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Preventing the Formation of the Long-Lived Colored *Transoid-Trans* Photoisomer in Photochromic Benzopyrans

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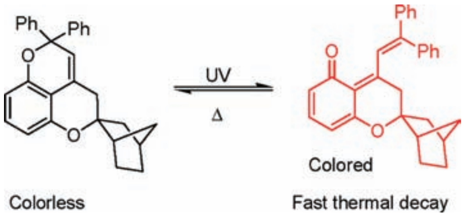
ABSTRACT



A new photochromic fused benzopyran presenting a bridge between the pyran double bond and the benzenic ring was prepared. While the UV irradiation of usual benzopyrans leads to the formation of two colored photoisomers with very different thermal stabilities, studies by laser flash photolysis showed that the presence of this particular bridge prevents the formation of the undesirable long-lived colored TT isomer and therefore after laser irradiation the colored solution fades following a fast monoexponential decay.

The photochromic properties of benzo- and naphthopyrans have been extensively studied in recent decades due to their use in the production of variable-transmission optical materials, namely photochromic plastic ophthalmic lenses that show a rapid and reversible color change when exposed to the sunlight.[1]

The reversible color change is due to the UV promoted pyran ring opening with formation of a *transoid-cis* colored isomer (TC, major product) that, upon isomerization of the double bond, leads to the more stable *transoid-trans* isomer (TT, minor product) (Scheme 1). A photostationary state between the uncolored and colored molecules is usually reached after several minutes of irradiation. The phenomenon occurs in solution or when the photoreactive molecules are incorporated in polymeric matrices although the relative amount of each photoisomer and the kinetic of the photoisomerization is strongly affected by the medium in which they are dispersed.[2]

These two photoisomers, with a strong absorption in the visible part of the spectrum, have very different lifetimes. As a result, after the removal of the light source the system returns to the original colorless state by a process following a biexponential kinetic. While the TC-isomer rapidly returns to the uncolored closed form, the TT-isomer is thermally more stable and is responsible for the persistence

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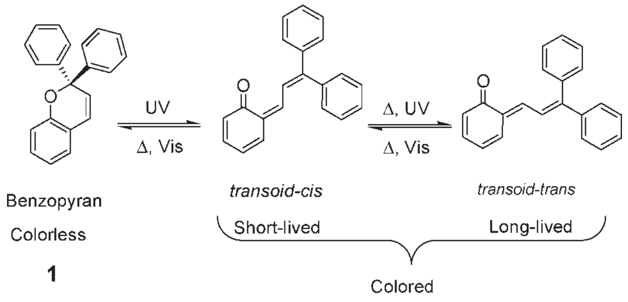
Scheme 1. Photochromic Equilibrium for 2,2-Diphenylbenzopyran **1**



of a residual color for several minutes after the removal of the light source (Figure 1).[3]

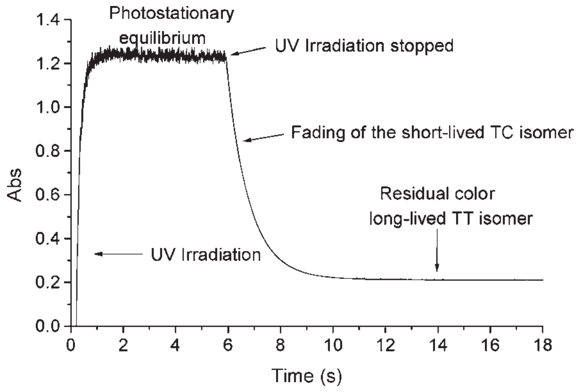
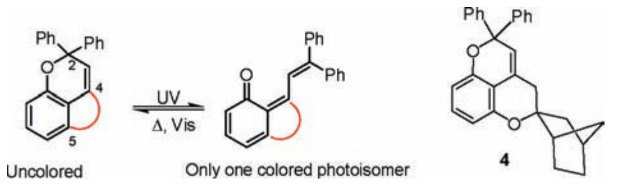


Figure 1. Color forming and color bleaching for usual naphthopyrans in solution measured at λ_{max}.

The color formed, and the kinetics of the bleaching process can be tailored by structural modifications at the benzopyran core or at the aryl rings attached to the sp^3 carbon atom.[4] In recent years many different benzopyran derivatives and especially the parent naphthopyrans have been prepared and patented.[5] However, after UV excitation two colored photoisomers are always formed, and in the absence of light an initial fast decay (thermal conversion of the TC-isomer to the closed form) followed by a slow decay (slow bleaching of the more stable TT-isomer) is persistently observed.

