsilon > 4$) ‡ at longer wavelengths.

Crystal Violet is a typical triphenylmethane dye which strongly absorbs in the visible region ($\lambda_{max} = 588$ nm). We reasoned that trivinylogs of Crystal Violet would cause large bathochromic shifts (vinylene red shifts amount to *ca.* 100 nm)[3] and hence lead to absorptions well within the NIR range. That this simple modification can indeed produce new NIR dyes with strong absorptions at longer wavelengths is now described in this paper.

Our synthesis started with the cheap commercial dye New Fuchsin (**1**) which *via* threefold diazotization ($NaNO_2$, aq. H_2SO_4) and Sandmeyer reaction (KI, H_2O) was converted to the tris(iodoaryl)methanol **2** in 40% overall yield (Scheme 1).[4] Threefold Heck reaction of **2** with *p*-dimethylaminostyrene, under Jeffery's conditions,[5] then produced the dye base **3** (50%). The latter, upon protonation with TFA,[6] gave rise to the desired dye **4** which was studied spectrophotometrically as a solution in CH_2Cl_2. The dye could also be generated in $CHCl_3$ solutions but no attempt has been made towards its isolation in the solid state. The electronic spectrum of **4** showed a strong absorption in the near-infrared region ($\lambda_{max} = 1003$ nm, $\log \varepsilon = 4.76$). Such a large bathochromic shift is no doubt caused by the extended π-conjugation in **4** which greatly lowered the energy of its charge-transfer transitions *vis-à-vis* Crystal Violet. The trigonal symmetry in **4** also plays a significant role towards this end. Thus, it ensures equal and extensive charge delocalization among all three arms leading to a large contribution of the resonance stabilized quinonoid forms to the ground state. Interestingly, the absorption spectra of **4** showed a pH dependent behavior (Fig. 1). Upon increasing the acid concentration, the NIR band of **4** gradually decreased and a new lower wavelength absorption band at *ca.* 530 nm gained in intensity. In the process, the former also underwent a small blue shift while the latter was shifted to longer wavelengths. In a strongly acidic solution (curve E, Fig. 1), the NIR absorption of **4** virtually vanished and the lower wavelength band at 615 nm ($\log \varepsilon = 5.08$) became the sole maximum. We attribute this to the formation of the *N*-protonated dye **4**H^+ whose reduced charge-transfer capabilities lead to absorptions at lower wavelengths. The solution concentration of **4**H^+ gradually increased with increasing acid strength and ultimately, in a strongly acidic medium, it became the predominant species. Similar acid-induced blue shifts have also been reported for some hemicyanine dyes.[7]

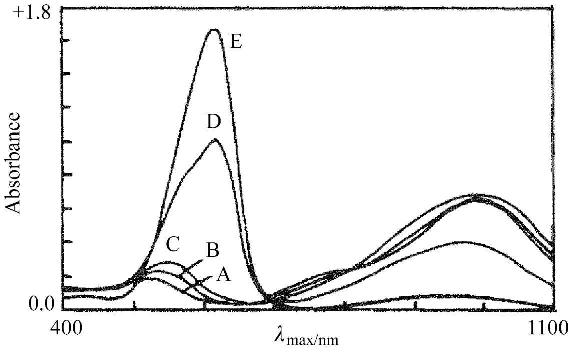


Fig. 1 Absorption spectra of **4** (0.013 mM) in CH_2Cl_2. TFA Concentration: (A) 1.5 mM; (B) 3.0 mM; (C) 6.1 mM; (D) 27.4 mM; (E) 71.0 mM.

