New Thermo and Photochromic 10-Methylspiro{dibenzo[*b,f*][1,4]oxazepino-11,3′-3*H*-naphtho[2,1-*b*]-1,4-oxazine}

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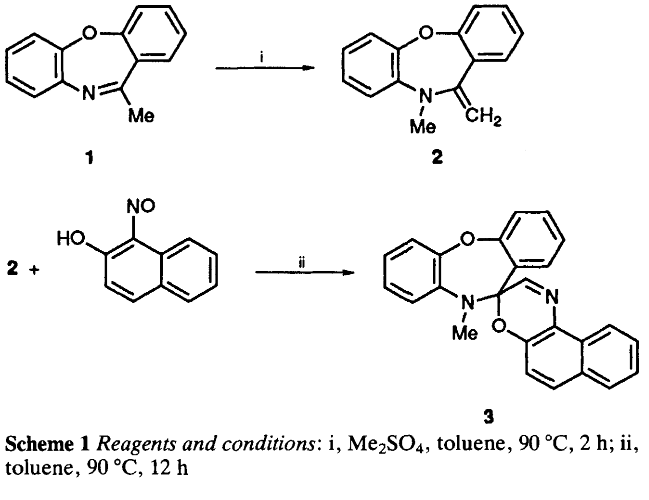
The synthesis of the new 10-methylspiro{dibenzo[*b,f*][1,4]oxazepino-11,3′-3*H*-naphtho[2,1-*b*]-1,4-oxazine **3** allows the influence of conformational factors on its thermal and photochemical behaviour to be studied.

Spironaphthoxazines are an important class of photochromic and/or thermochromic compounds[1] that undergo reversible structural modifications induced by either light or heat. Although spironaphthoxazines have attracted significant attention in view of possible practical applications such as in data storage or retrieval, displays, optical filters, *etc.*, no major commercial exploitation has so far been reported mostly because of their poor fatigue resistance to light or heat. The many structural modifications carried out on the parent compound have not helped to overcome in a satisfactory way these limitations.[2]

In this communication we present preliminary results on the synthesis, characterization and functional behaviour of compound **3**, the first of a new class of spiro{dibenzo[*b,f*][1,4]-oxazepino-11,3′-3*H*-naphtho[2,1-*b*]-1,4-oxazine}s (Scheme 1).[3]



Scheme 1 *Reagents and conditions*: i, Me_2SO_4, toluene, 90 °C, 2 h; ii, toluene, 90 °C, 12 h

Thus, 11-methyldibenzo[*b,f*][1,4]oxazepine **1**[4] was treated with dimethyl sulphate in toluene at 90 °C for 2 h to give the corresponding *N*-methyl-11-methylene derivative **2** in 50% yield. Further reaction of **2** with 1-nitroso-2-naphthol in

Table 1 Colouration and fading temperatures of **3** and absorption maximum of **4** in various solvents

Solvent	Activation temp./°C[a]	**4**, λ_{max}/nm	Fading temp./°C[b]
Pr^{i}OH	60–65	590	60 ± 2
$ClCH_2CH_2Cl$	70–75	576	70 ± 2
MeCN	80–85	570	80 ± 2
PhMe	90–95	572	90 ± 2

[a] Temperature range at which the coloured form is detectable. [b] Temperature at which the coloured form is not detectable.

Table 2 Photochromism of **3** in different solvents

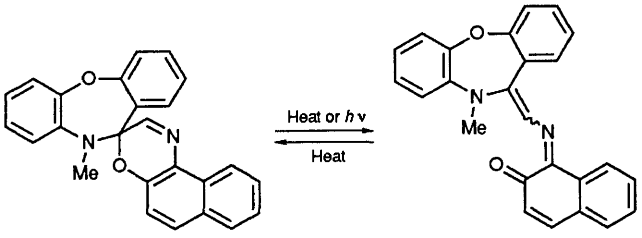
Solvent[a]	T/°C[b]	**4**, λ_{max}/nm[c]
n-hexane	−32	546
PhMe	−37	564
Me_2CO	−32	574
MeOH	−20	582, 608
MeCN	−29	576

[a] 10^{-4} mol dm^{-3} solutions. [b] Temperature at which the solutions were irradiated with a UV-A lamp. [c] The spiro-form **3** has weak absorption bands in the 300–390 nm region.

Table 3 Torsional angles of conformers of **3** resulting from quantum-mechanical calculation (MOPAC 5.0)

Conformer	ϕ_1	ϕ_2	$\phi_3{}^a$	ϕ_4	ϕ_5	ΔH/kcal mol$^{-1\,b}$
3a	68.9	−55.3	179.7	−73.8	4.8	113.08
3b	68.4	−51.2	62.7	−65.5	−8.6	109.26
3c	−66.7	51.1	−59.2	71.0	10.6	115.35
3d	−64.9	46.8	64.7	61.1	19.8	108.94
3e	45.4	−62.6	53.5	31.9	58.3	115.42
3f	54.6	−69.9	−46.1	−9.2	66.5	121.31
3g	−44.1	61.3	72.3	−31.9	−62.7	115.58
3h	−57.9	68.4	162.0	21.0	−67.9	118.78

[a] Dihedral angle between the nitrogen lone pair and the oxazine C–O bond. [b] 1 cal = 4.184 J.



