New Aspects of the Photophysical Properties of 1'*H*-2',3'-Dimethoxycarbonylspiro[fluoren-9,1'-pyrrolo[2,1-a]quinoline]

Christine Andreis, Heinz Dürr,* Véronique Wintgens, Pierre Valat and Jean Kossanyi

Dedicated to Prof. M. Hanack on the occasion of his 65th birthday

Abstract: In this paper we describe photophysical and mechanistic studies of spiro[fluorene-9,1'-pyrrolo[2,1-*a*]quinolines] (DHI) **1**–**4** and of their styryl homologues **5**–**11** (styryl DHI). DHIs **1**–**11** have low fluorescence quantum yields (approximately $\Phi_f = 10^{-3}$). The position of the fluorescence emission band is temperature-dependent. The ring-opened betaines **1'**–**11'** do not fluoresce at all. DHIs **1**–**11** exhibit phosphorescence, which is hypsochromically shifted by NO_2 substitution of the fluorene ring. The triplet can be populated only by sensitization (with benzophenone as sensitizer) and, therefore, the reaction that occurs under direct excitation of the molecule involves the singlet excited state only. On irradiation under time-resolved conditions, two transients were seen to be formed in the picosecond and microsecond domains. Slightly tilted educt or product-like geometries are attributed to these transients. An energy diagram is proposed for the photoreaction of the model compound spiro[pyrroloquinoline] **1** → **1'**, which takes into account the singlet pathway and the different transients of ca. 100 ps lifetimes formed from the singlet excited state of **1**–**11**.

Keywords
betaines · fluorescence spectroscopy · mechanistic approach · photochromism · spiro compounds

Introduction

The number of investigations of the spectroscopic and photophysical properties of photochromic materials has increased considerably in recent years as a result of potential commercial applications, besides their intrinsic scientific interest. When dispersed in a rigid polymeric matrix, the photochromic materials are expected to find uses as display systems, microfilms and communication systems.[1–3] The greatest advantage of photochromism is that it involves only a pure optical phenomenon; unfortunately, the materials involved in such processes are not highly stable to light. This is particularly the case for spiropyrans. However, spirooxazines present an interesting resistance toward light, that is, a large number of cycles are possible without significant deterioration of the material.[4–6] Depending upon the application, photochromic materials must show high isomerization quantum yields, efficient thermal back reaction and, indeed, high fatigue resistance; this last property is the key which will determine their potential applications.[7] For this reason, the preparation and the study of new photochromic materials are of current interest and draw the attention of many laboratories. One limiting factor for the industrial development of photochromic materials is the slow kinetics of the reverse thermal reclosure from the open form back to the starting material, when the compound is incorporated in a solid matrix. Electron-attracting or electron-donating substituents on the molecule can modify the kinetics of the forward or back reaction depending on the nature and on the position of these substituents.

Only a few photochromic materials show fluorescence emission. For instance, no emission has been reported for spiropyrans,[8] nor for fulgides,[9–11] and no mention of any fluorescence emission could be found for spiroindolinoxazines,[12–14] although the quantum yield for ring-opening of the spiro skeleton is ca. 0.50.[12] However, an intense fluorescence emission has been observed for the merocyanine form of spironaphthoxazines when chelated with transition-metal ions such as Co^{II}, Ni^{II}, Cu^{II} or Zn^{II}.[15] The only spiro derivatives for which a fluorescence emission has been reported (with a quantum yield of about 0.001) belong to the dihydroindolizine series.[16–19] For this reason, the determination of the singlet lifetime from the fluorescence decay of such spiro derivatives can give an evaluation of the different rate constants of the processes which deactivate the singlet excited state, including that of the formation of the open betaine form. For a potential application in information recording or as optical switches, a very fast ring-opening of the spiro molecule (A) into the betaine-type structure (B) (Scheme 1) is desirable.

We have prepared such systems,[20] which have the advantage of fluorescing with a quantum yield of almost 0.01 in certain

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[*] Heinz Dürr, Christine Andreis
Fachbereich 11.2 Organische Chemie, Universität des Saarlandes
D-66041 Saarbrücken (Germany)
Fax: Int. code +(681) 302-5612
e-mail: h.duerr@rz.uni-sb.de

Véronique Wintgens, Pierre Valat, Jean Kossanyi
Laboratoire des Matériaux Moléculaires, C. N. R. S.
2-8 rue Henri Dunant, F-94320 Thiais (France)

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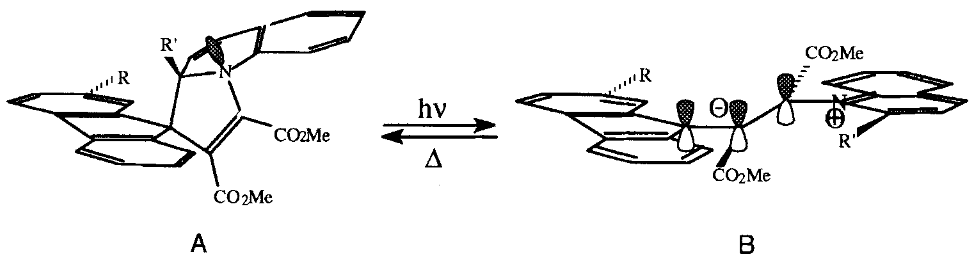
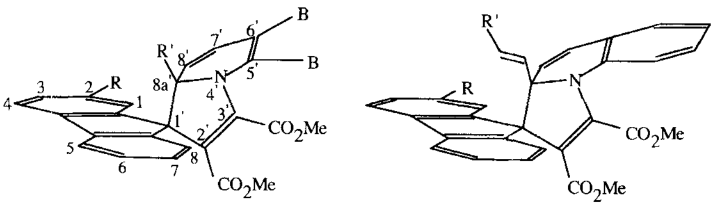


Scheme 1. Interconversion of spiro (A) and betaine (B) forms.

cases. In this article, we present a study of the singlet and triplet excited-state properties of the quinolinodihydroindolizines **1**–**11** and of their open betaine forms.



