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Synthesis and properties of 1,3,3-trimethylspiro[indoline-2,3′-naphtho[2,1-*b*][1,4]oxazin]-6′-amine, a novel, red colouring photochromic spirooxazine

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ABSTRACT

The synthesis and photochromic properties of 1,3,3-trimethylspiro[indoline-2,3′-naphtho[2,1-*b*][1,4]oxazin]-6′-amine, a novel red-colouring photochromic spirooxazine and derivatives is reported. The synthesis proceeds via an unusual one-pot transamination, oxime formation, N–O bond cleavage, spirooxazine formation process.

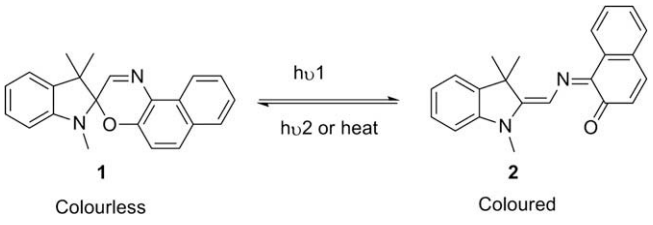
Spirooxazines are a commercially important class of photochromic dyes which upon irradiation with ultraviolet light undergo a reversible colour change (Scheme 1) from the colourless spirocyclic form, **1** to the coloured merocyanine form, **2**.[1,2]

Among the spirooxazines in commercial use are the 6′-amino compounds exemplified by such dyes as Reversacol Plum Red **3** (Fig. 1), which despite its name actually exhibits a purple colouration upon irradiation (λ_{max} = 578 nm in polyurethane).[3]

During the course of our research into the control of switching speeds of photochromic dyes,[4] we had reason to prepare a red spirooxazine dye with a functional group allowing conjugation to a functionalised polymer. As none of the published amino spirooxazines possessed such a functionality, the synthesis of the novel free amino spirooxazine, 1,3,3-trimethylspiro[indoline-2,3′-naphtho[2,1-*b*][1,4]oxazin]-6′-amine **4** (Fig. 1), was attempted.

The synthesis of 6′-amino spirooxazines is generally performed (in low yield) starting from Folin's reagent, 1,2-naphthoquinone-4-sulfonate, (**5**) which reacts with an amine **6** to give the corresponding 4-aminonaphthoquinone **7**. This is then converted with hydroxylamine hydrochloride into nitroso naphthol **8**, which upon reaction with methyleneindoline **9**, gives the spirooxazine product **10** (Scheme 2).[3] The desired spirooxazines can also be synthesised in similar yield by a one-pot direct alkylation of 1-nitroso-2-naphthol/cyclisation with methyleneindoline,[3,5,6] or from 1-amino-2-naphthol in the presence of an oxidising agent.[7]

Our initial approach to the amino functionalised spirooxazine, **4** began with the preparation of 4-amino-1,2-naphthoquinone (Scheme 2, 7, R,R′ = H) in 60% yield from the reaction of 1,2-naphthoquinone and azidotrimethylsilane.[8] This material was then converted in one-pot into **4** in 6% yield.



Scheme 1.

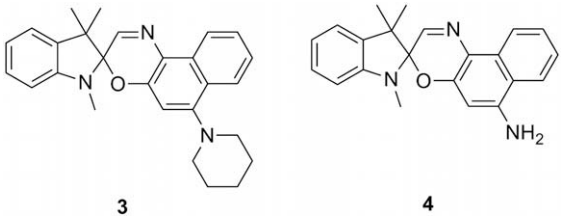


Figure 1.

