Solvatochromic and Photochromic Characteristics of New 1,3-Dihydrospiro[2*H*-indole-2,2'-[2*H*]-bipyrido[3,2-*f*][2,3-*h*][1,4]benzoxazines]

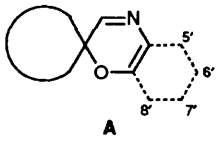
Jean-Luc Pozzo,[a] André Samat,[a] Robert Guglielmetti*,[a] and Denis De Keukeleire[b]
[a] *Université d'Aix-Marseille II, Faculté des Sciences de Luminy, Laboratoire de Chimie Organique et BioOrganique, URA 1320 163, Av. de Luminy, Case 901, F-13288 Marseille Cedex 9, France*
[b] *University of Gent, Faculty of Pharmaceutical Sciences, Harelbekestraat, 72 B-9000 Gent, Belgium*

The mono-oxime of 1,10-phenanthroline-5,6-quinone reacts with 1,3,3-trimethyl-2-methyleneindoline derivatives to give the corresponding spirooxazines, *i.e.* 1,3-dihydrospiro[2*H*-indole-2,2'-[2*H*]-bipyrido[3,2-*f*][2,3-*h*][1,4]benzoxazines]. These compounds exhibit particular solvatochromic behaviour, strongly dependent on the substitution pattern. At room temperature and without any light excitation, an equilibrium is established between closed and opened forms. The photochromic characteristics have been determined using flash photolysis coupled to a fast scanning spectrometer allowing the determination of rate constants for thermal bleaching, visible absorption and photocoloration. The coloured opened forms, either photoinduced or arising from the solvation effect, appear to be spectroscopically identical. Structural parameters of the short-lived photomerocyanines have also been obtained.

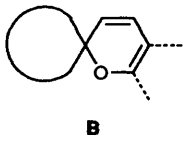
Spirooxazines **A**, first mentioned by Fox[1] in 1961, are structurally very similar to spiropyrans **B**. However, the replacement of the pyran ring by an oxazine ring induces greatly improved resistance to photodegradation.[2-5] This property is an important feature in connection with industrial applications in various fields (photochromic glasses, non-linear optics, biological probes, *etc.*).

While the spiro[indole-naphthoxazines] have been extensively studied[6,7] and patented, comparatively little work has been carried out on spiro[indole-benzoxazines] containing one or more heterocyclic nuclei, especially concerning the opened coloured forms. As for spiropyrans, the opened forms ('photomerocyanines') obtained after cleavage of the spiro linkage by absorption in the UV region return to the original spiroheterocyclic form *via* both thermal and photochemical pathways.

The thermal equilibrium between the ground state populations of the colourless and coloured forms is influenced by the solvent polarity as well as by the nature of the substituents.[6] A large number of spiro [indole-oxazines] were synthesized exhibiting a good compromise between efficient photocolouration and resistance to photodegradation. The presence of a heterobenzofused system gives rise to interesting properties which open up new prospects for synthesis and applications.[8]



A

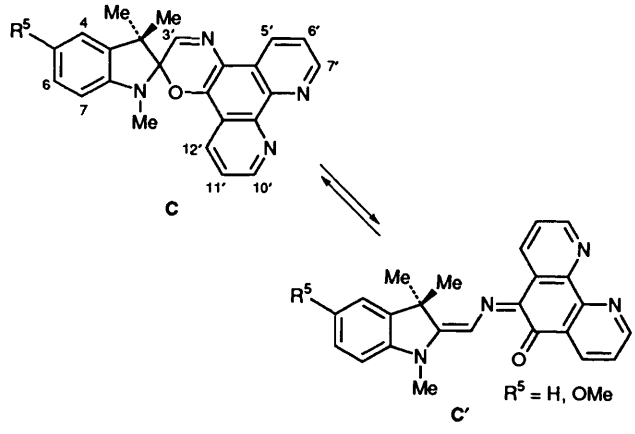


B

Thus, the purpose of the present work was to introduce two heterocyclic nuclei, respectively in the C(5')–C(6') and C(7')–C(8') positions and to investigate quantitatively the role of the heteroatoms in the oxazine moiety with respect to the photochromic properties and especially the stability of the opened forms.

These unstable species can be directly studied by flash-photolysis combined with a rapid spectrophotometer[9] or by ^{1}H NMR spectroscopy at low temperature.[10]

In the 1,3-dihydrospiro[2*H*-indole-2,2'-[2*H*]bipyrido[3,2-*f*]-[2,3-*h*][1,4]benzoxazine] series, an equilibrium occurs between the colourless closed form **C** and the coloured opened form **C'** at room temperature in the absence of light (Scheme 1, **C'** is represented here by its TTC conformation).



