

# The application of molecular modelling techniques in the prediction of the photochromic behaviour of spiroindolinonaphthoxazines

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## Abstract

Two isomeric photochromic compounds, spiroindolinonaphth[2,1-b] [1,4] oxazine **1** and spiroindolinonaphth[1,2-b] [1,4] oxazine **2**, were synthesised. During the synthesis of spirooxazine **2**, a coloured, non-photochromic spirooxazine **6** was isolated as an associated product and characterised as a mixture of geometric isomers. A range of readily available molecular modelling techniques were applied to provide an account of the behaviour of the photochromic materials. Heats of formation calculated using AM1, following MM2 geometry optimisation, for ring-closed and ring-opened spirooxazines, provide a method for assessing whether a spirooxazine might be expected to show photochromic behaviour. ZINDO calculations based on the molecular geometry optimised in this way provide a reasonable account of the UV–vis absorption profile of the ring-closed forms **1** and **2**. An approach that uses MM2 calculations to predict the most stable of the isomer(s) of the transient ring-opened photomerocyanines, used in combination with PPP-MO calculations using optimised parameterisation, may be used to provide a prediction of the  $\lambda_{\text{max}}$  values, although the method may not produce an unequivocal result when the energies of the geometrical isomers are similar.

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**Keywords:** Photochromism; Spirooxazine; Molecular modelling; Photomerocyanine

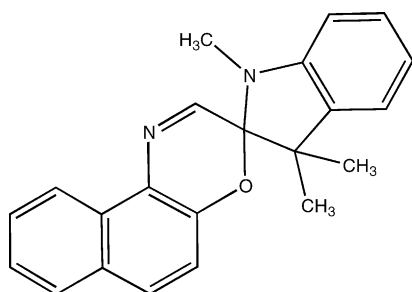
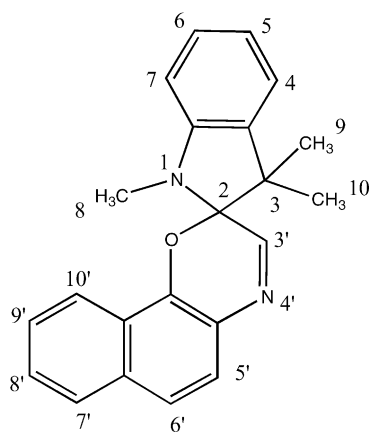
## 1. Introduction

Organic photochromic materials are of considerable current active interest because of their dynamic optical properties which offer potential for a wide range of applications in ophthalmics, optical recording, solar energy storage, non-linear optics and biological systems. [1–6] Spirooxazines as a class of organic photochromes are of interest due to their ability to impart intense photocolouration in appropriate application media, their reasonable fatigue resistance and relative ease of synthesis. Spirooxazines generally give colourless or only weakly coloured solutions which, when exposed to UV light, become intensely coloured, and when the light source is removed, the solutions once again become colourless. Absorption of UV light by the spirooxazine causes cleavage of the relatively weak spiro carbon–oxygen bond,

resulting in the formation of a coloured photomerocyanine, which reverts to the spirooxazine by a thermally induced ring-closure reaction when the light source is removed [7]. The commercial exploitation of photochromic spirooxazines has been limited by a number of factors including inadequate durability, the temperature sensitivity of the thermal decoloration process and the relatively restricted colour range available so that there remains considerable interest in the design of new compounds for improved technical performance. In the present investigation, we report the application of a range of relatively accessible molecular modelling techniques to account for properties of the spirooxazine system, with a view to developing the techniques as useful practical predictive tools in the molecular design of new photochromic materials. Two isomeric photochromic spirooxazines, **1** and **2**, were selected for this initial phase of the investigation, with a view to subsequent extension to a wider range of structural systems. There has been considerable research focus on the spiroindolinonaphth [2,1-b] [1,4] oxazine **1**, which has almost invariably been selected as the model compound

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for the series, and its photochromic properties are now reasonably well understood. [8–17] In contrast, and perhaps surprisingly, the spiroindolinonaphth [1,2-b] [1,4] oxazine **2** has been reported on only a few occasions, [18,19] although interest in this system may increase in view of its recently reported suitability for use in light-induced information memory systems. [20] In addition to our investigation of the application of molecular modelling, we report a comparison of the synthetic routes to compounds **1** and **2**, including the co-formation of a non-photochromic coloured spirooxazine in the synthesis of **2**, and the determination of the structure of the photomerocyanine derived from **2**.

