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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 λ_{max} values, although the method may not produce an unequivocal result when the energies of the geometrical isomers are similar.

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, nonlinear optics and biological systems. [1–6] Spirooxazines as a class of organic photochromes are of interest due to their ability to impart intense photocoloration 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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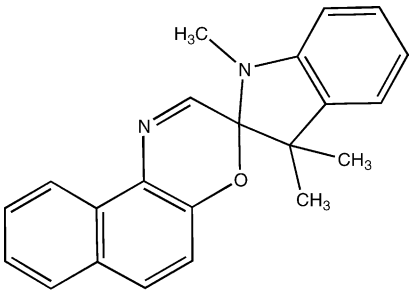
for the series, and its photochromic properties are now reasonably well understood. [8–17] In contrast, and perhaps surprisingly, the spiroindolinonaphth [1,2-b] [1,4] oxazine **2** has been reported on only a few occasions, [18,19] although interest in this system may increase in view of its recently 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**.



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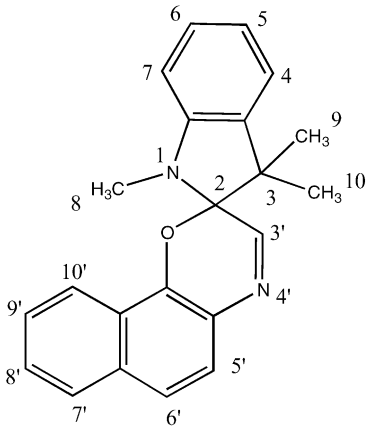

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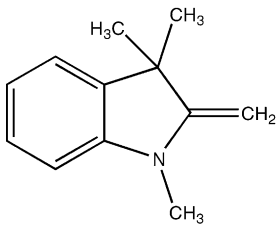
2. Results and discussion

The most important method of synthesis of spirooxazines involves the reaction of an *o*-nitrosophenol with an alkylidene 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%) 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}H and ^{13}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 $C_{34}H_{32}N_3O$. ^{1}H and ^{13}C NMR spectra of compound **6** measured in $CDCl_3$ 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 $CDCl_3$, 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}H, ^{13}C and ^{15}N chemical shifts are collected in Table 2.

Table 1
^{1}H and ^{13}C chemical shifts of compound **2** in $CDCl_3$

H/C atom no.	δ(^{1}H)	δ(^{13}C)	H/C atom no.	δ(^{1}H)	δ(^{13}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



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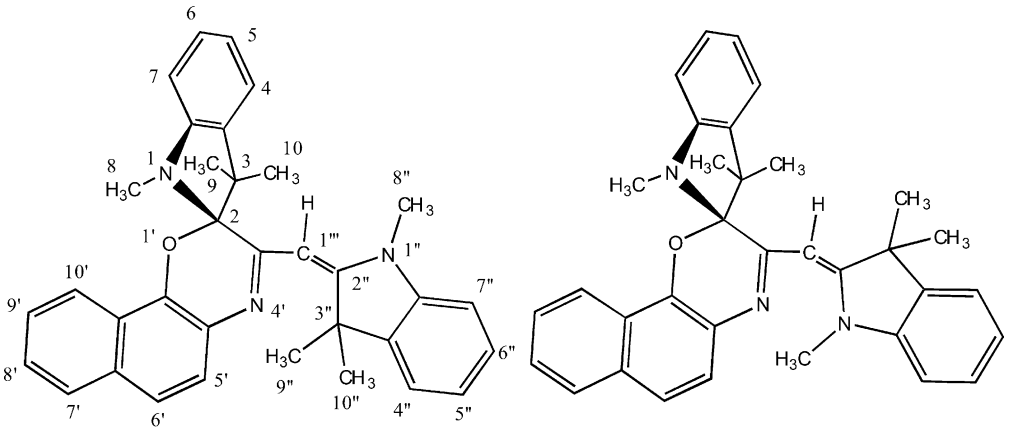
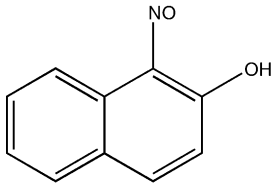


Fig. 1. Structures of geometric isomers of **6**, showing numbering scheme for NMR interpretation.



