

Spirodihydroazafluorenes — a new type of *cis*-fixed photochromic molecule with rigid region B showing extremely fast back reaction

Rolf Fromm^a, Roland Born^a, Heinz Dürr^{a,*}, Jörg Kannengießer^b,
Hans Dieter Breuer^b, Pierre Valat^c, Jean Kossanyi^c

^a *Fachbereich 11.2, Organische Chemie, Universität des Saarlandes, 66041 Saarbrücken, Germany*

^b *Fachbereich 11.3, Physikalische Chemie, Universität des Saarlandes, 66041 Saarbrücken, Germany*

^c *CNRS-Laboratoire de Photochimie Solaire, 2-8 Rue Henri Dunant, 94320 Thiais, France*

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Abstract

New 2',3'-diacetyl spirodihydroindolizines (DHI) **1** and four new spirodihydroaza-fluorenes (DHF) **3** were synthesized by condensation of **1** with hydrazine. The high reaction rate of the thermal 1,5-electrocyclization results in half lives of the colored betaines **4** range from 4.0 to 6.7 ns, thus showing the existence of the shortest lived colored form observed so far for pyrazoline based photochromes. The color of betaine **4** can only be observed in a matrix at 77 K liquid air absorbing between 483 and 545 nm. Fluorescence lifetimes of **3** were determined to be in the picosecond domain. Time resolved transient spectroscopy shows the geometry of the betaines **4** to be related to one of two detectable intermediates **2'** or **2''**. © 2000 Published by Elsevier Science S.A.

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1. Introduction

In recent years many photochromic spirodihydroindolizines (DHI) **1** were synthesized with remarkable properties concerning their photochromic behavior. The thermal back reaction — the 1,5-electrocyclization — from the ring-open betaine **2'''** to the DHI **1** shows rates extending from milliseconds to several weeks [1–6] depending on the substituents and the structure of the molecule involved (Scheme 1). Even stable betaine forms **2'''** can be isolated [4].

Based on time resolved spectroscopy we assume that at least three possible betaine conformers **2** are involved [6]. Two intermediates, one having the cisoid structure **2'** with a similar geometry as the ring-closed DHI **1**, arising from the heterolytic bond cleavage between C1' and C8'a, and an intermediate **2''** with a more distorted geometry. The third showing the transoid structure **2'''**, the most relaxed conformer resulting from **2''** by a change of conformation. The rates measured for the electrocyclization are attributed to the reaction of transoid betaine form **2'''** → **1**, but efforts to prove and detect **2'** were not undertaken so far because of the short lifetime of the species involved [6].

Klauck [7], Andreis [6,8] and Bleisinger [9] could detect intermediates with lifetimes in the microsecond range.

