

## Photophysical Properties of Biphotochromic Dihydroindolizines. Ring-Opening into Extended Bis-Betaines

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New photochromic spirodihydroindolizines (DHI) that are mono- (**1a–e**) or biphotochromic (**3a–e**) have been prepared. The monophotochromic DHIs **1d** and **1e** contain sterically highly demanding substituents. Photophysical studies, both static and time-resolved, were carried out with **1** and **3**. Monophotochromic DHIs **1a–e** show fluorescence and phosphorescence. Temperature decrease produces a hypsochromic shift in the fluorescence spectra. Time-resolved studies demonstrate that the photochromism is based on a one-photon electrocyclic photoreaction of **1** to the colored betaine. Only one transient of 0.6–6  $\mu$ s lifetime could be detected for the transformation of **1a–e**. For the bichromophoric DHIs **3a–e**, two different transients were recorded with lifetimes of 1 and 45–680  $\mu$ s. It was proved that the ring opening **1**  $\rightarrow$  **4** (as well as **3**  $\rightarrow$  **9**) results from an excited singlet species, as demonstrated by the absence of an oxygen effect and by sensitization experiments. Viscosity effects underline the conformational transformations involved in the sequence **1**  $\rightarrow$  **T**  $\rightarrow$  **4** and **3**  $\rightarrow$  **T**<sub>1</sub>  $\rightarrow$  **T**<sub>2</sub>  $\rightarrow$  **9** to occur in distinct steps, thus showing the detailed reaction paths of photochromic molecules **1** and **3**.

### 1. Introduction

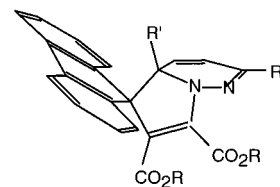
Photochromic dihydroindolizines have proved to constitute a highly efficient class of versatile molecules.<sup>1</sup> Their easy accessibility, superior to that of many other photochromic materials, and their potential use in ophthalmic lenses,<sup>2</sup> information recording or storage, and photoswitches,<sup>3</sup> as well as their recent application in dental materials<sup>4</sup> have made these molecules a highly attractive class of photochromes.

The limiting factor for the potential use of the photochromic materials is the slow kinetics of the reverse thermal reclosure of the open betaines to the starting materials when incorporated into a polymeric matrix.

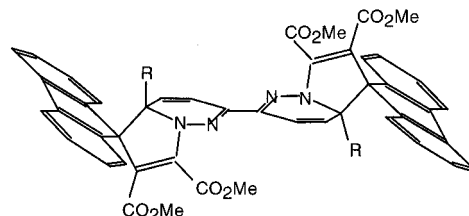
The extension of the photochromic concept to biphotochromic systems has been referred to in some cases<sup>5,6</sup> but an unambiguous study of the complicated properties and of the behavior of such systems has not been published in detail until now.<sup>7</sup>

Changing the previously employed pyridine-derived<sup>5</sup> structural elements by bipyridazine partial structures affords compounds which show a higher thermal stability.

In the present paper, we present a survey of polyether-functionalized biphotochromic dihydroindolizines (DHI)



- 1a** R = Me R' = R'' = H  
**1b** R = R'' = Me R' = H  
**1c** R = R' = R'' = Me  
**1d** R = 1-adamantyl R' = R'' = H  
**1e** R = 2-norbornyl R' = R'' = H



- 3a** R = Me  
**3b** R = OMe  
**3c** R = (OCH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>-OCH<sub>3</sub>  
**3d** R = (OCH<sub>2</sub>CH<sub>2</sub>)<sub>3</sub>-OCH<sub>3</sub>  
**3e** R = (OCH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>-O-C<sub>6</sub>H<sub>4</sub>-OCH<sub>3</sub>  
**3f** R = (OCH<sub>2</sub>CH<sub>2</sub>)<sub>4</sub>-OCH<sub>3</sub>

**3a–e**, their synthesis and basic photophysical properties, as well as a detailed study of the photophysical primary process (the photoinduced ring-opening reaction), based on the suitable model compounds **1a–e**.

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(1) Dürr, H.; Bouas-Laurent, H. In *Photochromism, Molecules and Systems*; Elsevier: New York, 1990; p 193.

(2) McArdle, C. B. In *Applied Photochromic Polymer Systems*; Blackie and son Ltd: Glasgow, 1992.

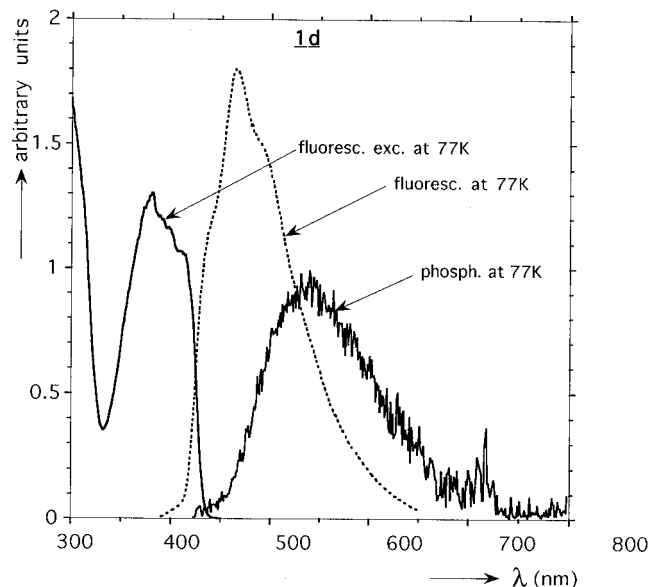
(3) Willner, W.; Rubin, S. *Angewandte Chem. Inter. Ed. Engl.* **1996**, *35*, 367.

(4) Dürr, H. *Praxis Naturwiss. Chem.* **1991**, *4/40*, 22.

(5) Spang, P. Ph.D. Dissertation, Saarbrücken (Germany), 1985.

(6) Scheidhauer, P. Ph.D. Dissertation, Saarbrücken (Germany), 1987.

(7) Spang, P.; Dürr, H. *Angew. Chem.* **1984**, *3*, 227.



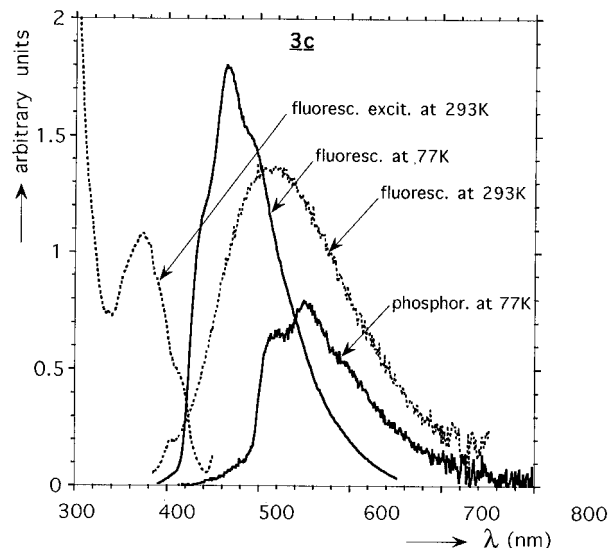
**Figure 1.** Compound **1d**: fluorescence, fluorescence excitation and phosphorescence spectra at 77 K in ethanol solution.

## 2. Results

**2a. Emission Spectroscopy.** The fluorescence emission of compounds **1a–c** and **3a–e** has been characterized at room temperature in dichloromethane and ethanol solutions under steady-state excitation. The fluorescence emission has been also examined at 77 K in ethanol solution while the phosphorescence of the compounds was obtained under the same conditions but with a chopper in order to eliminate the (prompt) fluorescence. The fluorescence quantum yield is very low at room temperature ( $\Phi_f = 7 \times 10^{-4}$  to  $2 \times 10^{-2}$  in dichloromethane), but it increases when the temperature is decreased. The phosphorescence intensity, although no quantum yield determination has been carried out, appears to be low also. The room temperature and 77 K fluorescence spectra, as well as the fluorescence excitation spectra and the phosphorescence spectra of compounds **1d** and **3c**, are depicted in Figures 1 and 2, respectively.

Attempts to measure the singlet lifetime of the compounds were limited by the technological limit ( $\tau_f > 0.4$  ns) of the detection system used. Thus, the fluorescence of compounds **1a–e**, **3a**, and **3c** decays with a lifetime shorter than 0.4 ns. On the other hand, the lifetime of the singlet excited state of compounds **3b** and **3d** is on the order of 0.6 ns while that of **3e** is about 1.0 ns.

In the case of the bichromophoric DHI molecules **3a–e**, the fluorescence quantum yields are more than double that of the monochromophoric systems (Table 1). This increase in fluorescence intensity, together with the slight bathochromic shift, could be considered as coherent with an extended conjugation of the singlet excited state and with the increased stabilization of the system. This also is verified by the longer lived singlet state of compounds **3b**, **3d**, and **3e** as compared to that of the corresponding compounds **1**. The influence of the polarity of the solvent upon the position of the fluorescence emission is weak, as one could have expected for a symmetrical molecule. The small (3 nm) hypsochromic shift observed for the position of the fluorescence when the polarity of the solvent is increased from dichloromethane ( $\epsilon = 9.1$ ) to acetonitrile ( $\epsilon = 37.5$ ) corresponds to an excited state which is only slightly more polar than the ground state.



