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Short communication

A thermochromism study in the ferrocenyl-benzopyran series

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The synthesis and the photochromic behaviour of a series of benzopyrans (otherwise called 2*H*-chromenes), substituted in the 2-position by a metallocene, have been previously described. Some of these compounds also present thermochromic properties. As the thermochromism has been scarcely studied in the benzopyran series, we describe here a study of the thermochromic properties of ferrocenyl benzopyrans. The correlations between the structure of the compounds investigated and their thermochromic properties are discussed. Copyright © 2004 John Wiley & Sons, Ltd.

KEYWORDS: ferrocenyl benzopyrans; photochromism; thermochromism

INTRODUCTION

The cleavage of the 2*H*-benzopyran's C–O bond leads to open forms[1] (OFs) which are more conjugated than the initial closed forms (CFs) (Scheme 1). The result of this process is a shift of the absorption range from the UV to the visible region. The reclosing of the OF to the initial CF is generally a thermal process, but in some cases it may also be observed under visible irradiation.

Two processes can lead to the cleavage of the 2*H*-benzopyran's C–O bond (Scheme 1): the well known and reviewed photochemical one (under UV irradiation), and a thermal one. The latter is quite uncommon,[2] but it has been already described in our group for 2-aryl-2-methyl-[2*H*]benzopyrans.[3] Generally, these two processes are concomitant, their relative importance depending on the structures and the temperature.

In previous studies on the photochromic properties of metallocenyl-benzopyrans,[4,5] thermochromic behaviour was observed for the compounds characterized by the presence of a ferrocenyl group in the 2-position and by a [7,8] or [5,6–7,8] annellation (Scheme 2).

It must be noted that, contrariy to the ferrocenyl-benzopyrans, the ruthenocenyl- and osmocenyl-benzopyrans[6] do not present any thermochromic properties; in the latter case, a 'normal' behaviour, i.e. increase of the thermal ring closure kinetics, is observed when temperature increases.

Because of this characteristic behaviour, the ferrocenyl-benzopyrans **1** to **5** were studied and their thermochromic properties were compared with those of their phenyl analogues **6** and **7**.

The structures of the compounds studied (Scheme 2) are reported in Table 1. Their synthesis has been described previously (see references in Table 1).

EXPERIMENTAL

Photochromic data were obtained using a Beckman DU-7500 spectrophotometer; irradiation was performed with an Oriel 150 W high-pressure xenon lamp using an optical fibre and a thermostated quartz cell. The thermochromism study has been realized using a Cary 50 Scan spectrophotometer fitted with a thermostated quartz cell. With this equipment, the temperature can be controlled between 10 and 80 °C. All the experiments were made in the dark in order to observe the thermochromic ring-opening process. The optical density (OD) values have been measured in anhydrous toluene solutions (high-performance liquid chromatography grade) using concentrations of 5×10^{-4} mol l^{-1}.

Compounds **1** to **7** were prepared according to procedures listed in the references indicated in Table 1.

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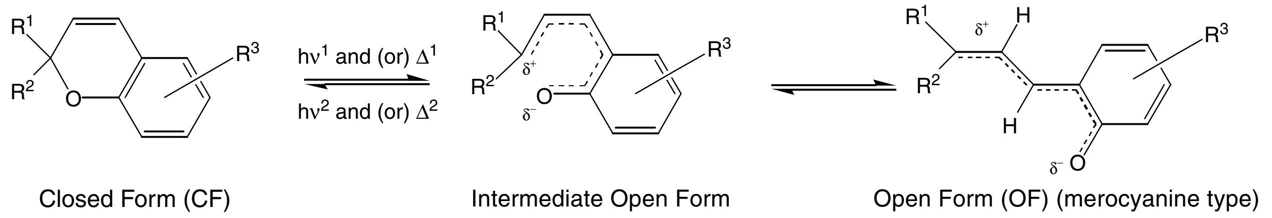
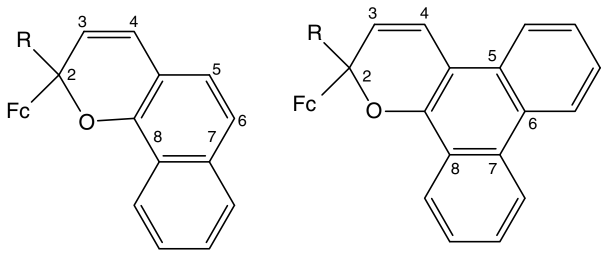


Scheme 1.



Scheme 2. The [7,8] and [5,6–7,8] annellatted ferrocenylbenzopyrans.

Table 1. Structures of the compounds studied

Compound	Ref.	R^1	R^2	Annellation
1	4	Fc	Ph	[7,8]
2	6	Fc	Me	[5,6–7,8]
3	5	Fc	Ph	[5,6–7,8]
4	5	Fc	*p*-(F_3C)Ph	[5,6–7,8]
5	5	Fc	*p*-MeOPh	[5,6–7,8]
6	5	Ph	Ph	[7,8]
7	7	Ph	Ph	[5,6–7,8]

RESULTS AND DISCUSSION

The λ_{max} of the OF (λ_{max}/Δ, determined under heating at 50 °C in toluene) and the λ_{max} of the OF under UV irradiation ($\lambda_{max}/h\nu$; measured at 25 °C, also in toluene) are reported in Table 2.

