

Spectrokinetic studies of two 6,6a-dihydrochromeno(3,4-b)chromene derivatives

Aimé-Jhustelin ABOGO MEBALE,^{1*} Alain MAGGIANI,² Roger ONDO NDONG,¹ Guy Buntinx,³

Jean Aubin ONDO,¹ Honoré GNANGA,¹ André SAMAT.²

¹Laboratoire Pluridisciplinaire des Sciences (LAPLUS), Ecole Normale Supérieure
BP 17009 Libreville, Gabon.

²CINaM, CNRS UMR 7325, Aix-Marseille Université
Faculté des Sciences de Luminy, 163 Avenue de Luminy, Case 901
F-13288 Marseille Cedex 9 France.

³Laboratoire de Spectrochimie Infrarouge et Raman, UMR-CNRS 8516
Université des Sciences et Technologies de Lille
Cité Scientifique, 59650 Villeneuve d'Ascq.

* E-mail of the corresponding author: abogo.mebale@yahoo.fr

Abstract

Benzo and Naphthopyrans (chromenes) have been extensively studied since the discovery of photochromic reaction of 2H-1-benzopyrans in 1966 by Becker and Michl. Researchers have investigated chromenes for their use in sunglass lenses and also other potential applications such as optical memories and optical switches. Femto/picosecond and nano/microsecond experiments were released on two 6,6a-dihydrochromeno(3,4-b)chromene derivatives. After disappearance of the singlet state S_1 formed from each compound, photoproducts with short lifetime (2.2 to 21 μ s) obtained were attributed to the open forms.

Keywords: 6,6a-dihydrochromeno(3,4-b)chromene, photochromic, nano/microsecond domain, femto/picosecond domain, wavelength, lifetime.

1. Introduction

Chromenes (benzopyrans) are compounds with excellent pharmacological (Cassidi *et al*, 1992) and photochromic (Guglielmetti *et al*, 1999) properties. Since the industrial marketing of the first photochromic lenses (Crano *et al*, 1992), the studies moving towards the development of new systems of photochromic compounds (Maggiani *et al*, 2005). Many studies showed that the bichromenes can develop a persistent staining after UV irradiation (Berthet *et al*, 2004; Samat *et al*, 2004). On the over hand, the photochromic properties observed can be consider as the sum of those of each chromene unit (Berthet *et al*, 2004; Samat *et al*, 2004).

This paper presents the study of the photochemical behavior of two compounds derived from 6,6a-dihydrochromeno(3,4-b)chromene to elucidate the process of ring opening who occurs (Delbaere *et al*, 1998).

2. Results and discussion

2.1 Description of the spectra.

Analysis were performed on the compounds **A** and **B** represented in the figure 1 (Abogo Mebale *et al*, 2006; Abogo Mebale *et al*, 2012). Their absorption spectra in the ultraviolet and visible (UV-Visible) showed similar maximum wavelength (λ_{max}) : 352 nm for **A** and 348 nm for **B** (Figure 2).

In femto/picosecond domain, the spectra obtained after photo-irradiation show a strong absorption band centered at 530-560 nm and a negative signal (bleaching signal) to 400 nm (Figure 3).

After excitation in the nano/microsecond domain, the spectra show intense bleaching signal (Figure 4) whose shape corresponds to the electronic absorption spectra of compounds **A** and **B**.

2.2 Interpretation of results.

In femto/picosecond experiments, absorption bands and bleaching signals disappear with the same kinetics. This is due to the excited singlet state S_1 (Aubard et al, 2000; Birks, 1973). After the disappearance of S_1 , new chemical species with wide spectrum absorption, very low intensity and stable in the 100-1500 ps are observed. The maximum wavelength of the spectrum, better seen in the nano/microsecond experiment, is at 420 nm for the compound **C** and 400 nm for compound **D** respectively formed from the excitation of **A** and **B** (Table 1).