**Figure 2.** Compound **3c**: fluorescence and fluorescence excitation spectra in ethanol solution. Fluorescence and phosphorescence spectra at 77 K in the same solvent.

**Table 1. UV-Visible Absorption Spectra and Fluorescence Data of the Starting DHI Molecules 1a–1e and 3a–3e ( $10^{-4}$  mol L $^{-1}$  in CH $_2$ Cl $_2$  at Room Temperature)**

compd	$\lambda_{\max}$ (nm) DHI/betaine <sup>a</sup>	$\log \epsilon$ DHI/betaine <sup>a</sup>	$\tau_{1/2}$ (s) <sup>b</sup> (betaine)	$\lambda_{\max}$ (nm) (fluoresc)	$\Phi_f$ $\times 10^3$
<b>1a</b>	389/505	3.92/4.29	49.5	484	3.8
<b>1b</b>	382/525	3.93/	73.2	494	1.5
<b>1c</b>	405/444–639	4.02/	864	490	0.7
<b>1d</b>	389/350–517	3.97/4.16	37.4	508	0.8
<b>1e</b>	389/355–525	3.94/4.21	25.6	515	1.5
<b>3a</b>	486/452–619	4.60/	221	517	6.7
<b>3b</b>	383/365–607	4.19/4.21	40.7	511	13.3
<b>3c</b>	373/360–608	4.16/4.24	26.6	508	18.4
<b>3d</b>	344/625	4.16/	12.0	508	12.3
<b>3e</b>	387/360–624	4.23/4.21	14.7	507	8.6

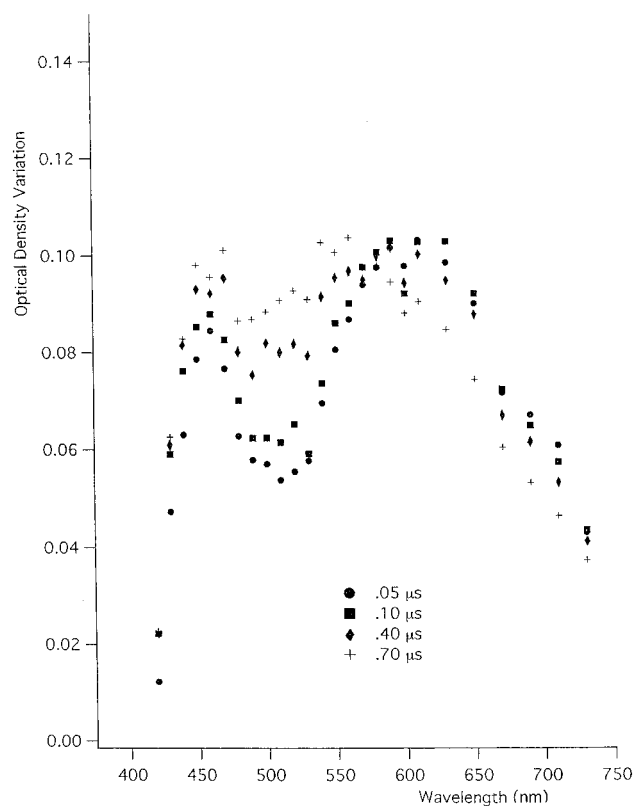
<sup>a</sup> Absorption and <sup>b</sup> half-life ( $\tau_{1/2}$ ) of the corresponding *trans*-betaines.

**Table 2. 77 K Fluorescence and Phosphorescence Results of the Monochromophoric DHI Compounds 1d and 1e and of the Bichromophoric DHI Molecules 3b–e ( $10^{-5}$  mol L $^{-1}$ ) in Ethanol**

compd	$\lambda_{\text{exc}}$ (nm)	$\lambda_f$ (nm)	$\lambda_{\text{ph}}$ (nm)	$E_{S1}$ (kJ mol $^{-1}$ )	$E_{T1}$ (kJ mol $^{-1}$ )	$\tau_{\text{ph}}$ (s)
<b>1d</b>	390	475 (508) <sup>a</sup>	540	283	258	0.4
<b>1e</b>	390	485 (515) <sup>a</sup>	550	280	255	
<b>3b</b>	390	480 (511) <sup>a</sup>	580	275	247	1.0
<b>3c</b>	370	470 (508) <sup>a</sup>	550	285	260	0.3
<b>3d</b>	360	470 {508} <sup>a</sup>	550	289	264	0.5
<b>3e</b>	390	470 (507) <sup>a</sup>	550	285	255	0.55

<sup>a</sup> Fluorescence maximum at room temperature (see Table 1).

The position of the maximum of the phosphorescence spectra (taken at 77 K in ethanol solution) and the phosphorescence lifetime (which ranges in the millisecond to the second time scale) are listed in Table 2. For all the compounds studied here, the phosphorescence emission is shifted to longer wavelengths—by 35–65 nm for the monochromophoric molecules and by 60–100 nm for the bichromophoric molecules—by reference to the corresponding fluorescence position taken at 77 K.



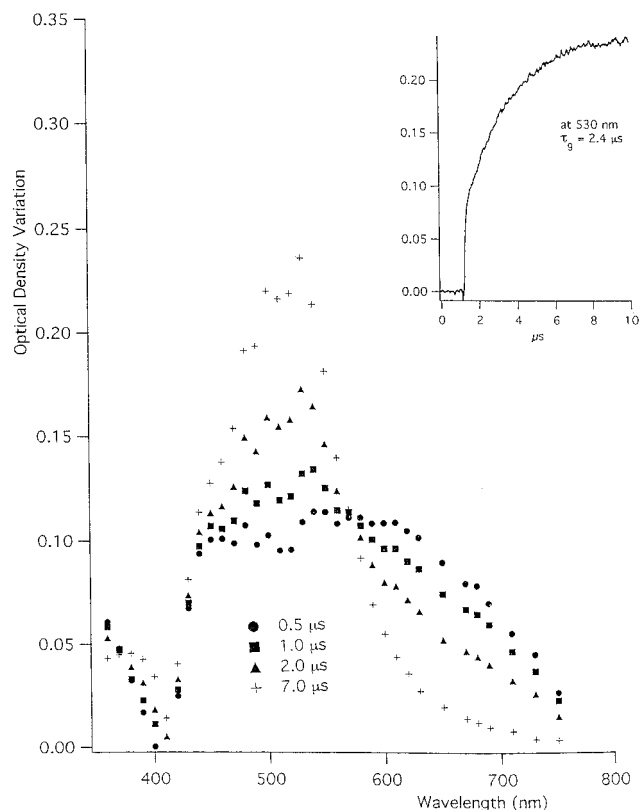
**Figure 3.** Transient absorption spectra of compound **1a** in  $\text{CH}_2\text{Cl}_2$  solution at different times shortly (50, 100, 400 and 700 ns) after the laser pulse.

**2b. Laser Flash Photolysis Experiments.** Excitation of dichloromethane solutions of compounds **1a–e** and **3a–e** leads to detectable photobetaines absorbing in the 515–625 nm range. As in the case of many betaines, those formed here by irradiation of the DHI molecules have lifetimes ranging from 12 to 864 s (Table 1), depending on the compound.

**Monochromophoric DHI 1a–e.** Time-resolved transient absorption spectroscopy was carried out using a pulsed ruby laser with a time resolution in the nanosecond time domain (20 ns fwhm) to detect any transient species formed after irradiation.

Figures 3 and 4 show the time-resolved absorption spectra in the nano- and microsecond time scales, respectively, of the transients formed by irradiation of the monochromophoric DHI molecule **1a**. The formed intermediate shows (Figure 3) two absorption bands (at 460 and 600 nm); the one at the lower energy absorbs at longer wavelengths than the more stable *trans*-betaine **5a**, which absorbs at 500–530 nm (Figure 4) in dichloromethane solution; a value to be compared to the ca. 505 nm obtained by conventional UV–visible spectroscopy in the same solvent. The isosbestic points observed at 370 and 570 nm (Figure 4) are a clear indication that this intermediate, for which we have attributed the structure of the *cis*-betaine **4a** (Scheme 1), is transformed into the long-lived transient, the absorption of which corresponds to the *trans*-betaine **5a**.

The growing-in of the final *trans*-betaine at 530 nm, as shown in the inset of Figure 4, occurs with a rise time (2.4  $\mu\text{s}$ ) identical with that of the decay of the short-lived transient absorbing at 460 and 600 nm. This transformation from **4a** into the long-lived *trans*-betaine **5a** is



**Figure 4.** Transient absorption spectra of compound **1a** in  $\text{CH}_2\text{Cl}_2$  solution at different times (0.5, 1.0, 2.0 and 7  $\mu\text{s}$ ) after the laser pulse. Inset: growing-in of the transient (betaine) at 530 nm.