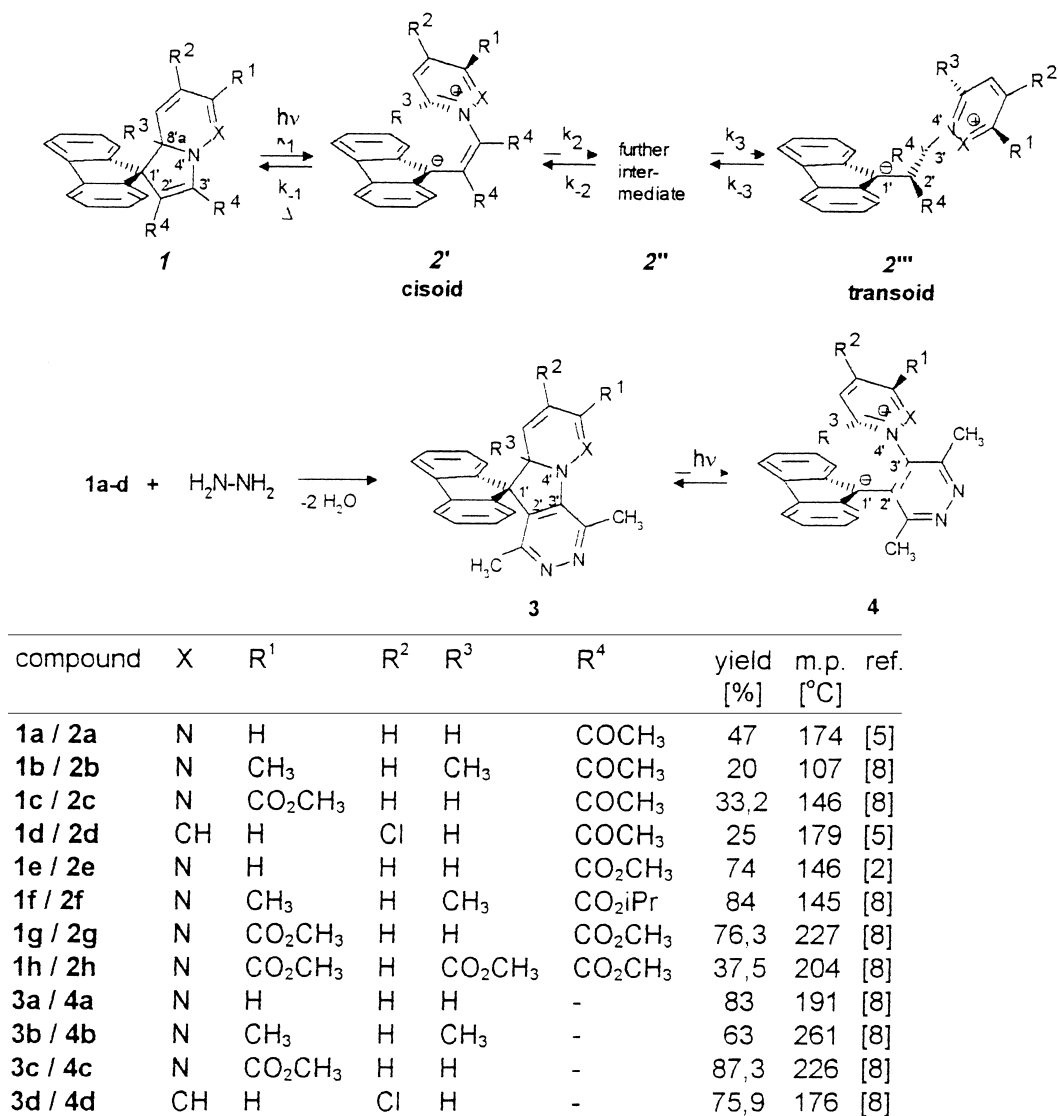
In order to assign a clear structure to a fast bleaching betaine, it was necessary to conceive a system with a very fast thermal back reaction of the ring-open form **2**. So one would prevent rotation and thus the formation of **2''** and the transoid isomer **2'''**. One possibility to achieve this goal is to create a molecule with a cyclic structure involving the substituents R⁴ in region B(C-2'=C-3') [1]. In this paper, we describe (1) the preparation of new compounds of type **3/4** and (2) time resolved single photon counting and LASER absorption studies that shed light on the potential intermediates involved in the ring opening process of **3** compared to **1**.

2. Results and discussion

2.1. Preparation

The molecules **3** were synthesized from the diacetyl-dihydro-indolizines (DHI) **1a–d**. The two acetyl groups R⁴ of **1a–d** [7,10] were transformed to dihydrofluorene (DHF) **3a–d** by condensation with hydrazine [10]. **1d–h** were prepared as model compounds by known procedures. Details will be published elsewhere.

* Corresponding author.

Scheme 1. Preparation and ring-opening reaction of the new DHI **1** and DHF **3**.

2.2. Photophysical properties of the DHI **1** and DHF **3**

The UV-spectra of the yellow DHI **1a–d** show a maximum between 405 and 421 nm, whereas the structurally related DHF **3** show a hypsochromic shift up to 46 nm (Table 1). The maxima of the betaines **4** are between 483 and 545 nm, and give a small hypsochromic shift. This indicates reduced conjugation of the π -electrons. To a smaller degree, low temperature (77 K, liquid air) during the measurement, is responsible for the hypsochromic shift of **4**. The color is probably caused by a charge transfer in **4** between the positive pyridazinium ring and the negative fluorenyl ring.

2.3. Thermal ring closure

In solution the DHI **1** show coloration on irradiation with visible light. The colored betaines **2'''a–h** have half-lives $\tau_{1/2}$ between 0.40 and 487 s.

However, there is no visible change of color on irradiation of **3a–d** in solution neither at room temperature nor at 183 K (dry ice/methanol). Only in a matrix, e.g. in solid ethanol at 77 K on irradiation of **3** the color of **4** persisting some seconds up to a few minutes was observed.

The kinetics of the thermal 1,5-electrocyclization of **4** were measured with a laser flash absorption apparatus described earlier [11]. Solutions of **3** ($c=10^{-4}$ mol/l) in degassed ethanol were irradiated at 298 K with a nitrogen laser ($\lambda=337$ nm), pulse length=600 ps. The analytic light from a Xenon lamp (150 W) was adjusted with a monochromator to the betaine maximum. An interference filter absorbed scattered and fluorescence light of the probe. The absorption spectra were recorded by time resolved spectroscopy.