One possible way to prevent the formation of this long-lived TT-isomer is to connect the pyran double bond to the benzenic core (Scheme 2).[6] The introduction of a bridge between carbons 4 and 5 would give rise to a new type of fused benzopyrans where the rotation of the double bond, which produces the long-lived TT isomer, is precluded. Therefore, UV irradiation of such fused benzopyrans should produce only the TC colored photoisomer and then bleach following a monoexponential kinetic thus avoiding the problem of the residual color. To evaluate the feasibility of this approach we prepared the new fused benzopyran **4** (Scheme 2).

Scheme 2. Photochromic Equilibrium for a Fused Naphthopyran



Benzopyrans are usually prepared by condensation of a phenol with 1,1-diarylprop-2-yn-1-ol in an acid medium. This reaction is very general and has been used for the preparation of thousands of double bond unsubstituted benzo- and naphthopyrans.[7] However, to prepare a benzopyran substituted at the double bond a different synthetic approach is needed. Due to the high reactivity of the pyran ring,[6] we decided to create, in a first stage, the dihydropyran bridge and then construct the pyran ring from a lactone system. The new benzopyran **4** was thus prepared in 3 steps from 2′,6′-dihydroxyacetophenone as shown in Scheme 3. The reaction of the 2′,6′-dihydroxyacetophenone with norcamphor in a basic medium gave the benzopyranone **2** as a mixture of two diastereoisomers (75/25). Then the Reformatsky reaction with ethyl bromoacetate/Zn/I_2 followed by reflux in acetic acid afforded directly the fused lactone **3**. Finally, the reaction of this lactone with the Grignard reagent PhMgBr provided, after hydrolysis, the new fused benzopyran **4**.

NMR studies on this compound showed that after 24 h in solution an equilibrium mixture of two benzopyrans is established due to the migration of the pyran double bond. For the benzopyran **4a**, H-3 appeared at 5.75 ppm as a singlet, while protons 9 were observed at 2.63 ppm. After 24 h, a new singlet at 5.41 ppm and an AB system between 3.11 and 3.36 ppm were observed. These signals were attributed to the parent **4b** compound. The C-2 signal

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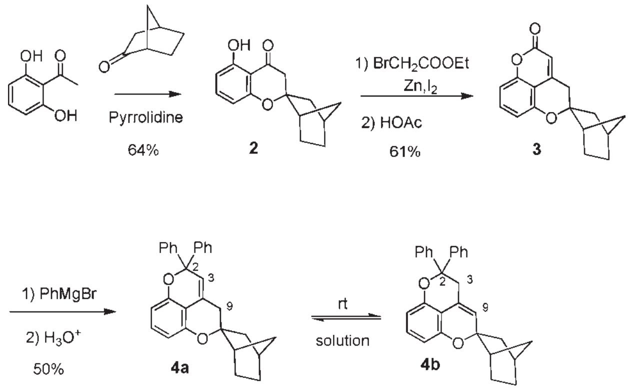
Scheme 3. Synthesis of the New Fused Benzopyran **4**



which is characteristic of 2,2-diarylbenzopyran systems was observed at 83.2 and 82.9 ppm respectively. The full NMR characterization of these two compounds can be found in the Supporting Information (SI). The presence of this equilibrium in solution means that two potential photoreactive benzopyran compounds are present in solution, and therefore, under irradiation, two TC photoisomers corresponding to the overture of each pyran ring are possible.

In toluene solution the known unsubstituted 2,2-diphenylbenzopyran **1** is colorless with a strong absorption in the UV region at 310 nm. Continuous UV−vis irradiation of this solution at 10 °C leads to the development of a slightly yellow coloration with two maxima at 410 and 480 nm (see SI). When the light source was removed the absorbance decreased following, as usual, a biexponential decay with two rate constants: 8.3 s^{-1} for the fast decay TC-isomer (73%) and 0.13 s^{-1} for the bleaching of the long-lived TT-isomer (23%) (see SI).

In acetonitrile solution the new fused benzopyran **4** is also colorless with a strong absorption at 280 nm (Figure 2); however, under continuous UV−vis irradiation no change in the absorption spectrum was observed which indicates that probably the lifetime of the colored species is very short. Since the flash photolysis technique is more adequate for fast fading systems, we decided to investigate the photochromic properties of the fused benzopyran **4** using this method.[8] Laser irradiation at 266 nm of fused benzopyran **4** in acetonitrile, methylcyclohexane, or ethanol solutions led to the fast development of a broad absorption band with two maxima at 390 and 520 nm that can be attributed to a highly conjugated benzopyran open form (Figure 2, Scheme 4).