1 R = R' = H BB = benzene ring
2 R = H R' = CH_3 BB = benzene ring
3 R = NO_2 R' = B = H
4 R = NO_2 R' = CH_3 BB = benzene ring

5 R = H R' = C_6H_5
6 R = H R' = *p*-CH_3O-C_6H_4
7 R = H R' = *p*-$(CH_3)_2N$-C_6H_4
8 R = H R' = *p*-NO_2-C_6H_4
9 R = H R' = *o*-NO_2-C_6H_4
10 R = NO_2 R' = *p*-NO_2-C_6H_4
11 R = NO_2 R' = *m*-NO_2-C_6H_4

Results and Discussion

Fluorescence and phosphorescence emission: All compounds show a weak fluorescence emission with a quantum yield which varies from 7×10^{-5} (compound **9**) to 1.2×10^{-3} (compound **1**). In dichloromethane solution the position of the fluorescence maximum is found around 590 nm (see Table 1) or even at longer wavelengths (660 nm for compound **8**) for each compound (except **7** and **9**) as long as the fluorene ring is not substituted by a nitro group (Figure 1). The presence of such a substituent at position 2 on the fluorene ring results in a hypsochromic shift of the emission by ca. 80 nm (compounds **3**, **4**, **10** and **11** in Table 1).

With the exception of compounds **1** (for which $\tau_s = 0.11$ ns), **2** and **5** (for which $\tau_s = 0.06$ ns), the fluorescence decays in less than 30 ps, the lower limit of our instrumentation. It is noteworthy that an electron-donating or electron-withdrawing group on the phenyl ring of the styrene substituent appears to have no influence on the stability of the excited state which fluoresces.

However, it is surprising to observe that the fluorescence emission, which should originate from one of the two orthogonal moieties (each being independent of the other), can be shifted from the absorption maximum in different DHIs by between 80 and over 220 nm. It has been already pointed out that, for compounds related to those studied here and by comparison of the radiative lifetime measured experimentally with the radiative lifetime calculated from Strickler and Berg's equation, the excited state that fluoresces is different from the one which absorbs the light.[18] One possibility would be the formation of a twisted intramolecular charge-transfer state, since the two entities of the molecule have the ideal geometry. However, if this

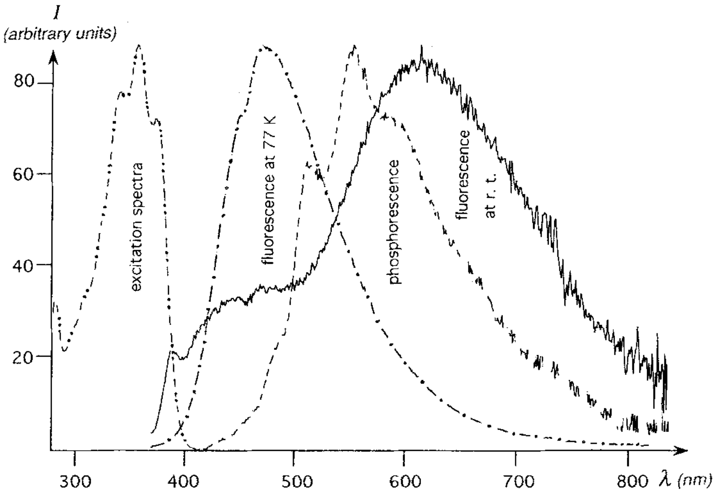


Figure 1. Compound **1**: room-temperature fluorescence (—) and fluorescence excitation spectra (· · · · · ·); 77 K fluorescence (– · –) and phosphorescence (- - - -) spectra in ethanol solution.

Table 1. Absorption (compounds **1**–**11**) and fluorescence data (compounds **1'**–**11'**) at room temperature in dichloromethane solution.

Compound	Absorption λ_{max} (nm) (ε ($M^{-1}cm^{-1}$))	Compound	Fluorescence $\Phi_f \times 10^3$	λ_{max} (nm)	$\tau_s \times 10^9$	$k_f \times 10^6\,s^{-1}$
1	360 (12500)	**1'**	1.2	596	≤0.11	11
2	365 (9440)	**2'**	0.61	585	≤0.06	10
3	324 (16100)	**3'**	0.2	508	≤0.25	
4	339 (35200)	**4'**	0.1	502	≤0.03	≥3
5	365 (6970)	**5'**	0.23	450, 585	≤0.06	4
6	365 (8120)	**6'**	0.37	588	≤0.03	≥12
7	338 (13740)	**7'**	0.45	502	≤0.03 and 0.21	≥15
8	320 (15750)	**8'**	0.54	660	≤0.03	≥18
9	343 (8900)	**9'**	0.07	554	≤0.03	≥2.3
10	328 (23900)	**10'**	0.24	498	≤0.03	≥8
11	332 (15450)	**11'**	0.5	500		?

