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## Photochromic Spirotetrahydroazafluorenes: Part V. Why Photochromic Molecules with Rigid Region B Exhibiting Extremely Fast Bleaching Process?

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*Spirotetrahydroindolizines (THIs) 1a-g and Spirotetrahydroazafluorenes (THF) 2a-g were previously synthesized. The high reaction rate of the thermal 1,5-electrocyclization results in the half-lives of the colored betaines 2'a-g range from 3.9 to 5.4 ns, thus showing the existence of the shortest lived colored form observed so far for pyrazoline based photochromes. However, laser flash spectroscopy was successfully used for the determination of both the half-life and absorption maxima of the colored betaines 2'a-g. Time resolved transient spectroscopy shows the geometry of the betaines 2'a-g to be related to one of the two detectable intermediates 1'a-g or 1''a-g.*

**Keywords:** flash photolysis; short-lived photochromes; spiroetrahydroazafluorenes

## INTRODUCTION

Photochromic dihydroindolizines DHIs and tetrahydroindolizines THIs undergo a photo-induced change of color in solutions and in polymer matrices when exposed to UV radiation or direct sunlight exposure.

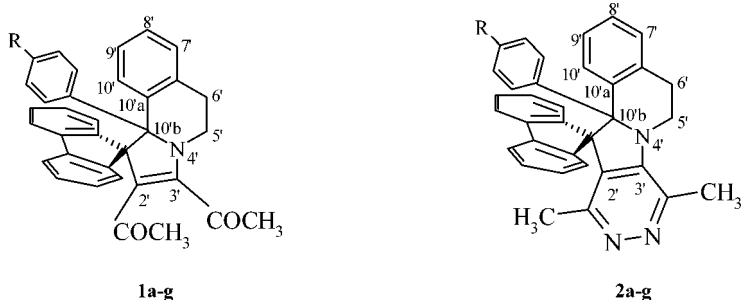
Many thanks are due to Prof. Dr. Aboel-Magd A. Abdel-Wahab for his helpful discussions and Dr. Thomas Hartmann for his assistance with the laser measurements.

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The thermal back reaction- the 1,5-electrocyclization- from the ring-open betaine to DHI shows rates extending from milliseconds to several weeks [1,2–5] depending on the substituents and structure of the involved molecule. This manuscript will shed light on the different intermediates controlling the photochromic behavior of the ultra-fast bleaching process of the *cis*-fixed betaine forms of THFs **2**.

## RESULT AND DISCUSSIONS

Photochromic THIs **1a–g** and THF **2a–g** were previously prepared [6]. The kinetic of the 1,5-electrocyclization of betaine forms of THIs **1a–f** was measured using UV/VIS in CH<sub>2</sub>Cl<sub>2</sub> at ambient temperature (Table 1). The colored betaine forms of THIs **1a–f** showed half-lives ( $t_{1/2}$ ) between 10–96s depending on the substituents in the 10'b-phenyl ring. Millisecond (ms) flash photolysis (Table 1) was successfully used to determine, in addition to  $\lambda_{\max}$  of betaine form of THI **1g**, the kinetics of the thermal back reaction. In the case of the betaines **2'a–g**, the extremely fast bleaching process hindered the measurement of both half-lives and absorption maxima of the ultrafast electrocyclization process of the betaine **2'a–g** to the **2a–g**.



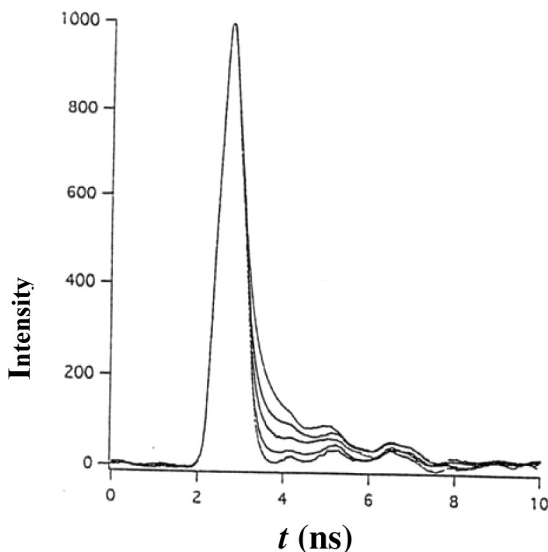
The kinetic of the thermal 1,5-electrocyclization of **2'a–g** were measured with a laser flash absorption apparatus described earlier [7–9]. The absorption spectra were recorded by time resolved spectroscopy. The time domains from  $10^{-3}$  to  $10^{-9}$  were monitored. Thus only half-lives for **2'a–g** in the range of a few nanoseconds ( $t_{1/2} = 3.1$ – $5.4$  ns) were found (Table 1, Figure 1). So ring fusion in region B of **2a–g** results in an acceleration of the thermal 1,5-electrocyclization of **2'a–g** to **2a–g**. A stabilization of **2'a–g** by protonation in position 1' with mineral acids that has been shown previously [1,10,11] was not possible in this case.