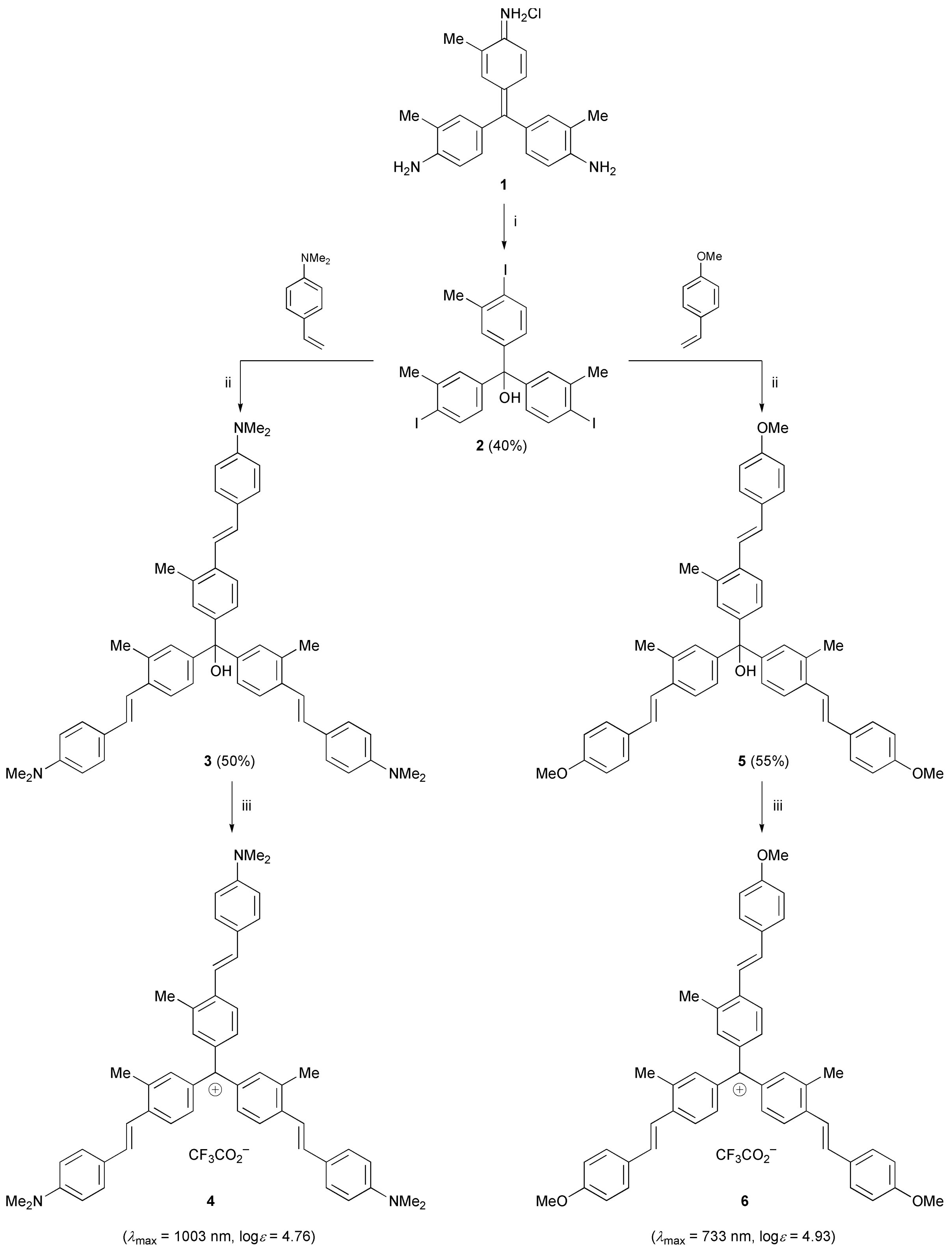
For comparison, we have also prepared the methoxy analog of **4** *i.e.* **6**. Thus, threefold Heck reaction of **2** with *p*-methoxystyrene produced the dye base **5** (55%) which upon protonation (TFA, CH_2Cl_2), as before, gave rise to the trimethoxy dye **6** (Scheme 1). The latter showed a λ_{max} value at 733 nm ($\log \varepsilon = 4.93$) which is greatly blue-shifted from that of **4**. This was, nevertheless, quite expected since the OMe group is a weaker auxochrome than NMe_2. However, the fact that **6**, despite having a weak auxochrome like OMe, is indeed capable of a NIR absorption, is a significant result and attests to the efficacy of the design elements (strong cationic acceptor group, trigonal symmetry, extended π-conjugation) leading to its preparation.

In summary, we have shown that new strongly absorbing NIR dyes can be easily prepared by extending the π-conjugation of the existing octupolar visible dyes. Further studies

---

† The IUPAC name for Crystal Violet is *N*-(4-{bis[4-(dimethylamino)-phenyl]methylene}cyclohexa-2,5-dien-1-ylidene)-*N*-methylmethanaminium chloride.

