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The molecular design, synthesis and photochromic properties of spirooxazines containing a permanent azo (hydrazone) chromophore

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ABSTRACT

A range of molecular modelling techniques has been applied to predict optimized geometrical conformations and energies of the ring-closed oxazine form and ring-opened merocyanine forms of three azospirooxazines. A comparison of the relative stabilities of the possible isomers of the merocyanines was carried out by applying molecular mechanics (augmented MM2), while the prediction of the potential for photochromic behaviour was made by comparison of the heats of formation calculated by AM1. Synthetic routes were explored and as a result two azospirooxazines were isolated, one of which showed interesting and unusual photochromic behaviour. The instability of this compound towards purification by chromatography was investigated. The decomposition product was isolated and characterized with the aid of single crystal x-ray crystallography. The correlation between predicted and observed photochromic behaviour is discussed.

1. Introduction

There is considerable interest in photochromic materials arising from the many current and potential applications which are associated with their ability to undergo reversible, light-induced colour change. Photochromic dyes are used most widely in ophthalmic sun-screening applications, and are potentially useful in security printing, optical recording and switching, solar energy storage, nonlinear optics and biological systems [1–9]. There has also been considerable recent interest in their application to textiles in view of the potential for functional and design applications [10–17]. Spirooxazines constitute a particularly significant chemical class of photochromic dyes, due to their intense colour generation properties, good fatigue resistance and ease of synthesis. The existing range of products generally undergo positive photochromism, a light-induced transition from colourless to coloured due to a ring-opening reaction. This paper describes the molecular design, using computer-aided molecular modelling techniques, synthesis and evaluation of the photochromic performance of spirooxazine dyes also containing a permanent azo chromophore, which exists in the hydrazone form, aimed at producing materials which undergo a photochromic change from one colour to another. It was anticipated that the observed colour changes, determined by the differences in the visible spectra of the ring-closed and ring-opened forms, would be significantly different from those given by physical mixtures of permanently coloured dyes and photochromic dyes, thus providing the potential for niche applications, for example in anti-counterfeit security printing and brand protection.

2. Experimental

2.1. Instrumental methods

Melting points were determined as peak temperatures using a Mettler DSC 12E at a heating rate of 10 °C min^{-1} from 30 to 400 °C. Fourier Transform Infrared spectra were recorded as KBr discs with

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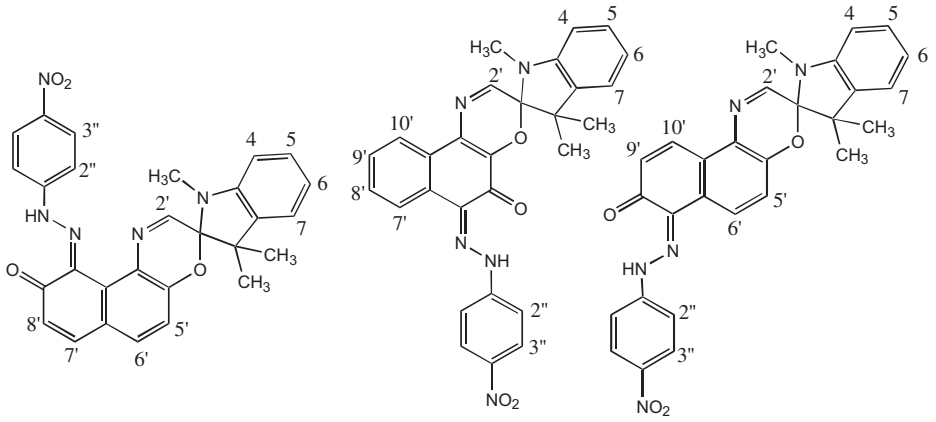


Fig. 1. Structures of azospiroxazines (illustrated in ketohydrazone forms) **1**–**3**, with numbering scheme for spectral interpretation.

a Nicolet Protégé 460 Spectrophotometer. ^{1}H NMR spectra were recorded on a Bruker AC 200 instrument at 200 MHz. Mass spectra were recorded in low resolution Electron Impact mode at 180 °C, on a Kratos Concept 1S spectrometer. Microanalysis for C, H and N was carried out on an Exeter Analytical CE440 analyser. UV–Visible spectra were recorded on a Perkin–Elmer UV–VIS Lambda 2 spectrophotometer. The photochromism was investigated by irradiating solutions contained in silica cells using a Phillips TL 20W/05 UVA bulb, with an emission maximum at 365 nm.

A single crystal of compound **10** suitable for X-ray crystallographic analysis was obtained by slow cooling of a solution in ethanol from its boiling point. The single crystal was covered in Paratone-N and mounted on a cryoloop on a Bruker Nonius X8-Apex2 CCD diffractometer. Data were collected with MoK_α radiation (0.7107 Å) at 100 K, cooled by an Oxford Cryosystems Cryostream. No significant crystal decay was found. Data were collected for adsorption by psi scans. The structure was solved by direct and difference Fourier methods and refined by full-matrix least-square on F^2. All non-hydrogen atoms were refined with anisotropic displacement parameters. Crystallographic computing was performed with SHELXTL programs.

Compound **10**: $C_{28}H_{25}ClN_5O_5$, M_r = 511.53; intense orange crystal 0.16 × 0.10 × 0.08 mm^3; triclinic, a = 9.3585(14), b = 11.1009(17), c = 13.201(2) Å; α = 111.358(8), β = 103.385(8), γ = 95.229°; V = 1219.1(3) Å^3; space group $P\bar{1}$; Z = 2, D_c = 1.394 Mg m^{-3}, T = 100(2) K; λ = 0.71073 Å (MoK_α radiation); μ = 0.098 mm^{-1}. $R1$ = 0.0507, wR2 = 0.1073 for $I > 2\sigma(I)$, Goodness-of-fit on F^2 0.973.

2.2. Synthesis of azospirooxazine **1** (route 1)

2,7-Dihydroxy-1-nitrosonaphthalene (**5**) was obtained by nitrosation of 2,7-dihydroxynaphthalene (**4**) according to a literature procedure [10]. Spirooxazine **7** was obtained by reaction of compound **4** with 1,3,3-trimethyl-2-methyleneindoline (Fischer's base) (**6**) according to a literature procedure [18].

2.2.1. Azo coupling of spirooxazine **7** with diazotized p-nitroaniline

p-Nitroaniline (1.04 g, 0.0075 mol) was stirred with concentrated hydrochloric acid (7.5 mL). A solution of sodium nitrite (0.53 g, 0.0075 mol) in water (6.8 mL) was added with stirring over 2 min keeping the temperature below 5 °C with ice cooling. An excess of nitrous acid was demonstrated by a positive reaction with starch/KI paper. The mixture was stirred for 20 min at 5 °C. Just before coupling, a few drops of aqueous sulphamic acid solution were added to remove the excess of nitrous acid. One fifth of the total volume was used for the coupling reaction. Spirooxazine **7** (0.34 g, 0.001 mol) was dissolved in ethanol (25 mL). A solution of sodium hydroxide (0.6 g, 0.15 mol) in water (3.2 mL) was added and the mixture stirred for 20 min. Anhydrous sodium acetate (2.5 g) was then added and stirring continued for 30 min. The *p*-nitrobenzenediazonium chloride solution was added to the solution of spirooxazine **7** over 30 min. No diazo excess was observed (H-acid test). The reaction mixture was stirred overnight. The pH was then adjusted to 6 by addition of dilute acetic acid. The precipitate was filtered, washed with water, allowed to dry in air and then recrystallized from ethanol to provide azospirooxazine **1** (0.27 g, 55%) as

