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Photolysis of *m*-phenylene-bis(chlorodiazirine) + 2-vinylpyridine: does an indolizine chromophore inhibit the photolysis of a diazirine?

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Abstract

The photolysis of *m*-phenylene-bis(chlorodiazirine) in the presence of 2-vinylpyridine (VP) yields the *m*-phenylene-bis(indolizine) by a mechanism involving two consecutive photoreactions. Photolysis of a first diazirine ring generates a carbene which reacts with 2-VP to give, via a sequence of fast thermal reactions, a first product including both the indolizine and the chlorodiazirine moieties. Although in the lowest excited singlet state of the primary product, the excitation is localized on the indolizine unit, the photolysis of this product induces the decomposition of the second diazirine ring to give a second carbene which yields the final product via the same sequence of reactions: formation of a 2-vinylpyridinium ylide, cyclization and elimination of HCl. Analysis of the absorption and fluorescence spectra indicates that an upper excited singlet state, with the excitation localized on the diazirine ring, is only a few kJ/mol above S_1. It can therefore be populated by thermal activation of S_1 so that there is, seemingly, an endothermic intramolecular energy transfer from the indolizine moiety to the diazirine ring.

Keywords: Carbene; Ylide; Diazirine; Indolizine; Photolysis; Energy transfer

1. Introduction

Phenylchlorocarbene (PCC) reacts with 2-vinylpyridine (2-VP) to form an ylide which rearranges to give, after elimination of HCl, a phenylindolizine [1] according to Scheme 1.

When phenylchlorodiazirine, the parent compound of PCC, is changed to *m*-phenylene-bis(chlorodiazirine) (**1**) photolysis or thermolysis in the presence of VP should give the *m*-phenylene-bis(indolizine) (**4b**). This occurs most probably stepwise (i.e. via **2** and **4a** but not via **3**) since the photolysis of **1** and of its *para* isomer in rigid matrices at low temperature has been shown [2,3] to proceed in similar fashion. However, the mechanism of the photolysis of **1** at room temperature in fluid solutions may be different from that which exists at low temperatures. The bis(indolizine) (**4b**) was indeed obtained after thermolysis but under photolysis in semi-preparative conditions, the reaction was reported to stop at **4a**, after the formation of the first indolizine ring [4].[3] This is potentially interesting for synthesis because, after elimination of the unreacted VP and addition of another reactant, thermolysis of the second diazirine ring will give an unsymmetrical product (e.g. the *N*-arylpyrrole-phenyl-indolizine (**4c**) when the second reactant is an *N*-aryl-1-aza-1,3-butadiene) (Scheme 2).

Several hypotheses may be proposed to explain why, in semi-preparative conditions, the photolytic process would stop after the formation of the first indolizine ring:

- after some time, the intense diffusion due to the precipitate of VP hydrochloride salt could slow down and nearly stop the photolysis;
- the intense absorption of the indolizine chromophore of **4a** could prevent the photolysis of the second diazirine ring by a screening effect; or
- the second diazirine unit could be protected by the trapping in the indolizine moiety of the excitation energy provided to **4a**.

In order to elucidate this question, we investigated the system **1** + VP by laser-flash-photolysis and by continuous irra-

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[3] After extensive photolysis of **1** + VP, the isolated amounts of **4a** and **4b** were, respectively, 43 and 11% of **1** consumed. We thank Dr. Romashin for giving us the sample of the *m*-phenylene-bis-amidine used to prepare **1**.

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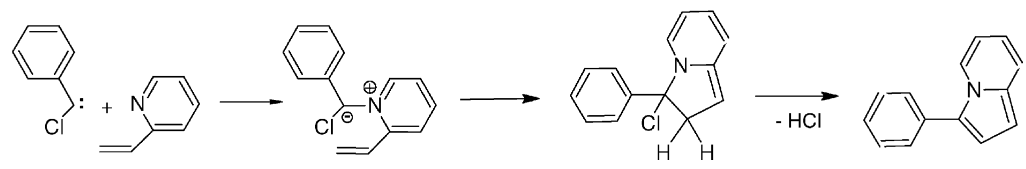
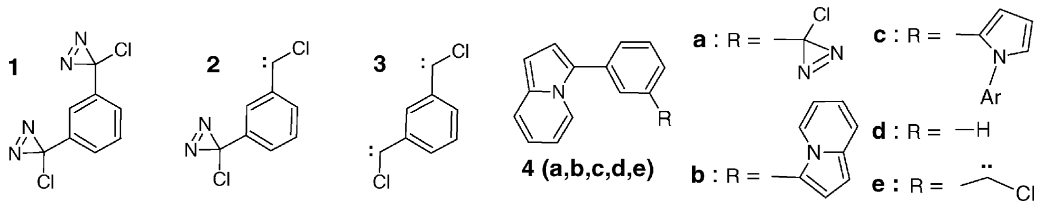


Scheme 1.



Scheme 2.

diation under “photophysical” conditions of monochromatic irradiation and low concentrations, monitoring the progression of the reaction by UV spectroscopy and fluorimetry.