Scheme 1

In this paper, a complete study (solvatochromism, photochromism) of spiro[indole-phenanthrolinoxazines] is presented, using ^{1}H NMR spectroscopy, electronic spectroscopy, and spectrokinetic (flash photolysis) experiments.

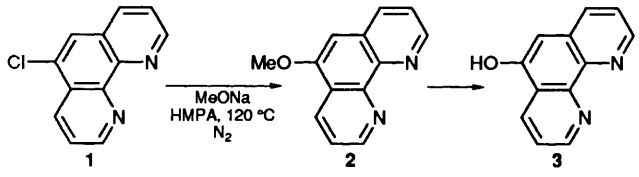
We were able to quantify the substituent and the solvent effects with regard to both solvatochromic and photochromic properties.

The concentration of the opened forms increases with solvent polarity. Precise measurements allow the molar absorptivities to be evaluated.

Results and Discussion

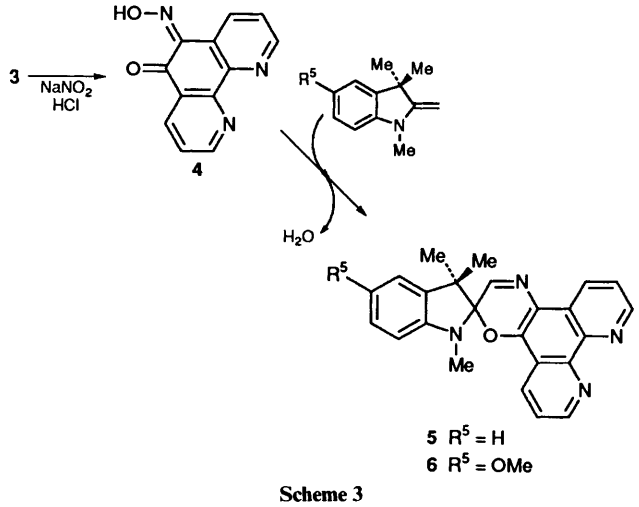
Synthesis.—The synthesis of 1,3-dihydrospiro[2*H*-indole-2,2'-[2*H*]bipyrido[3,2-*f*][2,3-*h*][1,4]benzoxazines] includes nucleophilic substitution and demethylation of 5-chloro-1,10-phenanthroline **1** in a one-pot process to give the hydroxy compound **3**. Sodium methoxide reacts in hexamethylphosphor-

amide with the chloro derivative **1** to give the 5-methoxy-1,10-phenanthroline **2** (S_NAr process). The excess base then effects demethylation of the ether to give the corresponding 1,10-phenanthrolinol **3** (S_N2 reaction). L. Testaferri *et al.*[11] have shown that the reaction of unactivated aryl halides with sodium methoxide gives better yields using HMPA as solvent. Thus, nucleophilic substitution followed by demethylation affords 5-hydroxy-1,10-phenanthroline **3** (90%) (Scheme 2).



Scheme 2

The mono-oxime of 1,10-phenanthroline-5,6-quinone **4** was prepared using sodium nitrite in acidic medium (86%). This bifunctionalized phenanthroline was then condensed with 1,3,3-trimethyl-2-methyleneindoline derivatives (Fischer's bases) leading to the spirooxazines **5** (26%) and **6** (39%) (Scheme 3).



5 $R^5 = H$
6 $R^5 = OMe$

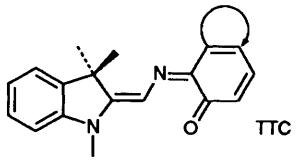
Scheme 3

The yields are low despite the positive influence of an electron-donating substituent in the indole moiety.[8] In fact, the purification of these compounds is difficult, owing to the appearance of an equilibrium between closed and opened forms depending on the nature of the solvents. The spiro[indole-phenanthrolinoxazines] could only be obtained after several separations by flash chromatography.

Solvatochromism.—Solvatochromism arises when a solute in solvents of varying polarity manifests a pronounced change in position, intensity and shape of its absorption bands. This phenomenon has been extensively used to study the polarity of merocyanine dyes and photomerocyanines.[12] Moreover, since in spiro[indole-phenanthrolinoxazines] the cleavage of the spirolinkage occurs simply by solvation, the solvatochromism involves two species, *i.e.* the closed and opened forms. The equilibrium is shifted towards the coloured forms as the polarity of the solvent increases.

Here, the overall solvation induces changes in the visible spectra of the coloured forms and modification of the ratio between the colourless and coloured forms. Furthermore, solvatochromism influences the chromogenic properties.