‡ The units of ε are $dm^3\ mol^{-1}\ cm^{-1}$ throughout.



Scheme 1 *Reagents and conditions*: i $NaNO_2$, H_2SO_4, 0 °C then KI, rt; ii $Pd(OAc)_2$, Bu_4NBr, KOAc, 80 °C; iii CF_3CO_2H, CH_2Cl_2, rt.

on these dyes, especially on their aggregation phenomena,[8] are currently in progress.

Experimental

All melting points are uncorrected. IR spectra were taken on a Perkin-Elmer R-297 spectrometer. NMR spectra were recorded in $CDCl_3$–TMS on a Bruker Avance 300 (300 MHz) instrument and coupling constants, *J*, are given in Hz. Electronic spectra were taken on a Shimadzu UV-160A spectrophotometer. Light petroleum refers to the 60–80 °C fraction.

Tris(4-iodo-3-methylphenyl)methanol 2

To a solution of New Fuchsin§ (**1**, 1.0 g, 2.73 mmol) in conc. H_2SO_4 (1.70 cm^3) and water (5 cm^3), was added a solution of $NaNO_2$ (0.62 g, 3.0 mmol) in water (2 cm^3) at 0 °C. After 15 min, the diazotized solution was treated dropwise with a solution of KI (7.0 g, 42.1 mmol) in water (5 cm^3). The mixture was stirred at room temperature for 5 h and then at 80 °C for 30 min. It was then cooled, filtered and the residue thoroughly

---

§ The IUPAC name for New Fuchsin is 4-[bis(4-amino-3-methylphenyl)-methylene]-2-methylcyclohexa-2,5-dien-1-ylidenaminium chloride.

washed with water. The residue was purified by column chromatography over silica gel (5% EtOAc in light petroleum) to give **2** (0.74 g, 40%); mp 98–99 °C (MeOH); ν_{max} ($CHCl_3$)/cm^{-1} 3650, 3560, 1450, 1365, 1185, 1000; δ_H ($CDCl_3$) 2.40 (9 H, s), 6.72 (3 H, dd, *J* 8.4, 2.1), 7.18 (3 H, d, *J* 2.1), 7.74 (3 H, d, *J* 8.4); δ_C ($CDCl_3$) 28.2, 81.0, 100.3, 126.9, 128.9, 138.5, 141.2, 146.2; found C, 39.12, H, 2.56; $C_{22}H_{19}I_3O$ requires C, 38.86, H, 2.79%.

A general procedure for threefold Heck reaction of 2: preparation of the dye bases 3 and 5

$Pd(OAc)_2$ (0.003 g, 0.014 mmol) was added to a solution of **2** (0.10 g, 0.15 mmol), 4-substituted styrene (0.90 mmol), Bu_4NBr (0.14 g, 0.44 mmol) and KOAc (0.11 g, 1.10 mmol) in DMF (3 cm^3) and the mixture heated at 80 °C for 30 h. It was then diluted with water (5 cm^3) and extracted with CH_2Cl_2. The organic layer was washed with water, dried and evaporated under reduced pressure. The residue was purified by preparative thin-layer chromatography over silica gel (10% EtOAc in light petroleum) to give **3** or **5**.

Compound 3. Yield 50%; mp 195–196 °C (EtOH); ν_{max} (KBr)/cm^{-1} 3450, 2916, 1606, 1521, 1354, 1164; δ_H ($CDCl_3$) 2.37 (9 H, s), 2.97 (18 H, s), 6.71 (6 H, d, *J* 8.5), 6.93 (3 H, d, *J* 16.1), 7.10 (3 H, d, *J* 16.1), 7.25–7.27 (6 H, m), 7.40 (6 H, d, *J* 8.5), 7.50 (3 H, d, *J* 7.9); δ_C ($CDCl_3$) 20.2, 40.4, 86.2, 112.5, 122.0, 124.1, 126.4, 126.6, 127.5, 129.8, 130.3, 134.5, 135.4; found C, 84.50, H, 7.50, N, 5.70; $C_{52}H_{55}N_3O$ requires C, 84.67, H, 7.45, N, 5.69%.