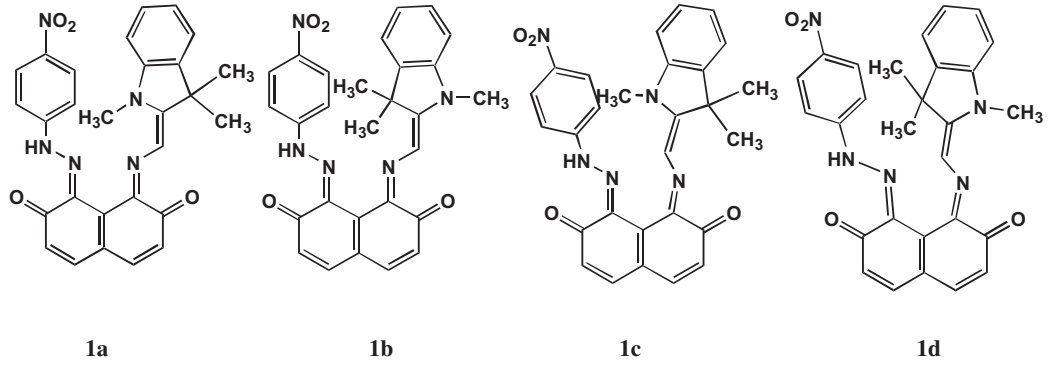


Fig. 2. The structures of the four possible transoid photomerocyanines from compound **1**.

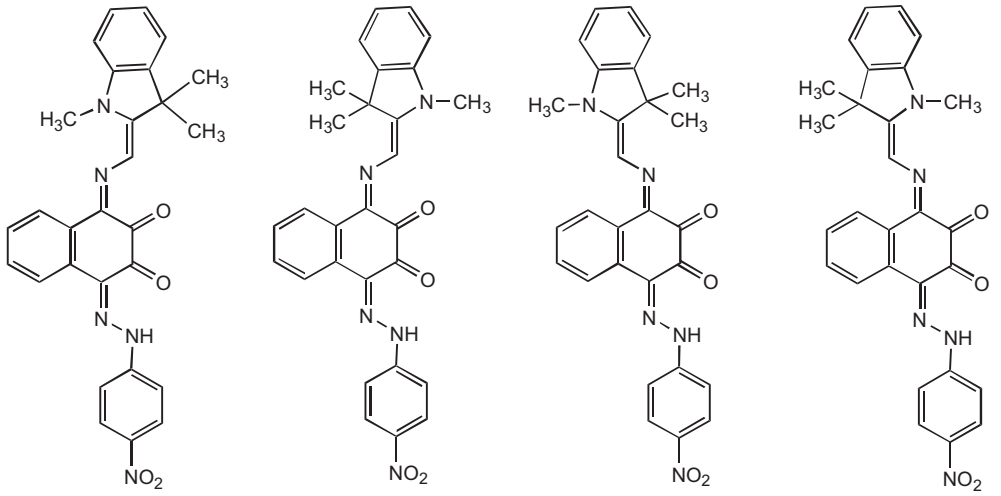


Fig. 3. The structures of the four possible transoid photomerocyanines from compound **2**.

orange-brown crystals. Because of apparent instability of the dye in solution, carefully-conducted recrystallisation was required. This involved addition of an optimized volume of boiling ethanol to the dye and chilling the solution in ice as soon as the dye had dissolved completely. The purified dye was filtered as soon as a reasonable quantity of crystals appeared, washed with cold ethanol and dried in a vacuum dessicator. The compound thus obtained was homogeneous by TLC examination. A further recrystallization was used to provide the analytical sample. The product decomposed without melting at 220 °C. ν_{max}(KBr)/cm^{-1}: 3435 (N–H st), 2975 (C–H st), 1626 (C=O, weak), 1595, 1572 (aromatic C–C st), 1487, 1334 (NO_2 st), 1160, 977 (C_{spiro}–O st), 845, 745, def); m/z (EI) (relative intensity, %): 493 (M^+, 5), 356 (38), 340 (39), 158 (56), 138 (79), 108 (4), 83 (100), 65 (57), 48 (92); δ_H ppm (200 MHz, $CDCl_3$) 1.26 (6H, s, $(CH_3)_2$), 2.86 (3H, s, NCH_3), 6.58 (1H, d, 7′-H, $J_{7',8'} = 9.4$ Hz), 6.63 (1H, d, 4-H, $J_{4,5} = 8.0$ Hz), 6.94 (1 H, m, 5-H), 7.20-7.45 (4H, 6-H, 7-H,5′-H, 6′-H, m, overlapping signals), 7.58 (1H, d, 8′-H, $J_{8',7'} = 9.8$ Hz), 7.71 (2H, d, 2′′-H, $J_{2'',3''} = 9.2$ Hz), 7.88 (1H, 2′-H, s), 8.31 (2H, d, 3′′-H, $J_{3'',2''} = 9.0$ Hz). The UV–Visible spectrum in dichloromethane gave λ_{max} values of 481 nm, 355 nm and 343 nm with respective molar extinction coefficients of 2.42×10^4 M^{-1} cm^{-1}, 1.42×10^4 M^{-1} cm^{-1} and 1.58×10^4 M^{-1} cm^{-1}

In attempts to purify compound **1** (0.27 g, 0.00054 mol) in a separate experiment, the product was chromatographed on a column of silica using dichloromethane initially and subsequently DCM/0.5% acetone. Amide **10** (0.17 g, 33%) was obtained from the eluates as orange crystals (from ethanol). The product decomposed without melting at 287 °C. ν_{max}(KBr)/cm^{-1}: 3436 (N–H, st), 1698 (C=O st), 1594, 1490 (Aromatic C–C st), 1336 (NO_2 st), 910 (C_{spiro}–O st), 746; *m/z* (EI) (relative intensity, %): 511 (M^+, 7), 509 (79), 481 (15), 372 (40), 359 (18), 344 (11), 331 (4), 254 (6.5), 158 (100), 144 (45)); δ_H ppm (200 MHz, $CDCl_3$); 1.59 (6H, s, $(CH_3)_2$), 2.51 (3H, s, NCH_3), 3.63 (1H, s, C–H), 6.50 (1H, d, 7′-H, $J_{7',8'} = 9.6$ Hz), 6.61 (1H, 4-H, m), 6.70(1H, m, 6-H), 7.06 (1H, m, 8′-H), 7.18 (1H, d, 7-H, $J_{7,6} = 8.3$ Hz), 7.38 (1H,d, 5′-H, $J_{5',6'} = 7.9$ Hz), 7.61 (1 H, m, 5-H), 7.65 (1H,d, 6′-H, $J_{6',5'} = 8.2$ Hz), 7.86 (d, 2H, 2′′-H, $J_{2'',3''} = 9.1$ Hz), 8.43 (2H,d, 3′′-H,