^1H NMR study. The 400 MHz ^1H NMR assignments for the colourless and coloured forms of the spirooxazines **5** and **6** are reported. For the closed forms, total assignments were realized in a non-polar medium in which the equilibrium is shifted towards the spiroheterocyclic form. M. I. Cherkachine *et al.*[10] described for the first time the ^1H NMR features of the coloured photoinduced form in the spiro[indole-oxazine] series. From spectra with and without irradiation obtained at −72 °C in deuteriotoluene and deuterioacetone, these authors concluded that the conformation was predominantly TTC.



In our case, the signals of different characteristic groups (*i.e.* azomethine proton $H^{3'}$, N-Me, gem di-Me) of the opened forms could be easily detected and measured at room temperature in the absence of light, and total assignments of the opened form were only performed for compound **6** (Table 1).

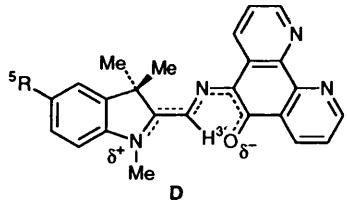
NMR spectroscopy is a suitable technique to investigate the geometry and the electronic structure of opened forms which is usually a very difficult task in the spiro[indole-oxazine] series.

The gem-dimethyl group is shifted towards low field when the opened form is compared to the closed one. This corresponds to the *trans*-stereoisomers of the coloured planar forms. The lone pair of the azomethinic nitrogen then affects strongly the electronic environment.[10] $\Delta\delta CMe_2$ between the closed and the opened forms is not affected by substituent or solvent effects (0.5–0.6 ppm). This signal is not dependent on electronic distribution and therefore does not allow distinction between the quinoidal and zwitterionic character.

The proton $H^{3'}$ for both compounds **5** and **6** is drastically shifted towards low field (10.1–10.3 ppm, $\Delta\delta H^{3'}$ *ca.* 2.4). For comparison, the chemical -CH-shift of diarylazomethines XC_6H_4-CH=N-C_6H_4Y is about 8.3–8.6 ppm. We assume therefore that the 'merocyanines' are planar and present a much more conjugated system.

$\Delta\delta$N-Me (1.15 in CD_3OD or $CDCl_3$; 0.88 in C_6D_6) indicates an electronic deficiency on the indole-nitrogen atom. In the opened form the lone pair is more involved in the conjugated system and so less localized on the nitrogen atom compared to the closed form.

According to these observations, we assign a delocalized electronic structure **D** to the coloured form which acquires more quinoid character on decreasing the polarity of the solvent. Indeed, the difference between $\Delta\delta$N-Me in deuteriomethanol and deuteriobenzene is 0.3 ppm for both compounds **5** and **6**.



D

A zwitterionic structure does not appear to be present, even in polar media, as found for merocyanines or photomerocyanines of some benzothiazolinic spiropyrans[13] which exhibit a pronounced negative solvatochromism. Indeed, the chemical shift

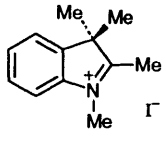


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Table 1 Chemical shifts (ppm) of closed and opened forms of compounds **5** and **6**

		'Closed form' C			'Opened form' C				
Compound	Solvent	CMe_2	NMe	$H^{3'}$	CMe_2	NMe	$H^{3'}$	r^a	p^b
5	CD_3OD	1.38, 1.41	2.79	8.00	1.92	3.91	10.32	0.12	10.5%
	$CDCl_3$	1.38, 1.42	2.79	7.87	1.91	3.87	10.21	0.09	8%
	C_6D_6	1.07, 1.15	2.37	7.59	1.72	3.24	10.10	0.01	1%
6	CD_3OD	1.37, 1.41	2.71	7.97	1.91	3.88	10.28	0.36	26.5%
	$CDCl_3$	1.34, 1.40	2.70	7.82	1.87	3.87	10.19	0.31	24%
	C_6D_6	1.09, 1.13	2.36	7.62	1.72	3.24	10.18	0.11	10%

$^a r = [C']/[C]$. $^b p = [C']/([C] + [C'])$.

Table 2 Solvent effect on the absorption maxima (nm) of compound **5** (**C** + **C'**)

Solvent	λ_{max}/nm			
Methanol	594	557	374	345
Ethanol	592	556	371	343
Acetonitrile	590	553	373	340
Acetone	591	554	373	342
Chloroform	589	555	373	341
Dioxane	587	553	372	337
Benzene	576	550	371	338
Cyclohexane	571	—	370	339

Table 3 Solvent effect on the absorption maxima (nm) of compound **6** (**C** + **C'**)

Solvent	λ_{max}/nm						
Methanol	611	571	375	353	276	244	209
Ethanol	610	572	373	349	275	246	210
Acetonitrile	609	570	377	348	281	250	—
Acetone	604	566	373	349	—	—	—
Chloroform	606	568	370	348	274	243	—
Dioxane	598	561	372	348	274	238	—
Benzene	596	562	369	344	—	—	—
Cyclohexane	585	—	374	350	275	236	209

