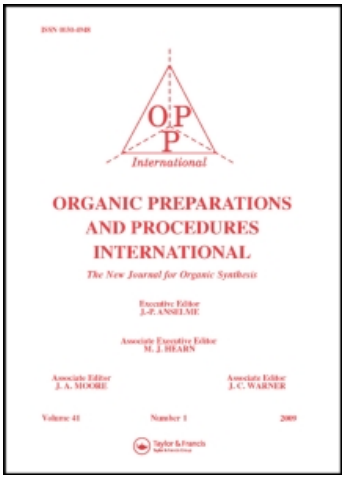


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# FACILE ONE-POT SYNTHESIS OF FLUORESCENT BENZOTHIENO[2,3:c]QUINOLINE

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6. H. Esterbauer, *Monasth. Chem.*, **101**, 782 (1970).

7. N. Munsch, A. M. de Kecondo and Ch. Frayssinet, *FEBS Letters,* **30,** 286 (1973).

8. H. M. Tilliam, E. Schauenstein and H. Esterbauer, *Europ. J. Cancer,* **14**, 533, (1978).

9. H. M. Tilliam, E. Schauenstein, E. Ertl and H. Esterbauer, *Europ. J. Cancer,* **12**, 989 (1976).

10. I. R. Schmolka and P. E. Spoerri, *J. Org. Chem.*, **22**, 943 (1957).

11. M. Seki, Y. Mori, M. Hatsuda and M. Yamada, *J. Org. Chem.*, **67**, 5527 (2002).

12. V. M. Kulkarni and H. P. Tipnis, *Curr. Science*, **41**, 637 (1972).

13. J. C. Perkin and B. Love, *Biochim. Biophys. Acta,* **78,** 753 (1963).

14. H. Esterbauer, A. Ertl, N. Scholz, *Tetrahedron*, **32**, 285, (1976).

15. R. Kuhn and C. Grundmann, *Ber.*, **70**, 1318 (1937).

16. E. R. Blout and M. Fields, *J. Am. Chem. Soc.*, **70**, 189 (1948).



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## FACILE ONE-POT SYNTHESIS OF FLUORESCENT BENZOTHIENO[2,3:c]QUINOLINE

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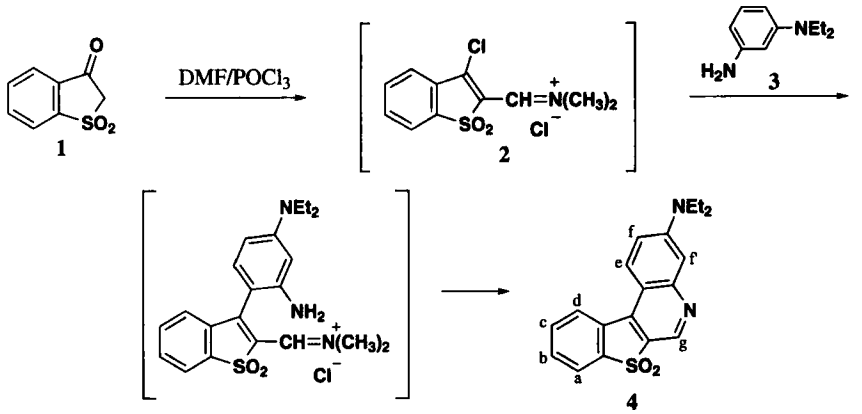
Fluorescent heterocyclic compounds are of interest as functional materials for applications in tunable dye lasers,[1] molecular probes for biochemical research,[2] polymers[3] and dyes.[4] Fluorophores are also useful tools in the search for new pharmacological agents and in the development of new diagnostic methods.[5] The literature[6] abounds with examples of the use of

β-chlorovinyl aldehydes of five-membered benzofused heterocycles in the preparation of anti-tumor agents,[7] psychotropic drugs,[8] fungicides [9] among other drugs. Interesting dyes and fluorescent brighteners have been synthesised by the annelation of other heterocyclic rings to β-chlorovinyl aldehydes by our group.[10,11] Extrapolating these concepts further to our ongoing quest to design novel fluorescent compounds,[12-15] we utilized the Foron Blue SR[16] precursor benzo[b]thiophene-3(2H)-one-1,1-dioxide(**1**)[17] to devise a one-pot synthesis of the fluorescent benzothieno[2,3:c]quinoline **4** through the cyclization of the intermediate halomethyleniminium salt, generated during the Vilsmeier reaction.[18]




Benzo[b]thiophene-3(2H)-one-1,1-dioxide (**1**) was treated with the Vilsmeier reagent derived from DMF and $POCl_3$ at 80°C. After the usual aqueous work-up, α β-hydroxy aldehyde was isolated instead of the expected β-chlorovinyl aldehyde, suggesting that the chlorine atom of intermediate **2** is highly labile. This is attributable to the conjugation of the chlorine atom with the $-SO_2$ group, thereby making the chlorine atom susceptible to nucleophilic substitution. The elemental analysis of the isolated product further confirmed the absence of chlorine. Hence, we pursued reaction conditions wherein the formylation of **1** was followed by *in situ* reaction with *m*-(diethylamino)aniline (**3**) to yield the yellow benzothieno[2,3:c]quinoline **4**. This compound is bright fluorescent yellow shade on poly (ethylene terepthalate). The reaction could be extended to suitably substituted *m*-(dialkylamino) anilines to synthesise a wide variety of fused heterocycles. One property of this class of compounds that could prove beneficial from a commercial viewpoint is the excellent sublimation fastness exhibited by the compound during evaluation of the dyed polyester.