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Table 2. Absorption at room temperature of the long-lived *trans*-betaines **1′**–**11′** in dichloromethane solution. Fluorescence and phosphorescence data for compounds **1**–**11** in ethanol glass at 77 K. n.p. = no phosphorescence.

Compound	Betaine		Compound	Phosphorescence		Fluorescence
	λ_{max} (nm)	$\tau_{1/2}$ $\times 10^3$ s		0–0 band (nm)	λ_{max} (nm)	λ_{max} (nm)
1′	470	123	**1**	482	515–552–588	472
2′	455	6930	**2**	520	600	470
3′	450	3500	**3**	488	525–558–600	large overlap with phosphorescence
4′	440	2115	**4**	485	520–556–595	545
5′	460	7.7	**5**	515	592	465
6′	465	10.7	**6**	520	598	466
7′	475	54	**7**	518	604	465
8′	450	4.2	**8**	526	565–605	526
9′	470	1.3	**9**	512	594	550
10′	450	11.8	**10**	n.p.	n.p.	524
11′	400	18.4	**11**	478	515–550–584	large overlap with phosphorescence

had been the case, then one would not expect a lifetime on the picosecond timescale. In addition, the position of the emission of compound **1** is red-shifted by only 36 nm when benzene is replaced by acetonitrile as solvent. A much larger shift should be expected for the fluorescence in the two solvents (owing to the large change of dipole moment of the molecule in the excited state with respect to its ground state value) if an intramolecular charge-transfer state was operating. A similar conclusion was drawn for spiro[1,8-*a*]dihydroindolizines,[17] for which it was stated, based on the short lifetime of the emission, that the emitting state is a ^1A_g state that cannot be seen in absorption. In the present case, this ^1A_g state does not seem to be present in the fluorescence excitation spectra.

In the case of the pyrrolo[2,1-*a*]quinoline compounds studied here, the energy of the excited state emitting at long wavelengths is ca. 460 nm (21740 cm^{-1}) for the molecules with an absorption maximum between 330 nm (30300 cm^{-1}) and 340 nm (29500 cm^{-1}). For the molecules absorbing around 365 nm (27400 cm^{-1}) the energy of the excited state emitting at the long wavelengths is ca. 520 nm (19230 cm^{-1}). These values indicate that the energy difference between the absorption and the long-wavelength fluorescence emission is of the order of 8000 cm^{-1}, that is, 96 kJ mol. From the kinetic activation parameters for thermal breakage of the spiro bond of spiro[indoline naphthoxazines] to give the merocyanine form, the energy of this bond has been reported to vary between 56 kJ mol^{-1} and 102 kJ mol^{-1}, depending upon the substituents on the molecule.[21] In our case, there is a ≈96 kJ mol^{-1} energy loss at room temperature to form the state emitting at long wavelengths. If we extend the results found by Favaro et al.[21] in the ground state (56–102 kJ mol^{-1} necessary to break the spiro bond and form the open merocyanine) to compounds **1**–**11**, but in the excited state, then the energy to break the spiro bond would be of the same order as the energy loss that leads to the fluorescing state. Therefore, the molecule could still remain on the potential energy surface of the excited state once the spiro bond has been broken. Consequently, the fluorescence emission observed at long wavelengths would originate from an excited state with a twisted open structure.

No triplet emission could be detected in the case of molecules having a skeleton similar to that of **1**–**11** when incorporated in a polymeric matrix.[17] On the other hand, all the molecules studied here, with the surprising exception of **10**, do phosphoresce when cooled down to 77 K in an ethanol glass (Table 2). This seems to be the first report of a phosphorescence emission in this series. The phosphorescence appears between 515 nm and 605 nm, depending on the compound. In some cases (compounds **1**, **3**, **4**, **8** and **11**), and this is valid for almost all compounds substituted with a nitro group, the spectrum is well-structured (Figure 1) and shows a 1270 cm^{-1} separation between two consecutive vibrational structures. The triplet energy has been estimated from the vibrational structure of the phosphorescence spectra of the compounds. Two series of triplets are found: for the one $E_T \approx 230$ kJ mol^{-1} (compounds **2**, **5**–**7** and **9**) and for the other $E_T \approx 246$ kJ mol^{-1} (compounds **1**, **3**, **4**, **8** and **11**). The energy of the triplet state of the molecules that bear a nitro group at position 2 on the fluorene ring is higher (by about 16 kJ mol^{-1}) than that of the molecules without such substitution, **1** excepted.

In most cases, recording the total emission spectra (fluorescence + phosphorescence) of the compounds in ethanol glass at 77 K shows only the fluorescence emission, with the exception of those compounds which contain a nitro group at position 2 on the fluorene ring. In these cases, the phosphorescence overlaps considerably with the fluorescence emission and becomes the principal, if not the only, detected emission. This is in agreement with the results already obtained for the formation of photomerocyanines from spirooxazines:[22–25] in the absence of a nitro substituent, the photomerocyanine is found to originate exclusively from the singlet excited state, while the triplet pathway becomes important when such a nitro group is present in the molecule. This has been attributed to an increased singlet to triplet intersystem crossing process as a result of the influence of the nitro substituent.