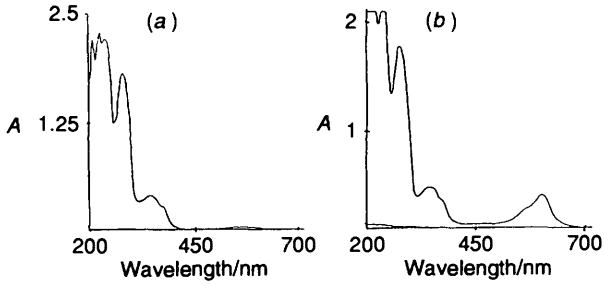


Fig. 1 Absorption spectra of **5** C + C' (*ca.* 8 × 10^{-5} mol dm^{-3}) in (*a*) cyclohexane and (*b*) methanol

of the N-Me group in the opened forms of **5** and **6** is lower than the chemical shift of the same group in 1,2,3,3-tetramethylindoleninium iodide **7** (N-Me: 4.25 ppm).

Absorption spectra of colourless and coloured forms of **5** *and* **6**. The investigation involved a set of eight solvents which span the polarity scale according to Kosower.[14] The absorption spectrum (from 200 to 800 nm) of a dark blue methanolic solution of compound **5** shows the presence of both species (closed and opened forms) while a solution in cyclohexane is quite colourless corresponding to the closed form only (Fig. 1.).

A detailed study was carried out for the spirooxazine **6**. Two intense maxima in the far UV region are centred at 210 and 240 nm. The other three absorption maxima in the UV region, close to 275, 350 and 375 nm, have moderate intensity but are much more interesting as they are associated with the oxazine moiety of the molecule in its closed form. The most prominent absorption peaks in the visible region are close to 605 (maximum) and 570 nm (shoulder), corresponding to the opened form.

According to the aforesaid description, we will focus attention on the four peaks centred at 595, 555, 370, 345 nm respectively for the unsubstituted spirooxazine **5** and at 605, 570, 375, 350 nm for the methoxy derivative **6**, in order to study the equilibria.

A red shift with increasing solvent polarity is observed for compounds **5** and **6** (Tables 2 and 3, respectively). It follows that the excited states of the opened forms are more polar than the ground states.

In fact, the solute dipole moment of the phenanthroline derivatives, should increase during the electronic transition ($\mu g < \mu e$) as the Franck–Condon excited state is formed in a solvent cage of already partly oriented solvent dipoles.[15] The better stabilization of the excited state relative to the ground state with increasing solvent polarity results in a bathochromic shift.

As found for other spiro[indole-oxazine] series,[8a] the absorption maxima are rather insensitive to the solvent. Nevertheless, the positive solvatochromism is consistent with a delocalized charge structure of the coloured species (quinoid structure when decreasing medium polarity).

In addition to the solvatochromic effect, a change in solvent also affects the positions of the equilibrium between the closed and the opened forms. In Table 4, the absorption peaks at the lowest wavelengths (at 350 and 340 nm for compounds **5** and **6** respectively) are considered as references and the corresponding absorbances are normalized in order to compare the relative intensities of the maxima of the opened forms at 5 × 10^{-5} mol dm^{-3} and 25 °C.

Polar solvents promote the formation of the coloured forms. However, even in the most unfavourable conditions (*i.e.* the unsubstituted spirooxazine compound **5** in cyclohexane, at a concentration of *ca.* 5 × 10^{-5} mol dm^{-3}), the opened form can be detected.

Table 4 Ratio between absorbances at λ_{max} of opened forms **5C'** and **6C'** and at λ *ca.* 345 nm of closed forms **5C** and **6C**

Solvent	$A_{5C'}/A_{5C}$	$A_{6C'}/A_{6C}$
Methanol	0.85	3.89
Ethanol	0.79	3.12
Acetonitrile	0.70	2.56
Acetone	0.64	2.04
Chloroform	0.63	1.76
Dioxane	0.58	0.76
Benzene	0.19	0.54
Cyclohexane	0.06	0.50

Table 5 Estimated molar absorptivities (± 10%) of the photomerocyanines of compounds **5** and **6**

Solvent	5C′ shoulder	5C′ λ_{max}	6C′ shoulder	6C′ λ_{max}
Methanol	24 400	42 800	—	—
Acetonitrile	26 020	46 200	—	—
Acetone	22 500	39 000	—	—
Chloroform	22 600	40 100	21 800	40 100
Benzene	—	—	19 500	33 500

Table 6 Spectrokinetic properties of spiro[indole-naphthoxazines] **5–10**. Solvent: toluene. Temperature 25 °C. (s) = shoulder

Compound	k_Δ s^{-1}	λ_{max} (s)/nm	A_0 (Colourability)	Reference
5	0.40	578–(543)	1.08[a]	
6	0.21	595–(555)	0.82[a]	
7	0.54	594–(564)	1.08	9
8	0.16	574–(547)	2.10	8
9	0.36	607–(571)	0.62	9
10	0.34	590–(561)	0.77	9

[a] A_0 is the additional value of the absorbance induced by flash photolysis.