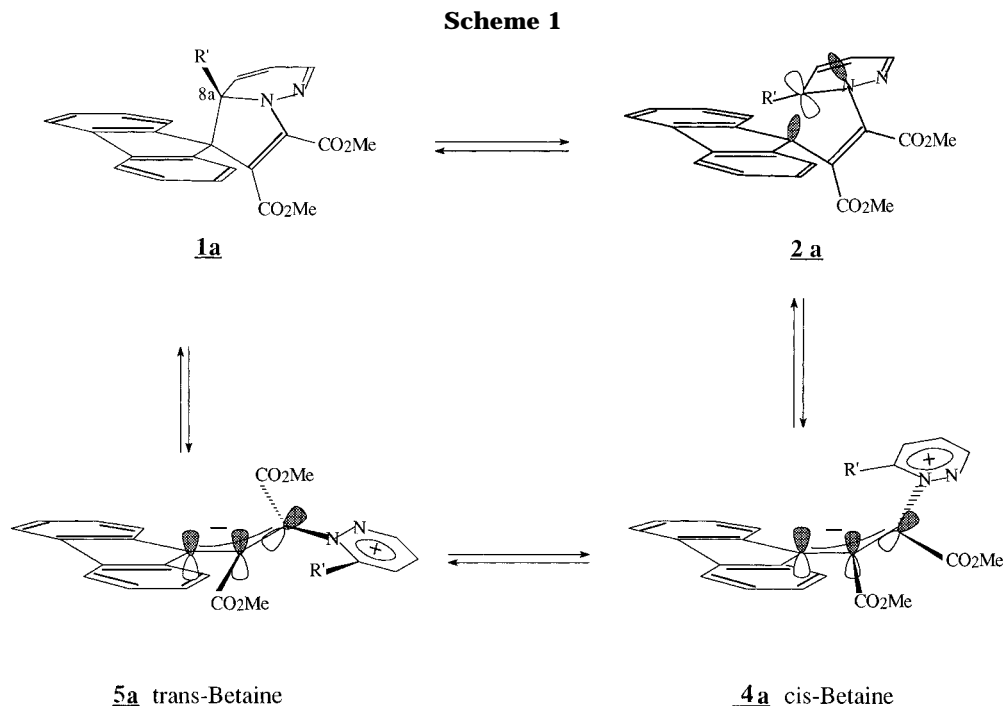
not influenced by the presence of oxygen, as demonstrated by the same decay of **4a**, whether the  $\text{CH}_2\text{Cl}_2$  solution is flushed with argon or not.

Compounds **1b** to **1e** show similar short-lived (a few microseconds) transients with two absorption maxima, one around 460 nm and the other between 590 and 650 nm, depending on the compound (Table 3).

**Bichromophoric DHI 3a–e.** The bichromophoric systems were examined under the same experimental conditions than in the case of the monochromophoric compounds **1a–e**. However, two transients are now observed with the bichromophoric systems **3a**, **3c**, and **3d**. The first transient is short-lived, as indicated by its rapid decay in the microsecond or fraction of microsecond time scale, while the second transient is longer lived, from 45 to 860  $\mu\text{s}$ , depending on the compound, as characterized by the growing-in of the relatively stable final betaine. A special attention will be devoted to compounds **3b** and **3d**.

With compound **3b**, the first transient detected has two maxima, one at about 470 nm and the other around 710 nm (full circles in Figure 5). This transient decays with a lifetime of 860  $\mu\text{s}$  and forms the relatively stable final *trans*-betaine as indicated by the two isosbestic points around 480 and 730 nm (Figures 5 and 6) and shown in the inset of Figure 6 by the growing-in of the optical density at 610 nm. The absorption of the *trans*-betaine (at 490 and 620 nm) is depicted by crosses in Figure 6.

A different behavior is observed for the bichromophoric DHI **3d** showing a short-lived transient, which peaks at 440 nm with a large shoulder around 660 nm and decays with a 0.65  $\mu\text{s}$  lifetime. A longer lived transient is



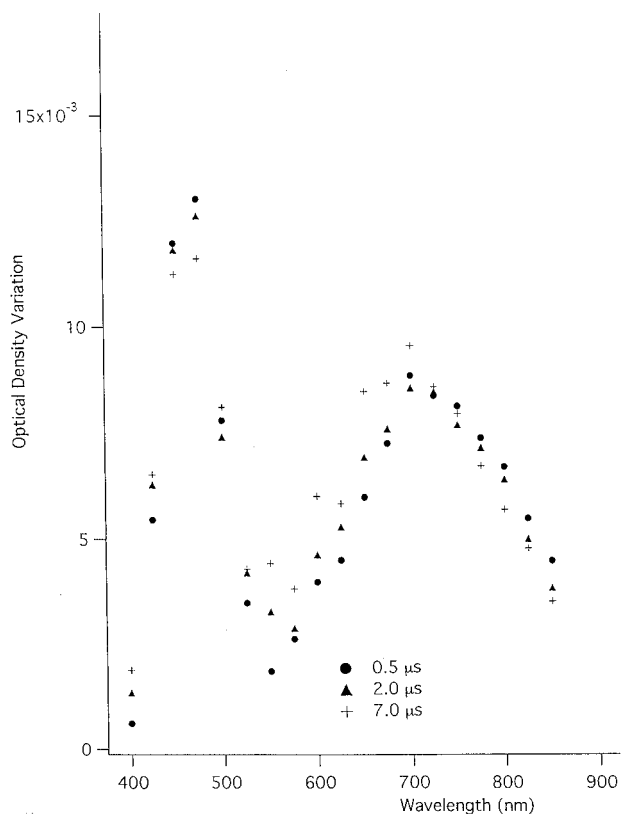
**Table 3. Maxima of the Absorption and Lifetime of the Transients Formed after Laser Excitation of the DHI Compounds in Dichloromethane Solution**

monophotocromic compounds <b>1a–e</b>	biphotocromic compounds <b>3a–e</b>
<b>1a:</b> 460 and 600 nm ↓ $\tau = 2.4 \mu\text{s}$	<b>3a:</b> 640 and 670 nm ↓ $\tau = 0.82 \mu\text{s}$
<b>4a:</b> 500 and 530 nm	<b>7a:</b> 660 nm ↓ $\tau = 45 \mu\text{s}$
<b>1b:</b> 460 and 620 nm ↓ $\tau = 0.6 \mu\text{s}$	<b>8a:</b> 630 nm
<b>4b:</b> 510 nm	<b>3b:</b> 470 and 710 nm ↓ $\tau = 860 \mu\text{s}$
<b>1c:</b> 460 and 650 nm ↓ $\tau = 5.6 \mu\text{s}$	<b>8b:</b> 490 and 620 nm
<b>4c:</b> 460 and 610 nm	<b>3c:</b> 460 and 740 nm ↓ $\tau = 1.1 \mu\text{s}$
<b>1d:</b> 470 and 590 nm ↓ $\tau = 3.9 \mu\text{s}$	<b>7c:</b> 470 and 740 nm ↓ $\tau = 680 \mu\text{s}$
<b>4d:</b> 510 nm	<b>8c:</b> 470 and 610 nm
<b>1e:</b> 470 and 590 nm ↓ $\tau = 3.2 \mu\text{s}$	<b>3d:</b> 440 and 610 nm ↓ $\tau = 0.65 \mu\text{s}$
<b>4e:</b> 520 nm	<b>7d:</b> 470 and 720 nm ↓ $\tau = 610 \mu\text{s}$
	<b>8d:</b> 470, 500 and 610 nm
	<b>3e:</b> 460 and 730 nm ↓ $\tau = 630 \mu\text{s}$
	<b>8e:</b> 490 and 610 nm

observed, absorbing at 470 and 720 nm and leading to the final relatively stable *trans*-betaine absorbing at 470, 500, and 610 nm. The formation of the transient may also have some triplet origin in this case, since the 0.65  $\mu\text{s}$  decay of this transient obtained in an aerated solution is increased to 1.1  $\mu\text{s}$  in an argon-flushed solution.

The spectroscopic data obtained in the case of the biphotocromic systems **3** are compiled in Table 3.