Temperature effect: The fluorescence spectrum recorded at 77 K in ethanol glass (Figure 1) shows a large hypsochromic shift which can reach more than 100 nm (≈ 4000 cm^{-1}) for several compounds compared with their emission at room temperature (Table 1). It is known that the polarity of an organic medium increases when the temperature decreases.[26, 27] For instance, the dielectric constant of ethanol increases from $\varepsilon = 24.3$ at 298 K to $\varepsilon = 41.0$ at 213 K. A large solvatochromic effect would be expected from the temperature decrease for molecules that have a large difference in dipole moment between their ground and excited states, as reported previously.[3, 17] However, we know from the ca. 36 nm shift found for the fluorescence emission when the solvent is changed from benzene to acetonitrile that a large modification of the dipole moment between the ground and the excited state cannot apply to the molecules studied here. Therefore, the large shift of the emission observed must be attributed to a process different from solvent reorganization around the excited molecule in a fluid medium. The position of the fluorescence emission at 77 K (Figure 1) is more compatible with the position of the long-wavelength absorption band of the molecules. It is noteworthy that the excitation spectra recorded at the maximum of the fluorescence emission corresponds well to the absorption spectra of the molecule.

A more careful study of the temperature effect has been carried out with compound **1** in ethanol solution by analyzing the fluorescence emission when the temperature is reduced by intervals from room temperature to 103 K (Figure 2). Two main modifications can be observed during this experiment. First, the intensity of the emission increases as the temperature decreases (Table 3); it is multiplied by a factor of 75 between room temperature and 103 K. This means that the species is emitting with a quantum yield of the order of 0.1 at 103 K. The other modification that occurs during the temperature decrease is the clear hypsochromic displacement of the emission (negative solvatochromic process), which shifts the fluorescence by more than 140 nm between room temperature and 77 K. Two factors can be put forward to explain this blue shift of the emission: when the temperature starts to decrease, the fluorescence band is blue-shifted by ca. 40 nm between 293 and 183 K (Figure 3). Then between 183 and 143 K a shift of more than 80 nm occurs; this corresponds to the temperature range of the glass transition of ethanol. At lower temperatures, the position of the fluorescence band is stabilized and shifts by only 10 nm between 130 K and 77 K. Similar temperature effects have already been observed with pyrylium ions in ethanol solution, and have been attributed to the polar solvent rearrangement around the excited molecule.[28]

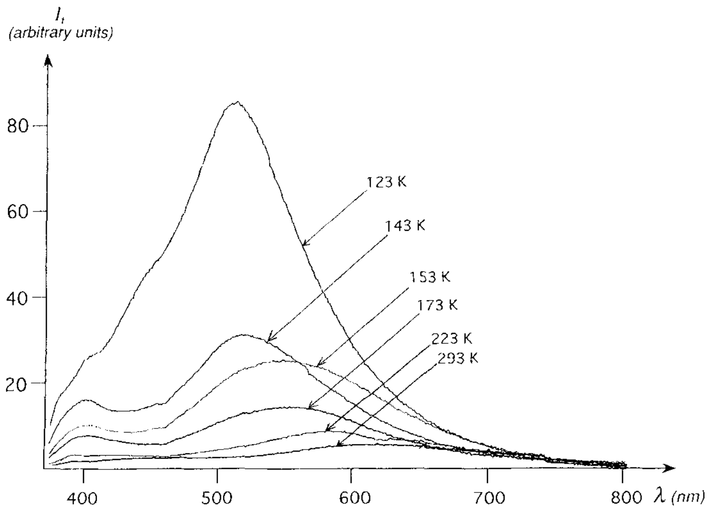


Figure 2. Fluorescence emission of compound **1** in ethanol solution at different temperatures between 293 K and 123 K.

Table 3. Variation of the fluorescence intensity of compound **1** and of the position of its maximum as a function of the absolute temperature. All measurements in ethanol solution.

Temperature (K)	293	223	183	163	150	123	103	77
λ^{f}_{max} (nm)	610	582	570	526	508	480	484	472
relative intensity	1	1.56	2.4	5.5	15.6	41.3	74.8	

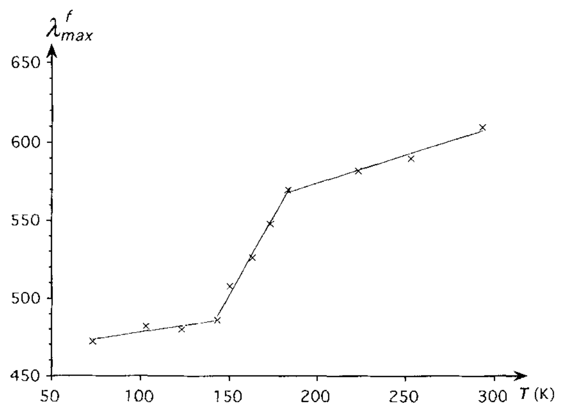


Figure 3. Plot of the fluorescence maximum of compound **1** in ethanol solution as a function of the absolute temperature of the medium.