Table 7 Variation of the spectrokinetic parameters (k_Δ, λ_{max}, ΔA_0) of **6** with the solvent. $\Delta A_0 = A_0 - A_i$ with A_0 = absorbance immediately after the flash and A_i = absorbance of the original solution

Solvent	$k\Delta$ s^{-1}	ΔA_0	λ_{max}/nm	Shoulder/nm
Cyclohexane	0.24	0.14	584	545
Toluene	0.21	0.49	595	555
Dioxane	0.50	0.47	597	555
Acetonitrile	0.22	0.56	601	557
Dimethyl sulfoxide	0.27	0.37	610	571
Ethanol	0.16	0.81	605	566
Methanol	0.22	0.86	609	567

Direct comparison of the data given in the tables shows a bathochromic shift when an electron-donating group is placed in the 5-position. The result has also been observed for other spiro[indole-oxazine] series.[8]

The substituent effect on the absorption intensities is important. According to Chu,[6] alkyl and alkoxy substituents on the indole moiety have a less pronounced influence. To our knowledge, this phenomenon should be observed at a higher concentration (*ca.* 5×10^{-3} mol dm^{-3}) and for an absorbance less than 0.1. In our case, the methanolic solution of **6** presents an $A = 1.12$ at 5×10^{-5} mol dm^{-3} (λ_{max} = 611 nm).

The C–O bond in compound **6** is much more polarizable, hence the opening of the oxazine ring is facilitated by simple solvation.

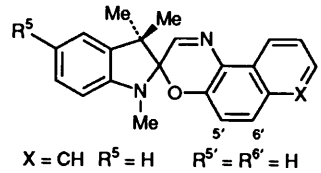
Estimation of molar absorptivities. The results of the UV–VIS and the 400 MHz ^{1}H NMR studies allow us to propose values for molar absorptivities in the spiro[indole-oxazine] series. The only assumption is that the ratio is unchanged for the different concentrations (*i.e.* 2.5×10^{-3} mol dm^{-3} for NMR and 5×10^{-5} mol dm^{-3} for UV–VIS). Variations of the concentrations of **6** in chloroform solution (UV–VIS) seem to validate our assumption in the range of concentrations employed. NMR spectra afford the ratio of the opened to the closed forms and therefore the concentration of the opened form. The molar absorptivities can be calculated from the Beer–Lambert law ($A = \varepsilon_{OF}\, l.r.[C_i]$). Table 5 displays the estimated ε values for compounds **5** and **6**.

Different molar absorptivities of opened forms have been reported in the spiro[indole-naphthoxazine] series. Chu[2] assumes that molar absorption coefficients are temperature-independent and that total conversion towards the opened form is achieved at high UV irradiation intensities and at low temperature. The value is 7.3×10^{-4} dm^3 mol^{-1} cm^{-1} in EtOH for 1,3,3-trimethylspiro[indole-naphthoxazine].

K. Dyumaev and A. Kholmanskii[16] have measured molar absorptivities in both a polymeric matrix (polystyrene) and in a polar solvent (EtOH). Taking several assumptions into account the absorptivities were in the range $2.7–5.2 \times 10^{-4}$ dm^3 mol^{-1} cm^{-1} in EtOH depending on substitution and temperature. The values presented here are in good agreement with those found by Wilkinson.[17] In this study, the molar absorptivities ($3.1–4.5 \times 10^{-4}$ dm^3 mol^{-1} cm^{-1}) depend on the determination of quantum efficiencies.

Photochromic Properties of **5** *and* **6** *in Solution.*—The spectra of the photomerocyanines in the selected set of solvents and the rate constants of thermal bleaching (ring closure) k_Δ were determined using flash photolysis (flashes of *ca.* 60 J, duration of *ca.* 20 μs) coupled to a Warner and Swasey fast scanning spectrometer capable of recording the whole transient absorption spectrum in the visible region in 1.25 ms in a 10 cm quartz cell.