**2c. Complexation with Alkaline-Earth Ions.** It was interesting to examine the behavior of compounds **3**, which contain multiple glycol ether groups and, therefore, can give rise to host–guest effects such as complexation of alkaline-earth ions similar to what are



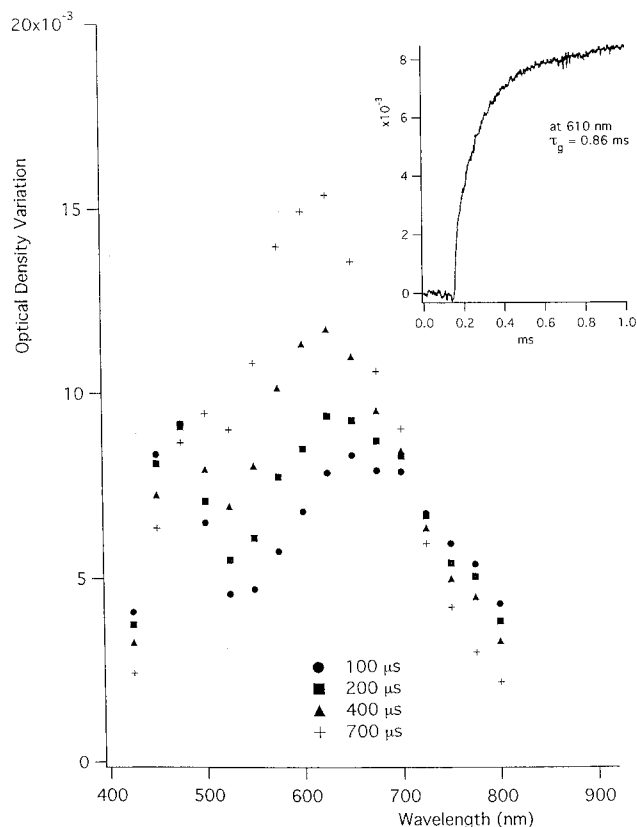
**Figure 5.** Transient absorption spectra of compound **3b** in  $\text{CH}_2\text{Cl}_2$  solution at different times shortly (0.5, 2.0 and 7  $\mu\text{s}$ ) after the laser pulse.

found with other supramolecular systems. The influence of such effects on the photochromic properties of similar molecules had been demonstrated with DHI molecules containing crown-ether units.<sup>10a</sup> In the present case, the

(8) Andreis, C.; Dürr, H.; Valat, P.; Wintgens, V.; Kossanyi, J. *Chem. Eur. J.* **1997**, *3*, 509.

(9) Zhou, J. W.; Zhao, F. Q.; Li, Y. T.; Zhang, F. S.; Song, X. Q. *J. Photochem. Photobiol. A, Chem.* **1995**, *92*, 193.

(10) (a) Kranz, C.; Dürr, H. *Mol. Cryst. Liq. Cryst.* **1994**, *62*, 135. (b) Ma, Y.; Dürr, H. DEOS P. 44 244 09, 1994. (c) Dürr, H.; Kilburg, H.; Kranz, C.; Bossmann, S.; Blasius, E.; Janzen, K.; Thome, A. *J. Phys. Org. Chem.* **1992**, *5*, 689.



**Figure 6.** Transient absorption spectra of compound **3b** in  $\text{CH}_2\text{Cl}_2$  solution at different times (100, 200, 400 and 700  $\mu\text{s}$ ) after the laser pulse. Inset: growing-in of the transient (betaine) at 610 nm.

**Table 4. Host–Guest Effects in the Supramolecular Systems **3c**, **3d**, and **3e** ( $10^{-5}$  mol  $\text{L}^{-1}$ ) in Methanol at Room Temperature**

compd	cation	$\lambda_f$ (nm)	relative fluorescence intensity
<b>3c</b>	none	475	1.0
<b>3c</b>	$\text{Ca}^{2+}$	475	1.28
<b>3c</b>	$\text{Mg}^{2+}$	475	1.37
<b>3d</b>	none	480	1.0
<b>3d</b>	$\text{Ca}^{2+}$	480	1.28
<b>3d</b>	$\text{Mg}^{2+}$	480	1.37
<b>3e</b>	none	520	1.0
<b>3e</b>	$\text{Ca}^{2+}$	520	1.33
<b>3e</b>	$\text{Mg}^{2+}$	520	1.40

introduction of  $\text{Ca}^{2+}$  (as  $\text{CaCl}_2$ ) and  $\text{Mg}^{2+}$  (as  $\text{Mg}(\text{NO}_3)_2$ ) cations at concentrations of  $10^{-3}$  mol  $\text{L}^{-1}$  in the methanol solution of DHI **3c**, **3d**, and **3e** at room temperature shows no detectable effect on the UV–visible absorption spectra of the three compounds, while their fluorescence intensity increases by up to 40% in the presence of the cations (Table 4).

This effect, which is more prominent for  $\text{Mg}^{2+}$  than for  $\text{Ca}^{2+}$ , can be tentatively interpreted as resulting from a reduced interaction of the polyether side chain, owing to the increased volume of the corresponding rotating moieties.

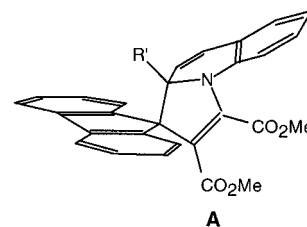
### 3. Discussion

**3a. Luminescence of the Compounds.** We have already pointed out<sup>8</sup> that the fluorescence emission from photochromic systems is a rather scarce phenomenon. The merocyanine form of spiroindolinonaphthoxazines has been

found<sup>9</sup> to luminesce when chelated with transition metal ions such as  $\text{Co}(\text{II})$ ,  $\text{Ni}(\text{II})$ , and  $\text{Zn}(\text{II})$ . However, for the photochromic molecules of the dihydroindolizine (DHI) series, it appears<sup>8,10–13</sup> that fluorescence emission is a common deactivation process of the singlet excited state, although occurring with a low quantum yield, as is the case of the compounds studied here (Table 1).

Spiroanthroxazines have been reported<sup>14,15</sup> to fluoresce at room temperature in nonpolar solvents, but this luminescence was postulated to originate from a dimeric species owing to the increase of its intensity with the concentration of the molecules in the solution. On the other hand, fluorescence has been observed<sup>16,17</sup> recently for the 6-piperidino and 6-morpholino derivatives of spiroindolinonaphthoxazine, but only at low temperature. It has been claimed that, in that case, the emission cannot originate from a dimeric form, on the basis that the unsubstituted spiroindolinonaphthoxazine shows no fluorescence at all, whatever the solvent and temperature conditions are.

The position of the absorption and fluorescence bands of compounds **1a** and **1c** can be compared to that of their analogues **A** of the spiro[fluorene-9,1'-pyrrolo[2,1a]quinoline] series.<sup>8</sup> By reference to the corresponding bands of compounds **1a** and **1c**, the absorption of **A** is shifted to the blue by ca. 25 nm while the fluorescence is shifted to the red by almost 100 nm. However, the position of the fluorescence of the two types of compounds is almost the same at 77 K: around 470 nm for **A** and at ca. 480 nm for the DHI compounds **1d** and **1e**. It is noteworthy that the position of the fluorescence emission of the compounds **3** at 77 K (Table 2) is not different from that of the compounds **1**, thus indicating that the singlet excited state which emits at the level of the biphotocromic compounds **3** is localized on one-half of the molecule.



The position of the fluorescence maximum of compounds **1** and **3** is blue-shifted by 30–38 nm when the temperature of the medium is decreased from room temperature to 77 K (Table 2). For the same change in temperature, the maximum of the fluorescence of compounds **A** is blue-shifted by more than 100 nm. The fluorescence of compounds **A** has been postulated<sup>8</sup> to originate from a twisted species in which the spiro C–C bond of the pyrroloquinoline moiety is broken, and the formation of a planar structure with an extended conju-

(11) Dürr, H. In *Photochromism, Molecules and Systems*; Dürr, H., Bouas-Laurent, H., Eds.; Elsevier: Amsterdam, 1990, p 238.

(12) Gross, H.; Dürr, H.; Rettig, W. *J. Photochem.* **1984**, *26*, 165.

(13) Blanc, J.; Ross, D. L. *J. Phys. Chem.* **1968**, *72*, 2817.

(14) Luchina, V. G.; Marevtsev, V. S.; Sychev, I. Y.; Vlasenko, T. Y.; Khamchukov, Y. D.; Cherkashin, M. *Izv. Akad. Nauk, Ser. Khim.* **1992**, 99.

(15) Luchina, V. G.; Sychev, I. Y.; Marevtsev, V. S.; Vlasenko, T. Y.; Khamchukov, Y. D.; Cherkashin, M. *Izv. Akad. Nauk, Ser. Khim.* **1992**, 2118.

(16) Luchina, V. G.; Sychev, I. Y.; Marevtsev, V. S. *Izv. Akad. Nauk, Ser. Khim.* **1995**, 684.

(17) Luchina, V. G.; Sychev, I. Y.; Shienok, A. I.; Zaichenko, N. L.; Marevtsev, V. S. *J. Photochem. Photobiol. A, Chem.* **1996**, *93*, 173.

gation has been proposed to be the driving force in that case. This does seem not to be the case for compounds **1**, according to the ca. 30 nm blue-shift of their fluorescence when the temperature is decreased from room temperature to 77 K (Table 2), nor for compounds **3**, for which the blue-shift is 30–40 nm in the same temperature range. Therefore, a fluorescence emission originating from the starting spirodihydroindolizines **1** and **3** themselves may be questioned.

The phosphorescence of spiro compounds was never reported before our recent investigation<sup>8</sup> on the spiro[fluorene-9,1'-pyrrolo[2,1a]quinoline] molecules **A**. No phosphorescence could be detected for molecules having a skeleton similar to that of compounds **1a–e** when they are inserted in a polymeric matrix.<sup>11</sup> However, a weak phosphorescence emission has been observed in ethanol glass at 77 K for several of the molecules studied here (Table 2). The phosphorescence of compounds **3c** and **3d** is structured (Figure 2), as in the case of molecules **A**,<sup>8</sup> while that of **1d**, **1e**, **3b**, and **3e** is structureless (Figure 1). Compound **3a** shows no phosphorescence.