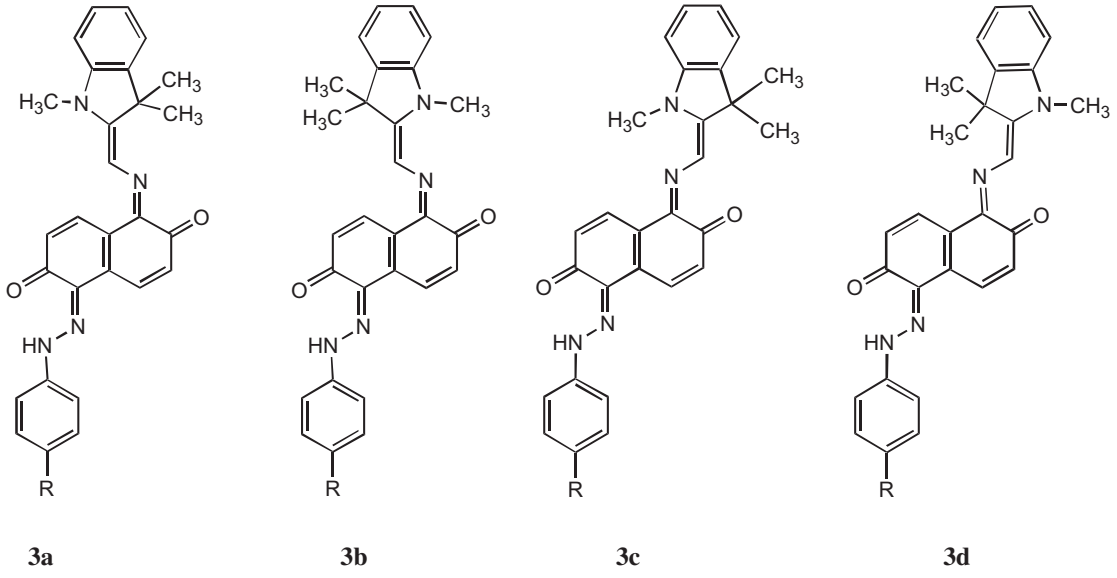


Fig. 4. The structures of the four possible transoid photomerocyanines from compound **3**.

Table 1
Steric energies (kcal mol^{-1}) from MM2 calculations for azospirooxazines **1**–**3** and their ring-opened merocyanine isomers **a**–**d**.

	1	2	3
Closed form	−1.65	−2.76	−2.32
a	3.42	2.14	2.53
b	4.47	−0.44	−0.05
c	3.76	3.39	3.93
d	4.65	5.17	5.17

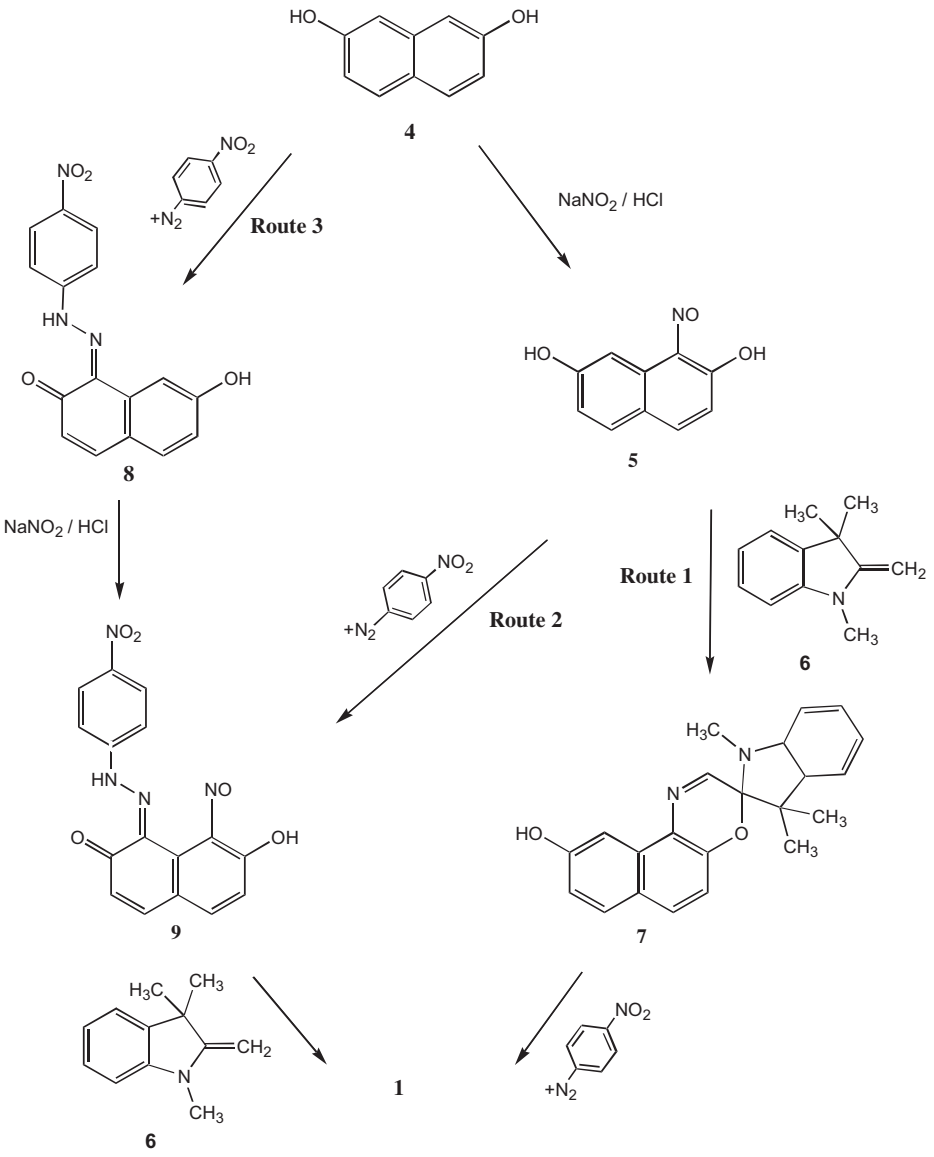
Table 2
Heats of formation (kcal mol^{-1}) from AM1 calculations for azospirooxazines **1**–**3** and their ring-opened merocyanine isomers **a**–**d**.

	1	2	3
Closed form	126.83	126.99	124.51
a	137.33	123.20	135.92
b	140.45	125.75	138.70
c	142.79	126.62	141.71
d	140.14	123.78	137.10

$J_{3'',2''} = 9.1$ Hz), 9.80 (s, 1H, OH), 11.65 (br s, 1H, NH), 12.50 (br s, 1H, NH). Found C, 65.8; H, 4.8; N, 13.2. $C_{28}H_{25}N_5O_5$ requires C, 65.7; N, 4.8; N, 13.6%.The UV–visible spectrum in dichloromethane showed λ_{max} values of 490 nm and 338 nm with respective molar extinction coefficients of 2.36×10^4 M^{-1} cm^{-1} and 1.33×10^4 M^{-1} cm^{-1}.