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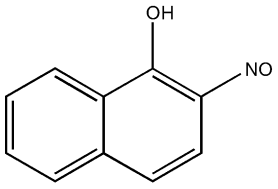

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The key starting structural information was obtained from the 2D ^{1}H-^{15}N HMBC spectrum in which three ^{15}N resonances for the major component were observed, two being close to that given by Fischer's base (**3**) (δ −283.8 ppm) [22] and the third giving a cross-peak with the alkene proton signal at δ 5.35 ppm, assigned to the azomethine nitrogen. Only two very weak ^{15}N signals were found for the minor component differing only slightly from those in the major component. Proton signals were assigned using gs-COSY. Proton-bearing carbons were assigned by gs-HMQC optimised for $^{1}J(^{13}C, ^{1}H) = 145$ Hz, and quaternary carbons were assigned using gs-HMBC, optimised for $^{n}J(^{13}C, ^{1}H) = 8$ and 4 Hz. We found appropriate cross-peaks due to the through-space correlation of the C(1‴)H proton with the C(8″) methyl protons in the NOESY spectrum. Thus, the major component is the (*E*)-isomer **6a**.

The formation of isomeric mixture **6** as the major product from the reaction of 2-nitroso-1-naphthol (**5**) with Fischer's base (**3**) mechanistically requires two molecules of Fischer's base and an oxidation step. When 2-nitroso-1-naphthol (**5**)

Table 2
^{1}H, ^{13}C and ^{15}N chemical shifts in major and minor (values in parentheses) components of compound **6** in C_6D_6

H/C/N atom no.	δ(^{1}H)	δ(^{13}C)	H/C no.	δ(^{1}H)	δ(^{13}C)	H/C no.	δ(^{1}H)	δ(^{13}C)
1	–	−299.8[a]	3′	–	155.02	1″	–	−267.0[a] (-263.3[a])
2	–	104.25	4′	–	−94.4[a] (−89.3[a])	2″	–	166.54
3	–	52.04	4a′	–	130.39	3″	–	48.51
3a	–	137.49	5′	7.81	125.96	3a″	–	141.10
4	7.12	122.37	6′	7.52	121.75	4″	6.95	122.57
5	6.97	119.67	6a′	–	133.85	5″	6.95	121.79
6	7.3[b]	[c]	7′	7.73	128.63	6″	7.14	127.99
7	6.59	106.34	8′	7.3[b]	126.30	7″	6.31	107.42
7a	–	141.26	9′	7.3[b]	126.06	7a″	–	144.86
8	2.96 (3.01)	30.39 (30.19)	10′	8.33	122.19	8″	2.41 (3.64)	29.27 (36.29)
9	1.44 (1.47)	26.66	10a′	–	125.29	9″	2.23 (1.21)	24.07 (29.29)
10	1.42 (1.45)	25.11	10b′	–	149.80	10″	2.14 (1.08)	24.65 (29.14)
						1‴	5.35 (5.15)	93.87 (90.83)

[a] δ(^{15}N).
[b] Unresolved overlapped signals.
[c] Probably overlapped by C_6D_6.

(1 mol) was reacted with two moles of Fischer's base (**3**) (2 mol), the yield of both products increased, compared with the reaction using equimolar quantities, (spirooxazine **2** from 6 to 10%, and compound **6** from 15 to 20%). When the reactions were carried out under nitrogen, the yield of compound **6** remained essentially unchanged. This indicates that air is not essential for the oxidation, which may thus involve one of the reactants, possibly the nitrosonaphthol **5**, and its consumption in this way may account for the relatively low yields obtained. Attempts to react compound **2** directly with Fischer's base (**3**) under a range of reaction conditions failed to produce compound **6**, the starting materials remaining essentially unchanged. The mechanism of the competitive reaction in which compound **6** is formed thus remains unclear.

Computer-aided molecular modelling techniques have the potential for practical application to the calculation of a variety of parameters relevant to photochromic systems to enhance understanding of photochromic behaviour and to provide a predictive tool for use in the design of new photochromic materials for optimised properties. The ability to calculate the electronic spectral properties of spirooxazines and their ring-opened forms is useful in the design of materials with a view to extending the available colour range or to provide improved colourability. In addition, calculation of molecular geometries and the relative energies of the various ring-closed and ring-opened species provides an insight into the nature of the photochromic process and is likely to lead to improved accuracy of spectral predictions. In this paper, we report on the results of an investigation, using relevant features of the molecular mechanics and quantum mechanics programmes accessible using the CaChe software package, in combination with the PPP-MO approach, to compounds **1** and **2**. This study provides a comparison of their application to these distinctly different, though structurally related, photochromic systems and provides the basis for future extension to other structural types of photochromic materials.