The energy of the triplet state, as estimated from the phosphorescence spectra, is on the order of 245–260 kJ mol<sup>-1</sup> depending on the compound; it is lower by 28 kJ mol<sup>-1</sup> (or less) than the energy of the lowest singlet excited state. Except for compounds **3c** and **3d** (vide supra), no triplet seems to be involved in the formation of the final betaines from compounds **1** and **3** (vide infra). It can be concluded from this observation that the rapid ring-opening of the spiro structure probably prevents the access to the triplet state under direct excitation conditions. However, as discussed below, no triplet–triplet absorption could be detected for the spiro molecules, nor could betaine formation be characterized under benzophenone-sensitized conditions.

**3b. Transient Absorption. Monochromophoric Molecules 1a–e.** The spectroscopic investigations carried out with compounds **1a–e** have shown that one transient is easily characterized in the reaction pathway from the dihydroindolizine to the betaine. The lifetime of this transient (Table 3) lies between 2 and 6  $\mu$ s.

In these experiments, the formation of both the transient and the long-lived *trans*-betaine is found to be independent of the presence of oxygen, indicating clearly that, under direct excitation conditions, the transient does not proceed through the triplet excited state but rather from the sole singlet excited state. Such a conclusion agrees with the quenching experiments<sup>6</sup> as well as with the triplet sensitization experiments<sup>8</sup> carried out with similar DHI molecules for which no reaction from the triplet excited state could be detected. Effectively, an attempt to open the ring of dihydroindolizine **1a** has been made under triplet energy transfer conditions in dichloromethane solution (HCl free), using benzophenone as sensitizer. In this experiment, where benzophenone absorbed more than 92% of the laser light and energy transfer to DHI is possible, the only transients which can be detected in the microsecond time scale correspond to triplet benzophenone and to the ketyl radical formed from solvent hydrogen abstraction by triplet benzophenone.

A singlet mechanism also has been found<sup>18,19</sup> for the formation of the photomerocyanines from spiro[indoli-

noxazines]. Then, the quantum yield for merocyanine formation is found to be on the order of 0.5; the efficient closure of the ring back to the spiro molecule just after its opening is made possible by the singlet nature of the intermediate. Of course, the formation of merocyanines by triplet sensitization, when such a reaction can occur, has a high quantum yield due to the triplet nature of the intermediate, which brings a spin-inversion energy barrier for the open form to revert back to the spiro configuration.<sup>18</sup>

The evolution of the transients, as characterized by laser flash photolysis, has been used to put forward a plausible explanation to the photoreactivity of the conjugated bichromophoric systems and to their evolution toward the open bis-betaine form. This will be discussed later.

**Influence of the Size of the Substitution.** The lifetimes obtained for the transients of compounds **1a** to **1e** (Table 3) lie in the 0.6–5.6  $\mu$ s range, in the upper end of the time scale obtained for the transients of DHI molecules. This long lifetime can result from the steric hindrance introduced by the substituents located at or near the reaction center. The influence of the substitution pattern on the lifetime of the transient formed through the ring-opening of the spiro bond of the DHI molecules can be visualized at best with DHI **1c**, for which we consider that the spatial demand of the methyl group located at the key position 8a' is the main cause for the relatively long lifetime (5.6  $\mu$ s) of the transient, about 2 times longer than the transient formed from **1a**. This assumption is also in agreement with the lifetime of the transient of compounds **1d** and **1e**. Thus, the impact of the substituent's bulkiness (1-adamantyl in the case of **1d**, and *exo*-norbornyl in that of **1e**) on the lifetime of the corresponding transient (3.9 and 3.2  $\mu$ s for **1d** and **1e**, respectively) is decreased as a result of their greater distance to the key reaction center C-8a'. Since the photoreaction leading to the open betaine form **2** implies the rotation of a voluminous part of the molecule, the torsional movement which enables the formation of **5** will be hindered by the bulkiness of the rotating moiety.

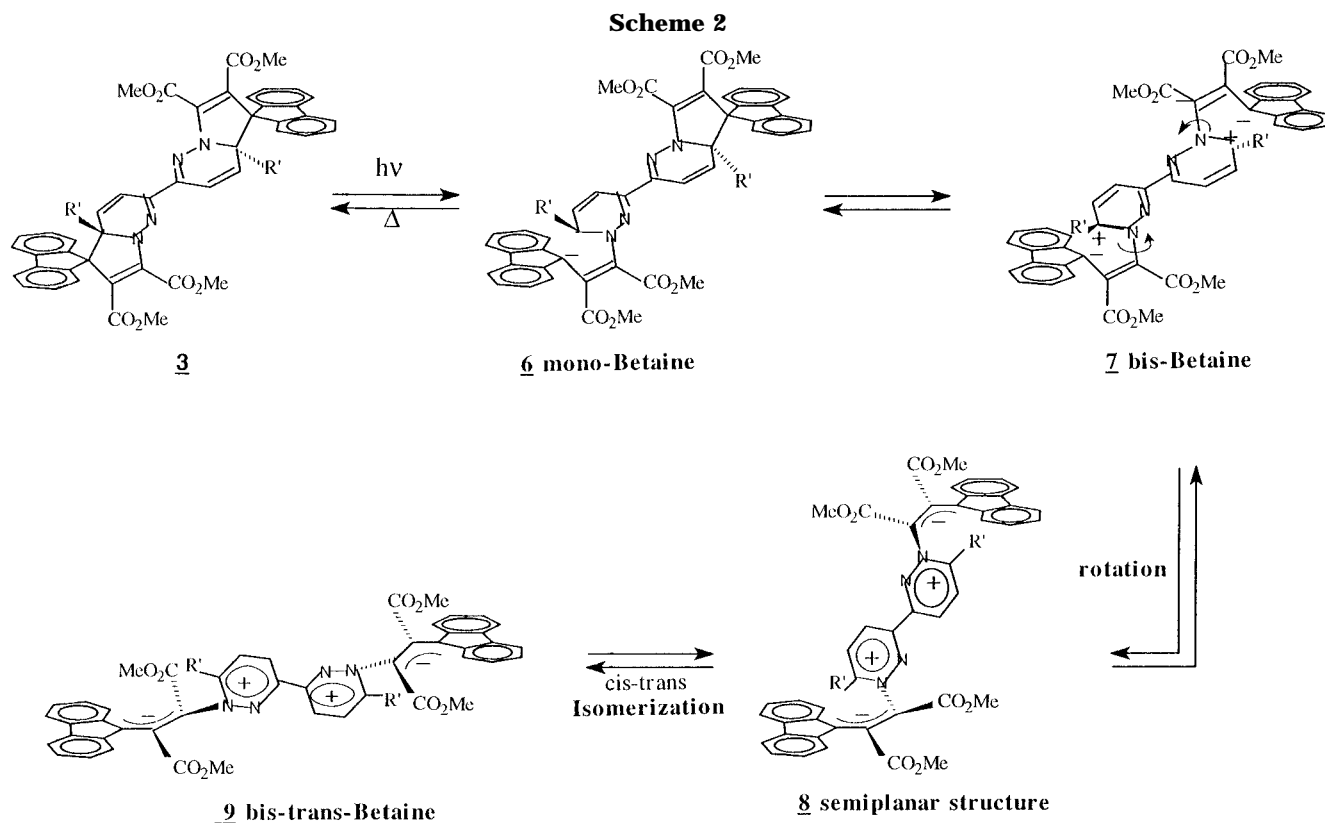
An interesting result is obtained also by comparing **1a** with **1b**, which differ from each other by the presence of an electron-donating methyl group at carbon C-6' for compound **1b**. The stabilization of the cationic part of the betaine by this methyl group appears to accelerate its formation from the transient.

To confirm the twisting conformational change of the *cis*-betaine **4a** into the *trans*-betaine **5**, the viscosity of the medium has been increased by using a 80:20 glycerol/ethanol mixture, and the decay of the transient formed in this solution has been compared to that of the same transient given by **1a** in pure ethanol solution, both experiments being carried out at room temperature. The increase of the transient lifetime from 0.43  $\mu$ s in pure ethanol to 0.81  $\mu$ s in the 80:20 glycerol/ethanol mixture supports a hypothesis of a hindered conformational change of the intermediate during its course to the final *trans*-betaine **5a**, and this increase can be taken as the indication of the rotation of one moiety of the molecule with respect to the other.

All the intermediates characterized by transient absorption do absorb at longer wavelengths than the long-

(18) Favaro, G.; Malatesta, V.; Mazzucato, U.; Ottavi, G.; Romani, A. *Mol. Cryst. Liq. Cryst.* **1994**, *246*, 299.