**1****2**

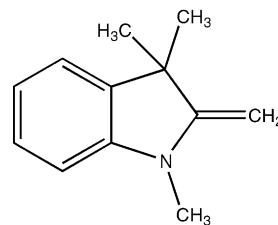
## 2. Results and discussion

The most important method of synthesis of spirooxazines involves the reaction of an *o*-nitrosophenol with an alkyldene heterocycle, the most common of which is 1,3,3-trimethyl-2-methyleneindoline, Fischer's base (**3**). 1-Nitroso-2-naphthol (**4**) reacts with Fischer's base to give the well-known spirooxazine **1**. [7] Consistent with a previous study of this reaction using factorial experimental design methodology, [21] we found that reaction in toluene at reflux for 1 h provided a reasonable yield (ca. 60%)

Table 1  
 $^1\text{H}$  and  $^{13}\text{C}$  chemical shifts of compound **2** in  $\text{CDCl}_3$

H/C atom no.	$\delta(^1\text{H})$	$\delta(^{13}\text{C})$	H/C atom no.	$\delta(^1\text{H})$	$\delta(^{13}\text{C})$
2	–	99.2	3'	7.69	152.1
3	–	51.7	4a'	–	125.0
3a	–	135.9	5'	7.53	125.8
4	7.09	121.5	6'	7.42	120.4
5	6.91	119.8	6a'	–	141.7
6	7.23	127.9	7'	7.75	127.6
7	6.58	107.1	8'	7.43	126.9
7a	–	147.6	9'	7.35	125.6
8	2.76	29.6	10'	7.99	121.9
9	1.363	25.5	10a'	–	123.6
10	1.355	20.9	10b'	–	134.5

while minimising the formation of the numerous highly coloured side products which were commonly observed by TLC. Use of more polar solvents, acid and base catalysts and longer reaction times generally lowered the yield and increased coloured product formation. Attempts to isolate the coloured products chromatographically demonstrated that they were present only in trace amounts, were highly insoluble and of high molecular weight. Only outline reaction conditions for the formation of spirooxazine **2** have been previously reported. [18–20] We report details in this paper, together with a complete interpretation of its  $^1\text{H}$  and  $^{13}\text{C}$  spectra using standard 1D and 2D methods (Table 1). The reaction of 2-nitroso-1-naphthol (**5**) with Fischer's base (**3**) in equimolar quantities gave spirooxazine **2** in relatively low yield (ca. 6%) together with a somewhat larger quantity (15%) of an orange-yellow material, which proved to be a chromatographically inseparable mixture of isomeric spirooxazines **6a** and **6b** (Fig. 1). The formation of this material has been reported recently without reference to isomers. [20] The authors report that it was not obtained pure and was not completely characterised. Our mass spectra and elemental analysis confirmed a molar mass of 498 and a molecular formula of  $\text{C}_{34}\text{H}_{32}\text{N}_3\text{O}$ .  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of compound **6** measured in  $\text{CDCl}_3$  gave two sets of signals in a dynamic equilibrium. This was demonstrated by the presence of positive cross-peaks in a 2D NOESY spectrum. The ratio of the two components was ca. 3:1 in  $\text{CDCl}_3$ , and there was considerable overlap of NMR signals. We found that the ratio was ca. 9:1 in perdeuteriobenzene, and thus a complete NMR analysis in this solvent was performed in that solvent. The  $^1\text{H}$ ,  $^{13}\text{C}$  and  $^{15}\text{N}$  chemical shifts are collected in Table 2.

**3**

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