The other interesting observation that can be made from this temperature dependence of the fluorescence emission is the presence of one band, appearing around 420 nm, which is barely shifted when the temperature is decreased. The fluorescence quantum yield of the species emitting here would be of the order of 1.5×10^{-4}. Judging by the position of this emission, it could correspond to that of the closed spiro compound **1**.

Transient absorption: Excitation of deaerated dichloromethane or acetonitrile solutions of compounds **1**–**11** leads to detectable photobetaines absorbing in the 400–520 nm range. As in the case of many betaines, those formed here by irradiation of molecules **2**–**4** have a lifetime in the second timescale (Table 2). However, for the other compounds, the lifetime of the *trans*-betaine is found to be rather short: 123 ms for **1**, and between 1 and 54 ms for all the other compounds.

Owing to their lifetime in the ms range, the open betaines could absorb a second photon and undergo a photochemical process, even under conventional steady-state irradiation. The transient is formed with the same efficiency whether the solution is degassed or not. This indicates that the transient characterized does not correspond to a triplet–triplet absorption and, in addition, that the triplet state is not involved in the formation of the betaine under direct excitation conditions. Furthermore, because of the very short lifetime of the singlet excited state, the singlet to triplet intersystem crossing process is expected to be very inefficient.

Compound 1: The transient obtained in dichloromethane solution by excitation of compound **1** at 347 nm with a ruby laser is depicted in Figure 4. It presents two distinct maxima at 450 and 470 nm. As seen in the figure, this spectrum evolves with time in that the band at 450 nm decreases slowly while that at 470 nm remains practically constant over 7 μs. This change in the transient absorption spectrum is better visualized by examining the

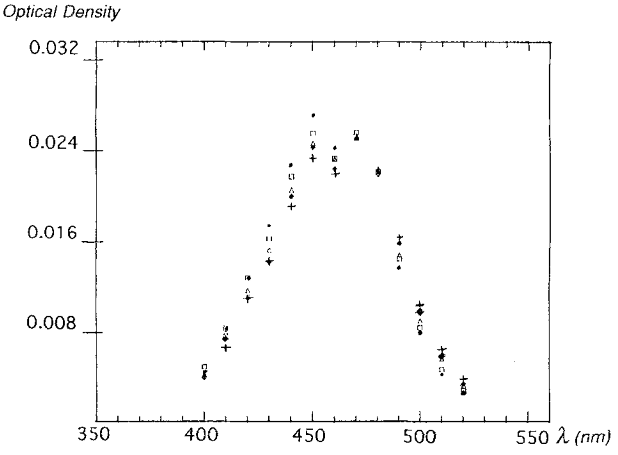


Figure 4. Transient absorption spectra of compound **1** in dichloromethane solution excited at 347.5 nm with a ruby laser and analyzed at different times: 0.5 (●), 1 (□), 2 (△), 4 (◆) and 7 (+) μs after the laser pulse.

spectral change a) at 430 nm, where the transient absorption *decreases* by almost 20% during the period 0.5–7 μs after the laser pulse and b) at 500 nm, where the transient absorption *increases* by about 16% in the same time interval. This change that occurs differently on the two sides of the transient absorption spectrum is indicative of the overlap of two different species absorbing in the same region. At 430 nm, the transient absorption first decays with an apparent lifetime of 1.7 μs, rapidly becoming constant within the analysis timescale (Figure 5); on the other hand, at 490 nm, the growing-in of the transient occurs with a shorter apparent lifetime (1.3 μs) and also becomes constant (Figure 5) on the analysis timescale. These two species should correspond to the (Z) and (E) (*cis* and *trans*) forms of the betaine, the latter being more stable than the former. From the small change of the transient absorption spectra with time, and from the large overlap of the (E) and (Z) isomers, it can be ascertained that the two isomeric forms have very similar electronic repartitions.

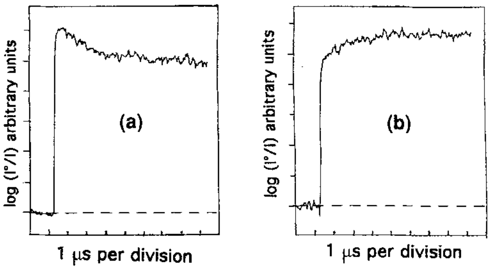


Figure 5. Oscilloscope trace of the growing-in and decay of the transient absorption of compound **1** in dichloromethane solution analyzed a) at 430 nm; b) at 490 nm.

The isomerization of the (Z) into the (E) isomer results, in principle, from a 180° rotation around a single bond and involves, in the excited state, an intermediate species formed by the 90° twisting of the "formal" double bond.[29, 30] However, it has been found by X-ray analysis of the crystals of similar molecules[31] that the double bond between the two carbon atoms which bear the carbomethoxy groups does not have an exact double-bond character. Effectively, the dihedral angle of the two bonds that bind the ester groups to the carbon atoms of the double bond is ca. 116° instead of 180° in the *trans*-betaine isomer. This nonplanar structure of the *trans*-betaine should also be valid for the *cis*-betaine, and the limited rotation between the two isomers would explain the strong overlap of their absorption spectra and the only minor difference between their electronic structures. Nevertheless, although limited, such a rotation with bulky substituents must be sensitive to the viscosity of the medium and its rate constant should decrease as the viscosity increases. That such a rotation occurs here has been verified by carrying out the experiment in ethanol/glycerol mixtures of various ratios. The decay of the *cis* isomer to form the *trans* isomer was found to be slowed down: its lifetime increased from 1.35 μs in pure ethanol to 4.9 μs in a 1:4 (v:v) ethanol/glycerol mixture, thus demonstrating the sensitivity of the isomerization to the viscosity of the medium.