## EXPERIMENTAL SECTION

Mps were determined in capillaries. $^1H$ NMR spectra were recorded in $CDCl_3$ with a Varian-300 MHz spectrometer, chemical shifts are in p.p.m. from the internal standard TMS. IR spectra were recorded on "Bomen, Hartmann and Braun" FTIR. Elemental analysis was done on "Hareus Rapid Analyser". UV-Visible spectra were recorded on "SPS –400 PYE UNICAM" spectrophotometer. The absorption spectra were recorded by dissolving 1.0 mg of the compound in 1 mL of

DMF and 9 mL of methanol. Further 1 mL of this stock solution was diluted to 10 mL with methanol. The dyeing of polyester was done on HTHP dyeing equipment.

**Benzo[b]thiophene-3(2H)-one-1,1-dioxide (1)** was synthesized according to the literature procedure[17] and *N,N*-diethyl-*m*-phenylenediamine **(3)** was obtained as an oil from commercially available *m*-(diethylamino)acetanilide by acid hydrolysis (15% $H_2SO_4$), neutralization (10% NaOH), extraction with solvent followed by distillation under reduced pressure (bp. 105°C/3 mm).

**Benzothieno[2,3-c]quinoline (4).**- To stirred DMF (10 mL) cooled to 0°C in an ice salt mixture, $POCl_3$ (2.52 g, 40.0 mmol) was added dropwise; after completion of addition, the mixture was stirred for 30 minutes. Subsequently **1** (3 g, 20.0 mmol) was added in one lot and the temperature of the reaction mixture was gradually raised to and maintained at 80°C on a water bath for 6 hrs. It was then cooled to room temperature and *N,N*-diethyl-*m*-phenylenediamine **(3)** (3.285 g, 20.0 mmol) was added under stirring. The temperature was raised to and maintained at 60°C for 2 hrs. The reaction mixture was cooled once again and poured into a well stirred ice-water mixture (25 mL). Neutralization to pH 4 with solid sodium acetate, yielded a yellow solid, which was collected, washed with water and dried. It was crystallized from a methanol-chloroform mixture to yield 3.62 g (65%) of **4**, mp. 220°C.

$^1$H NMR (300 MHz): d 1.23 (t, J = 7.05Hz, 6H), 3.55 (q, J = 7.08Hz, 4H), 7.12-7.15 (m, 2H, arom), 7.62-7.76 (m, 3H, arom), 7.89 (d, J = 7.14Hz, 1H, arom), 8.30 (d, J = 7.50Hz, 1H, arom), 8.33 (s, 1H, arom). UV(MeOH): $\lambda_{max}$ 441 nm, log ε 4.25.

*Anal.* Calcd for $C_{19}H_{18}N_2O_2S$: C, 67.45; H, 5.33; N, 8.28. Found: C, 67.42; H, 5.29; N, 8.21

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## REFERENCES

1. M. Matsuoka, *J. Soc. Dyers Colour*, **105,** 167 (1989).

2. E. R. Bissel, A. R. Mitchell and R. E. Smith, *J. Org. chem.*, **45,** 2283 (1980).

3. K. Venkatraman, "*Chemistry of Synthetic Dyes*", Vol. 5, p. 535-679, Academic Press, 1971.

4. J. Griffiths, V. Miller and G. S. Bahra, *Dyes and Pigments*, **28,** 327 (1995).

5. R. Kennedy, "*Coumarins*", John Wiley, New York, 1997.

6. P. R. Giles and C. M. Marson, *Tetrahedron*, **47**, 1303 (1991).

7. T. Nagai, I. Myokan, F. Keishi, K. Ohta, N. Taya, S. Miyabara, M. Shibata, H. Mikami and T. Hori, *Ger. Offen. DE 4,* 034, 687 (1991); *Chem. Abstr.*, **115**, 27992m (1991).

8. M. Debaret, P. Berthelot and C. Vaccher, *Eur. Pat. EP* 463, 969 (1992); *Chem. Abstr.*, **116**, 194138h (1992).

9. K. Bhandari, V.A. Murti, P.C. Jain and N. Anand, *Indian J. Chem. Sect. B*, **17B**, 246 (1979).

10. U. V. Gokhale and S. Seshadri, *Dyes and Pigments*, **8**, 157 (1987).

11. N. K. Chodankar, S. Sequeira and S. Seshadri, *Dyes and Pigments*, **7**, 231 (1986).

12. M. R. Jayanth, H. A. Naik, D. R. Tatke and S. Seshadri, *Indian J. Chem.*, **11**, 1112 (1973).

13. M. R. Jayanth and S. Seshadri, *Dyes and Pigments*, **8**, 399 (1987).

14. M. R. Jayanth, R. Krishnan, P. C. Sekhar and S. Seshadri, *Dyes and Pigments*, **8**, 405 (1987).

15. R. Rajagopal and S. Seshadri, *Dyes and Pigments*, **13**, 161 (1991).

16. B. Werner, (Sandoz Ltd), Brit. UK Pat 2, 026, 528 (1980); *Chem.Abstr.*, **93**, 48539e (1980).

17. M. A. Matskanova and G. Ya. Vanags, *Doklady Akad Nauk* SSSR., **132**, 615 (1960); *Chem. Abstr.*, **54**, 24636 (1960).

18. A. Vilsmeier and A. Haack, *Ber.*, **60**, 119 (1927).



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## SYNTHESIS OF PHENYLENE 1,3- AND 1,4-*bis*(METHYLENE)-3-CARBAMOYLPYRIDINIUM BROMIDES

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The B3 vitamin nicotinate (niacin) is needed by organisms for the synthesis of nicotinamide adenine dinucleotide ($NAD^+$) and its reduced form, NADH. These compounds are important nucleotide coenzymes in biotic electron transfer systems. There have been many studies of the biological oxidation and reductions related to the $NAD^+$/NADH pair.