The time domains from 10^{-3} to 10^{-9} were monitored. Thus only half-lives for **4a–d** in the range of a few nanoseconds for **4** ($\tau_{1/2}=4.0$ – 6.7 ns were found; Table 1). So ring fusion in region B of **1** results in an acceleration of the ther-

Table 1
UV-data of DHI **1** and DHF **3** and their colored forms **2** and **4** and kinetics of the 1,5-electrocyclization of the betaines **2** and **4**

Compound	UV-VIS (1/3) $\lambda_{(\max)}$ (nm)	$\epsilon \times 10^{-3}$	UV-VIS (2/4) $\lambda_{(\max)}$ (nm)	Color of betaine	$\tau_{1/2}$ (s) $2''' \rightarrow 1$	$k(2''' \rightarrow 1)$ ($\times 10^3 \text{ s}^{-1}$)	$\tau_{1/2}$ (ns) $2' \rightarrow 1/4 \rightarrow 3$	k_{-1} ($\times 10^{-8} \text{ s}^{-1}$)
1a/2a	406 ^a	11.4	497 ^a	Red	378 ^a	1.83	–	–
1b/2b	411 ^a	9.3	585 ^a	Blue	487 ^a	1.42	–	–
1c/2c	421 ^a	16.6	498 ^a	Red	191 ^a	3.63	–	–
1d/2d	405 ^a	7.4	531 ^a	Red-violet	132 ^a	5.25	–	–
1e/2e	389 ^a	9.5	505 ^a	Red	72 ^a	9.63	6.7 ^a	1.04
1f/2f	396 ^a	11.2	6.14 ^b (354,470)	Blue	284 ^a	2.44	5.3 ^a	1.31
1g/2g	408 ^a	14.1	506 ^a	Red	82 ^a	8.49	5.1 ^a	1.37
1h/2h	397 ^a	11.0	525 ^a	Red	0.40 ^a	1726.4	4.7 ^a	1.46
3a/4a	367 ^b	8.2	483 ^a	Red	–	–	4.7 ^b	1.47
3b/4b	374 ^b	8.6	545 ^a	Violet	–	–	4.1 ^b	1.70
3c/4c	390 ^b	11.7	515 ^b	Red	–	–	4.0 ^b	1.75
3d/4d	359 ^b	6.8	530 ^c	Red-violet	–	–	6.0 ^b	1.15

^a At 298 K in CH₂Cl₂, $c=1 \times 10^{-4}$ mol/l.

^b At 298 K in ethanol, $c=1 \times 10^{-4}$ mol/l.

^c At 77 K in ethanol glass, $c \sim 3 \times 10^{-4}$ mol/l.

mal 1,5-electrocyclization of **4a–d** \rightarrow **3a–d** by a factor of 10^{10} – 10^{11} . (A stabilization of **4** by protonation in position 1' with mineral acids that has been shown previously [1–3], was not possible in this case.)

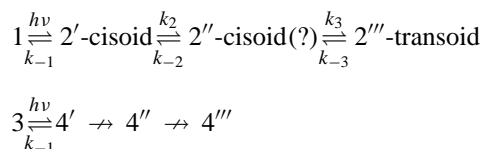
These results are explained as follows: The electron-withdrawing 3'-acetyl (R⁴) is stabilizing the ring—open form **2** by reducing the negative charge at C1'; which has sp² character. However, the ring closure is only initiated in the case of a sp³-hybridization of C1'. Dorweiler [12–14] showed that this is borne out by MINDO3 calculations. So the 1,5-electrocyclization is slowed down by a low electron density at C1'.

The transoid betaine conformer **2'''** is formed from the cisoid **2'** by rotations around the axes C2'–C3' and C3'–N4'. The energy barriers between the conformers **2'**, **2''** and **2'''** are small. C. Collet [15] could determine a rotational barrier C1'–C2' (with double bond character) to be 36 kJ/mol. The geometry of **2'''** was proved by X-ray analysis of a stable betaine by Münzmay [6]. According to this result, the most relaxed transoid betaine **2'''** is not totally planar but slightly twisted between C1' and N4'. The dihedral angle found is of the order of 116.5° between the axis R⁴2'–C2' and C3'–R⁴3' (R⁴: methyl ester). The geometry of **2''** is not exactly known whereas **2'** must be close to the one of DHI **1**.