**TABLE 1** UV-data of THI **1a-g** and THF **2a-g** and their Colored Forms of THIs **1a-g** and **2a-g** and Kinetics of the 1,5-Electrocyclization of the Betaine Forms of THIs **1a-g** and **2a-g**

Comp.	$\lambda_{\max}$ 1/2 [nm]	$\lambda_{\max}$ 1'''/2' [nm]	Color of betaine	$t_{1/2}$ (s) of betaine 1'''	$k_{(Y''')}\times 10^3\text{s}^{-1}$	$t_{1/2}$ (ns)	1'/1, 2'/2	$k_{-1}(\times 10^{-8}\text{s}^{-1})$
<b>1a/1'''a</b>	370 <sup>a</sup>	470/700 <sup>a</sup>	Green	47 <sup>a</sup>	14.75	—	—	—
<b>1b/1'''b</b>	375 <sup>a</sup>	469/698 <sup>a</sup>	Green	59 <sup>a</sup>	11.75	—	—	—
<b>1c/1'''c</b>	376 <sup>a</sup>	472/699 <sup>a</sup>	Green	58 <sup>a</sup>	11.95	—	—	—
<b>1d/1'''d</b>	387 <sup>a</sup>	475/680 <sup>a</sup>	Blue-green	25 <sup>a</sup>	27.73	—	—	—
<b>1e/1'''e</b>	364 <sup>a</sup>	477/684 <sup>a</sup>	Blue-green	15 <sup>a</sup>	46.21	5.4 <sup>a</sup>	5.2 <sup>a</sup>	1.28
<b>1f/1'''f</b>	363 <sup>a</sup>	476/689 <sup>a</sup>	Green-green	7 <sup>a</sup>	99.02	5.2 <sup>a</sup>	5.0 <sup>a</sup>	1.33
<b>1g/1'''g</b>	401 <sup>a</sup>	700 <sup>a</sup>	Green-green	0.023 <sup>a</sup>	30136.83	5.0 <sup>a</sup>	3.9 <sup>b</sup>	1.39
<b>2a/2'a</b>	343 <sup>b</sup>	455/620 <sup>b</sup>	Blue	—	—	3.1 <sup>b</sup>	2.23	1.78
<b>2b/2'b</b>	346 <sup>b</sup>	454/624 <sup>b</sup>	Blue	—	—	3.5 <sup>b</sup>	1.98	2.23
<b>2c/2'c</b>	352 <sup>b</sup>	449/625 <sup>b</sup>	Blue	—	—	3.7 <sup>b</sup>	1.87	1.98
<b>2d/2'd</b>	350 <sup>b</sup>	446/615 <sup>b</sup>	Blue	—	—	3.2 <sup>b</sup>	2.17	1.87
<b>2e/2'e</b>	341 <sup>b</sup>	444/620 <sup>b</sup>	Blue	—	—	3.1 <sup>b</sup>	2.26	2.17
<b>2f/2'f</b>	339 <sup>b</sup>	439/618 <sup>b</sup>	Blue	—	—	4.3 <sup>b</sup>	16.12	2.26
<b>2g/2'g</b>	373 <sup>b</sup>	454/634 <sup>b</sup>	Blue	—	—	—	—	16.12

<sup>a</sup>At 296 K in CH<sub>2</sub>Cl<sub>2</sub>, c = 1 × 10<sup>-4</sup> mol/l.

<sup>b</sup>At 296 K in Ethanol, c = 1 × 10<sup>-4</sup> mol/l.

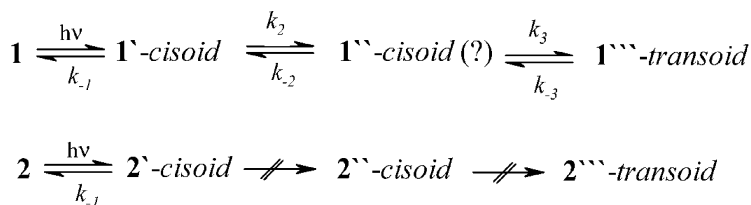


**FIGURE 1** Time-resolved fluorescence emission of **2c** measured with a Nd-Yag-laser at 500, 550, 600, 650 and 700 nm in  $\text{CH}_2\text{Cl}_2$  and by the single photon counting method ( $t_{4e} < 0.30$  ns).

