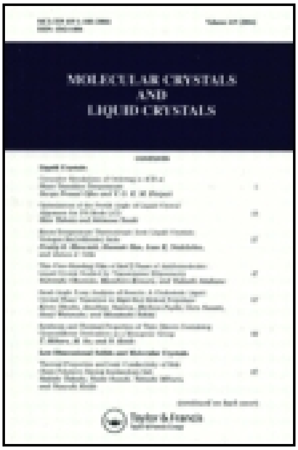

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Synthesis and Spectrokinetic Studies of a Series of 2-Ferrocenyl-2-methyl-[2H]-benzopyranes

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Synthesis and Spectrokinetic Studies of a Series of 2-Ferrocenyl-2–methyl-[2*H*]-benzopyranes

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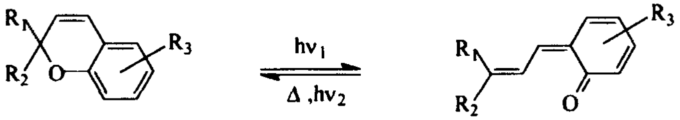
The synthesis of a series of 2-ferrocenyl-2-methyl-[2*H*]-benzopyranes and the results of a spectrokinetic study are presented. A broadening of the absorption band in the visible range and the apparition of a second absorption band is observed as compared with the reference compounds. Furthermore important kinetic modifications are observed. From these results a structure can be proposed for a permanent opened form which is observed in polar protic solvents.

Keywords: ferrocenyl benzopyrane; photochromic compounds

INTRODUCTION :

[2*H*]-benzopyranes (benzochromenes) [1] are an important class of photochromic compounds. Under irradiation these compounds are opened by cleavage of the C-O bond and the so formed opened forms (OF) absorb in the visible range. Generally these OF can be cyclized to the initial closed form (CF) by a thermal process and or by a photochemical one.

Scheme 1

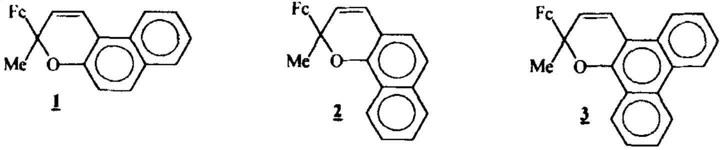


The photochromic properties can be described by 3 factors [2]: the λ_{max} of the opened form, the bleaching kinetic constant, the colorability which is the optical density determined at the λ_{max} under continuous irradiation or under flash photolysis. Previous results have shown that the presence of an aromatic ring on the –2 position of [*2H*]-benzopyranes increases the photochromic properties of these molecules [3]. Ferrocene is an aromatic organometallic group [4] in which an iron^{II} atom is complexed with two cyclopentadienyl systems. The replacement of a phenyl group by such a ferrocenyl one was shown to induce important modifications of the photochromic behaviour [5] with the apparition of a second absorption band in the visible range and also an increase of the kinetic of the closure process. In order to extend these observations we have synthesised a new series of 2-ferrocenyl benzopyranes in which the phenyl group is replaced by a methyl one and also in which we have modified the annulation (5-6, 7-8 and 5-6-7-8). The photochromic properties of these compounds were studied and our results are presented here.

RESULTS:

The synthesis of the three ferrocenyl benzochromenes used in this work (figure 1) was realised as previously described [5]. It must be noted that the condensation of the different phenols used with the propargylic alcohols is realised under acidic conditions. In the case of the ferrocenyl methyl propargylic alcohol, the acidity of the phenols was sufficient to induce the condensation.

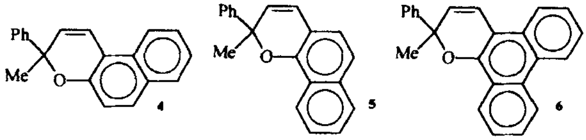
Figure 1



1 2 3

The spectrokinetic parameters of the compounds **1**, **2** and **3** were measured under continuous irradiation [6]. In order to determine the effect of the ferrocenyl group the behaviour of the ferrocenyl benzopyrane was compared with the one of the reference phenyl benzopyranes **4**, **5** and **6** which were prepared using described procedures [7, 8] (figure 2).

Figure 2



Our results are presented in table I.