Spirooxazines **1** and **2** are both photochromic in solution, changing from colourless to blue on irradiation with UV light due to merocyanine formation. The effect in both cases is observed more clearly as the temperature is lowered to reduce the rate of the thermal decoloration reaction. The calculation of the properties of the merocyanines is complicated by their existence as transient species capable of existing in a number of geometrical isomeric forms. There are, in each case, eight possible isomers of the photomerocyanines, four of which may be considered as cisoid and four as transoid. The four cisoid isomers are likely to be highly unstable due to steric constraints so that, in common with most of the discussion in the literature, the present investigation has centred on the transoid isomers **7a–7d** and **8a–8d** (Fig. 2). In the present investigation, the molecular geometries of spirooxazines **1** and **2** and of the transoid isomers of the photomerocyanines (**7a**–7**d** and **8a**–8**d**, respectively) were calculated using standard augmented MM2 within CaChe, with a fine convergence limit of $1e^{-5}$ used in the minimisations, and the approach was used to provide steric energies. Heats of formation were calculated using AM1. The results are given in Table 3. For both spirooxazines **1** and **2**, the calculated steric energies and heats of formation are lower than those of the relevant four ring-opened isomers **a**–**d**. This observation is consistent with photochromic behaviour in that the spirooxazines are observed to convert to the higher energy merocyanines by absorption of UV light and to revert thermally to the more stable ring-closed form when the light source is removed.

Table 3
Calculated energy data for spirooxazines **1** and **2**, and isomers of the respective ring-opened forms **7** and **8**, and dihedral angles at the azadiene bridge for ring-opened isomers

Compound	Final energy/kcal mol^{-1} (MM2)	Heat of formation/kcal mol^{-1} (AM1)	Dihedral angle at azadiene bridge
1	−5.93	81.7	
7a	−0.63	86.6	177.9°
7b	−3.43	89.2	179.6°
7c	2.99	88.8	171.7°
7d	0.79	91.7	170.8°
2	−6.63	81.8	
8a	−2.07	85.6	180.0°
8b	−4.27	88.3	179.8°
8c	−3.49	87.0	179.8°
8d	−5.92	90.1	180.0°

For most practical applications, photochromic materials such as spirooxazines are required to be UV-absorbing but colourless, and it is thus useful to be able to calculate their electronic absorption spectra. The PPP-MO method has proved to be particularly suitable for predicting the spectra of organic colorants. [23–25] However, the method is not suitable for the calculation of the spectra of spirooxazines **1** and **2** due to their non-planarity. In this study, the ZINDO approach, with geometry optimisation using MM2/AM1, was used to calculate the electronic spectra for these compounds. The results are illustrated in Fig. 3a and b. The calculated spectra provide confirmation of the absence of visible absorption and show reasonable, if not exact, agreement with the experimental UV absorption profiles.

UV–vis spectra of the photomerocyanines from compounds **1** and **2** were obtained for solutions in dichloromethane, selected as the common solvent, by irradiation with UV light at −60 °C at which temperature the thermal decoloration reaction effectively ceases. The visible absorption band of the merocyanine derived from compound **2** is observed to be shifted bathochromically compared with that of compound **1**, the λ_{max} values of the longest wavelength absorption bands being at 632 and 606 nm, respectively (Table 4). In a previous paper, we reported the results of an investigation using the PPP MO approach into the electronic spectra of the coloured merocyanine form derived from a wide series of spiroindolinonaphth [2,1-b] [1,4] oxazines. [14] The calculations carried out for the four transoid isomers of the merocyanines, assuming molecular planarity in each case, provided a reasonable correlation between calculated and experimental λ_{max} values. In our previous