Compound **2**: In the case of compound **2**, the transient absorption was approached by two different routes: by direct excitation and by triplet energy transfer from benzophenone, both experiments being carried out in dichloromethane solution. In the triplet-sensitized method, compound **2** (10^{-5} M) is irradiated with benzophenone (7.8×10^{-3} M) in dichloromethane solution. Under such conditions, 90% of the light emitted at 347.5 nm by the frequency-doubled ruby laser of 20 ns fwhm are absorbed by benzophenone. The time-resolved spectra obtained in this way are depicted in Figure 6. Triplet benzophenone absorbs at 530 nm and the benzyl radical, resulting from the solvent hydrogen abstraction by the lowest (n,π^*) triplet benzophenone, absorbs at 510 and 545 nm. Different evolutions can be seen in the spectra : 1 μs after the laser pulse, the spectrum shows two principal maxima, one at 450 nm (with a shoulder at 480 nm) and the other at 530 nm. The first one corresponds to the absorption of the open betaine form of compound **2**, and the

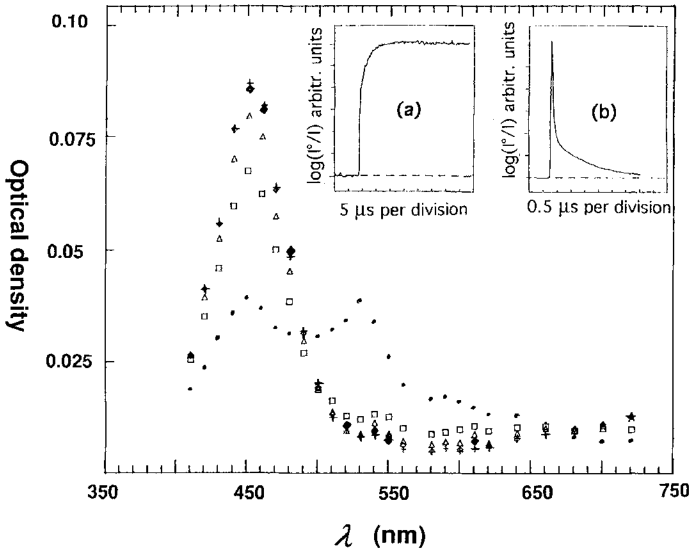


Figure 6. Transient absorption of **2** in CH_2Cl_2 solution sensitized by benzophenone; analysis at different times: 1 (·), 5 (□), 10 (△), 20 (◆) and 35 μs (+) after the laser pulse. Inset: oscilloscope traces a) of the growing-in and decay of the transient absorption of **2** analyzed at 450 nm; b) of the fluorescence (fast decay) of **2** and of benzophenone phosphorescence (slow decay) at 530 nm.

second one to that by triplet benzophenone. Then the 530 nm band of triplet benzophenone decreases rapidly (with a 1.51 µs decay) while a small amount of benzyl radical is formed. On the other hand, the peak at 450 nm, which was partly formed by direct excitation of **2**, increases with an apparent growing-in of 2.3 µs, owing to the formation of the (*E*)-betaine as the final step of the triplet sensitization reaction. The betaine then slowly disappears with a lifetime of 6.9 s.

In the direct excitation method, the transient absorption spectrum of **2** shows one principal peak at 450 nm and a smaller one above 700 nm (Figure 7). The main peak decays in almost seven seconds; it is very long-lived compared with the transient formed from **1**, which had a lifetime of 123 ms (vide supra). The single peak observed for the transient in the absorption spectrum of **2** cannot be attributed to a triplet species but rather to the most stable (*E*)-betaine form. This implies firstly that the triplet excited state of **2** also forms the open betaine species and, secondly, that all the intermediates, triplet, twisted open form and (*Z*)-betaine isomer, have lifetimes shorter than 1 µs and evolve to the more stable (*E*)-betaine.

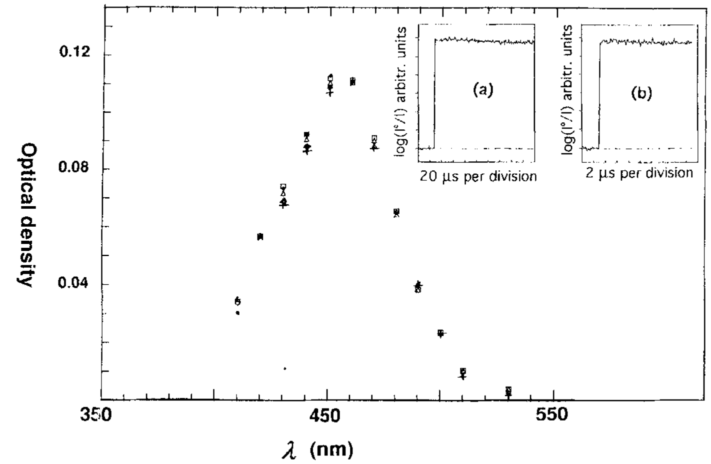


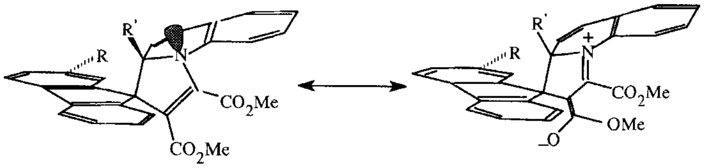
Figure 7. Transient absorption of **2** in CH_2Cl_2 solution excited at 347.5 nm with a ruby laser; analysis at different times: 5 (·), 20 (□), 40 (△), 80 (◆) and 140 µs (+) after the laser pulse. Inset: trace of the growing-in and decay of the transient absorption of compound **2** in dichloromethane solution analyzed at: a) 430 nm; b) 450 nm.