In contrast to this results in betaine **4** the rotation between C2' and C3' is impossible because of the annulated heterocyclic ring. The molecule **4** is *cis* fixed. There are only rotations possible around the C1'–C2' and C3'–N4' axis and the ring systems are interacting during the rotation. The sp³ character of C1' is maintained to a large extent because of the decreasing withdrawal of charge by the aromatic pyridazine ring (C2' and C3'). Thus the geometry of the betaine **4** is similar to the starting material, the DHF **3**. Therefore, these structure is favorable for fast thermal disrotatory [6] 1,5-electrocyclization of **4** (obtained by irradiation of **3**). Houk [16] demonstrated that in the carbocyclic analogue the ring-opening mechanism of the cyclopentenyl anion, the

transition state comes close to the possible transition state of the reaction **4** \rightarrow **3**.

Now the different steps and intermediates involved in the ring opening of **3** or **1'** and cyclization of **4** or **2'** can explained with the following reaction sequence:



involving the DHI **1** and the betaine conformers **2'**, **2''** and **2'''**. The rate constant k_{-3} ($\ln 2/k = \tau_{1/2}$) is much smaller than k_{-2} and k_{-1} (**2e**: $k_{-3} = 9.67 \times 10^{-3} \text{ s}^{-1}$, $k_{-2} = 4.17 \times 10^5 \text{ s}^{-1}$, $k_{-1} = 1.11 \times 10^8 \text{ s}^{-1}$). In order to confirm the reaction mechanism [1,17] we investigated the transient spectra obtained on irradiation of **1f–h** with regard to a conformer **2'**. The transients showed first order kinetics in the nanosecond range (Table 1).

2.4. Photochemical ring opening

The fluorescence and fluorescence lifetime data of **1** and **3** were measured (Table 2). The excitation maxima of **1/3** are between 335 and 457 nm, the emission maxima between 471 and 545 nm. The excitation and absorption maxima do not correspond. This means that the excited state is not identical with the state, from which fluorescence occurs. There are Stokes shifts between 62 and 180 nm. Thus the excited state S₁ of **3** is more polar than the ground state S₀, so that the polar solvent ethanol is able to stabilize S₁ more than S₀. The singlet energies E_{S1} of **3** and the low fluorescence quantum yields ($\phi_F \approx 10^{-3}$; reference: diacetyl) are in the normal range for DHI **1**. Only **3c** shows a strong yellow fluorescence in a matrix of ethanol glass at 77 K ($\phi_F = 1.51 \times 10^{-3}$ in liquid air); betaine **4c** was not detectable during irradiation with polychromatic light. The fluorescence lifetimes

Table 2

Emission data, singlet energies E_{S1} , fluorescence quantum yields ϕ_f and experimental fluorescence lifetimes τ_f of DHI **1** and DHF **3**^a

Compound	λ_{ex} (nm)	λ_{em} (nm)	$\Delta\lambda$ (nm)	$\lambda_{0 \rightarrow 0}$ (nm)	E_{S1} (kJ/mol)	ϕ_f^b ($\times 10^3$)	τ_F (%) ($\times 10^9$ s)
1a	419	490	71	444	269.4	0.28	0.98 [5]
1b	369	487	118	440	271.9	0.76	–
1c	457	545	88	481	248.7	1.08	–
1d	364	518	154	460	260.0	1.40	16.20 [5]
1e	340	493	153	430	278.0	–	0.68 [1]
1f	404	506	102	440	271.9	0.47	–
1g	420	512	92	456	262.3	1.49	–
1h	335	515	180	434	275.6	0.97	–
3a	430 ^c	507 ^c	77	457	261.8 ^c	1.19	0.876 (48)
3b	409	471	62	423	282.8	0.48	0.162 (93)
3c	410	498	88	453	264.1	1.51	0.300 ^d (80)
3c	453 ^c	535 ^c	61	472	253.4 ^c	–	–
3d	433 ^c	530 ^c	97	486	246.1 ^c	–	0.885 (24)

^a In dichloromethane at 298 K, if not mentioned otherwise; λ_{ex} : maximum of excitation wavelengths and λ_{em} : maximum of emission wavelengths.^b Reference: diacetyl.^c In ethanol at 298 K.^d Measured with a Nd-Yag-Laser.

of **3** were measured in dichloromethane at room temperature by single photon counting. We found an approximately monoexponential decay in the spectra of **3b** and **3c**, but a biexponential decay for **3a** and **3d**. The values are between $\tau_F=45$ –300 ps. A LASER flash photolysis study gave a value of $\tau_F=150$ ps for **3b** (Figs. 1 and 2).

Earlier investigations of DHI of type **1** have shown similar biexponential decays in a few cases [18,19]. An explanation could be the existence of two excited conformers being responsible for the photoproduct and the fluorescence [6].