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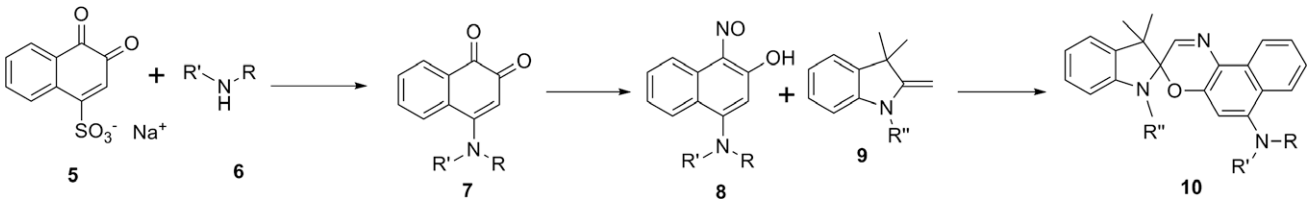
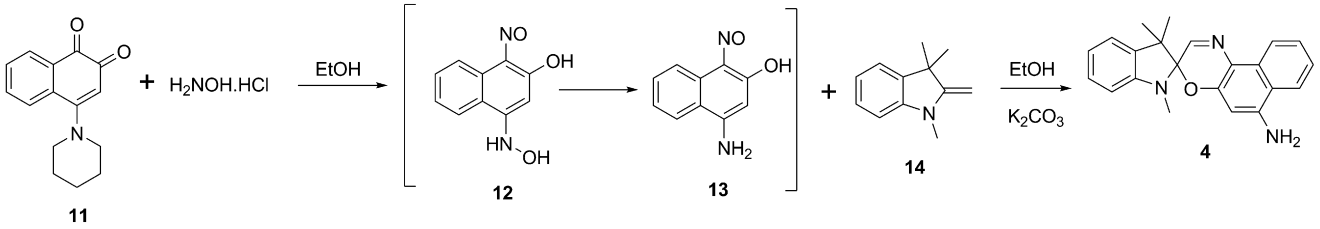


Scheme 2.



Scheme 3.

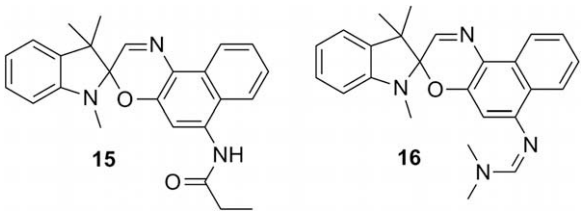


Figure 2.

As a result of this very poor yield and a desire to develop a synthesis which did not require the use of the very toxic reagent azidotrimethylsilane, a second approach was developed to take advantage of the reported propensity of 4-amino-1,2-naphthoquinones to undergo transamination reactions in the presence of 1° and 2° amines.[9] Thus, the reaction between 4-piperidinyl-1,2-naphthoquinone (**11**),[10] and an excess of hydroxylamine hydrochloride gave the putative intermediate hydroxylamine-functionalised nitroso naphthol, **12**.[11] Under the reaction conditions, cleavage of the hydroxylamine N–O bond occurred and on addition of K_2CO_3 and 1,3,3-trimethyl-2-methyleneindoline (**14**), to the reaction mixture and heating in a sealed vessel at 90 °C the desired amino spirooxazine **4** was isolated in 25% overall yield (Scheme 3).[12] A conceptually related direct formation of anilines with hydroxylamine hydrochloride has been reported.[13] In order to further explore the photochromic properties