(19) Favaro, G.; Ortica, F.; Malatesta, V. *J. Chem. Soc., Faraday Trans.* **1995**, *91*, 4099.



lived "stable" *trans*-betaines **5**, which originate from these intermediates. This observation can be explained if one assumes the semiplanar conjugated structure **4** (such as **4a** on Scheme 1) to this transient rather than the nonplanar conformation **2**.<sup>20</sup> This assumption is in accordance with previous results obtained by transient absorption spectroscopy<sup>21</sup> which did show the existence of another transient in the nanosecond time range and which could be attributed to structure **2**. The transformation of **2** into the semiplanar isomer **4** involves an  $sp^3 \rightarrow sp^2$  change in the hybridization of the C-8a' spiro carbon atom of **2**, which enables the planarity of the molecule and, as a consequence, leads to a species stabilized by electron delocalization (see Scheme 1). The structure of the *trans*-betaine **5** is known, owing to similar stable species which have been characterized by X-ray spectroscopy.<sup>22,23</sup> These investigations lead to the conclusion that the betaines obtained here have quite a distorted transoid conformation with a dihedral angle of about 117° (instead of 180°) between the ester substituents. In addition, it is probable that the ground-state energy of the transient lies higher than that of the betaines (otherwise the transient would not form the betaines) while the energy of its excited state is at about the same level as that of the betaines, leading to an energy difference between the two states lower for the transient than for the betaine (see for comparison Scheme 3 in ref 8).

**Bichromophoric Molecules 3a–3e. A One-Photon Ring-Opening of the Spiro Skeleton.** It has been

demonstrated with bichromophoric systems similar to **3a–e** but having a dissymmetrical structure that the excited state of the two chromophores decays differently, although the irradiation leads to the same bis-betaine **9**.<sup>5</sup> We have assumed, in the present case, that the symmetrical bichromophoric compounds **3a–e** react in a similar way and give also the bis-betaine by irradiation (Scheme 2).

The final structure resulting from this irradiation corresponds to the most stable *trans*-betaine. Owing to their lifetime of several tens of seconds, these open betaines could absorb a second photon and undergo a photochemical process, when using conventional steady-state or flash photolysis irradiation experiments. However, the ring-opening of similar monochromophoric DHI molecules, followed with isomerization into the *trans*-betaines **5** (**5a** in Scheme 1), has been shown<sup>8</sup> already to be a one-photon process. That the photoreaction is the same here has been verified by laser experiments carried out with compounds **3a** and **3e**.

Experiments, carried out with laser pulses of different intensities, reveal that the optical density of the solution, at the position of the final betaine absorption, varies linearly with the laser pulse intensity (Figure 7). Therefore, the ring-opening reaction of the conjugated bichromophores, which leads to the final *trans*-betaine, can unambiguously be interpreted as resulting from a one-photon process.

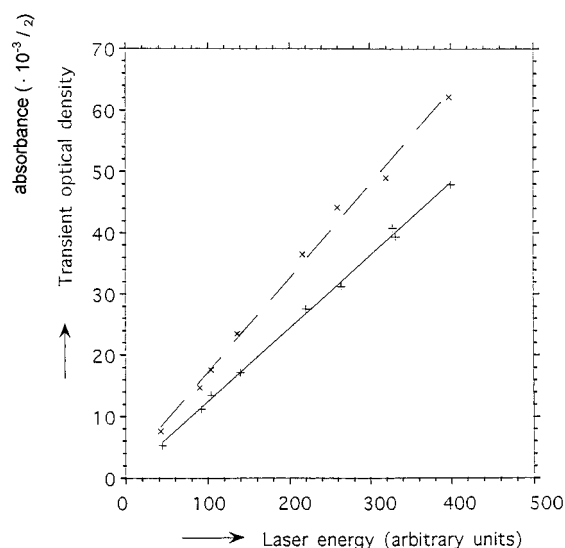
**3c. Betaine Formation from the Conjugated Bichromophoric DHI.** The primary step in the course of the light-induced ring-opening of compounds **1** is the cleavage of the bond between C-1' and C-8a', yielding the biplanar intermediate **2** which undergoes a planarization to the *cis*-betaine **4** which itself isomerizes into the energetically more stable *trans*-betaine **5**.

(20) Gehrtz, M.; Bräuchle, C.; Voigtländer, J. *J. Am. Chem. Soc.* **1982**, *104*, 2094.

(21) Fromm, R.; Dürr, H.; Breue, D., unpublished results.

(22) Dorweiler, C.; Spang, P.; Dürr, H.; Peters, K.; von Schnering, H. V. *Isr. J. Chem.* **1985**, *25*, 246.

(23) Dorweiler, C.; Holderbaum, M.; Münzmay, T.; Spang, P.; Dürr, H.; Raabe, E. *Chem. Ber.* **1988**, *121*, 843.



**Figure 7.** Optical density variation of the final *trans*-betaine structure of compounds **3a** and **3e** as a function of the laser intensity.

It is now possible from the above-discussed results to put forward a concise explanation to the light-induced ring-opening of the simple photochromic DHI molecules **1**. This includes the characterization of the main intermediates on the way to the *trans*-betaines **5**, which, in turn, revert back to the starting spiro materials following a concerted electrocyclic process.<sup>24</sup>

For all the mono- and bichromophoric molecules studied here, the singlet lifetime must be the few picoseconds time scale. Since no triplet absorption could be detected (except for **3d**, for which the lifetime of the transient is longer in a degassed solution than in an aerated solution), the opening of the spiro ring must constitute the main reaction pathway of the singlet excited state. The fact that no triplet is detected experimentally may not exclude its formation, but it could indicate that it is very short-lived, just like the singlet excited-state itself (due to the rapid ring-opening of the spiro structure). However, attempts to sensitize the triplet state of compounds **1a** and **3b** at room temperature, using benzophenone as sensitizer, show no evidence for any triplet absorption of the spiro form in the 400–700 nm range. If it is formed, then it must absorb in the short-wavelengths region (<410 nm), where it becomes difficult to characterize it. Since no betaine absorption could be detected, it is difficult to put forward a rapid ring-opening of the spiro form to explain the absence of any transient absorption in this triplet experiment. One possibility could be that the triplet reached by sensitization does not lead to the betaine. But this is contradictory with the results observed in many other cases where the betaine is formed from the triplet state with high quantum yield either under direct irradiation<sup>25–28</sup> or

under triplet-sensitized conditions.<sup>19,29–32</sup> The energy of the triplet state determined from the phosphorescence spectra is 24–41 kJ mol<sup>-1</sup> lower than that of benzophenone, indicating that triplet energy transfer to the spiroindolizines should be efficient. However, such absence of triplet sensitization could be related to the structure of the spiro compound itself, which has two independent chromophores in orthogonal planes: one localized on the fluorene part and the other on the dihydroindolizine moiety. Then, the triplet reached by sensitization could be different from the one which could open the ring of the spiro compound and form the betaine under direct excitation conditions. Such absence of electronic interaction between two orthogonal moieties of spiro molecules has been demonstrated previously by ESR experiments.<sup>33</sup> A similar deduction has been obtained from the observation that the triplet state responsible for the ring opening of the spiro molecule is different from the one which phosphoresces.<sup>31</sup>

The light-induced ring-opening of the conjugated bichromophoric systems **3** is a much more complex process from the mechanistic standpoint (see Scheme 2). Since the molecule contains two conjugated spiro moieties, a greater number of intermediate structures is involved in the course of the reaction. Two transients are observed in the case of compounds **3a**, **3c**, and **3d**, one of them decays in approximately 1  $\mu$ s, while the other has a decay which ranges from 45 to 860  $\mu$ s. We have taken **3c** as an example (Scheme 2) and assumed that the molecule remains on the potential energy surface of the singlet excited state immediately after the breaking of the first spiro bond has taken place. Then, an energy transfer can take place from one part of the molecule to the other, or a high vibrationally excited ground-state level is reached with structure **6**, which enables the ring opening of the second spiro part of the molecule to afford **7**. This implies that the energy of the photon which triggers the whole process is high enough to enable the breaking of the second spiro bond as well. Since energy absorption and bond cleavage are elementary processes, they occur in the picosecond rather than the nanosecond time domain. After the ring-opening of the second spiro bond, the molecule has reached the ground state of the short-lived intermediate **7**, which undergoes conformational transformation with a decay of 1.1  $\mu$ s lifetime, to yield the new delocalized semiplanar transient for which the cisoid conformation **8**—with a 680  $\mu$ s lifetime for **8c**—is put forward. The final step in this sequential reaction is the isomerization from the cisoid transient **8** into the transoid betaine **9** by the rotation around the ester-substituted single bond. Recent X-ray investigations of betaines having a similar but stable structure in the open form have revealed<sup>22,23</sup> that betaines such as **6c** have a slightly distorted transoid conformation which, therefore, is reached by a final rotation smaller than 180°.