The kinetics of disappearance of **C** (2.2 to 4 μ s) and **D** (4.1 to 21 μ s) is insensitive to the presence of oxygen (O_2). These compounds do not correspond to the triplet state T_1 (Birks, 1973; Turro, 1978). In addition, tests using hexane show that the absorbance is independent of the polarity of the solvent. There is linear variation of the intensity of the absorption spectrum with the intensity of the excitation whatever the solvent used. Species **C** and **D** are not the radicals cations (Lomoth et al, 1998; Stirk et al, 1992).

The rapid disappearance of **C** and **D** is accompanied by the almost total decline, with the same kinetic, of the bleaching signal restoring almost compounds **A** and **B** respectively. **C** and **D** are the products of the isomerization reaction of the closed form following the photo-excitation (Aubard et al, 2000). The maximum wavelength of **C** is higher than that of **A** and **D** higher than that of **B**; **C** and **D** correspond to the chemical structure of the intermediate open form **OF1** or the final open form **OF2** (Figure 5). The important difference of thermal stability of the compounds **C** and **D** shows a dual ring opening occurs directly after the photon excitation. The stability of **D** is due to the presence of the phenyl group which stabilizes the system by conjugation. Compounds **C** and **D** should correspond to the open form **OF2**.

After 100 μ s, a residual spectrum and a light bleaching signal is still after disappearance of **C** and **D** in each case. The presence of these signals indicates that a minority of molecules are not returned to the initial state. This residual spectrum could correspond to another open form more stable than the previous one. Compound **B** leads to a residual spectrum of significant amplitude (23 to 26%), which is clearly distinguishable from that of the compound **D**. Her maximum wavelength is on the blue. This molecule is therefore more conjugated than **D**.

3. Experimental section

3.1 Nano/microsecond domain

Experiments were performed using as excitation source the third harmonic (355 nm, 8 ns, 1 mJ) of a Nd: Yag laser (Thales Laser DIVA) and as a source of white light lamp xenon, an optical configuration in cross Bonneau et al, 1997). The light transmitted by the sample is dispersed by a monochromator and detected by a photomultiplier (Applied Photophysics Model 504) coupled to a digital oscilloscope (Tektronix TDS 540). It is therefore a single-channel detection. Each measurement provides, for a wavelength selected by the monochromator, the time variation of the transient absorbance (ΔOD). From these kinetics, spectra can be reconstructed at selected times. The spectral investigation covers the region 300-650 nm. The time domain extends from 0.1 to 100 μ s. The samples were placed in a quartz cell of 4 ml (section 1 cm x 1 cm) sealed with a device for degassing. Solutions were studied firstly under an inert atmosphere after degassing with N_2 during 15 min, secondly under an atmosphere of O_2 . The sample concentration (10^{-4} mol.L⁻¹) was adjusted so as to have an optical density of 1.0 at the wavelength 355 nm.

3.2 Femto/picosecond domain

Experiments were performed using a laser Ti: Sa oscillator (Coherent MIRA 900D + regenerative amplifier BM Industries alpha 1000) operating at 1 kHz (Buntinx et al, 1996). The excitation of pump (383 nm , 80 fs, 5 μ J) corresponds to the second harmonic of the system. A pulse characterized by a continuum of spectrally white light, covering the area from 390 to 700 nm (about 80 fs), generated by focusing a portion of the laser pulse in a window of CaF₂ is used as a probe. This is time-delayed relative to the excitation pulse using a delay optical line (Microcontrol Model MT160-250PP) with the precision ± 1 μ m. The polarizations of the pump pulses and probe are adjusted to 54° from each other. The overall time resolution of the experiment (full width at half-height of the cross-correlation signal pump-probe) is estimated at about 300 fs. The probe pulse is split into two parallel beams from both in the sample (Salin, 1998; Bonneau et al, 1997). The lights transmitted on the two channels are simultaneously analyzed by a multi channel detector (CCD camera Princeton Instrument LN/CCD-1340/400-EB) and provides a direct ratio of the variation range of transient absorption (ΔOD) generated by the excitation of the pump within the pump-probe selected by the delay line. From the spectra obtained for different possible pump-probe the kinetics may be reconstituted to selected wavelengths. The spectral investigation covers the region 390-700 nm. The time domain extends from 0.3 to 1500 ps. The sample (concentration of 10⁻³ mol.L⁻¹) is placed in a flow cell (to minimize the photodegradation). The spectra were accumulated during 3 minutes (or 180 000 pump-probe sequences).

