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4-*Tert*-Butyl-1-(4′-dimethylamino-benzylideneamino)pyridinium Perchlorate (BDPP): A Novel Fluorescent Dye

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ABSTRACT

4-Tert-*butyl-1-(4′-dimethylaminobenzylideneamino)pyridinium perchlorate (BDPP) is a novel dye showing unusual properties, viz. (i) it gives a yellow-green fluorescence which quenched on heating and in solution, and (ii) by heating at 180° or by simple squeezing, it is transformed into orange, non-fluorescent crystals (i.e. it is piezochromic). Surprisingly, among other 1-(benzylideneamino)pyridinium salts, BDPP was the only dye revealing the above properties.*

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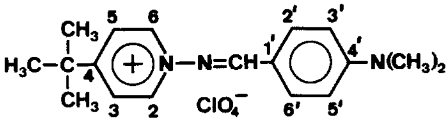
1 INTRODUCTION

The fluorescence of substances, both as solids and in solution, is due to their molecular structure.[1] For example, some benzylideneanilines with suitable substituents which allow intramolecular charge transfer, or with *ortho*-hydroxy groups, are effective luminescent materials, due to their rigid structures.[1] Particular crystal packing can also give rise to solid state fluorescence, as shown recently.[2] Solutions of such compounds very often do not fluoresce at all, and sometimes, there is more than one crystal modification showing a different fluorescence intensity.[2] Shortening of the distance between neighbouring molecules or, more exactly, between their chromogens, results in a diminution or quenching of the fluorescence, as well as a bathochromic shift of the band in the solid state absorption spectrum.[2] As a whole, fluorescent dyes belong to different chemical classes.[2,3] The present paper deals with the unusual properties of 4-*tert*-butyl-1-(4′-dimethylaminobenzylideamino) pyridinium perchlorate (BDPP).



Structure 1

RESULTS AND DISCUSSION

The synthesis of BDPP was performed by the general method of condensing benzaldehydes with 1-aminopyridinium salts.[4–6]

Besides the dyeing ability towards synthetic fabrics, elsewhere reported,[7] we stress, in this present paper, the ‘piezochromic’ and fluorescence properties of BDPP and their independence of heat treatments. At room temperature, the dye forms yellow-green leaflets showing a neat fluorescence. In the solid state absorption spectrum, the first long-wavelength band appears at 400 nm. The analogous fluorescence spectrum (excitation wavelength 313 nm) displays the band at 547 nm. The fluorescence disappears when the spectrum is recorded in methanol.

An orange-coloured modification of BDPP, which does not exhibit any fluorescence, can be obtained in two ways. By heating a sample on a melting point apparatus at *c.* 180°, its colour changes from yellow-green to orange. Further heating causes the melting of the sample over a wide temperature range (228–246°), a common phenomenon in this series of dyes, probably due to liquid crystal properties. Also, in differential scanning calorimetry

(DSC) experiments, a peak appears at 180°, thus indicating a possible crystalline transition. The second method for attaining the orange, non-fluorescent form, is quite unusual: simple pressure with a spatula is sufficient to promote a modification stable for several hours (on suitable standing, the original form is reversibly recovered). For this reason, BDPP can be considered a piezochromic dye. Examples of dyes showing this behaviour comprise of dehydrodianthrones,[8] metal complexes,[9-12] heterocycles[13-16] and polymers.[17-19]

^{1}H and ^{13}C NMR spectra in solution (figures not reported) and the ^{13}C-^{1}H COSY spectrum (Fig. 1) clearly sustain the structure of BDPP. The solid state ^{13}C NMR spectra are practically unaffected (Fig. 2) when the yellow-green form is compared with that obtained by crushing the orange form. The same phenomenon occurs for a specimen heated at 190° and quickly quenched in liquid nitrogen. Consequently, one can deduce that the specific intermolecular effects are too weak to be revealed by NMR spectra.

It is worth mentioning that BDPP shows a unique behaviour in the series. For example, if the *tert*-butyl group is replaced by a methyl, both