It can be seen from Table 2 that the observed λ_{max} values are quite similar for the two processes.[8] This means that the two opening processes lead to the same types of OF stereoisomer.

The ability of the ferrocene to enhance the thermochromic process is shown by comparing the behaviour of compounds **1** and **6**. The comparison of the behaviour of compounds **6** and **7** stresses another relation between the structure and the thermochromic properties: the thermal C–O bond cleavage is easier for the phenanthrenopyran (**7**) than for the naphthalenopyran (**6**). It seems that extended π conjugation facilitates the thermochromic process. It must be noted that, in the case of compound **2**, thermochromism is not observed at 50 °C; the replacement of a phenyl group by a methyl group increases the necessary activation energy $\Delta G^{\ddagger}$ and the thermal ring-opening process was not observed at 50 °C. However, a small thermochromic behaviour can be detected for **2** at higher temperature.

Table 2. λ_{max} of the OF observed under thermal (Δ) and photochemical (hν) conditions

Compound	λ_{max}/Δ (nm)	$\lambda_{max}/h\nu$ (nm)
1	459,605	467,600
2	Not thermochromic	440,563
3	444,584	447,600
4	440,585	443,591
5	450,580	454,583
6	Not thermochromic	472
7	420	425

In Fig. 1, the OD determined at the λ_{max} of the OF of compounds **3** and **7** is plotted as a function of the temperature. The curves **3**-1L (first λ_{max}) and **3**-2L (second λ_{max}) represent the OD variation for compound **3** measured at 444 nm and 584 nm respectively. The curve for **7**-1L represents the OD variation for compound **7** measured at 420 nm.

The curves representing the variation of the optical density for the OF of compound **3** are higher than the corresponding one for compound **7**; this result again shows the ferrocene's ability to enhance the thermochromic properties.

Another interesting result can be observed: the shapes of the two curves for compound **3** are not similar: above 30 °C, the thermal ring-opening process for **3**-1L is accelerated compared with **3**-2L. This result shows that the thermal

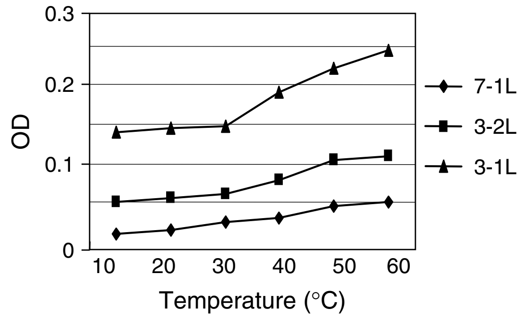


Figure 1. Variation in OD as a function of the temperature for compounds **3** and **7**.

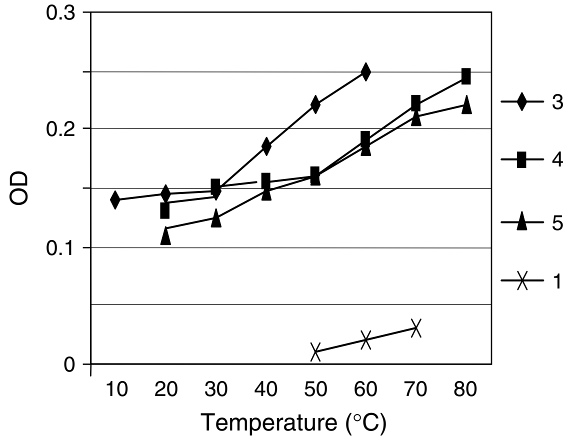


Figure 2. Variation in OD as a function of the temperature for compounds **1, 3, 4** and **5**.

process leads to the formation of two or more different OF stereoisomers.

The OD variation of the ferrocenyl compounds **1, 3, 4** and **5** as a function of the temperature is presented in Fig. 2; the ODs are measured at the lowest λ_{max}, respectively at 459 nm, 444 nm, 440 nm and 450 nm.

The main result shown by Fig. 2 is the decrease of the thermal ring-opening process when the phenanthrene ring is replaced by a naphthalene ring: as noted previously, the thermal opening process for compound **1** starts at higher temperature and the ODs are lower than those of the other compounds at the same temperature.

The similar thermal behaviour of compounds **4** and **5** shows that the electron-donating or electron-withdrawing nature of a group in the para position on the phenyl nucleus has no effect on the thermochromic behaviour.

CONCLUSION

This study has shown another characteristic property of the ferrocenyl-benzopyrans; in addition to their good photochromic behaviour,[4–6] these ferrocenyl-benzopyrans present enhanced thermochromic properties compared with their phenyl homologues. The type of annellation also has a direct influence on the concomitant opening processes, with the [5,6–7,8] annellation being favourable to the thermal process. The different thermochromic behaviours of compound **3**, when measured at two different λ_{max}, show that two or more thermally induced OFs are generated.

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