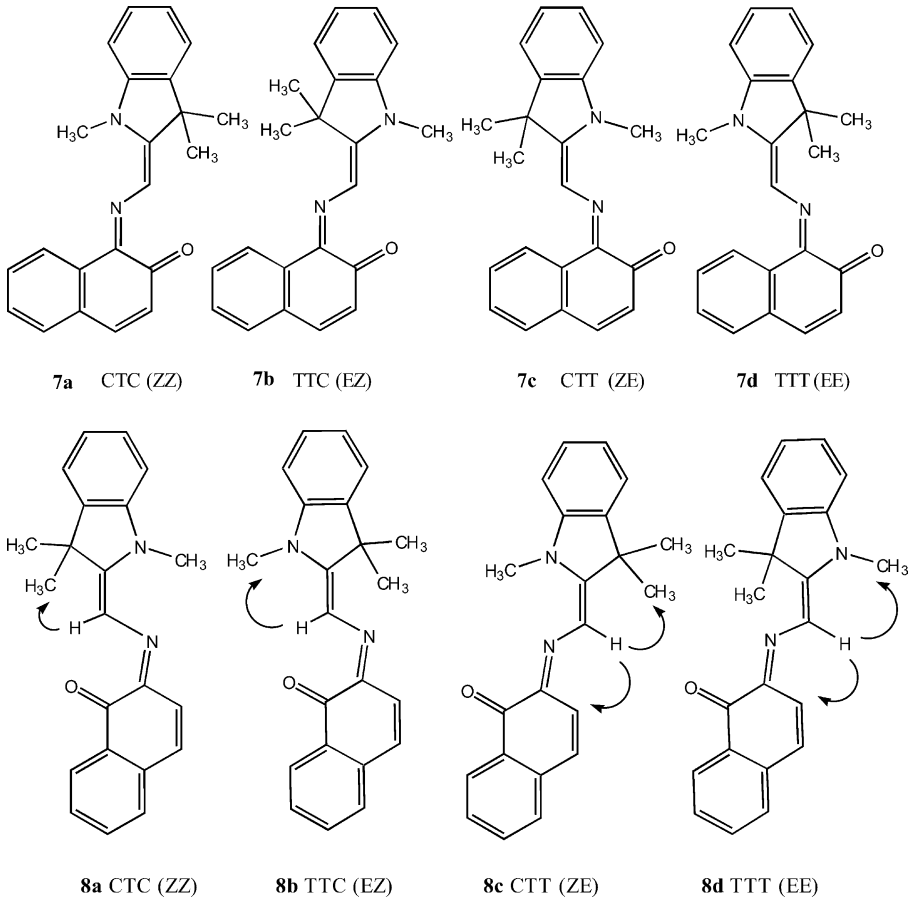

Fig. 2. Transoid isomers of photomerocyanines, showing expected NOE contacts in the case of isomers **8a**–**8d**.

investigation, no account was taken of the relative stabilities of the isomers. It has been proposed by Nakamura et al. using a ^{1}H NMR NOE study of a solution of compound **1** in CD_3OD photoirradiated at −45 °C, a temperature at which the thermal reverse reaction effectively ceased, that the most stable merocyanine form is the TTC (EZ) structure **7b**. [11] The authors provided supporting evidence that this is the thermodynamically most stable isomer on the basis of ab initio MO calculations. With this information available, we repeated the PPP-MO calculations, with further refinement by adjustment of parameters for the azomethine nitrogen atoms, the electron affinity value to 6.0 eV (from 4.5 eV) and the valence state ionisation potential to 19.5 eV (from 18.0 eV), to provide a calculated λ_{max} value for structure **7b** of 614 nm (experimental value 606 nm, Table 4). The results obtained using these parameters for the remaining isomers of **7** and for merocyanines **8a**–**8d** are also given in Table 4. It is of interest that higher oscillator strengths are calculated for merocyanines **8** compared with **7**, suggesting that this system offers potentially higher colorability.

We have carried out an NMR study on compound **2** and its photomerocyanine, using a procedure similar to that used by Nakamura et al. for compound **1**. In this case, CD_2Cl_2 was used as the NMR solvent for consistency with the UV–vis spectral data. UV irradiation of a solution of compound **2** at −60 °C gave ca. 20% conversion to the merocyanine as judged from the ^{1}H NMR spectrum. A distinctive feature of the spectrum was the characteristic singlet at δ 9.87 ppm

Table 4
Correlation between experimental and calculated visible absorption spectra for photomerocyanines **7** and **8**

Isomer	Calculated (PPP) electronic spectral data [λ_{max}/(nm) (f_{osc})]for merocyanines **7**	Experimental electronic spectral data [λ_{max}/(nm)] for merocyanines **7**	Calculated (PPP) electronic spectral data [λ_{max}/(nm) (f_{osc})] for merocyanines **8**	Experimental electronic spectral data [λ_{max}/(nm)] for merocyanines **8**
a	620 (0.83)		634 (1.01)	
b	614 (0.85)	606, 578(sh)	627 (1.03)	632, 596
c	609 (0.80)		620 (1.13)	
d	594 (0.79)		605 (1.15)	