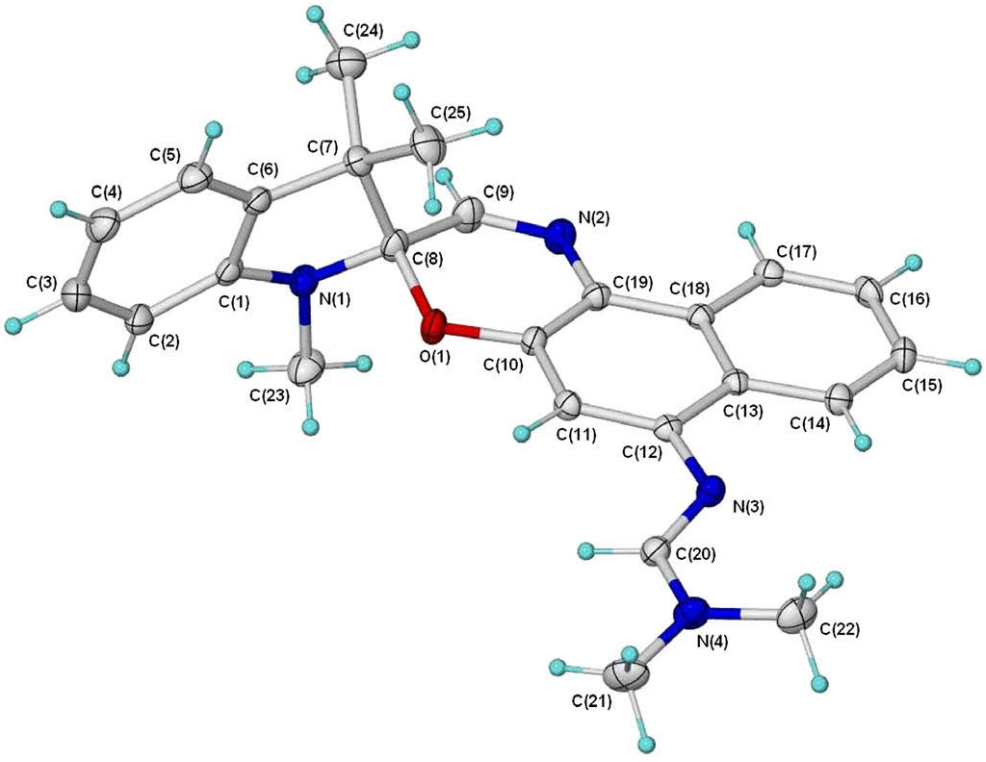


Figure 3.

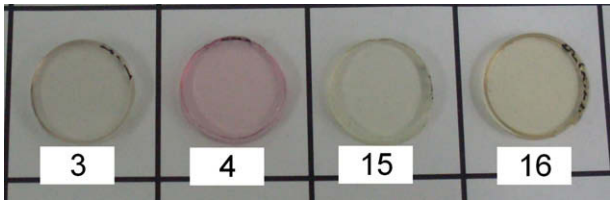


Figure 4.

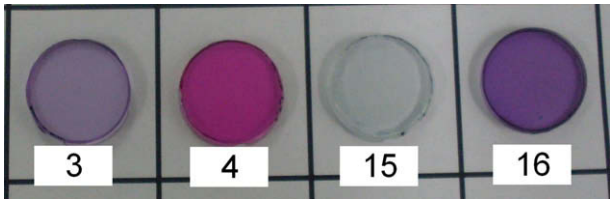


Figure 5.

of this novel scaffold the corresponding propionyl amide **15**,[14] and formamidine **16**,[15] were also prepared (Fig. 2). The topology of **4** was confirmed by X-ray crystallography of crystalline derivative **16** (Fig. 3).[16]

To evaluate the photochromic performance of the novel compounds **4**, **15** and **16** in comparison with commercially available material, **3**, test lenses were prepared using a matrix composed of polyethyleneglycol 400 dimethacrylate and 2,2′-bis(4-methacryloxy)phenyl propane in a 1:4 weight ratio with 0.4% AIBN by mass as initiator. 1.2×10^{-7} mol of spirooxazine per gram of matrix was thoroughly mixed into the lens matrix and the lenses thermally cured before irradiation at 365 nm with a hand-held UV source. The lenses before and after irradiation can be seen in Figs. 4 and 5, respectively.

Reversacol Plum Red (**3**) displays a purple colouration upon irradiation contrasting strongly with the red colouration of free amino compound, **4**. The conjugation of the amino group as an amide has the effect of greatly reducing the colour developed, with only a faint blue colouration observed for compound **15**. In contrast, formamidine **16** shows a strong purple colouration.