2. Experimental

2.1. Photolysis and spectroscopy

Continuous irradiations used either a HPK 125 medium pressure Hg-lamp through two glass filters (Schott UG 11 and WG 345) to isolate a spectral window where 366 nm is the only intense Hg line, or an Osram XBO 1500 Xe-arc combined with a Jobin-Yvon irradiation monochromator (2 mm slits, 5 nm bandwidth) for irradiation at other wavelengths.

The laser-flash-photolysis set-up involves a mode locked Nd-YAG laser (Quantel), frequency tripled, providing single pulses (200 ps, 20–30 mJ) at 355 nm as excitation in a crossed beams arrangement and has been already described [5]. The time response of the detection system is around 3 ns.

The absorption spectra of the solutions were recorded with a HP8452A photodiode-array spectrophotometer and fluorescence measurements were made with a SPEX Fluorolog spectrofluorimeter with full correction on both excitation and emission. We used isooctane or *n*-hexane (SDS, spectroscopic grade) as solvent, unless otherwise specified.

The NMR spectra have been recorded on a Bruker Avance 300 (300 MHz) instrument.

We used the software package “CAChe 3.2” (Oxford Molecular) to calculate the UV-Vis absorption spectrum of **4a** and visualize the molecular orbitals (MOs) involved in the first electronic transitions.

2.2. Chemicals

We prepared the bis-diazirine (**1**) from the *m*-phenylene-bis-amidine by oxidation with NaOCl, according to the Graham procedure [6] (CAUTION! This product is explosive![4]). It was identified by NMR since its UV absorption spectrum, very similar to that of the phenylchlorodiazirine, is probably nearly identical to the UV spectrum of the product where only one amidine group would be oxidized into diazirine. A diluted solution of **1** slowly develops an absorption in the 280–350 nm region, characteristic of an azine which is easily removed by chromatography over silica in a column of a few centimeters.

Spectral data for the bis-diazirine (**1**): ^{1}H NMR (CDCl$_3$), δ (ppm): 7.46 (t, 7.8 Hz, 1H), 7.13 (d, 7.8 Hz, 2H), 6.9 (s, 1H), identical to data from literature [2]. UV: structured absorption band in the 310–400 nm range with maxima at 348, 366 and 384 nm (see Fig. 1).

We prepared the bis-indolizine (**4b**) by thermolysis of **1** in boiling benzene in the presence of VP and chromatography of the resulting mixture on a silica column with isooctane eluent. The product was identified by NMR and by its UV-Vis absorption spectrum. In alkanes, this absorption spectrum, a broad band with a maximum at 332 nm and faint shoulders at 375 and 396 nm (see Fig. 1), closely resembles that of the phenylindolizine prepared from PCC + VP ($\lambda_{\max} = 324$ nm) and it is similar to that of the unsubstituted indolizine which presents a more structured absorption in the same region ($\lambda_{\max} = 345$ nm) with a well defined 0–0 transition at 390 nm [7]. Therefore, the absorption spectra of **4a** and **4b** are probably also similar.

Spectral data for the bis-indolizine (**4b**): ^{1}H NMR (CDCl$_3$), δ (ppm): 8.33 (d, 7.3 Hz, 2H), 7.77 (s, 1H), 7.57–7.53 (m, 3H), 7.43 (d, 8.8 Hz, 2H), 6.91 (d, 4 Hz, 2H), 6.69 (dd, 9.1, 6.4 Hz, 2H), 6.56 (d, 4 Hz, 2H), 6.50 (t, 6.4 Hz, 2H). UV, $\lambda_{\max}$ (nm): 267, 276 (sharp), 332 (broad).

2-VP, freshly received from Aldrich and kept in freezer, was used without further purification.

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[4] Working on diluted solutions is safe but, if the solvent must be removed, this must be done carefully in small amounts. Never freeze pure diazirine to a solid state.

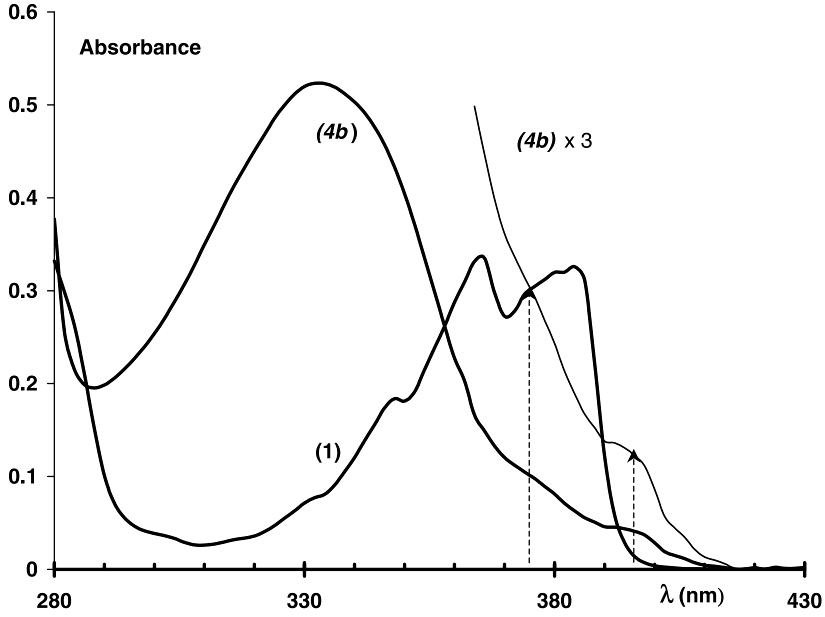

Fig. 1. UV-Vis absorption spectrum of alkane solutions of *m*-phenylene-bis(chlorodiazirine) (**1**) and *m*-phenylene-bis(indolizine) (**4b**).