Compound 5. Yield 55%; mp 126–127 °C (EtOH); ν_{max} (KBr)/cm^{-1} 3452, 2917, 1635, 1510, 1248 and 1173; δ_H ($CDCl_3$) 2.38 (9 H, s), 3.83 (9 H, s), 6.90 (6 H, d, *J* 8.6), 6.96 (3 H, d, *J* 16.2), 7.09 (3 H, d, *J* 8.1), 7.17 (3 H, s), 7.18 (3 H, d, *J* 16.2), 7.45 (6 H, d, *J* 8.6), 7.52 (3 H, d, *J* 8.1); found C, 84.15, H, 6.50; $C_{49}H_{46}O_4$ requires C, 84.25, H, 6.58%.

Sample preparation for absorption measurements

Stock solutions of the dye base **3** or **5** (0.135 mM) and TFA (30.50 mM) were prepared in CH_2Cl_2. The dye solutions (**4** or **6**) were prepared by mixing 1 cm^3 of the dye base solution with the TFA solution (0.5 cm^3 for **4**, 9 cm^3 for **6**) and the final volumes adjusted to 10 cm^3 with CH_2Cl_2. For the pH dependent study of **4**, the solutions A–E (Fig. 1) were prepared by adding varying amounts of the TFA solution (0.5, 1, 2, 9 cm^3 and 9 cm^3 + 50 mg TFA) to a 1 cm^3 aliquot of the stock solution of **3** and the final volumes were adjusted to 10 cm^3 with CH_2Cl_2.

Acknowledgements

The authors are grateful to Professor S. P. Moulik and S. K. Hait for absorption measurements and to S. K. Ghorai for some experimental assistance. Financial support for this work was provided by DST (SP/S1/G-14/97) and CSIR (research fellowship to S. K. S.).

References

1 (*a*) M. Matsuoka, *Infrared Absorbing Dyes*, Plenum Press, New York, 1990; (*b*) J. Fabian, H. Nakazumi and M. Matsuoka, *Chem. Rev.*, 1992, **92**, 1197.

2 M. Zollinger, *Colour Chemistry. Synthesis*, *Properties and Applications of Organic Dyes and Pigments*, VCH, Weinheim, 1987.

3 (*a*) W. Z. König, *Angew. Chem.*, 1925, 743; (*b*) H. Kuhn, *Angew. Chem.*, 1959, **71**, 93; (*c*) H. Schmidt and R. Wizinger, *Justus Liebigs Ann. Chem.*, 1959, **623**, 204; (*d*) S. Dähne and R. Radeglia, *Tetrahedron*, 1971, **27**, 3673; (*e*) S. Akiyama, K. Yoshida, M. Hayashida, K. Nakashima, S. Nakatsuji and M. Ioyada, *Chem. Lett.*, 1981, 311; (*f*) J. L. Brédas, R. Silbey, D. S. Boudreaux and R. R. Chance, *J. Am. Chem. Soc.*, 1983, **105**, 6555; (*g*) S. Nakatsuji, N. Okamoto, K. Nakashima and S. Akiyama, *Chem. Lett.*, 1986, 329; (*h*) S. Akiyama, S. Nakatsuji, K. Nakashima and S. Yamasaki, *Dyes Pigm.*, 1988, **9**, 459; (*i*) S. Akiyama, S. Nakatsuji, K. Nakashima, M. Watanabe and H. Nakazumi, *J. Chem. Soc.*, *Perkin Trans. 1*, 1988, 3155.

4 S. Sengupta and S. K. Sadhukhan, *Tetrahedron Lett.*, 1999, **40**, 9157.

5 T. Jeffery, *Tetrahedron*, 1996, **52**, 10113.

6 (*a*) D. Hellwinkel, H. Stahl and H. G. Gaa, *Angew. Chem.*, *Int. Ed. Engl.*, 1987, **26**, 794; (*b*) B. Abarca, G. Asensio, R. Ballesteros and T. Varca, *J. Org. Chem.*, 1991, **56**, 3224.

7 (*a*) G. L. Gaines, Jr., *Angew. Chem.*, *Int. Ed. Engl.*, 1987, **26**, 341; (*b*) G. Morowsky, L. F. Chi, D. Möbius, R. Steinhoff, Y. R. Shen, D. Dorsch and B. Rieger, *Chem. Phys. Lett.*, 1988, **147**, 420.

8 A. Mishra, R. K. Behera, P. K. Behera, B. K. Mishra and G. B. Behera, *Chem. Rev.*, 2000, **100**, 1973.