Table I: Spectrokinetic parameters for compound 1-6

	Acetonitrile	Toluene	Ethanol
1 λ_{max} : $k_{\Delta}(10^{-3}s^{-1})$:	441/ 580 -	425/ 587 -	437/ 584 -
2 λ_{max} : $k_{\Delta}(10^{-3}s^{-1})$:	472/ 609 10.8/ 4.2 (472 nm)	473/ 608 0.9 (473 nm)	396/425/ 608 0 (396 nm) 1.4 (609)
3 λ_{max} : $k_{\Delta}(10^{-3}s^{-1})$:	440/ 563 157.9/ 1.6 (440 nm)	440/563 144.1/ 0.1 (440 nm)	400/530 0 (396 nm)
4 λ_{max} : $k_{\Delta}(10^{-3}s^{-1})$:	410 100/ 0.2	411 160/ 0.4	417 210/ 0.9
5 λ_{max} : $k_{\Delta}(10^{-3}s^{-1})$:	458 21.9/ 1.1	450 14.8/ 0.5	461 5.6/ 0.8
6 λ_{max} : $k_{\Delta}(10^{-3}s^{-1})$:	400 60.8/ 0.8	400 40.5/ 0.2	400 65.9/ 22.8

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DISCUSSION

In the visible range the absorption spectra of the OF of 1, 2 and 3 shows two λ_{max} (400 and 600 nm) while only one absorption band is observed for the parent compounds 4, 5 and 6 (figure 3).

For compound 1 the spectrokinetic parameters cannot be determined because its closure process is too fast. This is not the case for compounds 2 and 3 which present stable OF in ethanol. After irradiation of 2, absorption bands are observed at 396nm, 425nm and 608nm. At 396 nm the optical density does not decrease after the end of the irradiation while the absorptions at 425-608 nm decrease (k_8=1.4 10^{-3} at 608 nm). This is shown in figure 4.

Figure 3

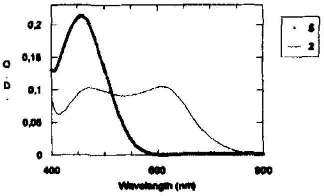
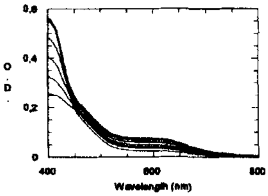


Figure 4



This result indicates that under irradiation different OF are generated: a permanent one (λ_{max}=396nm) and two others (425 and 608nm) which are closed back when the irradiation is stopped. The same behaviour is observed for compound 3. In order to get more informations on this phenomenon we have realised the same studies in different alcohols. Our results are indicated in table II which shows that the behaviour of the OF is controlled by the size of the alcohol used as solvent. This effect is more important in the case of the compound 3.

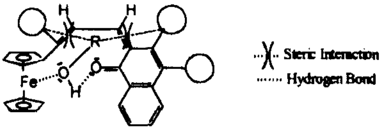
Table II: Spectrokinetic properties of the compounds 2 and 3

	MeOH	EtOH	PrOH	iPrOH	BuOH	iBuOH
2	$k_\Delta = 0$	$k_\Delta = 0$	$k_\Delta = 0$	$k_\Delta \neq 0$	$k_\Delta \approx 0$	$k_\Delta \neq 0$
3	$k_\Delta = 0$	$k_\Delta = 0$	$k_\Delta \approx 0$	$k_\Delta \neq 0$	$k_\Delta \neq 0$	$k_\Delta \neq 0$

The relative acidity of the different alcohols is not responsible for the observed behaviour as the addition of a trace of acid does not modified anything.

In order to accommodate the different observations made : stabilisation by small alcohols, stabilisation for methyl-ferrocenyl derivatives and not for phenyl-ferrocenyl ones, λ_{max} of the stable OF not very different from the one of the CF, we postulate that these permanent OF are of the cisoïde type as represented in figure 5.

Figure 5



When the C-O bond is broken a molecule of a small alcohol can enter in the cavity of such a cisoïde form and by hydrogen bonding and interaction of the oxygen with the iron atom, stabilises it enough, so that a permanent OF is observed. In such a model it is easy to see that when the methyl substituent is replaced by a bulky phenyl group or when a bulky substituent is introduced on the cyclohexadienone moiety such a stabilisation is not any more effective because of steric repulsions. In the absence of alcohol this stereoisomer is transformed into more stable ones which absorption bands appear at 425 and 608 nm.

CONCLUSION

We have prepared a new series of ferrocenyl benzopyranes and we have described their photochromic properties. It was shown that for methyl ferrocenyl benzopyranes, permanent OF can be observed in polar protic solvents. To explain the observed behaviour a cisoïd geometry is proposed and actually NMR studies are under progress in order to get more informations on the geometry of such systems.

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