#### 4. Conclusions

The results presented above lead to the following conclusions:

(24) Dürr, H. *Angewandte Chem. Inter. Ed. Engl.* **1989**, *28*, 415.  
 (25) Kholmanskii, A. S.; Chudakov, V. M.; Piraev, A. K. *Khim. Fiz.* **1986**, 1329.  
 (26) Kellmann, A.; Lindqvist, L.; Tfibel, F.; Guglielmetti, R. *J. Photochem.* **1986**, *35*, 155.  
 (27) Goebel, L.; Brede, O.; Zimmermann, T. *Radiat. Phys. Chem.* **1996**, *47*, 369.  
 (28) Kellmann, A.; Lindqvist, L.; Monti, S.; Tfibel, F.; Guglielmetti, R. *J. Photochem.* **1985**, *28*, 547.

(29) Hobley, J.; Wilkinson, F. *J. Chem. Soc., Faraday Trans.* **1996**, *92*, 1323.  
 (30) Sakuragi, M.; Aoki, K.; Tamaki, T.; Ichimura, K. *Bull. Chem. Soc. Jpn.* **1990**, *63*, 74.  
 (31) Reeves, D. A.; Wilkinson, F. *J. Chem. Soc., Faraday Trans., 2* **1973**, *69*, 1381.  
 (32) Bach, H.; Calvert, J. G. *J. Am. Chem. Soc.* **1970**, *92*, 2608.  
 (33) Kropf, M. Ph.D. Dissertation, Saarbrücken (Germany), 1995.





2980–2890 (C–H, aliphatic), 1740 (C=O), 1695 (C=O), 1635, 1600, 1590 (C=C), 1440, 1310, 1270, 1225, 1120, 1080, 1030, 770, 670;  $^1\text{H}$  NMR  $\delta$  7.84–7.62 (m, 10H), 7.48–7.18 (m, 18H), 7.12 (d,  $^3J = 7.50$  Hz, 2H), 6.99–6.93 (m, Ar–H), 6.77 (d,  $^3J = 9.85$  Hz, 2H), 6.07 (d,  $^3J = 9.85$  Hz, 2H), 5.99 (d,  $^3J = 9.85$  Hz, 2H), 5.62 (d,  $^3J = 9.85$  Hz, 2H), 4.09 (s, 6H), 3.84 (s, 6H), 3.82 (s, 6H), 3.47 (s, 6H), 3.54 (s, 6H), 3.26 (s, 6H);  $^{13}\text{C}$  NMR  $\delta$  164.53, 162.23, 160.03, 158.17, 156.12, 155.05, 154.73, 153.52, 152.26, 151.17, 150.97, 150.03, 148.09, 141.57, 140.28, 133.74, 133.52, 133.02, 132.52, 132.04, 130.12, 120.85, 117.37, 114.83, 114.02, 110.88, 110.02, 71.38, 71.25, 67.18, 66.12, 59.17, 57.04, 53.45, 52.63, 51.14, 50.76; MS (FAB, Xe, Gly/MeOH)  $m/z$   $M^+$  830.9. Anal. Calcd for  $\text{C}_{48}\text{H}_{38}\text{N}_4\text{O}_{10}$ : C, 69.39; H, 4.61; N, 6.74. Found: C, 69.58; H, 4.68; N, 6.69.

**Bis[8a'-methoxy-(2-ethoxy(2-ethoxy))spiro[fluorene-[9,1']-(8a'-H)-2',3'-dimethoxycarbonylpyrrolo[1,2-b]pyridazine-6'-yl]] (3c).** Standard Procedure. Educ: 320 mg (0.81 mmol) of 3,3'-bipyridazine **11c** and 500 mg (1.63 mmol) of spirene **12**. Reaction time: 14 days. A:B isomer ratio of **3c** = 1:1.5; 147 mg (18%) of yellow crystals of **3c** was obtained: mp 195 °C;  $\text{UV}_{\text{DHI}} \lambda_{\text{max}}$  = (290 nm), 373 nm,  $\log \epsilon$  = 4.16;  $\text{UV}_{\text{Betaine}} \lambda_{\text{max}}$  = 360 nm, 608 nm,  $\log \epsilon$  = 4.24;  $\text{IR } \bar{\nu}$  ( $\text{cm}^{-1}$ ) = 3040 (C–H, aromat), 2980–2890 (C–H, aliphatic), 1740 (C=O), 1695 (C=O), 1630, 1600, 1590 (C=C), 1445, 1350, 1315, 1270, 1225, 1120, 1030, 765, 735, 670;  $^1\text{H}$  NMR  $\delta$  7.76–7.64 (m, 10H), 7.48–7.21 (m, 18H), 7.03 (d,  $^3J = 7.50$  Hz, 2H), 6.92–6.86 (m, Ar–H), 6.73 (d,  $^3J = 9.80$  Hz, 2H, 2H, 8',8''-H, A), 6.09 (d,  $^3J = 9.80$  Hz, 2H, 8',8''-H, B), 5.98 (d,  $^3J = 9.80$  Hz, 2H, 7',7''-H, A), 5.65 (d,  $^3J = 9.80$  Hz, 2H, 7',7''-H, B), 4.81–4.21 (m, 10H), 4.08 (s, 6H), 3.95–3.82 (m, 12 H, 6H), 3.72–3.57 (m, 14H, 8H); 3.65 (s, 6H), 3.41–3.57 (m, 20H, 8H; 12H), 3.26 (s, 6H);  $^{13}\text{C}$  NMR  $\delta$  164.38, 162.21, 159.56, 158.14, 155.74, 155.02, 154.87, 154.23, 153.47, 151.52, 150.88, 150.12, 148.03, 141.72, 140.14, 134.17, 133.28, 133.03, 132.21, 130.1, 120.74, 117.21, 115.79, 114.72, 111.62, 110.3, 73.08, 72.74, 71.48, 71.41, 70.74, 70.53, 69.38, 68.54, 67.19, 66.14, 56.47, 53.62, 52.81, 51.60, 50.96; MS (FAB, Xe, Gly/MeOH/HCO<sub>2</sub>H)  $m/z$   $M^+$  1007.1. Anal. Calcd for  $\text{C}_{56}\text{H}_{54}\text{N}_4\text{O}_{14}$ : C, 66.79; H, 5.40; N, 5.56. Found: C, 66.85; H, 5.54; N, 5.48.

**Bis[8a'-methoxy-(2-ethoxy(2-ethoxy))spiro[fluorene-[9,1']-(8a'-H)-2',3'-dimethoxycarbonylpyrrolo[1,2-b]pyridazine-6'-yl]] (3d).** Standard Procedure. Educ: 390 mg (0.81 mmol) of 3,3'-bispyridazine **11d** and 500 mg (1.63 mmol) of spirene **12**. Reaction time: 16 days. A:B isomer ratio = 1:1.6; 151 mg (17%) of yellow crystals of **3d** was obtained: mp 187 °C,  $\text{UV}_{\text{DHI}} \lambda_{\text{max}}$  = (290 nm), 344 nm,  $\log \epsilon$  = 4.16;  $\text{UV}_{\text{Betaine}} \lambda_{\text{max}}$  = 625 nm;  $\text{IR } \bar{\nu}$  ( $\text{cm}^{-1}$ ) = 3040 (C–H, aromat), 2980–2890 (C–H, aliphatic), 1735 (C=O), 1695 (C=O), 1630, 1600, 1590 (C=C), 1440, 1350, 1310, 1265, 1225, 1120, 1095, 1030, 770, 735, 670;  $^1\text{H}$  NMR  $\delta$  7.75–7.18 (m, 28H), 7.07–7.00 (m, 4H), 6.78 (d,  $^3J = 9.80$  Hz, 2H), 6.08 (d,  $^3J = 9.80$  Hz, 2H), 5.97 (d,  $^3J = 9.80$  Hz, 2H), 5.65 (d,  $^3J = 9.80$  Hz, 2H), 4.77–4.76 (m, 4H), 4.59 (s, large, 4H), 4.22–3.80 (m, 12H), 4.08 (s, 6H), 3.76–3.48 (m, 20H), and 3.76 (s, 6H), 3.55 (s, 6H), 3.45–3.32 (m, 12H; 8H), 3.26 (s, 6H);  $^{13}\text{C}$  NMR  $\delta$  164.25, 162.19, 159.36, 158.02, 155.09, 154.96, 154.62, 153.23, 151.62, 150.84, 150.06, 148.02, 141.58, 140.11, 134.01, 133.27, 132.99, 132.19, 130.11, 120.74, 117.20, 115.78, 114.73, 111.52, 110.13, 72.61, 72.28, 71.54, 71.47, 71.22, 71.02, 70.90, 70.13, 69.33, 68.71, 67.95, 67.17, 66.10, 57.03, 53.61, 52.76, 51.57, 50.98; MS (FAB, Xe, Gly/MeOH/HCO<sub>2</sub>H)  $m/z$   $M^+$  1095.2. Anal. Calcd for  $\text{C}_{60}\text{H}_{62}\text{N}_4\text{O}_{16}$ : C, 65.80; H, 5.71; N, 5.12. Found: C, 66.08; H, 5.79; N, 5.09.