3. Results

3.1. Laser-flash-photolysis

Under excitation of a solution of the bis-diazirine (**1**) in isooctane, a transient absorption appears in the 290–330 nm region, within the 3 ns time resolution of our set-up, and then decays by a mixture of first- and second-order processes, with a "decay time" of approximately 2 μs in our experimental conditions. This transient absorption is assigned to carbene **2** because of its similitude with the absorption spectrum of PCC [8]. Upon addition of VP, the decay, monitored at 312 nm, becomes first order and the linear plot of the reciprocal lifetime vs. [VP] yields a value of $k_{\text{yl}} = 7.7 \times 10^8\,\text{M}^{-1}\,\text{s}^{-1}$ as shown in Fig. 2.

Simultaneously with the decay of the absorption of carbene **2**, a broad absorption band appears in the spectral range 420–750 nm, with a maximum around 550 nm. This absorption, similar to that previously observed [1] for the (*p*-Cl-PCC ← VP) ylide and therefore assigned to the 2-vinylpyridinium ylide of carbene **2**, grows according to an approximately first-order kinetics, the rate constant of which depends linearly on [VP]. When it is measured at 550 nm, this pseudo-first-order rate constant is similar to,

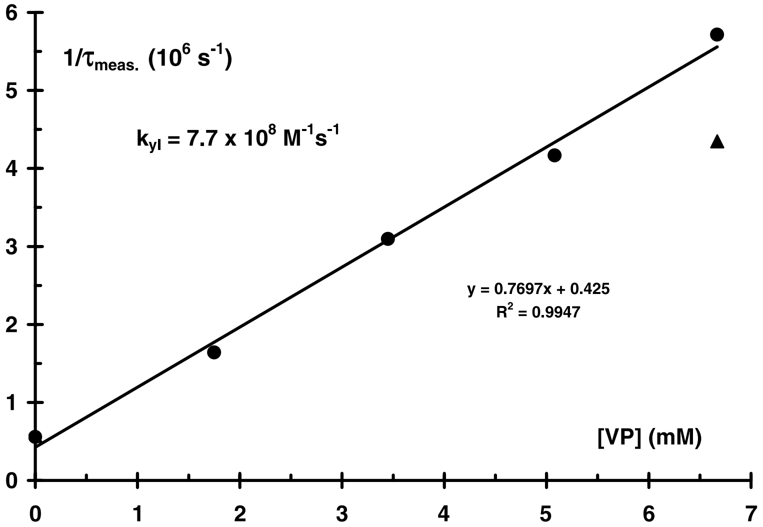

Fig. 2. Reciprocal lifetime of the carbene, monitored by its absorption at 312 nm, as a function of the 2-vinyl-pyridine concentration (●). The triangle (▲) indicates the rate constant for the growth of the vinyl-pyridinium ylide absorption at 550 nm.

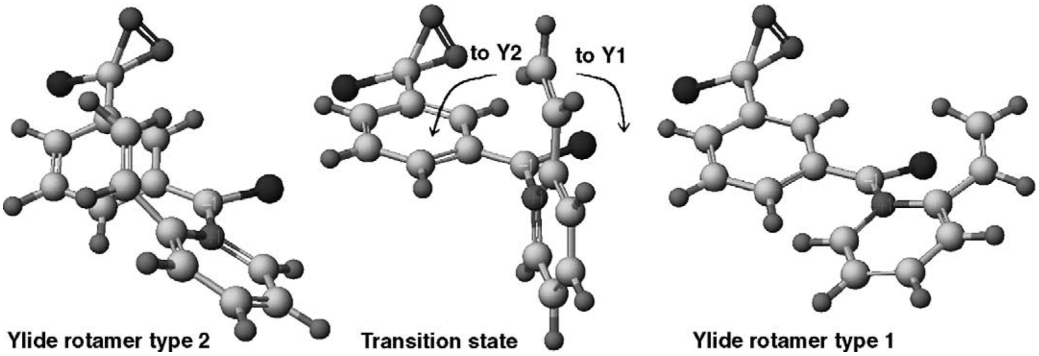

Fig. 3. Structures of the two ylide rotamers and the transition state between these two species as calculated using MOPAC with PM3 parameters (CAChe 3.2 software).

but significantly lower than, the rate constant for the decay of **2** in the same conditions: e.g., for $[VP] = 6.67$ mM one gets a 230 ns rise time at 550 nm and a 175 ns decay time at 312 nm. In addition, the rate of formation and the rate of decay of the ylide absorption depend on the wavelength of measurement: both are noticeably slower at 550 nm (230 ns and 50 μs) than at 450 or 750 nm (≈120 ns and 33 μs).[5] This clearly indicates that the observed transient absorption is due to at least two species.