The absorption maxima, evaluated with an accuracy of 2 nm, show that the photoinduced opened forms are identical to those due to the solvation. The 'colourability' is evaluated by monitoring the absorbance A_0 at λ_{max} immediately after the flash. The spectrokinetic parameters (k_Δ, λ_{max} and A_0) of compounds **5** and **6** are reported in Table 6 and are compared with the spiro[indole-oxazines] **7–10** previously synthesized.[8a,18]



7 X = CH R^5 = H $R^{5'} = R^{6'}$ = H
8 X = CH R^5 = H $R^{5'} = R^{6'}$ = Benzo
9 X = CH R^5 = OMe $R^{5'} = R^{6'}$ = H
10 X = N R^5 = H $R^{5'} = R^{6'}$ = H

Table 6 shows that the visible absorption of the spiro[indole-phenanthrolinoxazines] **5** and **6** undergoes an hypsochromic shift compared to the spiro[indole-naphthoxazines] **7** and **9**, respectively. The spiro[indole-phenanthrenoxazines] **8** exhibits a similar behaviour. The predominant effect is due to the benzo- or heterobenzo-annelation at C(5′)–C(6′). A bathochromic shift ascribed to the methoxy group at C(5) is also found. The effects on k_Δ are less important, but a stabilization of the opened forms is observed by introduction of the two nitrogen heteroatoms.

Solvent effect. The study was performed for the spiro[indole-phenanthrolinoxazines] **6** in dilute solution. A polar solvent shifts the equilibrium towards the opened form. In Table 7 are reported the ΔA_0 values corresponding to the enhancement of the absorbances observed after flash photolysis.

Attention is drawn to the fact that unlike for other spiro-oxazines, the rate of bleaching does not increase with increasing solvent polarity. On the other hand the bathochromic shifts with increasing solvent polarity are similar to those determined by UV–VIS experiments. The relative intensities between the maxima and the shoulders are not modified. These latter could be assigned to a mixture of stereoisomers.[19]

Temperature effect. Fig. 2 shows clearly that two competitive pathways to the opened coloured form are operating in toluene, *i.e.* photocolouration and thermochromism.

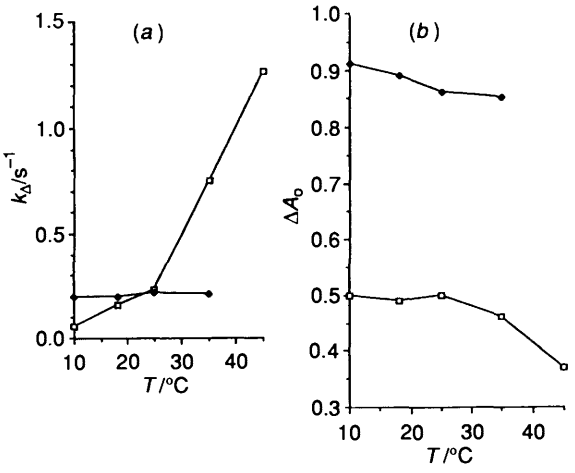


Fig. 2 Plots of (*a*) k_Δ and (*b*) ΔA_0 *versus* temperature for solutions of **6** in toluene (□) and methanol (◆)

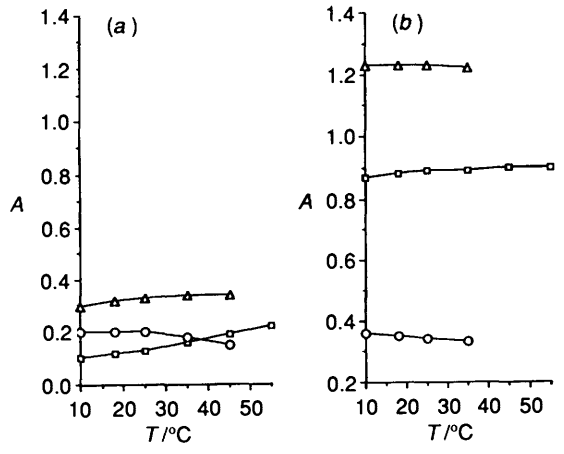


Fig. 3 Plot of absorbance *versus* temperature for solutions of **6** in (*a*) toluene and (*b*) methanol: □, thermochromin; ○, photolysis; △, total

On the contrary, in methanolic solution a weak decrease of the photocolouration from 10 to 35 °C is observed. Partial compensation occurs by thermochromism.

Thermochromism.—In order to verify the results found during the study of the photochromic properties, the spectra of **6** were recorded on a spectrophotometer (300–650 nm) equipped with a thermostatted cell (10–60 °C) in toluene and methanol (Fig. 3).

Fig. 3(*a*) indicates that the formation of the opened form is dependent on the temperature in toluene ($A_{\lambda max}$ 55 °C/$A_{\lambda max}$ 10 °C = 2) and Fig. 3(*b*) shows the lack of variation in methanol.

In the experimental conditions used for flash photolysis (*i.e.* 6 kV), the photochemical and the solvation pathways compensate each other in the temperature range studied.