In summary, a route to a novel red-colouring spirooxazine, 1,3,3-trimethylspiro[indoline-2,3′-naphtho[2,1-*b*][1,4]oxazin]-6′-amine (**4**) has been developed, involving an unusual one-pot transamination, oxime formation, N–O bond cleavage, spirooxazine formation process. The compound develops a red colouration upon irradiation in contrast to related commercially available material **3** which is purple upon irradiation. Furthermore, the free amino group of **4** serves as a convenient handle for further functionalisation, allowing rapid access to additional novel photochromics.

Acknowledgements

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Supplementary data

Supplementary data (experimental procedures and data for all new compounds) associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2010.02.105.

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10. Obtained in near quantitative yield from the reaction of an ethereal suspension of 1,2-naphthoquinone with piperidine.
11. Such displacement of the amino group by hydroxylamine may explain the low yields observed in the conversion of 4-aminonaphthoquinones into the corresponding nitroso naphthols in the reported synthesis of amino spirooxazines (e.g., **11** gives a reported 8% yield of the corresponding nitroso naphthol).[3]
12. *Experimental procedure*: A suspension of 4-(piperidin-1-yl)naphthalene-1,2-dione (1.00 g, 4.14 mmol) in EtOH (15 mL) was treated with hydroxylamine hydrochloride (0.58 g, 8.29 mmol) and stirred at 22 °C for 18 h. The mixture was then treated with K_2CO_3 (0.74 g, 5.39 mmol) and 1,3,3-trimethyl-2-methyleneindoline (1.44 g, 8.29 mmol), sealed and heated to 90 °C for 18 h. The mixture was cooled, diluted with CH_2Cl_2 (40 mL), filtered through Celite, evaporated in vacuo and purified by column chromatography eluting with 0–50% v/v EtOAc/Petroleum ether to give 1,3,3-trimethylspiro[indoline-2,3′-naphtho[2,1-*b*][1,4]oxazin]- 6′-amine, **4** as a purple solid (0.35 g, 25%). Mp = 175–177 °C; ^{1}H NMR (acetone-d_6, 400 MHz) δ 8.49 (d, J = 8.5 Hz, 1H), 7.96 (d, J = 8.4 Hz, 1H), 7.51–7.48 (m, 2H), 7.29 (t, J = 8.1 Hz, 1H), 7.17–7.10 (m, 2H), 6.82 (t, J = 7.4 Hz, 1H), 6.61 (d, J = 7.7 Hz, 1H), 6.26 (s, 1H), 5.61 (s, 2H), 2.74 (s, 3H), 1.32 (d, J = 7.3 Hz, 6H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 147.7, 146.1, 145.5, 144.4, 136.2, 131.8, 127.9, 127.2, 123.0, 122.0, 121.4, 120.5, 119.6, 119.1, 116.5, 107.0, 98.9, 98.7, 51.5, 29.5, 25.5, 20.7; HRMS (EI) calcd for $C_{22}H_{21}N_3O$ [M^+]: 343.1685, found: 343.1675.
13. For a recent example, see: Shchekotikhin, A. E.; Makarov, I. G.; Buyanov, V. N.; Preobrazhenskaya, M. N. *Chem. Heterocycl. Compd.* **2005**, *41*, 914–920.
14. *N*-(1,3,3-Trimethylspiro[indoline-2,3′-naphtho[2,1-*b*][1,4]oxazine]-6′-yl)propionamide, **15** was prepared in 95% yield from reaction of a THF solution of **4** and pyridine with propionyl chloride at room temperature for 1 h.
15. *N*,*N*-Dimethyl-*N*′-(1,3,3-trimethylspiro[indoline-2,3′-naphtho[2,1-*b*][1,4]oxazine]-6′-yl)formamidine, **16** was prepared in 51% yield from reaction of a benzene solution of **4** with *N*,*N*-dimethylformamide dimethylacetal at reflux for 2 h.
16. Crystallographic data (excluding structure factors) for compound **16** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no CCDC 755252. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK, (fax: +44 (0) 1223 336033 or email: deposit@ccdc.cam.ac.uk).