Origin of the fluorescence emission: The structure of the species which fluoresces in the 550–650 nm range is puzzling. We have shown (vide supra) that the ring-opening of the spiro system could lead to a twisted open form that would remain on the potential energy surface of the singlet excited state. In order to determine whether or not the emission originates from one of the two isomeric forms of the photobetaine, a two-photon experiment was carried out with the aid of two different techniques.

In the first experiment, the intensity of the fluorimeter excitation light was attenuated by neutral filters of various optical densities put in front of the 1 × 1 cm Suprasil cell containing the sample. Then the intensity of the fluorescence was recorded for the various light intensities. The linear correlation obtained with a slope of unity demonstrates that the fluorescence of the compounds does not originate from a two-photon process.

In the second experiment, the solution of the spiro compound was irradiated by two successive pulsed laser beams: first, with a ruby laser (20 ns fwhm) at 347.5 nm and then, after a delay of ca. one microsecond, with a YAG laser (30 ps fwhm) at 354 nm. No fluorescence emission could be observed as a result of the excitation by the second laser pulse; therefore, it can be concluded that the *cis*- and *trans*-betaines in their quasistable form are not emitting.

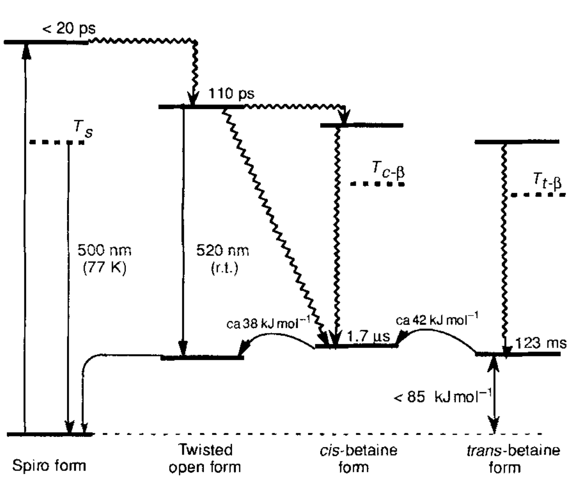
One possibility could have been a delocalization of the nonbonded electron pair fixed to the nitrogen atom at the ring junction, leading to an extended conjugation in the dihydroindoquinolizine moiety of the molecule, as depicted in Scheme 2. Such a possibility could be accounted for in ethanol solution, from which protons could be easily transferred to the negatively charged oxygen atom.



Scheme 2. Delocalization of the nonbonded electron pair on the nitrogen atom at the ring junction resulting in extended conjugation in the dihydroindoquinolizine moiety.

Nevertheless, the decrease in temperature should not prevent the formation of such a mesomeric form unless the process is conditional upon the flattening of the pyramidal nitrogen atom. Then it would resemble the umbrella-like motion (ULM) that has been proposed recently in the case of xanthenes[32] and rhodamines,[33] and that has been demonstrated to be one of the conditions for the well-characterized intramolecular charge transfer mechanism of *p*-dimethylaminobenzonitrile.[34, 35]

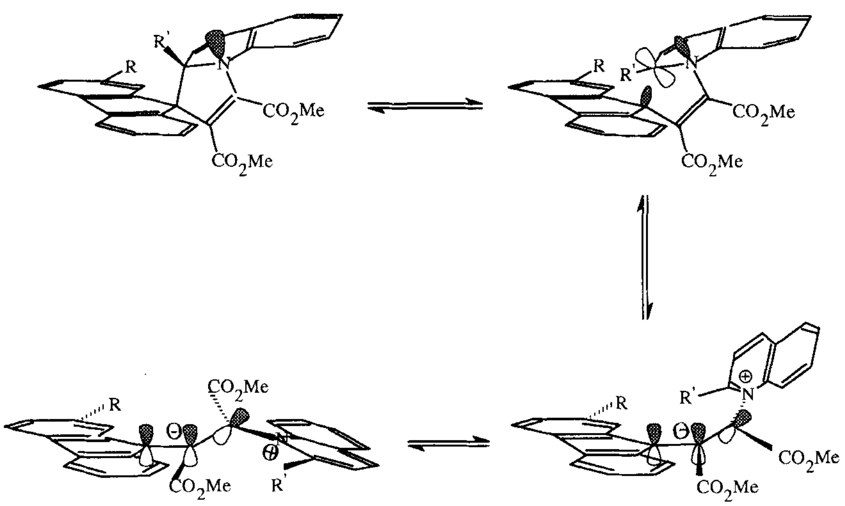
However, in the case just discussed, one would not expect the fluorescence emission to be so short-lived and red-shifted at room temperature by almost 200 nm as it is found to be for most of the compounds studied here, which fluoresce with a maximum around 590 nm. From the data obtained for the DHI (**1**–**11**) → betaine (**1'**–**11'**) interconversion, the energy diagram in Scheme 3 can be put forward. It emphasizes the singlet reac-