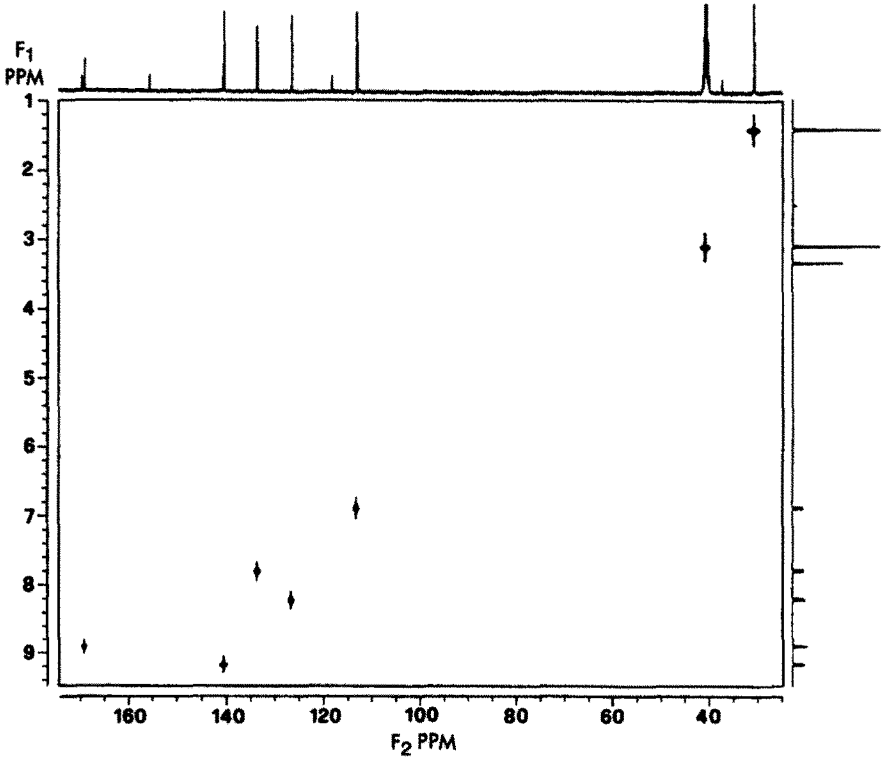


Fig. 1. ^{1}H-^{13}C COSY spectrum of BDPP.

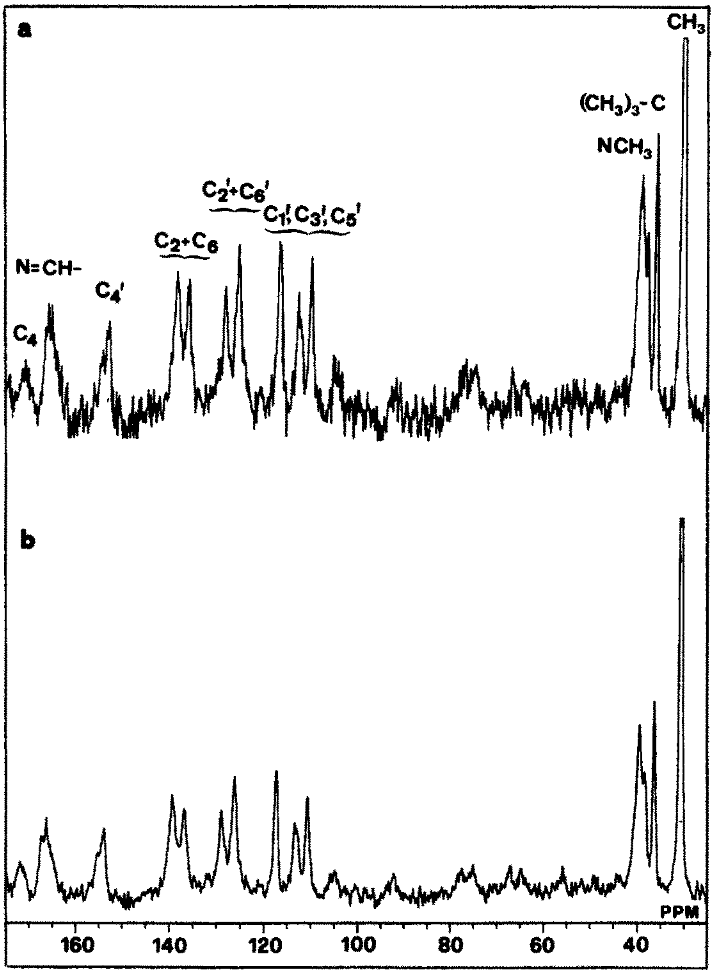


Fig. 2. Solid state ^{13}C spectrum of BDPP: (a) yellow-green fluorescent crystals; (b) crushed orange crystals.

fluorescence and colour change on compression disappear.[4] To explain the unusual properties of BDPP, the synthesis of similar dyes is in progress. In particular, we are interested to obtain suitable crystals of BDPP for a complete X-ray analysis. Unfortunately, with the perchlorate counterion, the samples obtained are too thin and, therefore, different anions must be selected.

3 EXPERIMENTAL

The synthesis of BDPP has been reported elsewhere.[4]

The solid state absorption and fluorescence spectra were recorded on a

Hewlett-Packard 8452 spectrophotometer and a MSF 102 spectrofluorimeter (PAN, Waesaw, Poland) respectively. The internal wall of the quartz cell was sprayed with a concentrated solution of BDPP in methanol; the solvent was then slowly evaporated to obtain the crystals covering the surface.

^1H and ^{13}C NMR spectra were obtained with a Jeol EX 400 spectrometer in DMSO-d_6 solution.