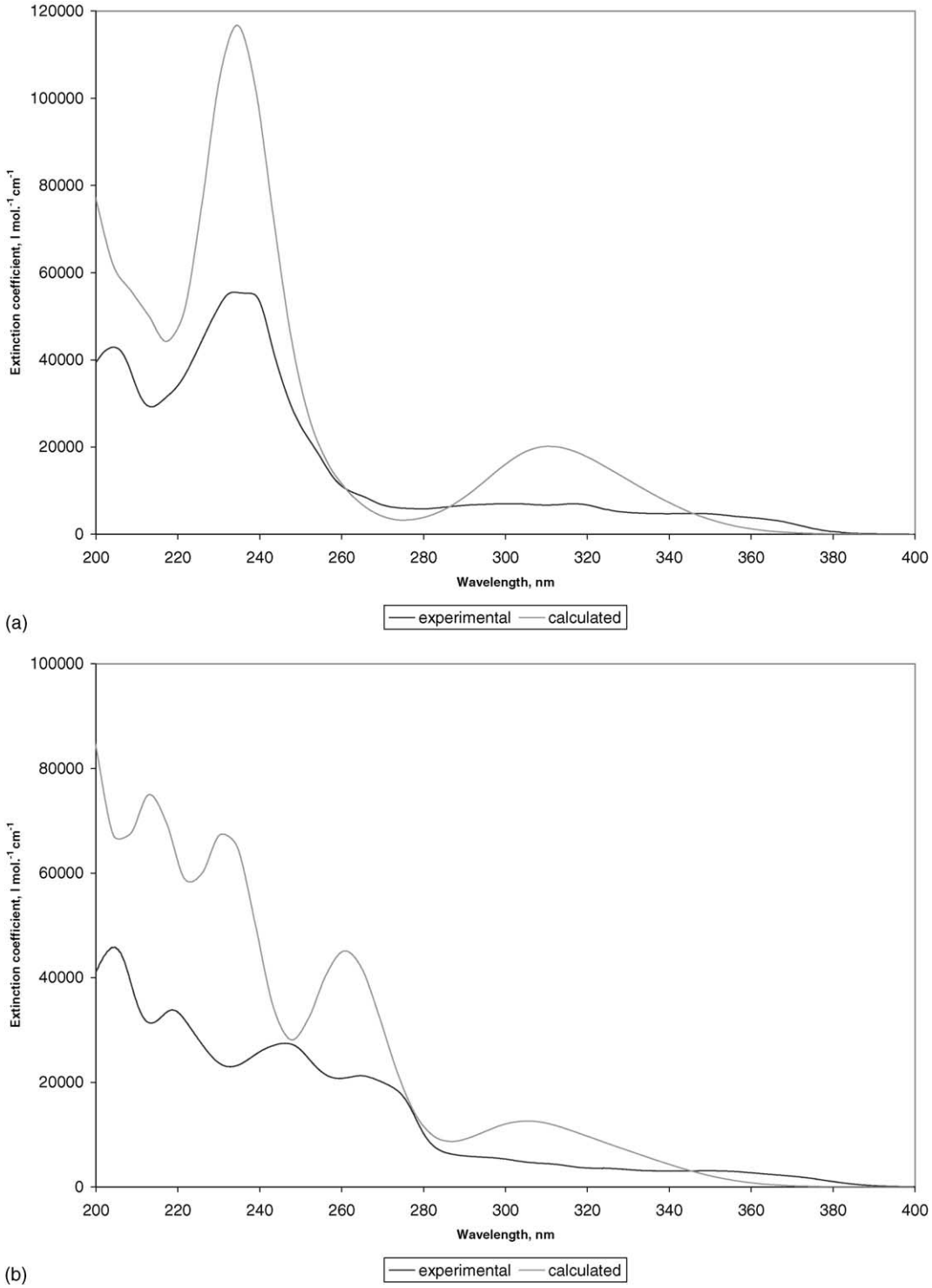

Fig. 3. (a) Experimental and calculated (ZINDO) UV–vis spectra of spirooxazine **1**. (b) Experimental and calculated (ZINDO) UV–vis spectra of spirooxazine **2**.

due to the azomethine proton H_α (Fig. 4). This proton in isomer **7b** is reported at δ 10.22 ppm. [11] In our case, NOE contact was observed between the signal due to H_α and that due to the NCH_3. This result excludes isomers **8a** and **8c** and is most consistent with isomer **8b** (Fig. 2). Isomer **8d** would be expected to show NOE contact with one of the protons in the aromatic region, but no such contact was observed. The assignment of the most stable isomer as **8b** is supported by the optimised PPP-MO calculation (Table 4), which predicts the visible absorption of **8b** to be, at 627 nm,