Scheme 3. Energy diagram of the different intermediates between the starting spiro compounds and the final *trans*-betaines.

tion pathway under direct excitation. The diagram also shows the energy difference between the spiro form and the *trans*-betaine, both in their ground states. The indicated value of 85 kJ mol^{-1} corresponds to the variation in enthalpy between the two forms measured[36] for several compounds in this series. The energy barrier between the *trans*-betaine and the *cis*-betaine has been estimated to be of the order of 40 kJ mol^{-1}. It is reasonable to think that when the molecule has reached its twisted form from the *cis*-betaine, the ring closure to the spiro form is instantaneous. Therefore the energy necessary to go from the *cis*-betaine to the twisted intermediate is of the order of 40 kJ mol^{-1}. However, during the rotation of the *trans*-betaine to form the *cis*-betaine, some of the molecules attain the favourable conformation of the twisted form and ring-close easily.

The question as to whether the product is formed adiabatically in the excited state $^1A^* \rightarrow {}^1(cis\text{-betaine})^*$ or diabatically $^1A^* \rightarrow cis$-betaine is left open. The results discussed above seem to favour an adiabatic process to an open twisted excited intermediate which gives the *cis*-betaine through a diabatic process. The spectroscopic intermediates are represented in Scheme 4.



Scheme 4. The spectroscopic intermediates between spiro and *trans*-betaine forms. R = R' = H, Hal, CH_3, phenyl.

Conclusions

DHIs **1**–**11** show low fluorescence quantum yields of the order of 10^{-3}. The position of the fluorescence maximum is temperature dependent. Betaines **1'**–**11'** do not fluoresce at all. DHI phosphorescence is hypsochromically shifted by NO_2 substitution on the fluorene ring.

Upon pulsed laser irradiation, two transients have been characterized which decay in the ps and μs domains. We attribute slightly tilted educt or product-like geometries to these transients.

The triplet state could be populated only by sensitization; direct excitation involves the singlet state only.

An energy diagram is proposed for the photoreaction **1** → **1'** that takes into account the singlet pathway and the different transients formed from the singlet state of **1**–**11** having lifetimes of the order of ca. 100 ps.

Experimental Procedure

Products and solvents: Dichloromethane (OSI, HPLC grade), benzene (Aldrich, spectrophotometric grade), ethanol (Prolabo, RP Normapur) and acetonitrile (Prolabo, HPLC grade) were used as received. The preparation and characterization of compounds **1**–**11** will be published elsewhere.[20]

Absorption and emission: The UV/visible absorption spectra were obtained in dichloromethane solution with a Varian-Cary model 219 apparatus or with a Kontron apparatus, model Uvikon 860, equipped with a lambda-scan module. Corrected fluorescence spectra were recorded with a SLM-Aminco 8000C model apparatus. Fluorescence quantum yields were measured in various solvents by comparison with that ($\Phi_f = 0.010$) of 2-(phenyl)-1*H*-benz[*f*]isoindole-1,2-(2*H*)-dione in dichloromethane solution, the latter being itself measured by reference to quinine sulfate in 1 N aqueous sulfuric acid solution for which $\Phi_f = 0.55$.[37] Phosphorescence spectra were obtained at 77 K in ethanol solution by means of a SLM-Aminco 8000C model apparatus equipped with a phosphorescence accessory coupled to an oscilloscope that can measure phosphorescence decay over times as short as 3 ms.

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 were stored in an Apple II + microcomputer, could be displayed on a Hewlett-Packard 7470A graph plotter. Average decays could be analyzed directly by the computer. For shorter-lived fluorescent species, a TSN 505 streak camera was used with ca. 50 ps time resolution; the fluorescence was focused through an optical couple on the slit of the streak camera, and the data were transferred to a multichannel analyzer to permit accumulation of several decay measurements. In this way, lifetimes of 60 ps or more could be analyzed, in the same way as described for data storage in the digitized oscilloscope.

Temperature effects: Variable-temperature measurements were carried out in ethanol solution for both absorption and fluorescence with a liquid-nitrogen-cooled Dewar (from Oxford Instruments) that permitted measurements down to ca. 85 K. Stabilization of the temperature to ±1° was accomplished before each measurement. Fluorescence quantum yields were corrected for the change in optical density at the excitation wavelength.

Triplet state: Flash-photolysis experiments were carried out with a frequency-doubled pulsed ruby laser (347.5 nm; 20 ns fwhm) from JK Laser Company. The usual crossed beam system was used, the analyzing light being a conventional pulsed xenon lamp from Applied Photophysics. Triplet-triplet absorption spectra were tentatively determined by direct excitation as well as by triplet energy transfer with benzophenone as sensitizer (the intersystem crossing quantum yield of which being unity). The transient decay was recorded with a 7A13 differential comparator amplifier of a Tektronix 7912AD digitalized oscilloscope. A detailed description of the experimental setup has been given already.[38]

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