2.3. Synthesis of azospirooxazine *1* (route 2)

P-Nitroaniline (0.276 g, 0.002 mol) was diazotised as described for Route 1. 2,7-dihydroxy-1-nitrosonaphthalene (**5**) (0.39 g, 0.002 mol) was dissolved in a solution of sodium hydroxide (0.66 g, 0.016 mol) in water (28 mL) to which anhydrous sodium acetate (2.76 g) was added as in Route 1. *P*-Nitrobenzenediazonium chloride was added to the solution of compound **5** over 30 min. No diazo excess was observed (H-acid test). The reaction mixture was stirred overnight and the pH was then adjusted to 6 by addition of dilute acetic acid. After filtration, washing with water and drying at 60 °C, compound **9** (0.59 g, 85%) was obtained as a highly insoluble brown powder. Mp 161 °C. ν_{max}(KBr)/cm^{-1} 3431 (N-H, st), 3167 (C–



Scheme 1. Synthetic routes to azospirooxazine **1.**

H st), 1636 (C═O), 1576, 1437 (Aromatic C–C st), 1343 (NO_2 st), 749 (Ar–H); δ_H ppm (200 MHz, DMSO-d6); 6.24 (1H, d, 5-H, $J_{5,6}$ = 9.5 Hz), 6.77 (1H,d, 3-H, $J_{3,4}$ = 8.3 Hz), 7.32 (1H, d, 4-H, $J_{4,3}$ = 8.2 Hz), 7.86 (1H,d, 6-H, $J_{6,5}$ = 9.6 Hz), 7.92 (2H,d, H *o*– to NH, J = 9.0 Hz), 8.71 (1H, br s, OH), 8.23 (2H,d, H *o*– to NO_2, J = 8.7 Hz). The compound was unstable to recrystallisation and so was used subsequently without further purification.

1,3,3-trimethyl-2-methyleneindoline (Fischer's base) (**6**) (0.19 g, 0.0011 mol) in ethanol (0.65 mL) was added over 30 min to a solution of nitrosoazo compound **9** (0.338 g, 0.001 mol) in ethanol (3.8 mL) and the mixture heated under reflux for 2 h. The reaction mixture was then rotary evaporated to approximately one third of the original volume and allowed to stand overnight. Filtration, washing with cold ethanol and drying at 60oCprovided azospirooxazine **1** (0.06 g, 12%) (identical FTIR and NMR spectrum compared with the product obtained by route 1).

2.4. Attempted synthesis of azospirooxazine *1* (route 3)

P-nitroaniline (3.04 g, 0.022 mol) was diazotised as described for Route 1. 2,7-dihydroxynaphthalene (**4**) (3.88 g, 0.024 mol) was dissolved in a solution of sodium hydroxide (5.48 g) in water (200 mL). The solution was stirred for 30 min after the addition of anhydrous sodium acetate (22.85 g). The diazotized *p*-nitroaniline solution was added dropwise to the coupling component solution over 30 min. The final pH was 4.2. The solution was stirred for 75 min, heated to 80–90 °C, filtered, washed with hot water, hot ethanol and then dried at 60 °C. Azo compound **8** (5.53 g, 75%) was obtained as an insoluble red powder. Mp. 302 °C. ν_{max}(KBr)/cm^{-1}: 3404 (N–H, st), 3112 (C–H st), 1653 (C═O), 1590, 1497 (Aromatic C–C st), 1375 (NO_2 st), 748(Ar–H); found C, 61.9; H, 3.4; N, 13.6; $C_{10}H_7NO_3$ requires C, 62.1; H, 3.6; N, 13.6; δ_H ppm (200 MHz, DMSO-d6); 6.40 (1H,d, 5-H, $J_{5,6}$ = 9.6 Hz), 6.88 (1H, d, 3-H, $J_{3,4}$ = 8.2 Hz), 7.70–7.80 (2H, m, 1-H and 6-H, overlapping signals), 7.50 (1H, d, 4-H, $J_{4,3}$ = 8.3 Hz), 7.86 (2H,d, H *o*– to NH J = 9.2 Hz), 8.31 (2H,d, H *o*– to NO_2, J = 9.1 Hz). Found C, 61.9; H, 3.4; N, 13.6. $C_{16}H_{11}N_3O_4$ requires C, 62.1; N, 3.6; N, 13.6%

Attempted nitrosation of compound **8** using a range of standard procedures led only to recovery of starting material.

2.5. Synthesis of azospirooxazine *2*

Spirooxazine **13** was prepared from 2,3-dihydroxynaphthalene (**11**), via 2,3-dihydroxy-1-nitrosonaphthalene (**12**) according to literature procedures [18].

Diazotisation of *p*-nitroaniline and coupling with spirooxazine **13** was carried out as for the synthesis of dye **1** by route 1. Azospirooxazine **2** (0.27 g, 77%) was provided as brown crystals obtained by recrystallisation from ethanol (x 2). The compound decomposed without melting at 196 °C. ν_{max}(KBr)/cm^{-1}: 3436 (N–

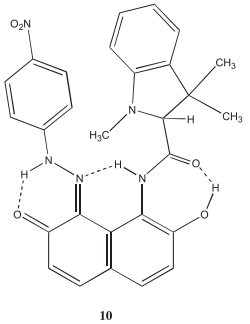


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Fig. 5. Structure of amide **10**.

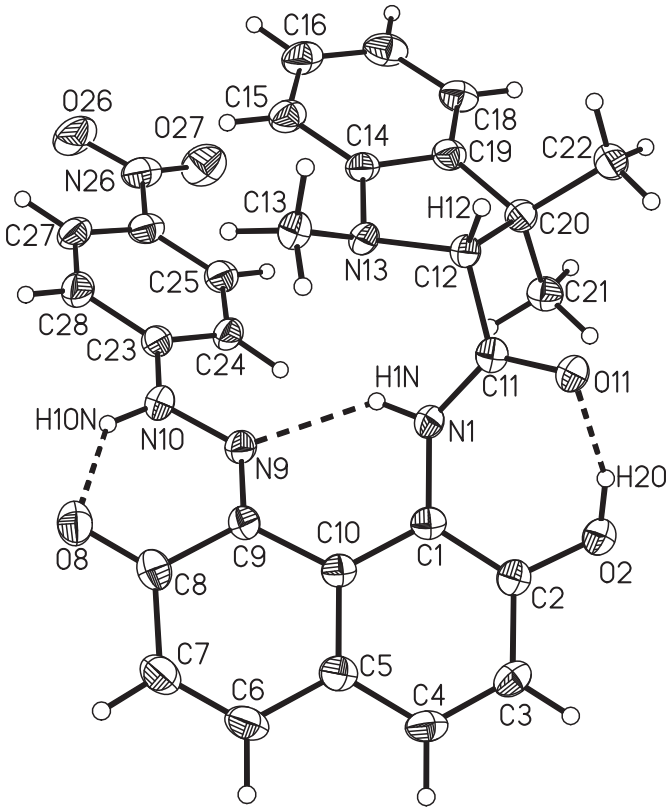


Fig. 6. The single crystal x-ray structure of amide **10**, with numbering scheme, showing intramolecular hydrogen bonding.

H st), 1610 (C═O st, weak), 1599, 1572, 1493, 1334 (NO_2 st), 1299, 1150, 930(C_{spiro}–O st), 760, 747; *m*/*z* (EI) (relative intensity, %): 493 (M^+, 80), 477 (71), 369 (30), 353 (72), 343 (31), 309 (13), 160 (100), 138 (90), 69 (64); δ_H ppm (200 MHz, $CDCl_3$) 1.30 (3H, s, C–CH_3), 1.42 (1H, s, C–CH_3), 2.79 (3H, s, NCH_3), 6.52 (1H, d, 4-H, $J_{4,5}$ = 7.7 Hz), 6.89 (1H, m, 5-H), 7.06 (1H, dd, 7-H, $J_{7,6}$ = 7.79), 7.20 (1H, m, 6-H), 7.45-7.55 (4H, m, 7′-H, 8′-H, 9′-H, 10′-H), 7.60 (2H, d, H *o*– to NH, $J_{10,11}$ = 9.16 Hz), 7.97 (s, 1H, 2′-H), 8.30 (2H, d, H *o*– to NO_2, $J_{12,13}$ = 9.0 Hz), 15.8 (1H, br s, NH). The UV–Visible spectrum in dichloromethane showed λ_{max} values of 495 nm and 345 nm with respective molar extinction coefficients of 2.9 × 10^4 M^{-1} cm^{-1} and 1.3 × 10^4 M^{-1} cm^{-1}. Since the compound was not obtained in analytically pure form, these molar extinction coefficients should be regarded as approximate.