4. Conclusion

Spectrokinetic studies released on compounds **A** and **B** in the nano/microsecond and femto/picosecond domains showed that 6,6a-dihydrochromeno(3,4-*b*)chromenes derivatives can undergo a double ring opening after photoirradiation . The thermal instability of the species **C** and **D** is a limiting factor for photochromic applications of these compounds. More investigations should therefore continue to improve on this very important parameter.

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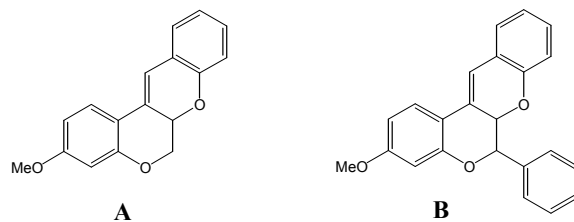
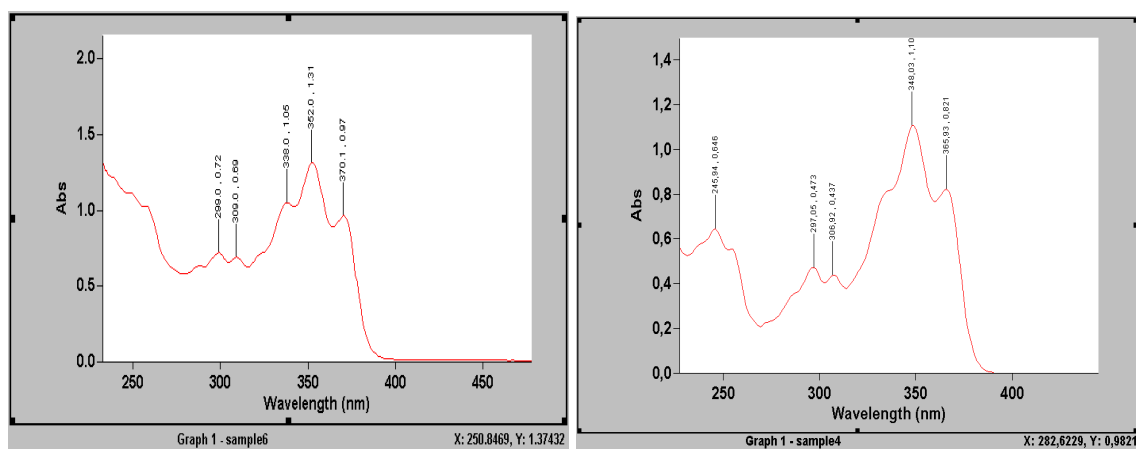


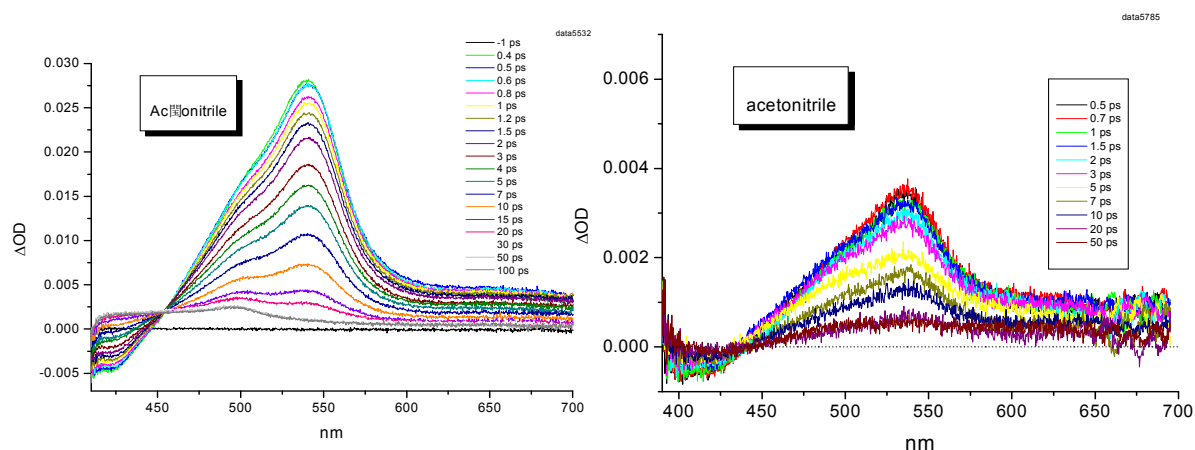
Figure 1. Structure of compounds **A** and **B**.