3 **4**

Scheme 2

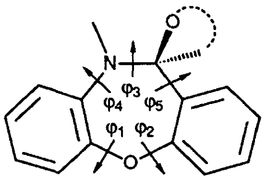


Fig. 1 Torsion angles considered in the theoretical calculation (MOPAC 5.0) defining the eight more stable conformers of **3**

toluene at 90 °C for 12 h afforded compound **3** in 30% yield. Compound **3** was fully characterized by elemental analysis, ^{1}H and ^{13}C NMR, IR, UV, and mass spectrometry.†

Compound **3** exhibits thermochromism and photochromism due to the reversible ring opening to the coloured aza-merocyanine **4** as depicted in Scheme 2.

As reported in Table 1, compound **3** shows thermochromic properties in various solvents; the λ_{max} of the aza-merocyanine form is red shifted when the solvent polarity is increased and the activation temperature is strongly affected by the nature of the solvent. It is also worth noting that the colour fading takes place within a very narrow temperature range, *i.e.* ±2 °C.

Furthermore, derivative **3** shows photochromic properties at low temperatures in the range −20 to −40 °C as shown in Table 2. The reason for the apparent lack of photochromism at temperatures higher than −20 °C may be kinetic in nature, *i.e.* a very fast ring closure would not allow a high enough concentration of the coloured aza-merocyanine **4** to be formed for it to be detected by the eye. On the other hand, as conformational factors seems to control the ring opening of spironaphthoxazines[5,6] requiring a charge-transfer from the nitrogen lone-pair n_N into the anti-bonding orbital σ^*_{C-O} of the adjacent C–O bond it is likely that when the dihedral angle (ϕ_3) between n_N and the C–O bond is in the range $45° < \phi < 90°$ the charge transfer would be not too effective and hence the colouration reaction sluggish.

The results of a preliminary quantum-mechanical study (MOPAC 5.0) on the title compound indicate that the two most stable isomers **3b** and **3d** adopt a *gauche* conformation (ϕ = *ca.* 65°) (Table 3). In Fig. 1 are reported the torsional angles defining the geometry of the most stable conformers of the oxazepine ring along with the ϕ_3 dihedral angle between the nitrogen lone pair and the oxazine C–O bond and their heats of formation.

We also note that compound **3**, unlike indolino-spironaphthoxazines, is not fluorescent at 77 K.[7] It is likely that the excited singlet state decays *via* a non-radiative mechanism because of the higher conformational mobility of the seven-membered ring that allows the interconversion between conformers **3d** and **3b** (Table 3). Kinetic studies on the thermal bleaching of the aza-merocyanine **4** back to **3** are in progress.

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References

1 R. C. Bertelson, in *Photochromism*, ed. G. H. Brown, Wiley-Interscience, New York 1971; *Photochromism: Molecules and Systems*, eds. H. Durr and H. Bouas-Laurent, Elsevier, Amsterdam, 1990.
2 S. Kawauchi, H. Yoshida, N. Yamashina, M. Ohira, S. Saeda and M. Irie, *Bull. Soc. Chem. Jpn.*, 1990, **63**, 267; E. Pottier, R. Dubest, R. Guglielmetti, P. Tardieu, A. Kellmann, F. Tfibel, P. Levoir and J. Aubard, *Helv. Chim. Acta*, 1900, **73**, 303; U. W. Grummt, M. Riechenbächer and R. Paetzold, *Tetrahedron Lett.*, 1981, 3945 and references cited therein.
3 G. Castaldi and P. Allegrini, Eur. Pat. Appl., 1990, No. 90203212.3.
4 R. Higginbottom and H. Suschitzky, *J. Chem. Soc.*, 1962, 2367.
5 S. M. Aldoshin and L. O. Atovmyan, *Izvest. Akad. Nauk SSSR, Ser. Khim.*, 1985, **9**, 2009.
6 R. Millini, G. del Piero, P. Allegrini, L. Crisci and V. Malatesta, *Acta Crystallogr., Sect. C*, 1991, in the press.
7 Unpublished results.

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† M.p. 144–145 °C (from acetone), satisfactory elemental analysis was obtained; mass (*m*/*z*): 378; ^{1}H NMR (200 MHz; CDCl$_3$; SiMe$_4$) δ: 2.98 (3H, s, MeN), 7.69 (1H, s, CH=N), 7.0–8.7 (14H, m, ArH); ^{13}C NMR (80 MHz; CDCl$_3$; SiMe$_4$) δ 35.86 (MeN), 89.24 (spiro-C), 116.5–131.1 (Ar–C), 150.47 (CH=N).