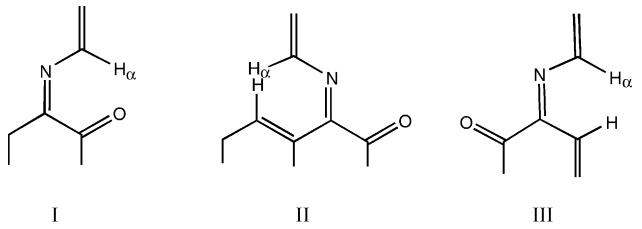

Fig. 4. Conformations in photomerocyanines.

bathochromically shifted relative to **7b**, consistent with the experimental observation (634 nm), whereas **8d** is predicted to be hypsochromic relative to **7b**. In the spectrum of the irradiated solution of compound **2**, a minor component was detected on the basis of a weak singlet at δ 9.73 ppm. It is conceivable that this is isomer **8d**, although the signal was too weak for NOE experiments.

Molecular mechanics (MM2) calculations on the photomerocyanines suggest that in all cases proximity of H_α to N–CH_3 is favoured compared with proximity to $C(CH_3)_2$ (Table 3). The calculations confirm the lowest steric energy for structure **7b** confirming it as the most stable isomer in that case, a result consistent with previous observations. [11,17] The instability of isomers **7c** and **7d** is attributed to the steric interaction of H_α with a naphthalene ring H-atom (conformation II, Fig. 4). The effect can be demonstrated from the dihedral angle at the azadiene bridge for the optimised geometric structure after the MM2 calculation shown in Table 3 for the ring-opened forms of compound **1,** which show significant deviation of isomers **7c** and **7d** from planarity. MM2 calculations indicate structure **8d** as having the lowest steric energy, although only slightly less than **8b**. In compound **8d**, due to the different structural situation, the steric interaction of H_α with the naphthalene ring H-atom (conformation III, Fig. 4) is significantly less. This is demonstrated by the corresponding dihedral angles (Table 3) calculated for the optimised geometric structures for ring-opened forms of compound **2**, all of which are essentially planar. A possible reason for the inconsistency with the result provided by NMR is the stabilisation of structure **8b** from a weak electrostatic interaction between H_α and the carbonyl oxygen (conformation I, Fig. 4) which molecular mechanics may not adequately address. A further contributing factor may be that the calculations apply strictly to the gas phase, while solvent effects may influence the experimental solution spectral data. Horii et al. [19] have examined the photochromism of compounds **1** and **2** by visible spectroscopy in hexane. They report significant changes in the shape of the visible absorption profile of the ring-opened forms derived from compound **2** when irradiated with light of wavelengths >600 nm. They have interpreted the outcome of this secondary photochromic behaviour as a change of position of the thermal equilibrium between the possible isomeric forms. The similarity in energies between forms **8b** and **8d** may provide an explanation for this secondary photochromic behaviour of compound **2**, which is not shown by compound **1**. Heats of formation of the photomerocyanines calculated by AM1 are not consistent with the experimental observations (Table 3). Other authors have previously reported similar inconsistencies in attempting to address the energies of the ring-opened species using quantum mechanical methods. [12,14] It is generally observed that molecular mechanics provides better energy predictions of geometric isomers, while AM1 is more appropriate to provide an account of the energies of dissimilar molecules.

It is of interest that the components of the isomeric mixture **6** are spirooxazines, but we have observed no photochromic behaviour under normal irradiation conditions. There are numerous hypothetical photomerocyanines derivable from ring-opening of compound **6**, all of which are likely to show considerable steric congestion and thus would be expected to be highly unstable.

3. Conclusions

Details of the synthesis of spirooxazine **2** are provided for the first time, and a coloured spirooxazine **6** formed as an associated product has been completely characterised as a mixture of geometric isomers. Heat 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 λ_{max} values, although the method may not produce an unequivocal result when the energies of the geometrical isomers are similar. The approach described in this paper, which makes appropriate use of a range of accessible molecular modelling methods, has considerable potential for the design of new photochromic materials, for example in the screening of potential synthetic target molecules. We will report the successful application of this approach to a wider range of systems in future publications.