Spectrum of **A**

Spectrum of **B**

Figure 2. Absorption spectra of compounds **A** and **B**. in acetonitrile at 5.10^{-4} mol.L $^{-1}$.



Spectrum of **A**

Spectrum of **B**

Figure 3. Spectra of compounds **A** and **B** in femto/picosecond domain.

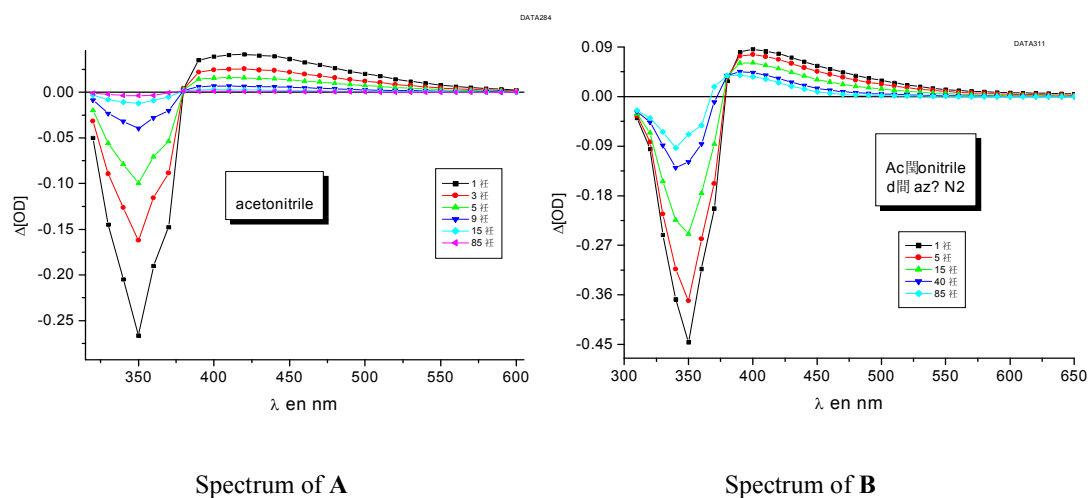


Figure 4. Spectra of compounds **A** and **B** in nano/microsecond domain.

Table 1. Spectrokinetic results.

	Absorption and lifetime of S_1		Absorption and lifetime of C and D		bleaching	Residual spectrum $t > 100 \mu s$
	λ_{max} / nm	$t_{1/2} / ps$	λ_{max} / nm	$t_{1/2} / \mu s$	λ_{max} / nm	%
A	542	6,1	420	acetonitrile : 4 hexane : 2,2	350, ep 370	acetonitrile: 1,5% hexane : 2%
B	535	5.8	400	acetonitrile: 21 hexane: 4,1	350, ep 370	acetonitrile: 23% hexane : 26%

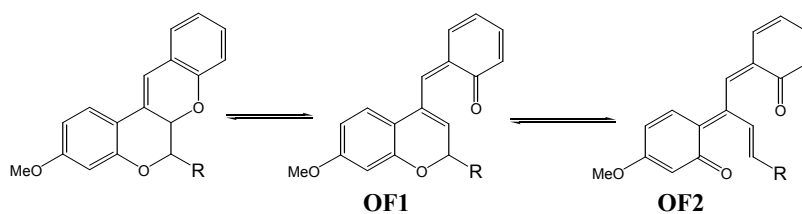


Figure 5. Photochemical opening of chromenes.

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