We first considered the simultaneous formation of the monoylide **2** ← VP and of the bis-ylide **3** ← VP assuming that the exothermic reaction $\mathbf{1}^* \rightarrow \mathbf{2} + N_2$ produces **2** in a "hot" state which, at least partially, thermally decomposes to give $\mathbf{3} + N_2$. However, we rapidly realized that the two ylide species are rotamers of the monoylide (see Fig. 3) because the absorption spectrum of the pyridinium ylide of **2** shows only one component whereas the absorption spectrum of the PCC ← VP ylide shows two components [9]. Consequently, the formation of two ylide species is a characteristic of VP and the photolysis of **1** produces only the mono carbene **2**, even under the very intense irradiation intensities used in laser-flash-photolysis.

3.2. UV spectroscopy and continuous irradiation

The evolution of the UV absorption spectrum of a solution of **1** (≈ 0.3 mM) + VP (10 mM) in *n*-hexane during the first stages of its photolysis under continuous irradiation at 385 nm is shown in Fig. 4. The spectra of the reaction product(s) are obtained by subtracting from the spectra recorded after 10, 20 and 65 s of irradiation, the initial spectrum (only due to **1** for wavelengths >340 nm) multiplied by the percentage of unreacted (**1**) (0.98, 0.96 and 0.90, respectively). These percentage values are adjusted in such a way that the shape of the resulting spectrum of the product(s) does not show the structured absorption of a diazirine in the 350–400 nm range, and that the percentage of reacted **1** is proportional to the irradiation time multiplied by the fraction of the excitation absorbed by **1**.

The absorption spectrum obtained in this manner for the product(s) with a maximum around 330 nm resembles that of the bis-indolizine (**4b**). The main difference is a "too large" absorption in the range of 300–320 nm, most probably due to the facts that:

- in this region the absorption is mainly due to VP, the concentration of which is nearly constant since VP is in large excess, so that the percentage of the initial spectrum to subtract should remain close to 100%;
- the effect of diffusion by a precipitate of VP-HCl salt, insoluble in alkanes, which rapidly makes impossible spectroscopic measurements when the photolysis is continued up to large conversion levels.[6]

The accuracy on the absorption spectrum of the product(s) is not sufficient to determine its (their) nature, **4a** and **4b** or a mixture of both since, as stated above, the absorption spectra of **4a** and **4b** are probably similar. Therefore we decided to use spectrofluorimetry, a technique well suited to detect the various components of a mixture since the results depend on four characteristics of each species: fluorescence excitation and emission spectra, fluorescence quantum yield and fluorescence lifetime.

3.3. Fluorescence measurements

The fluorescence emission spectrum of the bis-indolizine (**4b**) is poorly structured. It extends from 400 to 600 nm with a shoulder at 409 nm and maxima at 434 and 457 nm (see Fig. 5). The fluorescence excitation spectrum, with a maximum at 332 nm, closely resembles the absorption spectrum shown in Fig. 1b. The fluorescence quantum yield, determined using quinine sulfate as a standard [10],[7] turned out to be 0.08.

A non-irradiated solution containing $\mathbf{1} + \mathrm{VP}$ does not give any fluorescence signal under excitation in the 330–400 nm

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[5] Values measured at 24 °C for $[VP] = 6.67$ mM.

[6] The formation of each indolizine unit releases one HCl molecule. In dichloromethane solvent, the formation of the precipitate is minimised but not suppressed and a non-identified blue stuff, also absorbing in the UV region, is formed.

[7] $\phi_f = 0.59$ for quinine sulfate in water + $HClO_4$ 0.1 M.