2.6. Attempted synthesis of azospirooxazine *3*

Spirooxazine **16** was prepared from 2,6-dihydroxynaphthalene (**14**), via 2,6-dihydroxy-1-nitrosonaphthalene (**15**) according to literature procedures [18].

Table 3
Hydrogen bonds for compound **10** [Å and °].

D-H…A	d(D-H)	d(H…A)	d(D…A)	<(DHA)
N(1)-H(1N)…N(9)	0.865(18)	2.025(17)	2.711(2)	135.5(15)
N(1)-H(1N)…N(13)	0.865(18)	2.263(17)	2.734(2)	114.2(14)
N(10)-H(10N)…O(8)	0.93(2)	1.80(2)	2.569(2)	139.1(18)
O(2)-H(2O)…O(11)	0.96(3)	1.63(3)	2.5713(18)	163(2)
C(6)–H(6)..O(26)i	0.95	2.47	3.396(2)	165
C(13)–H(13C)..O(8)ii	0.98	2.49	3.288(2)	139
C(25)–H(25)..O(2)iii	0.95	2.52	3.206(2)	129

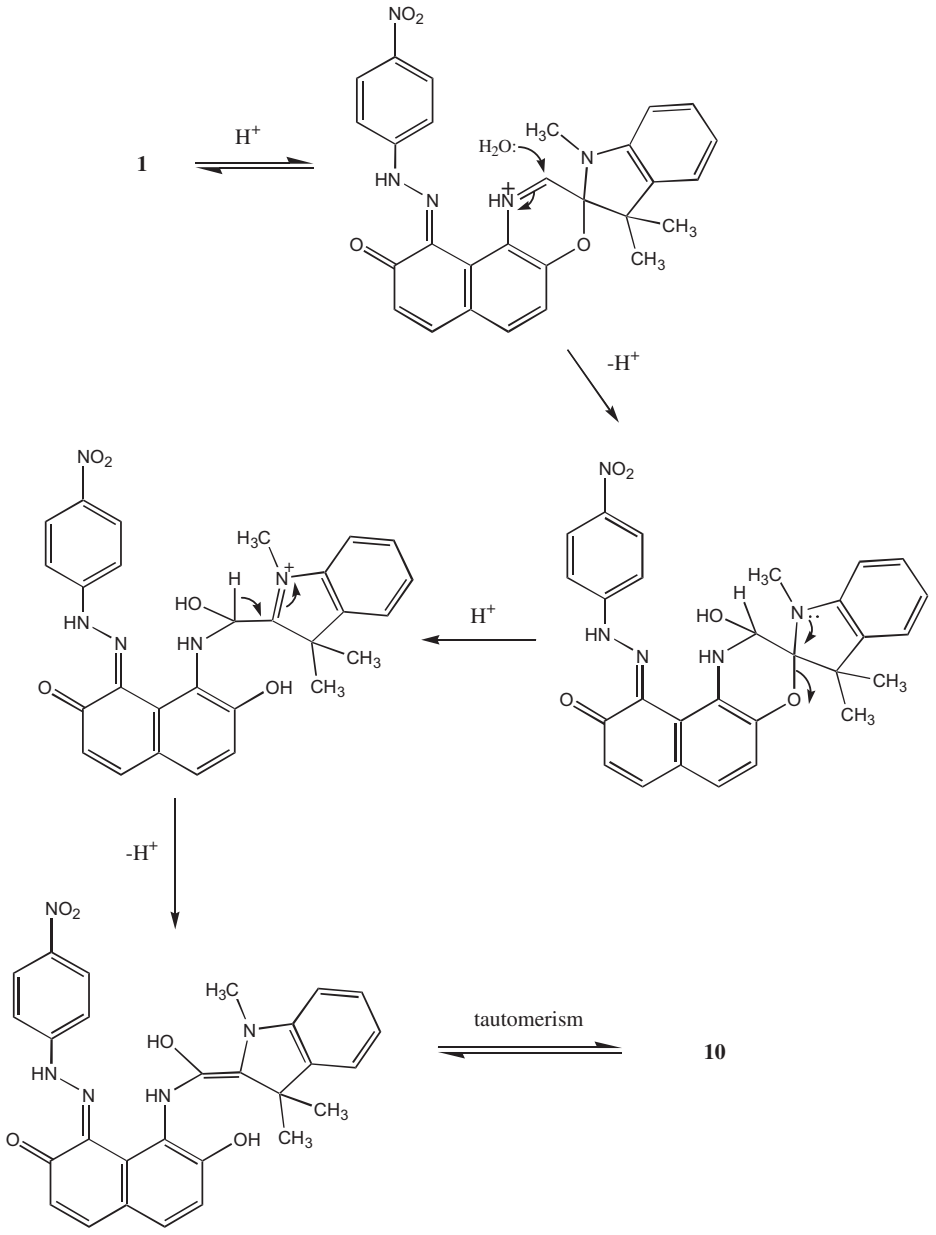
Symmetry transformations used to generate equivalent atoms: i: x, −1 + y, −1 + z; ii: 1 − x, 2 − y, −z; iii: 1 − x, 2 − y, −z.

An attempt was made to synthesise azospirooxazine **3** from compound **16** using a procedure as for the synthesis of dye **1** by route 1. A low yield of a crude brown product was obtained. Attempts to purify by column chromatography and recrystallization showed that compound is highly unstable, with a tendency to generate new impurities during the purification process.

3. Results and discussion

Azospirooxazines **1**–**3** (Fig. 1) were selected as target molecules based to a certain extent on an assessment of synthetic feasibility. Prior to attempted synthesis, the molecules were subjected to computer-aided molecular modelling to provide a prediction of features of their photochromism based on a methodology previously devised and verified in these laboratories using the facilities provided by the CAChe system [19]. It was assumed, based on established knowledge of the structures of azonaphthols, that the molecules are likely to exist in the ketohydrazone rather than the hydroxyazo tautomeric form and in a conformation which favours intramolecular hydrogen bonding as illustrated in Fig. 1 [20]. Spirooxazines owe their photochromic properties to a light-induced ring-opening to form a photomerocyanine, which reverts thermally to the ring-closed form when the light source is removed. There are eight possible isomers of the photomerocyanines, four of which may be considered as *cisoid* and four as *transoid*. The *cisoid* isomers are likely to be highly unstable due to steric constraints so that, in common with assumptions made previously, the investigation centred on the *transoid* isomers **a**–**d** (Figs. 2–4).

The molecular geometries of the azospirooxazines **1**–**3** and each of the isomers of the probable photomerocyanines were calculated using standard augmented MM2 within CaChe, with a fine convergence limit of $1e^{-5}$ used in the minimisations, and this approach was also used to provide steric energies (Table 1). Heats of formation were calculated using AM1 (Table 2).



Scheme 2. Mechanism proposed for the conversion of azospirooxazine **1** to amide **10**.