Conclusions

Two new 1,3-dihydrospiro[2*H*-indole-2,2′-[2*H*]bipyrido[3,-2-*f*][2,3-*h*][1,4]benzoxazines] were synthesized. They exhibited particular solvatochromic behaviour. The compounds are very polarizable, which leads to an equilibrium between the colourless closed and the coloured opened forms in the range of temperatures investigated (283–328 °K) in the absence of light. Thus, they represent good models to obtain structural information on the opened forms in the spiro[indole-oxazine] series. 400 MHz ^{1}H NMR experiments shows that those 'merocyanines' are transoid towards the azomethine bridge. The delocalized electronic structure tends to become more quinoidal with decreasing medium polarity. The features of the spiro-[indole-phenanthrolinoxazines] are strongly dependent on the substituents in the indole moiety and on the nature of the solvent. Thus, the bathochromic shift observed for the opened forms with increasing solvent polarity indicates that the excited states are more polar than the ground states. The concentration of the opened forms determined by ^{1}H NMR spectroscopy and the use of electronic spectroscopy allow one to evaluate the corresponding molar absorptivities. The opened forms generated by photolysis are spectroscopically identical to those arising from solvation.

Experimental

Melting points were taken on a Buchi 510 apparatus. ^{1}H NMR spectra were recorded on a BRUKER AMX 400 or on a BRUKER AM 200. Chemical shifts are given in ppm relative to TMS (0 ppm). *J* values are in Hz. UV–VIS spectra were recorded on a UVIKON 810. Spectra of the photomerocyanines and the rate constants of thermal ring closure k_Δ were determined using a modified flash photolysis apparatus (NORTECH) coupled to a Warner and Swasey fast scanning spectrometer.[20]

5-Hydroxy-1,10-phenanthroline **3**. To a stirred solution of 5-chloro-1,10-phenanthroline (1.06 g, 4.94 mmol) in HMPA (15 cm^3), kept under N_2 at 120 °C, NaOMe (0.75 g) was added (three portions in 1 h). After heating for 2.5 h, the reaction mixture was cooled and poured into 2 mol dm^{-3} sodium hydroxide solution. The organic layer was then extracted with dichloromethane, washed with 2 mol dm^{-3} sodium hydroxide solution, and dried over $MgSO_4$. Solvents were removed under reduced pressure to afford a mixture of 5-chloro- and 5-methoxyphenanthroline which was then subjected to the same procedure. The aqueous layer was then neutralized with dilute HCl solution to pH = 7, the precipitate was then filtered and dried to give 5-hydroxy-1,10-phenanthroline **3** (0.87 g, 90%), m.p. 217 °C (from xylene); δ_H (200 MHz; DMSO) 7.16 (1 H, s, 6-H), 7.61 (1 H, dd, *J* 8.2 and 4.2, 3-H), 7.76 (1 H, dd, *J* 8.2 and 4.2, 8-H), 8.24 (1 H, dd, *J* 8.2 and 0.9, 4-H), 8.64 (1 H, dd, *J* 8.2 and 0.8, 7-H), 8.83 (1 H, dd, *J* 4.3 and 0.8, 2-H), 9.08 (1 H, dd, *J* 4.2 and 0.9, 9-H) and 11.03 (1 H, br s, OH).

Mono-oxime of 1,10-phenanthroline-5,6-quinone **4**. A solution of sodium nitrite (0.48 g) in 4 cm^3 of water was added over 0.5–1 h with stirring and cooling to +2 °C to a solution of 5-hydroxyphenanthroline (1.25 g, 6.37 mmol) in 0.6 cm^3 hydrochloric acid and 4 cm^3 of distilled water. Stirring was continued for another 1.5–2 h, and the precipitate was filtered, washed with water, squeezed and dried to give 1.28 g (86%) of mono-oxime of 1,10-phenanthroline-5,6-quinone **4**, m.p. 209 °C (from EtOH); δ_H(200 MHz; DMSO) 7.8 (2 H, m, 3-H and 8-H), 8.56 (1 H, dd, *J* 8.1 and 0.9, 7-H), 8.89 (1 H, dd, *J* 4.1 and 0.8, 2-H), 9.09 (1 H, dd, *J* 4.2 and 0.8, 9-H) and 9.40 (1 H, dd, *J* 8.1 and 0.9, 4-H).