4. Experimental

NMR spectra of spirooxazine **2** were recorded on a Bruker DPX400 instrument: ^{1}H at 400 MHz, ^{13}C at 100 MHz**.** For the ring-opened form of compound **2**, the sample in CD_2Cl_2 at −60 °C was irradiated for 45 min using a 400 W mercury lamp emitting principally at 366 nm. The NMR spectra were also recorded at −60 °C. NMR spectra of compound **6** were measured on a Bruker AMX 360 spectrometer (360.13 MHz for ^{1}H, 90.56 MHz for ^{13}C, 36.50 MHz for

^{15}N) in C_6D_6 or $CDCl_3$. ^1H and ^{13}C chemical shifts are given on the δ scale (ppm) and are referenced to internal TMS. ^{15}N chemical shifts are referenced to external neat nitromethane in a co-axial capillary ($\delta = 0.0$). Positive values denote shifts to higher frequencies. All 2D experiments (gradient-selected (gs)-COSY, NOESY, gs-HMQC, gs-HMBC) were performed using manufacturer's software.

Mass spectra were recorded on a Vacuum Generators' MS9 instrument operated in FAB mode. Elemental analysis was carried out on an Exeter CE-440 Elemental Analyser. Infrared spectra were recorded as KBr discs with a Nicolet Protege 460 Fourier Transform spectrophotometer. UV–vis spectra of the spirooxazines were recorded on a Perkin-Elmer Lamda 2 spectrophotometer for solutions in acetonitrile. For the ring-opened form of compound **2**, the sample in dichloromethane was irradiated at −60 °C as for the NMR sample and the spectrum of the deep blue solution obtained using a Unicam UV300 spectrophotometer. Melting points were recorded as peak temperatures on a Mettler DSC 30 with a Mettler TC 10A processor using a heating rate of 10 °C min^{-1}.

A standard PPP-MO procedure was used within the fixed β approximation [13,22] for the calculation of the spectra of the ring-opened merocyanine structures. A generalised set of parameters was used with specific parameter modification as discussed in the previous section. Two-centre repulsion integrals were determined using the Nishimoto–Mataga relationship [26] and electronic excitation energies were refined by a limited configuration interaction treatment involving nine singly excited configurations obtained by promoting an electron from the three highest occupied molecular orbitals to the three lowest unoccupied molecular orbitals. Molecular mechanics, MOPAC and ZINDO calculations were carried out using the CAChe for Windows system [27].

1-Nitroso-2-naphthol (**4**) was obtained by nitrosation of 2-naphthol according to literature procedures. [28] 2-Nitroso-1-naphthol (**5**) and 1,3,3-trimethyl-2-methyleneindoline (Fischer's base) (**3**) were commercial products obtained from the Aldrich Chemical Company, The Old Brickyard, New Road, Gillingham Dorset, SP8 4JL, UK.

*4.1. Reaction of 1,3,3-trimethyl-2-methyleneindoline (Fischer's base) (**3**) with 1-nitroso-2-naphthol (**4**)*

1-Nitroso-2-naphthol (**4**) (1.73 g, 0.01 mol) was added to toluene (20 cm^3) and the mixture brought to reflux. Fischer's base (**3**) (1.75 cm^3, 0.01 mol) in toluene (5 cm^3) was added dropwise over 10 min and reflux continued for 1 h. The reaction mixture was cooled, poured into water (100 cm^3) and extracted with dichloromethane (2 × 100 cm^3). The combined organic extracts were washed with water, dried over anhydrous sodium sulphate and evaporated. Chromatography on a column of silica gel using dichloromethane/hexane (1:1) gave 1,3,3-trimethylspiro[indoline-2,3′-[2H]-naphth [2,1-b] [1,4] oxazine (**1**) (1.93 g, 59%) as colourless prisms (from ethyl acetate/hexane with charcoal screening), m.p 128 °C (lit. 124–125 °C).[1] (Found C, 80.3; H, 6.0; N, 8.5. $C_{22}H_{20}N_2O$ requires C, 80.5; H, 6.1; N, 8.5%); υ_{max}: 3049 (Ar–H, st), 2967, 2869 (C–H, st), 1606 (C=N, st), 1593, 1509, 1485 (aromatic C=C, st), 1386 (C–H, bd), 1173 (C–N, st), 959 (C_{spiro}–O, st), 749 (Ar–H, bd) cm^{-1}. *m/z* (FAB) 329 (M+1, 91.5), 314 (M+1-CH_3, 16.0), 299 (M+1-$(CH_3)_2$, 6.8), 285 (M+1-$(CH_3)_3$, 3.8), 160 (100.0).