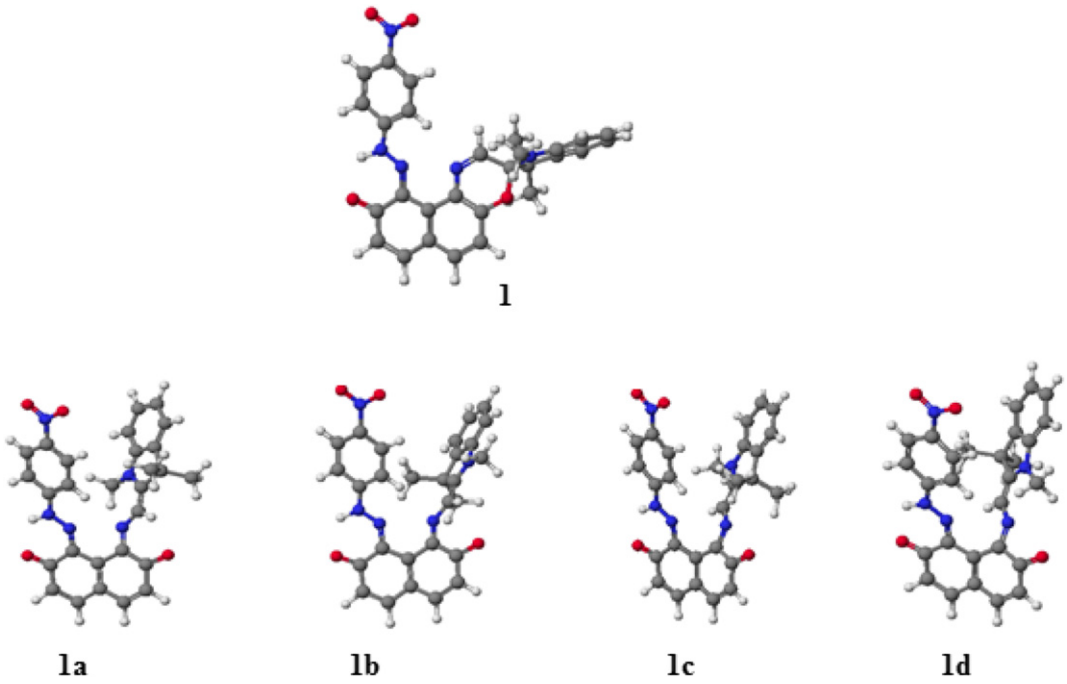


Fig. 7. The optimized (MM2) geometric structures of compound **1** and its ring-opened forms.

Both MM2 and AM1 calculations predict that compounds **1** and **3** would be expected to exist normally in the ring-closed form since, in each case, it is of lower energy than all of the isomers of the ring-opened forms. This suggests that these dyes might have the potential to show photochromism, by absorption of UV light to convert to the higher energy states, with thermal reversion to the more stable ring-closed form when the light source is removed. The prediction is ambiguous in the case of compound **2**. AM1 calculations suggest that the ring-opened forms are marginally more stable than the ring-closed form, predicting the possibility of a permanent merocyanine structure, while MM2 calculations suggest the opposite. However, the calculated values for the various species are very close in these cases.

For compound **1**, three complementary synthetic routes were attempted as illustrated in Scheme 1. Each route involved three stages: azo coupling of a dihydroxynaphthalene derivative with diazotized *p*-nitroaniline, nitrosation and reaction with Fischer's base (**6**). The three routes differed in the sequence in which the reactions were carried out. Azospirooxazine **1** was successfully synthesized by both routes 1 and 2. Isolation of compound **1** initially proved problematic. The compound was unstable to a range of chromatographic conditions, and to a certain extent thermally during recrystallisation. Ultimately an optimized synthetic procedure was developed, on the basis of repeated trials, leading to a product which TLC examination indicated was relatively free from impurities, and could be purified to a homogeneous product by a carefully-conducted recrystallisation process, as described in the experimental section. Route 1 proved to be the best. Under optimized conditions, azo coupling of spirooxazine **7** with *p*-nitrobenzenediazonium chloride in aqueous ethanol gave the orange-brown azospirooxazine **1** in 55% yield. Route 2 gave a much lower overall yield and presented more difficulties at the purification stage. Route 3 failed at the nitrosation stage, probably because of the extreme insolubility of azo compound **8** in the acidic medium. The existence of compound **1** as the ring-closed spirooxazine was demonstrated by ^{1}H NMR spectroscopy, for example showing the singlet characteristic of the oxazine proton (2′-H) at δ 7.88 ppm.

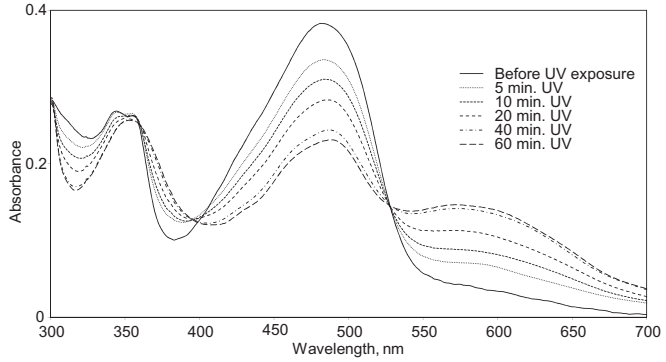


Fig. 8. UV/visible spectra of solutions of azospiroxazine **1** in ethanol with UV exposure with time up to 80 min.

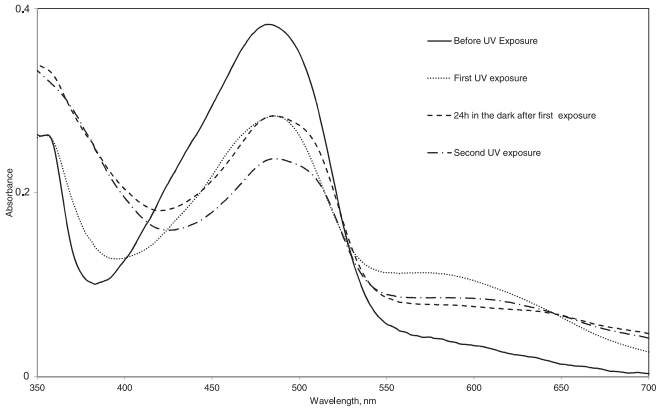


Fig. 9. UV/visible spectra of a solution of azospiroxazine **1** in ethanol following two cycles of UV exposure for 20 min, with 24 h in the dark between exposures.

It had been noted during our attempts at optimization of the synthesis that compound **1** was unstable to TLC on silica and to column chromatography, converting to an orange compound. By deliberately exposing compound **1** to preparative silica column chromatography, the orange product was obtained in 33% yield. This compound was demonstrated to be the secondary amide **10** (Fig. 5) on the basis of spectroscopic analysis confirmed by a single crystal x-ray structure determined from crystals grown from ethanol. The crystal structure (Fig. 6) demonstrates that the compound exists in the ketohydrazone form in which there is significant intramolecular hydrogen bonding in two 6-membered rings (between hydrazone N–H and ketone C=O and between amide N–H and hydrazone C=N) and in a 7-membered ring (between O–H and amide C=O). Table 3 shows relevant interatomic distances and angles. With regard to intermolecular interactions, there is potential π–stacking where the distance between the centroids of the two symmetry equivalent rings C23–C28 related by a centre of inversion is 3.5580(12) Å. The closest intermolecular contacts are three CH..O interactions where the C..O distances are in the range 3.206(2)–3.396(2) Å.