> ^1H NMR: δ (ppm): 1·42 (s, —$C(CH_3)_3$), 3·11 (s, —$N(CH_3)_2$), 6·89 (d, $H_{3',5'}$), 7·80 (d, $H_{2',6'}$), 8·21 (d, $H_{3'5}$), 8·91 (s, N=CH), 9·18 (d, $H_{2'6}$).
>
> ^{13}C NMR: δ (ppm): 29·67 —$C(\underline{C}H_3)_3$), 36·25 (s, —$\underline{C}(CH_3)_3$, 39·68 —$N(CH_3)_2$), 111·69 ($C_{3',5'}$), 116·88 ($C_{1'}$), 125·16 ($C_{3'5}$), 132·22 $C_{2',6'}$), 139·05 ($C_{2'6}$), 154·17 ($C_{4'}$), 167·64 (N—CH—), 168·27 (C_4).

The two-dimensional ^{13}C-^1H COSY spectrum was recorded with spectral windows of 15 000 and 3400 Hz in the F_2 and F_1 dimensions, respectively. The acquisition involved 160 scans for 256 experiments. The data were collected and transformed using a sine bell squared function.

High resolution solid state ^{13}C NMR spectra were recorded on a Joel GSE 270 spectrometer at 67·8 MHz under conditions of ^1H-^{13}C cross polarization, high-power proton decoupling, magic-angle spinning. Samples (100–200 mg) were contained in rotors of zirconia and spun at 3·5 kHz spinning rate. Chemical shifts (δ scale, high frequency positive) were referenced to external neat liquid tetramethylsilane (TMS). The assignments were made by comparison with a ^{13}C NMR spectrum in DMSO solution and examination of the shape of the signals. The =N—CH_3, C_4 and C_7, signals showed the characteristic multiplicity as result of second-order quadrupolar effects of ^{14}N[20], while $C_{2,6}$ and $C_{2',6'}$ appeared as doublets because of the closeness to the asymmetry center.

The DSC (Differential Scanning Calorimetry) curve of BDPP was recorded on a PERKIN-ELMER DSC 7.

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REFERENCES

1. Krasovitskii, B. M. & Bolotin, B. M., *Organic Luminiscent Materials*. VCH, Weinheim, 1988.

2. Langhals, H., Demmig, St & Potrawa, Th., *J. Prakt. Chem.*, 333 (1991) 733 and references therein.
3. Gold, H. & Theidel, H., *Ullmanns Encyclopädie der Technischen Chemie, Vol. 17*, 4th ed. VCH, Weinheim, 1979, p. 459.
4. Gawinecki, R., *Croat. Chem. Acta*, **63** (1990) 187.
5. Gawinechi, R., *J. Prakt. Chem.*, **330** (1988) 759.
6. Gawinecki, R. & Rasala, D., *Spectrosc. Lett.*, **20** (1993) 523.
7. Hanna, M. A., Girges, M. M. & Gawinecki, R., *J. Chem. Technol. Biotechnol.*, **52** (1991) 559.
8. Fortuem, G., *Ber Bunsenges. Phys. Chem.*, **78** (1974) 391.
9. Kotowski, M., Van Eldik, R., Razak Bin, A., Burgess, J. & Radulovic, S., *Inorg. Chim. Acta*, **131** (1987) 225.
10. Razak Bin, A., Burgess, J., Kotowski, M. & Van Eldik, R., *Transit. Met. Chem. (London)*, **12** (1987) 230.
11. Bray, K. L., Drickamer, H. G., Schmitt, E. A. & Hendrickson, D. N., *J. Am. Chem. Soc.*, **111** (1989) 2849.
12. Drickamer, H. G. & Bray, K. L., *Acc. Chem. Res.*, **23** (1990) 55.
13. Mataka, S., Takahashi, K., Tashiro, M., Lin, W. H., Iwasaki, S., Akiyama, S. & Yonemitsu, T., *J. Heterocycl. Chem.*, **26** (1989) 215.
14. Matsui, M., Shibata, K. & Muramatsu, H., *Bull. Chem. Soc. Jpn*, **63** (1990) 1845.
15. Reichardt, C., *Chem. Soc. Rev.*, **21** (1992) 147.
16. Maeda, K. & Hayashi, T., *Bull. Chem. Soc. Jpn*, **43** (1970) 429.
17. Nallicheri, R. A. & Rubner, M. F., *Macromolecules*, **24** (1991) 517.
18. Schilling, F. C., Lovinger, A. J., Davis, D. D., Bovey, F. A. & Zeigler, J. M., *J. Inorg. Organomet. Polym.*, **2** (1992) 47.
19. Song, K., Miller, R. D., Wallraft, G. M. & Rabolt, J. F., *Macromolecules*, **25** (1992) 3629.
20. Gobetto, R., Harris, R. K. & Apperley, D. C., *J. Magnet. Reson.*, **96** (1992) 119.