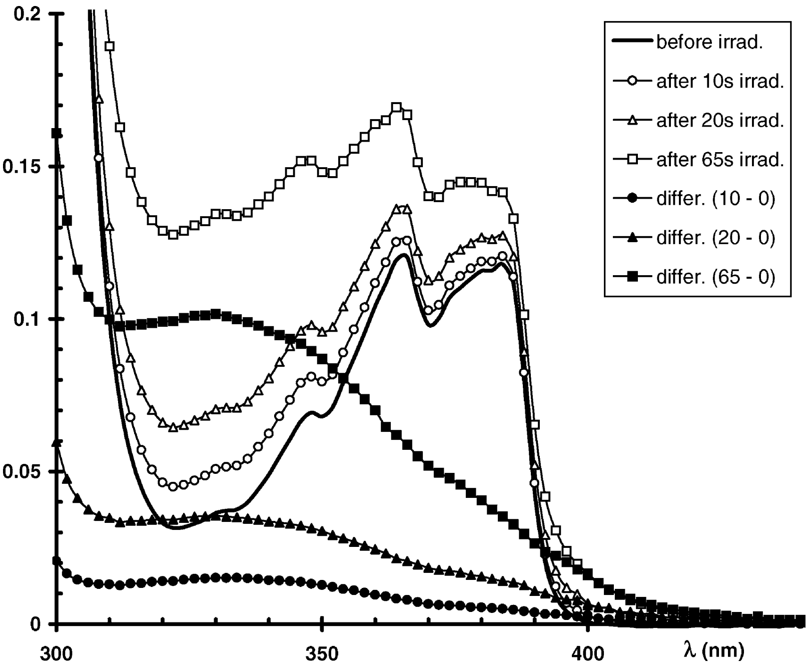

Fig. 4. Evolution of the absorption spectrum of a solution of **1** + VP in hexane under irradiation (open symbols) and absorption spectrum of the product(s) formed calculated as indicated in the text (closed symbols).

range because the bis-diazirine (**1**) does not provide any detectable fluorescence. After a few seconds irradiation at 384 nm, the same solution gives a fluorescence signal with an emission spectrum which fits that of **4b** and a fluorescence excitation spectrum with a maximum at 328 nm. Further irradiation induces an increase of the fluorescence intensity without any noticeable change of the emission spectrum but with a progressive shift of the maximum of the excitation spectrum to 332 nm.

We recorded the absorption spectrum and the fluorescence intensity at the emission maximum after each short period of irradiation (5–10 s). Then, plotting the increase of the absorbance at 330 nm and the fluorescence intensity at 457 nm as a function of the cumulated irradiation time, we obtained the curves shown in Fig. 6: whereas the increase of the absorbance shows a small downward curvature (expected since the fraction of the excitation absorbed by the diazirine chromophore decreases as the reaction progresses), the increase

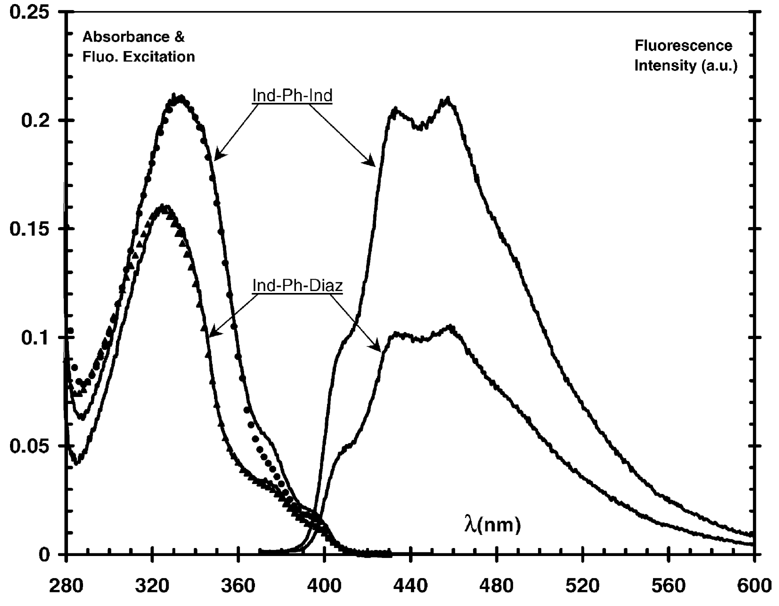

Fig. 5. Fluorescence emission and excitation spectra (lines) and absorption spectra (● and ▲) of **4a** and **4b** in isooctane solutions.

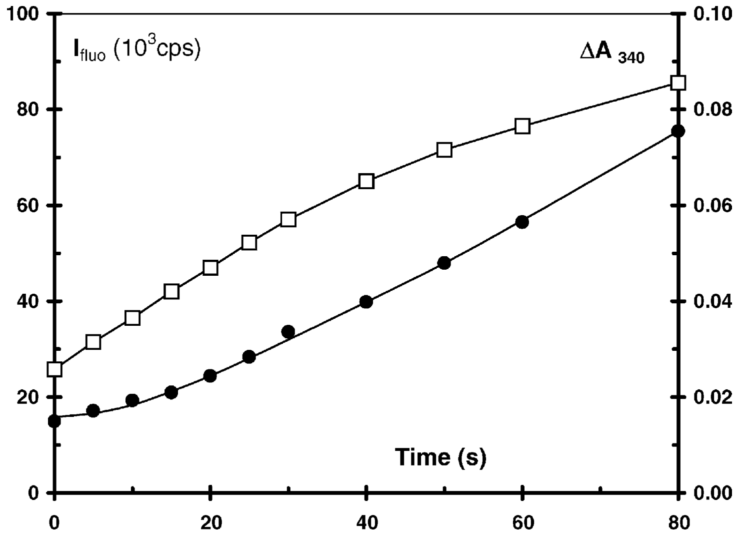

Fig. 6. Evolution of the absorbance at 340 nm (☐) and of the fluorescence intensity at 450 nm (●) for a solution of **1** + VP in isooctane as a function of the time of irradiation at 380 nm.

of the fluorescence intensity shows an upward curvature during the first irradiation steps.