In DHI's **1** (Andreis [8,20,21] and Scheidhauer [22]) the measured monoexponential fluorescence lifetimes lie in the

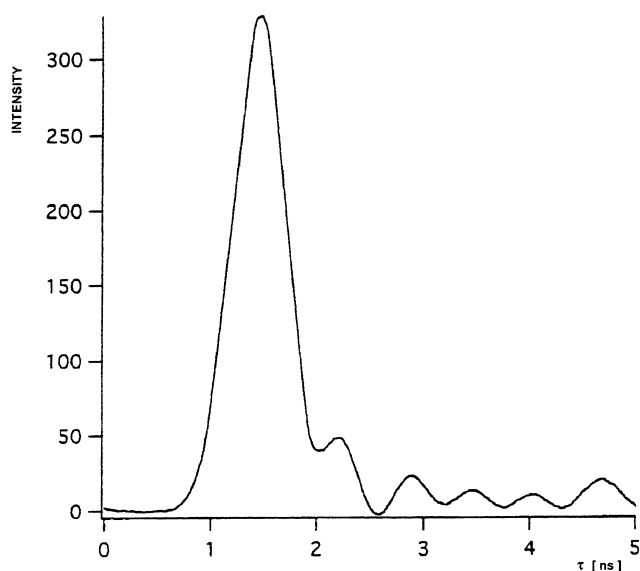


Fig. 1. Time-resolved fluorescence emission of **3b** measured with a Nd-Yag-Laser at 500 nm in CH_2Cl_2 and by the single photon counting method ($\tau_{3b} < 0.30$ ns).

range between 30 and ~ 700 ps. With **3** no fluorescence of the betaines **4** nor triplet states by quenching of **3** with azulene (in ethanol) was detected. A geometrical optimization (PM3/Sunwork Station, Solaris 25, MOPAC 7.00) for the structure of the DHF **3** (unsubstituted) shows that two conformers are possible ($\Delta H=28$ kcal/mol) which equilibrated via N-inversion with a barrier of $\Delta E=8.6$ kcal/mol. Thus for the photochemistry these different conformers may also interfere with the photochemistry.

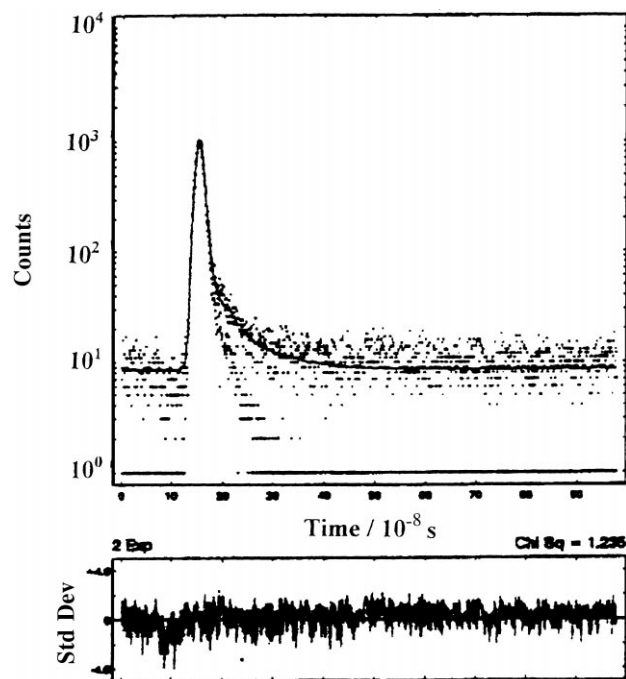


Fig. 2. Fluorescence lifetime decay determined by single photon counting of **3b** ($\lambda_{ex}=419$ nm, $\lambda_{em}=471$ nm; $\tau_{S1}=0.162$ ns (93.1%), $\tau_{S2}=8.12$ ns (6.9%)).

3. Conclusion

DHI systems **1** and **3** have been prepared and characterized showing a fast 1,5-electrocyclization **2** → **1** or **4** → **3** after irradiation of **1** or **3**. The transients formed on irradiation of **3** undergo a very fast electrocyclization **4** → **3**. Ring annulation in the *cis* fixed **4** molecules suppresses rotation and thus produces colored transients in the nanosecond domain. This the fastest thermally reverting systems in this series [1].

4. Experimental

4.1. Apparatus

UV- and F-spectra were measured with Uvikon 860, CONTRON and fluorescence spectrometer F-3000, HITACHI. The single photon counting experiments were carried out in a EDINBURGH INSTRUMENTS apparatus, Model FL-900.

LASER-fluorescence and absorption spectra were obtained with a 2 MW N₂-LASER ($\lambda=337$ nm) described in l.c. [11]. and a Nd-YAG-LASER ($\lambda=389$ nm).

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