**Bis[8a'-anisyl-(2-ethoxy(2-ethoxy))spiro[fluorene-[9,1']-(8a'-H)-2',3'-dimethoxycarbonylpyrrolo[1,2-b]pyridazine-6'-yl]] (3e).** Standard Procedure. Educ: 540 mg (0.81 mmol) of 3,3'-bipyridazine **11e**<sup>33</sup> and 500 mg (1.63 mmol) of spirene **12**. Reaction time: 16 days. A:B isomer ratio of **3e** = 1:1.2; 114 mg (11%) of yellow crystals of **3e** was obtained: mp 196 °C,  $\text{UV}_{\text{DHI}} \lambda_{\text{max}}$  = (290 nm), 387 nm,  $\log \epsilon$  = 4.23;  $\text{UV}_{\text{Betaine}} \lambda_{\text{max}}$  = 360 nm, 624 nm,  $\log \epsilon$  = 4.21.  $\text{IR } \bar{\nu}$  ( $\text{cm}^{-1}$ ) = 3040 (C–H, aromat), 2980–2890 (C–H, aliphatic), 1740 (C=O), 1695 (C=O), 1640, 1600, 1590 (C=C), 1440, 1350, 1310, 1265, 1220, 1120, 1095, 1030, 770, 735, 670;  $^1\text{H}$  NMR  $\delta$  7.71–7.67 (m, 10H), 7.53–7.49 (m, 6H), 7.37 (t,  $^3J = 7.30$  Hz,

4H), 7.27–7.16 (m, 8H), 7.05 (d,  $^3J = 7.50$  Hz, 2H), 6.86–6.80 (m, 18H, 16 H, 2H), 6.76 (d,  $^3J = 9.80$  Hz, 2H), 6.05 (d,  $^3J = 9.80$  Hz, 2H), 5.98 (d,  $^3J = 9.80$  Hz, 2H), 5.64 (d,  $^3J = 9.80$  Hz, 2H), 4.61–4.56 (m, 4H), 4.24–4.21 (m, 4H), 4.09–4.06 (m, 18H, 6H), 3.85–3.68 (m, 52H) 3.85 (s, 6H); 3.75 (s, 12H); 3.65 (s, 6H, 28H), 3.26 (s, 6H);  $^{13}\text{C}$  NMR  $\delta$  164.29, 162.14, 159.29, 157.86, 155.03, 154.83, 154.56, 153.21, 151.43, 150.72, 149.98, 147.86, 141.43, 140.03, 128.57, 128.12, 127.97, 127.14, 125.04, 120.71, 117.14, 115.75, 114.69, 111.43, 110.05, 72.50, 72.24, 71.43, 71.38, 71.04, 70.83, 70.04, 69.29, 68.57, 67.86, 67.14, 66.07, 55.75, 53.57, 52.74, 51.43, 50.93; MS (FAB, Xe, Gly/MeOH/HCO<sub>2</sub>H)  $m/z$   $M^+$  1279.4. Anal. Calcd for  $\text{C}_{72}\text{H}_{70}\text{N}_4\text{O}_{18}$ : C, 67.60; H, 5.52; N, 5.603. Found: C, 67.95; H, 5.67; N, 5.85.

**Bis[8a'-methoxy-(2-ethoxy(2-ethoxy(2-ethoxy(2-ethoxy(2-ethoxy))spiro[fluorene-[9,1']-(8a'-H)-2',3'-dimethoxycarbonylpyrrolo[1,2-b]pyridazine-6'-yl]] (3f).** Standard Procedure. Educ: 462 mg (0.81 mmol) of 3,3'-bipyridazine **11f** and 500 mg (1.63 mmol) of spirene **12**. Reaction time: 16 days. A:B isomer ratio of **3f** = 1:1.5; 115 mg (12%) of yellow crystals of **3f** was obtained: mp 188 °C,  $\text{UV}_{\text{DHI}} \lambda_{\text{max}}$  = (290 nm), 345 nm,  $\log \epsilon$  = 4.19;  $\text{UV}_{\text{Betaine}} \lambda_{\text{max}}$  = 622 nm.  $\text{IR } \bar{\nu}$  ( $\text{cm}^{-1}$ ) = 3040 (C–H, aromat), 2980–2890 (C–H, aliphatic), 1740 (C=O), 1695 (C=O), 1630, 1600, 1590 (C=C), 1450, 1350, 1320, 1270, 1230, 1120, 1030, 765, 670;  $^1\text{H}$  NMR  $\delta$  7.75–7.03 (m, 32 H), 6.77 (d,  $^3J = 9.80$  Hz), 5.99 (d,  $^3J = 9.80$  Hz, 2H), 5.78 (d,  $^3J = 9.80$  Hz, 2H), 5.54 (d,  $^3J = 9.80$  Hz, 2H), 4.74–4.68 (m, 8H), 4.25–3.83 (m, 22H) 4.08 (s, 6H, 16H), 3.77–3.42 (m, 32H, 6H; 6H, 20H, 6H), 3.37–3.33 (m, 32H, and 12H, 20H), 3.26 (s, 6H);  $^{13}\text{C}$  NMR  $\delta$  164.29, 162.25, 159.35, 158.09, 155.13, 154.88, 154.59, 153.18, 151.47, 150.76, 150.02, 148.09, 141.57, 140.04, 133.94, 133.21, 132.95, 132.16, 130.09, 119.82, 118.15, 115.72, 114.66, 111.44, 110.06, 72.65, 72.33, 74.72, 74.56, 73.24, 72.08, 71.67, 71.67, 71.35, 71.20, 70.97, 70.56, 70.08, 69.27, 68.84, 67.89, 67.61, 67.18, 66.18, 57.11, 53.60, 52.68, 51.52, 50.89; MS (FAB, Xe, Gly/MeOH/HCO<sub>2</sub>H)  $m/z$   $M^+$  1183.3. Anal. Calcd for  $\text{C}_{64}\text{H}_{70}\text{N}_4\text{O}_{18}$ : C, 64.96; H, 5.96; N, 4.74. Found: C, 64.78; H, 6.14; N, 4.67.

**5b. Spectroscopic Measurements.** IR spectra were recorded with an IR-4230 Beckman Instrument. Samples were run in KBr pellets.

NMR spectra were taken with a BR-500 Bruker instrument. The solvent used was  $\text{CDCl}_3$ , unless otherwise specified.

Mass spectra were recorded with a MAT-311 Varian instrument using the FAB technique.

The UV-visible absorption spectra have been obtained in dichloromethane solution with a Varian-Cary model 219 apparatus or with a Uvikon 860 model Kontron apparatus, equipped with a  $\lambda$ -scan-module.

Corrected fluorescence spectra were recorded with a SLM-Aminco 8100C model apparatus. Fluorescence quantum yields were measured in various solvents by comparison with that ( $\Phi_f = 0.010$ ) of 2-phenyl-1*H*-benzo[*f*]isoindole-1,3(2*H*)-dione in dichloromethane solution, the latter being itself measured by reference to quinone sulfate in 1 N aqueous sulfuric acid solution for which  $\Phi_f = 0.55$ .<sup>34</sup>

Phosphorescence spectra were obtained at 77 K in ethanol solution, using the SLM-Aminco 8100C model apparatus equipped with a phosphorescence accessory coupled to an oscilloscope which enables phosphorescence decay measurements at times as short as 3 ms.

**5c. Singlet Lifetime Measurements.** Singlet lifetimes were measured by excitation with a frequency-tripled pulsed YAG laser (from B. M. Industries) of 30 ps fwhm. For lifetimes greater than 1.0 ns, the light was focused through a cylindrical lens onto the sample placed in front of a photodiode. An appropriate filter is put between the cell and the photodiode in order to limit the analysis range. The output from the photodiode was fed into a Tektronix 7912 AD digitized oscilloscope and the data, which are stored in an Apple II+ microcomputer, could be displayed on a Hewlett-Packard model 7470A graphic plotter. Average decays could be analyzed directly by the microcomputer.

**5d. Low-Temperature Measurements.** Low-temperature measurements were carried out at 77 K in ethanol glass,

for absorption, fluorescence, and phosphorescence. A liquid nitrogen cooled Dewar was used with a chopper (for phosphorescence) or without the chopper (for absorption and fluorescence).

**5e. Flash Photolysis Experiments.** Flash photolysis experiments were carried out with a frequency-doubled pulsed ruby laser (347.5 nm; 20 ns fwmh) from JK Laser Co. The usual crossed beam system was used, the analyzing light being a conventional pulsed Xenon lamp from Applied Photophysics.

No triplet-triplet absorption spectra could be characterized by direct excitation nor by triplet energy transfer using

benzophenone as sensitizer, the intersystem crossing quantum yield of which being unity.

The transient decay is recorded with a 7A13 differential comparator amplifier of a Tektronix 7912 AD digitalized oscilloscope. A detailed description of the experimental setup has been given<sup>35</sup> already.

Under direct excitation conditions, the spiro compounds are transformed into the open betaine form and the transients characterized show no oxygen influence.

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(34) Melhuish, W. H. *J. Phys. Chem.* **1961**, *65*, 229.

(35) Valat, P.; Tripathi, S.; Wintgens, V.; Kossanyi, J. *New J. Chem.* **1990**, *14*, 825.