These observations indicate that the photolysis of the system **1** + VP does not yield directly the bis-indolizine (**4b**) after absorption of a single photon, either by formation of the bis-carbene **3** from the excited state **1***, a hypothesis already rejected on the ground of the laser-flash-photolysis study, or by decomposition of the second diazirine ring during the formation of the first indolizine ring.

The reaction must proceed stepwise and, to account for the observations, the intermediate species **4a** must be poorly- or non-fluorescent and its absorption spectrum should be blue shifted compared to that of **4b**. Then, it appeared necessary to prepare **4a** and to study its absorption and fluorescence characteristics to substantiate these deductions.

3.4. Preparation and spectroscopic properties of *4a*

We irradiated a few milliliters of a solution of **1** (≈5 mM) and VP (≈5 mM) in isooctane at 366 nm, up to decomposition of about 10% of the initial amount of **1**. The solution was concentrated under reduced pressure after filtration to eliminate the precipitate of VP-HCl. Chromatography of the residue on a 20 cm long silica gel column with isooctane as eluent gave the following fractions: **1**, **4b**, another product, X, and finally VP.

The absorption spectrum of X is similar to that of **4b** and nearly identical to that of **4d** with the faint structures at 375 and 395 nm and an intense absorption in the 320–340 nm region indicative of an indolizine unit but the maximum absorption is found at 324 nm (332 nm for **4b**, 324 nm for **4d**). There is no evidence in the 350–400 nm part of this spectrum for the absorption of a diazirine moiety but this is easily explained by the low absorption coefficient of the diazirine chromophore ($\varepsilon \approx 150$) combined with the low concentration of the sample ($\leq$75 μM since its absorption coefficient at 324 nm must be $\geq$2000 $M^{-1}\,cm^{-1}$).[8] The fluorescence excitation spectrum of the chromatographic fraction containing X is identical to its absorption spectrum over the 300–420 nm range, indicating that this fraction contains a reasonably pure product.[9]

The fluorescence emission spectrum of X is identical to that of **4b**, but its fluorescence quantum yield in N_2 flushed solutions, $\phi_f \leq 1.2\%$ determined by using quinine sulfate as a standard, is at least 6.7 and 8.5 times smaller than for **4b**, $\phi_f \approx 8\%$ and **4d**, $\phi_f \approx 10.2\%$. The value of 1.2% is a maximum for ϕ_f because the presence of a few percents of **4b** in the chromatographic fraction containing X could hardly be detected since the fluorescence emission spectra are identical and the absorption spectra similar.

In order to remove this uncertainty, we measured the quenching of fluorescence by molecular oxygen dissolved in the solution. A Stern–Volmer analysis of the fluorescence intensities measured in solutions deaerated by N_2 bubbling, aerated and saturated with a 1:1 mixture of O_2:N_2 or with pure O_2,[10] gave ($k_q\tau_0$) values equal to 133 for X and to 252 for **4b** (see Fig. 7a). With $k_q = 3.1 \times 10^{10}\,M^{-1}\,s^{-1}$,[11] this gives $\tau_0 = 4.3$ and 8.1 ns, respectively. These values are in agreement with the values obtained from the analysis

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[8] For the unsubstituted indolizine, $\varepsilon_{322} = 2000$ (see Ref. [7]) and for X, that will prove to be **4a**, ε_{324} should be larger than that because of the substitution by a phenylchlorodiazirine.

[9] Below 300 nm, the absorption spectrum is more intense than the excitation spectrum. This does not necessarily indicate the presence of impurities since such a difference in a wavelength range corresponding to excitation to higher excited states is not uncommon.

[10] For solubility of O_2 in isooctane, see [11].

[11] Mean value of the rate constant k_q for quenching by O_2 of the excited singlet state of several aromatics in solvents of viscosity comparable to that of isooctane. Values of k_q from "Handbook of Photochemistry" by Murov [12].