1,3,3-Trimethyl-1,3-dihydrospiro [2H-indole-2,2′-[2H]bipyrido[3,2-f][2,3-h][1,4]benzoxazine] **5**. Compound **5** was prepared by reacting mono-oxime of 1,10-phenanthroline-5,6-quinone **4** (0.5 g, 2.22 mmol) in EtOH (20 cm^3) with 1,3,3-trimethyl-2-methyleneindoline (0.39 g, 2.22 mmol) in EtOH (15 cm^3). After refluxing for 2 h, the reaction mixture was cooled. The solvent was removed under reduced pressure. The residue was purified twice by flash chromatography using a mixture of cyclohexane and dichloromethane from 50:50 to 5:95 as eluent to give 0.22 g (26%) of 1,3,3-trimethyl-1,3-dihydrospiro[2*H*-indole-2,2′-[2*H*]bipyrido[3,2-*f*][2,3-*h*][1,4]benzoxazine] **5**, m.p. 175 °C (Found: C, 77.8; H, 5.75; N, 11.9. $C_{23}H_{20}N_3O$ requires C, 77.94; H, 5.69; N, 11.85%); δ_H **5C** (400 MHz; CD_3OD) 1.37, 1.40 (6 H, CMe_2), 2.78 (3 H, s, N-Me), 6.66 (1 H, d, *J* 7.8, 7-H), 6.91 (1 H, td, *J* 7.5 and 0.9, 5-H), 7.15 (1 H, dd, *J* 7.8 and 1, 4-H), 7.21 (1 H, td, *J* 7.7 and 1.2, 6-H), 7.67 (1 H, dd, *J* 8.3 and

4.4, 6'-H), 7.81 (1 H, dd, *J* 8.3 and 4.4, 11'-H), 7.98 (1 H, s, 3'-H), 8.44 (1 H, dd, *J* 8.3 and 1.7, 12'-H), 8.97 (1 H, dd, *J* 4.4 and 1.7, 10'-H), 9.05 (1 H, dd, *J* 4.4 and 1.7, 7'-H) and 9.08 (1 H, dd, *J* 8.4 and 1.7, 5'-H).

5-*Methoxy*-1,3,3-*trimethyl*-1,3-*dihydrospiro*[2H-*indole*-2,2'-[2H]*bipyrido*[3,2-f][2,3-h][1,4]*benzoxazine*] **6**. Compound **6** was prepared by reacting the mono-oxime of 1,10-phenanthroline-5,6-quinone (0.72 g, 3.2 mmol) in MeOH (15 cm^3) with 5-methoxy-1,3,3-trimethyl-2-methyleneindoline freshly prepared according to Fischer's procedure (0.65 g, 3.2 mmol) in MeOH (10 cm^3), which was added over a period of 20 min. After refluxing for 3.5 h, the reaction mixture was cooled. The solvent was removed under reduced pressure. The residue was purified several times by flash chromatography using a mixture of dichloromethane and methanol (96:4) as eluent to give 0.51 g (39%) of 5-methoxy-1,3,3-trimethyl-1,3-dihydrospiro[2*H*-indole-2,2'-[2*H*]bipyrido[3,2-*f*][2,3-*h*][1,4]benzoxazine] **6**; m.p. 204 °C (Found: C, 74.9; H, 5.9; N, 10.85. $C_{24}H_{22}N_3O_2$ requires C, 74.98; H, 5.77; N, 10.93%); δ_H of **6C** (400 MHz, $CDCl_3$) 1.34, 1.40 (6 H, CMe_2), 2.70 (3 H, s, NMe), 3.80 (3 H, s, OMe), 6.49 (1 H, d, *J* 8.2, 7-H), 6.73 (1 H, d, *J* 2.5, 4-H), 6.75 (1 H, dd, *J* 8.3 and 2.5, 6-H), 7.53 (1 H, dd, *J* 8.3 and 4.4, 6'-H), 7.69 (1 H, dd, *J* 8.4 and 4.3, 11'-H), 7.82 (1 H, s, 3'-H), 8.4 (1 H, dd, *J* 8.3 and 1.9, 12'-H), 8.98 (1 H, dd, *J* 8.3 and 1.5, 5'-H), 9.09 (1 H, dd, *J* 4.3 and 1.5 10'-H) and 9.14 (1 H, dd, *J* 4.4 and 1.8, 7'-H). δ_H of **6C'** (400 MHz, $CDCl_3$) 1.87 (6 H, s, CMe_2), 3.87 (6 H, s, NMe and OMe), 6.92 (1 H, dd, *J* 8.8 and 2.5, 6-H), 6.99 (1 H, d, *J* 2.4, 4-H), 7.1 (1 H, d, *J* 8.9, 7-H), 7.6 (1 H, dd, *J* 8 and 4.1, 5'-H), 8.49 (1 H, dd, *J* 8 and 1.6, 11'-H), 8.77 (1 H, dd, *J* 8 and 1.6, 6'-H), 8.83 (1 H, m, 12'-H), 9.02 (1 H, m, 7'-H), 9.22 (1 H, dd, *J* 4.1 and 1.7, 10'-H) and 10.19 (1 H, s, 3'-H).

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