A plausible mechanism for the formation of **10** is proposed in Scheme 2. This proposition suggests an initial acid-catalysed (by silica) nucleophilic addition of water, presumably from within the silica, followed by ring-opening by cleavage of the weak C_{spiro}–O bond. This feature may account for observations of the instability of spirooxazines towards aqueous acidic conditions and this reaction may provide an insight into possible hydrolytic degradation mechanisms [12]. The ability to isolate a product, compound **10** in this particular case, is probably due to the stability provided by the extensive intramolecular hydrogen bonding.

Fig. 7 illustrates the structures of compound **1** and the possible photomerocyanines **1a**–**1d,** as modelled by MM2 calculations. Compound **1** shows a molecular geometry with the *p*-nitrophenylhydrazone system more or less in the same plane as the naphthoxazine system, which is orthogonal to the plane of the indoline system as a consequence of the spiro arrangement. As discussed earlier, the MM2 and AM1 calculations suggest that compound **1** has the potential to exhibit photochromism. Indeed, we have found that azospiroxazine **1** shows interesting and unusual photochromic properties, converting in ethanolic solution by UV irradiation from an orange colour to a neutral grey, progressively and slowly in comparison with commercial spirooxazine-based photochromic dyes.

Fig. 8 shows the UV/visible spectra of azospiroxazine **1** during irradiation with UV light with exposure times up to 60 min. The ring-closed compound shows a single visible absorption band (λ_{max} = 481 nm), associated mainly with the azo (hydrazone) group, which is responsible for its orange colour. The spectrum of the photoproduct after 60 min of UV exposure shows two absorption bands in the visible region, λ_{max} = 487 nm, close to the original absorption band but with lower intensity and a change of shape, and a broad longer wavelength band, λ_{max} = 571 nm. The absorption throughout the visible region accounts for the observed grey colour. There are also differences in the UV spectral region. An important observation in Fig. 8 is the definitive presence of isosbestic points at 353, 392 and 528 nm. Isosbestic points are locations in absorption spectra at which the species in solution absorb with equal intensity at particular wavelengths, and their presence provides evidence that only two principal species are present in the solution during the conversion [21–24]. This feature is consistent

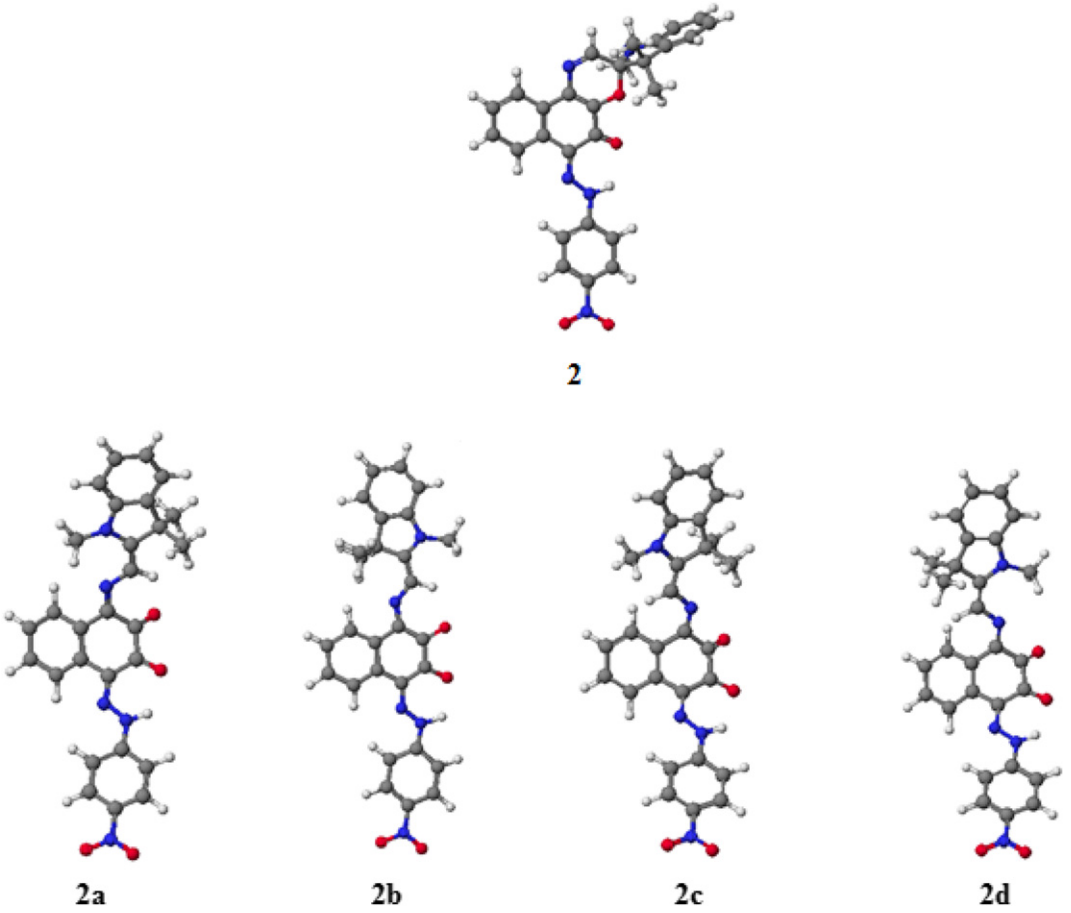
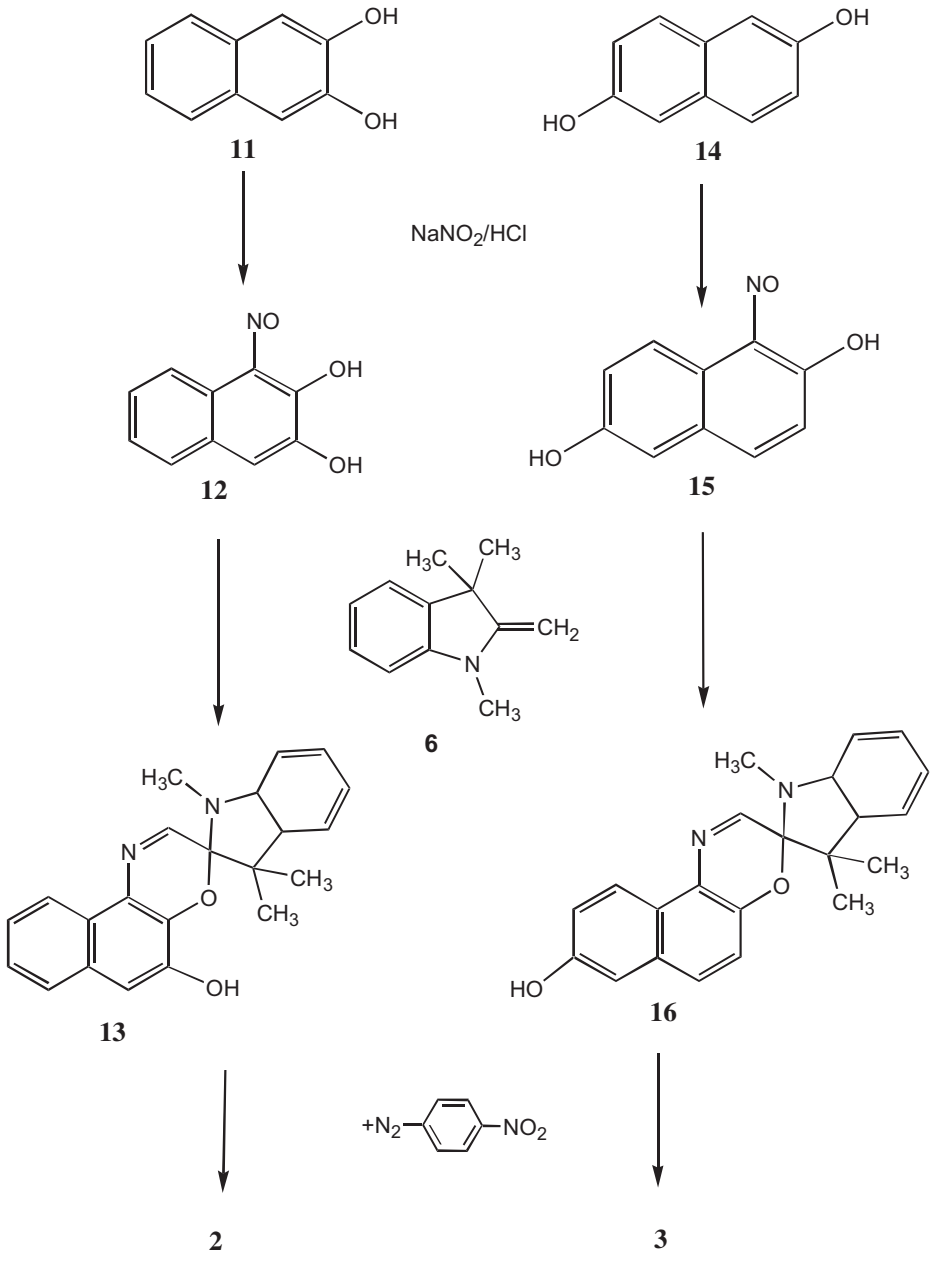