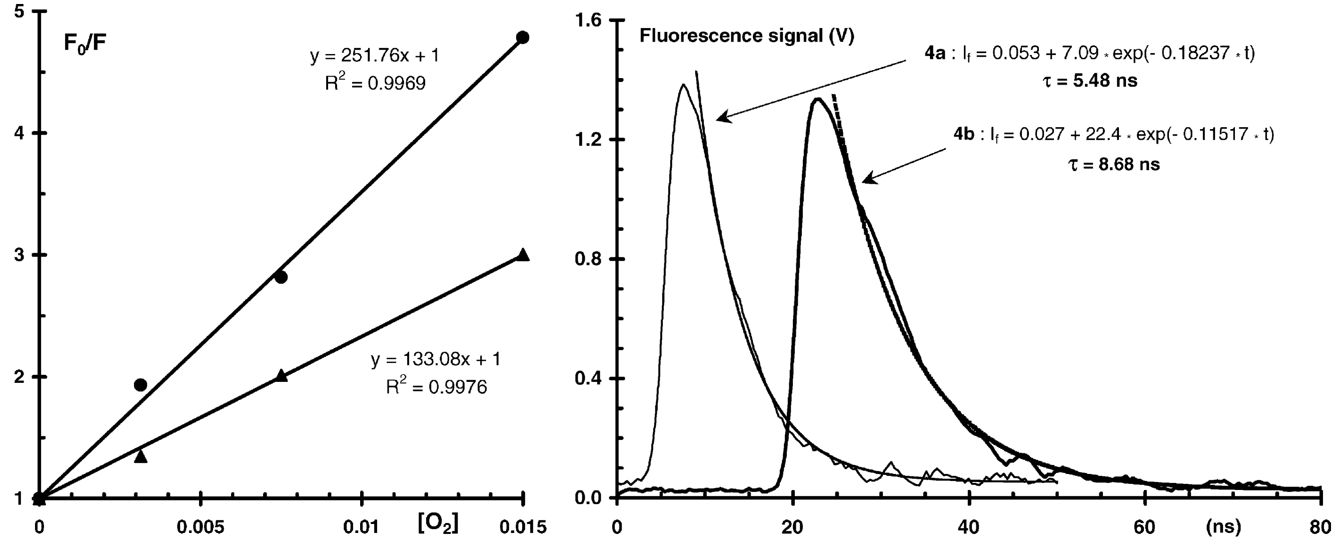

Fig. 7. Determination of the fluorescence lifetime of **4a** and **4b** by Stern–Volmer analysis of the quenching of the fluorescence intensity by O_2 (left) and by kinetic analysis of the fluorescence signal after excitation by a 200 ps laser pulse (right).

of the fluorescence signal of **4a** and **4b** recorded on the flash-photolysis system and shown in Fig. 7b, $\tau_0 = 4.58$ and 8.15 ns.[12] Clearly, the fluorescence signal of the chromatographic fraction containing X cannot be due to **4b**, since its fluorescence lifetime is about twice shorter than that of **4b**.

We identify X as **4a** on the basis of the following arguments: (i) the chemistry of the system; (ii) the absorption spectrum (see above); (iii) the fluorescence emission spectrum, identical for this product, **4b** and **4d**[13] indicates that these three compounds have the same phenylindolizine emitting chromophore, unaffected by a *meta* substitution; (iv) the fluorescence of a solution of this product in the presence of VP increases rapidly upon photolysis and, simultaneously, the maximum of the absorption spectrum shifts from 324 to 332 nm indicating the formation of **4b**.

NMR data for **4a**:[14] ^{1}H NMR ($CDCl_3$), δ (ppm): 6.50–6.57 (m, 1H) 6.69–6.74 (m, 1H), 7.02–7.07 (m, 1H), 7.34–7.37 (m, 1H), 7.40–7.53 (m, 3H), 7.59–7.65 (m, 1H), 8.23 (d, 7.5 Hz).

4. Discussion

The photolysis of the system **1** + VP yields the bis-indolizine (**4b**) via the intermediate **4a** which gives quite easily the final product by photolysis in the presence of VP in excess. The absorption coefficient of **4a** being much larger than that of **1** over the range of wavelengths generally used to photolyze diazirines, **4a** never accumulates to a large extent and its detection is made difficult by the similitude of its absorption and emission spectra with those of **4b**.

From the fluorescence lifetimes of **4a** and **4b**, one can estimate[15] the quantum yield of decomposition of the diazirine ring of **4a** to be ≈0.5 and the corresponding rate constant, $k_d \approx 1 \times 10^8\ s^{-1}$. The indolizine moiety of **4a** does not protect efficiently the remaining diazirine ring against photodecomposition. Yet, considering the ordering of the excited states of **4a**, one could expect a trapping of the excitation energy into the indolizine.

The absorption UV-Vis absorption spectrum of **4a** calculated using ZINDO after optimization of the geometry (MOPAC with PM3 parameters) shows five transitions in the range 400–300 nm. The MOs involved in the two first ones, at 373 and 362 nm, are localized on the indolizine only. The third transition, at 326 nm, implicates MO localized on the diazirine and on the 5-membered ring of indolizine whereas, for the two last ones, at 310 and 305 nm, the MO are localized on the diazirine, as shown in Fig. 8.

Thus, according to these calculations, the first excited state with an excited diazirine, S_3, would be 32 and 46 kJ/mol higher than the two excited states with excitation localized on the indolizine. If these values were correct, the indolizine would protect the diazirine moiety of **4a** against photolysis. The absorption and fluorescence spectra indicate that this

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[12] Obtained after correction for the response time of the experimental set-up, $\tau_{app} \approx 3$ ns, according to $(\tau_{real})^2 = (\tau_{meas})^2 - (\tau_{app})^2$. For **4d**, $\tau_0 = 7.9$ ns by kinetic analysis of the decay of the fluorescence induced by a 200 ps laser pulse or 7.1 ns by single photon counting.

[13] Obtained from PCC and VP.

[14] Data provided by Dr. Youri Romashin.