4.2. Reaction of 1,3,3-trimethyl-2-methyleneindoline Fischer's base (3) with 2-nitroso-1-naphthol (5)

(a) A similar reaction procedure was used with 2-nitroso-1-naphthol (**5**) (1.73 g, 0.01 mol) and Fischer's base (**3**) (1.75 cm^3, 0.01 mol). After reaction work-up, the residue was chromatographed on a column of silica gel using dichloromethane/hexane (1:1). Initial eluates gave an orange product which proved to be an inseparable mixture of spiro[1,3,3-trimethylindoline)-2,2′-{3′-(1,3,3-trimethylindolin-2-ylidinemethyl)-2'H-naphth[1,2-b] [1,4] oxazines}] **6a** and **6b** (0.36 g, 14.5%) as orange plates (from hexane), m.p.184.0 °C, (Found C, 81.4; H, 6.6; N, 8.3. $C_{34}H_{33}N_3O$ requires C, 81.7; H, 6.7; N, 8.4%); υ_{max}: 3056 (Ar–H, st), 2955 (C–H, st), 1606 (C=N, st), 1587, 1504, 1490 (aromatic C=C, st), 1384 (C–H, bd), 1184 (C–N, st), 959 (C_{spiro}–O, st), 742 (Ar–H, bd) cm^{-1}, *m/z* (FAB) 499 (M+1, 49.7), 484 (26.4), 340 (10.47), 158.1 (23.91), 28.0 (100). Further elution gave 1,3,3-trimethylspiro[indoline-2,3′-[2H]-naphth[1,2-b] [1,4]oxazine (**2**) (0.19 g, 5.8%) as very pale green crystals (from ethyl acetate/hexane 1:1), m.p. 137.1°, (Found C, 80.1; H, 6.1; N, 8.4. $C_{22}H_{20}N_2O$ requires C, 80.4; H, 6.1; N, 8.5; υ_{max}: 3050 (Ar–H, st), 2959 (C–H, st), 1609 (C=N, st), 1577, 1509, 1486 (aromatic C=C, st), 1386 (C–H, bd), 1184 (C–N, st), 961 (C_{spiro}–O, st), 745 (Ar–H, bd) cm^{-1}; *m/z* (FAB) 329 (M+1, 36.1), 314 (M+1-CH_3, 5.1), 299 (M+1-$(CH_3)_2$, 1.9), 285 (M+1-$(CH_3)_3$, 1.9), 160 (100.0); δ_H (ppm) 1.356 (3H, s, 9-CH_3), 1.363 (3H, s, 10-CH_3), 2.76 (3H, s, N–CH_3), 6.58 (^1H, m, 7-H), 6.91 (^1H, m, 5-H), 7.09 (^1H, m, 4-H), 7.23 (^1H, m, 6-H), 7.35 (^1H, m, 9′-H), 7.42 (^1H, d, $J_{6',5'}$ = 8.6Hz, 6′-H), 7.43 (^1H, m, 8′-H), 7.53 (^1H, d, $J_{5',6'}$ = 8.5Hz, 5′-H), 7.69 (^1H, s, 3′-H [N=CH]), 7.75 (^1H, m, 7′-H), 7.99 (^1H, m, 10′-H); δ_C (ppm) 20.9 (9-CH_3), 25.5 (10-CH_3), 29.6 (N–CH_3), 51.7 (3-C), 99.2 (spiro 2-C), 107.1 (7-C), 119.8 (5-C), 120.4 (6′-C), 121.5 (4-C), 121.9 (10′-C), 123.6 (10a′-C), 125.0 (4a′-C), 125.6 (9′-C), 125.8 (5′-C), 126.9 (8′-C), 127.6 (7′-C), 127.9 (6-C), 134.5 (1a′-C),135.9 (3a-C), 141.7 (6a′-C), 147.6 (7a-C), 152.1 (3′-C).

(b) The procedure as in (a) was used but with 2-nitroso-1-naphthol **5** (1.73 g, 0.01 mol) and Fischer's base (**3**) (3.5 cm^3, 0.02 mol). Spirooxazine **2** (0.33 g,10%) and orange mixture **6** (0.49 g, 20%) were obtained.

(c) The procedure in (a) was used except that a slow stream of nitrogen was passed through the mixture to prevent oxidation by air. Spirooxazine **2** (0.11 g, 3.4%) and orange mixture **6** (0.43 g,17%) were obtained.

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