According to Fromm et al. [12], these results are explained as follows: The electron withdrawing 3'-acetyl is stabilized the ring-open form **1'''a-g** by reducing the negative charge at C1'; which has  $\text{sp}^2$  character. However, the ring closure is only initiated in the case of a  $\text{sp}^3$ -hybridization of C1'. Dorweiler [13] showed that this is borne out by MINDO3 calculations. So the electrocyclization is slowed down by a low electron density at C1'. The *transoid* betaine conformer **1'''a-g** is formed from the *cisoid* **1'a-g** by rotations around the axes C2'-C3' and C3'-N4'. The energy barriers between the conformers **1'a-g**, **1''a-g** and **1'''a-g** are small. Collet [14] could determine a rotational barrier C1'-C2' (with double bond character) to be 36 KJ/mol. The geometry of **1'''a-g** was proved by x-ray of a stable betaine by Münzamy [15]. According to this result, the most stable relaxed *transoid* betaine **1'''a-g** 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  $\text{R}^4\text{-C2}$  and  $\text{C3-R}^4\text{3'}$  ( $\text{R}^4$ : methyl ester). The geometry of **1''a-g** is not exactly known whereas **1'a-g** must be close to the one of THIs **1a-g**.

In contrast to these results in betaine **2'a-g** the rotation between C2' and C3' is impossible because of the annulated heterocyclic ring.

The molecule **2'a-g** 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  $sp^3$  character of C1' is maintained to a large extent because of decreasing withdrawal of charge by the aromatic isoquinoline ring (C2' and C3'). Thus the geometry of the betaine **2'a-g** is similar to the starting material, the THF **2a-g**. Therefore, this structure is favorable for fast thermal disrotatory [9] 1,5-electrocyclization of **2'** (obtained by irradiation of **2a-g**). It is 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 **2'** → **1**. The rate constant  $k_{-3}$  ( $\ln 2/k = t_{1/2}$ ) is much smaller than  $k_{-2}$  and  $k_{-1}$ . Now the different steps and intermediates involved in the ring opening of **2** and cyclization of **2'a-g** can be explained with the following reaction sequence (for the structure of **1'**, **1''**, **1'''**, **2'**, **2''**, **2'''** see reference 6):



In conclusion, novel type of photochromic THF **2a-g** showed a fast 1,5-electrocyclization process, which cannot be detected by UV/Vis or millisecond flash photolysis technique. Ring annulation in the *cis*-fixed **2'a-g** molecules suppresses rotation and thus produces colored transients in the nanosecond domain. The new system is an interesting candidate for pattern recognition system and it will find its application.

## REFERENCES

- [1] Dürr, H. & Bouas-Laurent. H. (1990, 2003). *Photochromism: Molecules and Systems*. Vol 1,2., Elsevier: Amsterdam.
- [2] Ahmed, S. A., Hartmann, T., Huch, V., Dürr, H., & Abdel-Wahab, A. A. (2000). *J. Phys. Org. Chem.*, **13**, 539.
- [3] Tan, Y. S., Ahmed, S. A., Dürr, H., Huch, V., & Abdel-Wahab, A. A. (2001). *Chem. Commun.*, **14**, 1246.
- [4] Fromm, R., Ahmed, S. A., Hartmann, T., Huch, V., Abdel-Wahab, A. A., & Dürr, H. (2001). *Eur. J. Org. Chem.*, **21**, 4077.
- [5] Ahmed, S. A., Abdel-Wahab, A. A., & Dürr, H. (2003). *J. Photochem. Photobiol. A.*, **154**, 131.
- [6] Ahmed, S. A. (2005). *Mol. Cry. & Liq. Cry.*, **430**, 295.

- [7] Ahmed, S. A. (2002). *J. Phys. Org. Chem.*, *15*, 392.
- [8] Tan, Y. S., Hartmann, Th., Huch, V., Dürr, H., & Kossanyi, K. (2001). *J. Org. Chem.*, *66*, 1130.
- [9] Fromm, R., Born, R., Dürr, H., Kannengiesser, J., Breuer, H.-D., Valat, P., & Kossanyi, J. (2000). *J. Photochem. & Photobiol.*, *135*, 85.
- [10] Weber, C., Rustemeyer, F., & Dürr, H. (1998). *Adv. Mater.*, *10*, 1348.
- [11] Dürr, H. (1989). *Angew. Chem.*, *101*, 427. *Angew. Chem. Int. Ed. Engl.* *28*, 413.
- [12] Dorweiler, C., Münzmay, T., Spang, P., Holderbaum, M., Dürr, H., Raabe, E., & Kürger, K. (1988). *Chem Ber.*, *121*, 843.
- [13] Collet, C. (1994). *Master Thesis*, Universität des Saarlands, Saarbrücken.
- [14] Münzamy, T. (1986). *Ph. D Thesis*, Universität des Saarlands, Saarbrücken.