[15] For **4b**, $k_f + k_{nr} = 1/\tau = 1.2 \times 10^8\ s^{-1}$ and $k_f = \phi_f/\tau = 1.2 \times 10^7\ s^{-1}$ so that $k_{nr} \approx 1.1 \times 10^8\ s^{-1}$. Similar values are found for **4d**, $1/\tau = k_f + k_{nr} = 1.33 \times 10^8\ s^{-1}$ and $k_{nr} \approx 1.2 \times 10^8\ s^{-1}$. By contrast, for **4a**, $1/\tau = k_f + k_{nr} + k_d = 2.27 \times 10^8\ s^{-1}$ and $k_{nr} + k_d \approx 2.24 \times 10^8\ s^{-1}$. Assuming that the intersystem crossing and internal conversion processes are similar for **4a**, **4b** and **4d**, i.e., $k_{nr} \approx 1.2 \times 10^8\ s^{-1}$, one gets $k_d \approx 1 \times 10^8\ s^{-1}$ and a quantum yield around 50% for the decomposition of the diazirine moiety in **4a**.

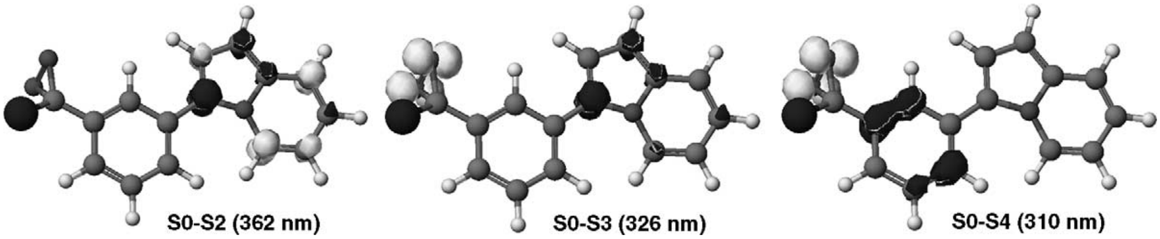

Fig. 8. Visualization of the MO involved in the first electronic transitions of **4a** as calculated using CAChe (ZINDO method after optimization of geometry by MOPAC and PM3).

energy gap is overestimated by the calculations and give more accurate values.

The absorption of the diazirine moiety, in the 350–400 nm region, is nearly the same for phenylchlorodiazirine and for **1**, indicating that the *meta* substitution does not affect this absorption. Therefore, although it is masked by the intense absorption of indolizine, the absorption of the diazirine moiety of **4a** is most probably the same as in **1** with a 0–0 transition at 384 nm (26 041 cm^{-1}). On the other hand, the absorption spectrum of **4a**, **4b** and **4d** in the 330–420 nm region can be decomposed as the sum of three Gaussian curves, with the last one (assumed to be the 0–0 band of the S_0–S_1 transition of the phenylindolizine chromophore) centered at 397.6 nm (25 151 cm^{-1}). Consequently, the first state with excitation localized on the diazirine is only 890 cm^{-1} (10.64 kJ/mol) above S_1 and it can be populated by thermal activation, at a level of about 1.5% at room temperature. The value of k_d estimated above ($\approx 10^8\,s^{-1}$) would therefore be due to only 1.5% of the excited molecules undergoing decomposition with a rate constant of approximately $7 \times 10^9\,s^{-1}$, which seems to be a reasonable value for the rate of decomposition of an electronically excited diazirine.[16]

5. Conclusion

The photolysis of the system **1** + VP yields the bis-indolizine (**4b**) according to the following mechanism. Photolysis of **1** produces the carbene **2** which reacts with VP to give the product **4a** by the sequence of reactions presented in Scheme 1. Then, photolysis of **4a** produces the carbene **4e** via a higher excited state **4a**** where the excitation is localized on the diazirine, slightly populated by thermal activation of the lowest excited singlet state **4a***. Finally, the carbene **4e** reacts with VP in excess to give **4b** by the same sequence of reactions. The key step of this mechanism is the formation of **4e** from **4a*** by an endothermic thermally activated intramolecular energy transfer from the indolizine moiety to the diazirine ring of **4a**.

That the reaction seems to stop after the formation of the first indolizine ring cannot be explained by either trapping of the excitation energy in the indolizine or the screening effect of the indolizine chromophore of **4a**. The only screening effect that can be invoked is that of the indolizine chromophores of **4b**. However, this product is only formed in low amounts. The best explanation seems to be the intense diffusion due to the milky precipitate of VP hydrochloride salt which rapidly slows down and nearly stops the photolysis process.

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[16] The energy splitting between S_1 and S_x (the lowest excited state of **4a** with excitation localized on the diazirine) may be a little bit larger than 890 cm^{-1}: the 0–0 line of fluorescence is at 407 nm, indicating some relaxation (geometry and solvent cage) of the S_1 state. The relaxed S_1 is therefore at 402.3 nm [(407 + 397.6)/2], i.e., 24 857 cm^{-1} above S_0. The S_x state is probably not affected by this relaxation process occurring in and around the indolizine and should stay at 26 040 cm^{-1} above S_0 so that the splitting S_1–S_x would be $\approx$1183 cm^{-1} (14.1 kJ/mol) giving a thermal population of S_x equal to only 0.35% at room temperature and a decomposition rate constant $2.7 \times 10^{10}\,s^{-1}$, still a reasonable value.

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