Fig. 10. The optimized (MM2) geometric structures of compound **2** and its ring-opened forms.

with the photochromic behaviour of azospiroxazine **1** involving a photochemical conversion of the ring-closed form to another species, the value of the absorption maximum of which (571 nm) is consistent with that anticipated for a photomerocyanine [20]. The spectrum of the unexposed solution passes through the isosbestic points at 353 and 528 nm, but does not pass so accurately through the isosbestic point at 392 nm, indicating that the mechanism may not be as simple as this. It is observed that the absorption spectrum after UV exposure for longer than 60 min begins to deviate from isosbestic behaviour, an effect which becomes more pronounced as exposure times are increased. This observation indicates the formation of new species, possibly due to photodegradation as a result of prolonged exposure to UV light. A further possibility which may contribute towards this observation is chemical degradation in ethanol, especially in view of the hydrolytic instability of dye **1**.

When the UV light source is removed after exposure, there is a slow colour change when the solution is stored in the dark, although it does not revert to the original orange colour. The spectral change when a sample is irradiated for 20 min and then is allowed to fade in the dark for 24 h at normal temperatures is shown in Figs. 9 and 10. The spectrum shows a decrease in the longer wavelength absorption, as might be expected from a thermal reversal by ring closure of the merocyanine form, although there is little change in the lower wavelength absorption. A second irradiation of this sample shows some, but rather limited, residual photochromic behaviour with an increase in the longer wavelength absorption and a decrease in the lower wavelength band intensity (Fig. 9). The level of photochromism due to the second irradiation is observed to reduce further with longer initial UV exposure times. This behaviour is consistent with partial reversible photochromism, but accompanied by degradation processes in solution leading to non-photochromic products. Additional investigation of the photochemical behaviour of the dye in solution has demonstrated its complexity, for example that it is strongly solvent-dependent.



Scheme 3. Synthetic routes to azospiroxazines **2** and **3**.

Details of an extensive study will form the basis of a future publication.

Steric energies from MM2 calculations and heats of formation values obtained from AM1 calculations (Tables 1 and 2) suggest that isomer **1a** is the lowest energy ring-opened form and thus is likely to be the dominant species in the photomerocyanine which is observed experimentally when compound **1** is irradiated with UV light, on the basis of the UV/visible spectra in Fig. 8. Inspection of the 3D structures calculated for **1a**–**1d** indicate that there is considerable steric congestion in each of the isomers forcing significant non-planarity, but that this is minimised in isomer **1a** which deviates least from planarity (Fig. 7).

Since route 1 proved to be optimal for synthesis of compound **1**, attempts were made to synthesise compounds **2** and **3** following analogous procedures. Azospirooxazine **2** was obtained as a brown solid in low yield starting from 2,3-dihydroxynaphthalene (**11**) by the route illustrated in Scheme 3. Isolation of dye **2** in analytically pure form proved problematic because of instability towards the purification process. In this case, the prediction of photochromic properties based on MM2 and AM1 calculations was ambiguous (Tables 1 and 2). However, the spectral data, especially by comparison of its ^{1}H NMR spectrum with that of the isomeric dye **1**, demonstrate that dye **2** exists as the ring-closed form, for example showing the singlet characteristic of the oxazine proton (2′-H) at δ 7.97 ppm, whereas the merocyanine would have given the corresponding proton at much higher field. In this case (Fig. 10), there is clearly much less steric interaction in the ring-opened forms **2a**-**2d** than in **1a**-**1d** and the isomers are calculated to be nearly coplanar. We have investigated UV irradiation of solutions of azospirooxazine **2**, but have not been able to demonstrate photochromic properties. However, photochromism can be dependent on a range factors, including the nature of the solvent, the temperature and the irradiation conditions and thus it cannot be stated with certainty that the dye is non-photochromic.

Attempts to synthesise dye **3** from 2,6-dihydroxynaphthalene (**14**) as illustrated in Scheme 3 gave, in the final stage, a low yield of a crude brown product which proved highly unstable towards attempts at purification both by recrystallisation and using chromatography, processes which invariably gave rise to the formation of a range of coloured impurities so that the compound could not be obtained with sufficient purity for rigorous characterization. Nevertheless, there is reasonable evidence from FTIR and ^{1}H NMR spectra, in comparison with those obtained for dyes **1** and **2**, and from TLC behaviour, that dye **3** in its ring-closed form is the major component of the crude product. Characteristic singlets in the ^{1}H NMR spectrum at δ 1.35 (C–CH_3), 2.70 (NCH_3) and 7.82 ppm (2′-H) were observed together with the signals due to the AB system characteristic of the *p*-nitroaniline derived aromatic ring system.

4. Conclusions

Spirooxazines containing an azo chromophore, which exists in the hydrazone form, have been synthesized in three stages from dihydroxynaphthalenes. Our previously-established methodology involving MM2 and AM1 calculations was used to predict aspects of photochromic behaviour in the selected synthetic target molecules. Azospirooxazine **1** shows interesting, unusual photochromic properties. The dye converts slowly by UV irradiation in ethanolic solution from an orange colour to grey, the spectrum being consistent with the formation of a photomerocyanine, in a process showing isosbestic spectral behaviour. However, the reverse thermal reaction appears to be incomplete and is complicated by degradation leading to non-photochromic products. Dye **1** was converted on a silica chromatography column to a secondary amide (**10**), whose structure was confirmed by single crystal x-ray crystallography. A mechanism for the conversion is proposed, which may provide an insight into the reasons underlying the instability of spirooxazines towards aqueous acidic conditions.

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