For benzopyran **4** in all the investigated solvents, the evolution of the absorbance at 390 and 520 nm indicates that the formation of the open form occurs within the laser pulse (ca. 20 ns) and no additional signal (in degassed solutions) could be observed, in the microsecond or millisecond time range, that could be attributed to the triplet state of the closed form (see data for acetonitrile in Table 1). Despite the existence of two absorption bands in Figure 2, we observed that upon excitation with the 266 nm laser pulse, the absorbance measured at 390 or 520 nm decays monoexponentially all over the spectra (instead of the usual biexponential decay observed with benzopyran **1**) (Figure 3) and with a decay time that is only dependent on the solvent polarity. This most likely indicates that only the TC colored open form is present (Scheme 4).

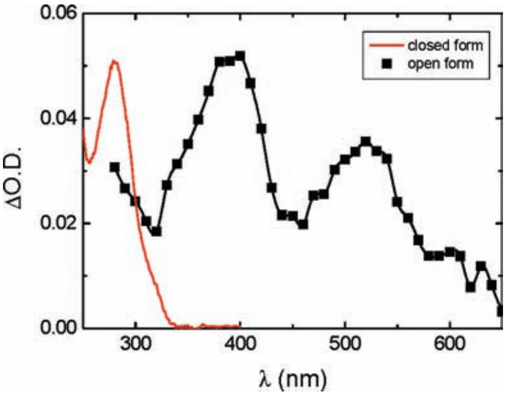


Figure 2. Normalized absorption spectra of the closed and open forms of benzopyran **4** in acetonitrile (10^{-4} M) collected before and after laser irradiation @266 nm (with a 0.16 ms delay after flash).

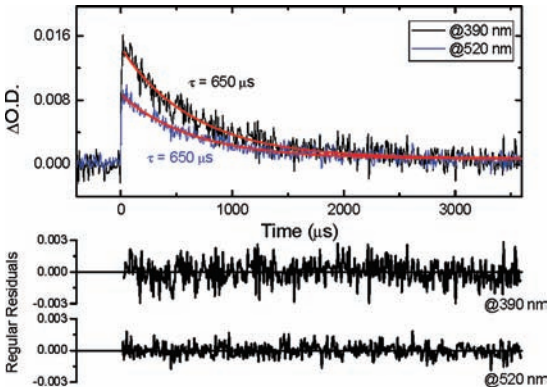


Figure 3. Decay traces for the open form in MeCN collected at 390 and 520 nm. Also displayed are the monoexponential fittings to the decays and the corresponding residual distribution.

The lifetimes of the colored open form of benzopyran **4** seem to be dependent on the solvent polarity since for polar solvents (MeCN, EtOH) a lifetime of ∼650 μs was found, while in methylcyclohexane (nonpolar solvent) a slightly higher value was found, ∼920 μs (Table 1). In addition, for all the solvents, similar lifetimes for the colored open form of compound **4** were obtained when the decays were

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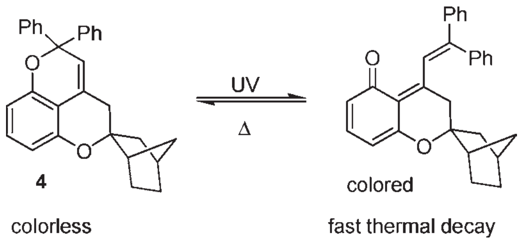
Scheme 4. Photochromic Equilibrium for the Fused Naphthopyran **4**



collected at 390 and 520 nm respectively (Figure 3, Table 1).

Although benzopyran **4a** undergoes equilibration in solution with formation of the isomeric benzopyran **4b**, the lifetimes of the colored species, measured in freshly prepared solutions or after 24 h, were the same which indicates that most likely only one of the benzopyrans opens in these conditions. The high value of the maximum wavelength of absorption of the colored open form and the observation that the whole visible spectra decay with the same first-order decay kinetics indicate that probably only the diphenylpyran ring of compound **4a** opens upon UV irradiation, with the formation of only one short-lived colored TC-isomer that fades in less than 1 ms to the initial uncolored state.

Consequently, the presence of the dihydropyran bridge on this benzopyran prevents the formation of the undesirable long-lived TT-isomer, and therefore the fading of the colored species to the uncolored closed form occurs without the persistence of a residual coloration, usually observed in these systems. Structural changes at the C-2 aryl substituents, or the use of this strategy in the parent naphthopyrans, should allow the increase of the lifetime of the TC colored species and thus permit observation of a color change at room temperature detectable to the naked eye. Such compounds could also be important for real-time image processing where the return of the colored species to the uncolored form must occur in tens of milliseconds.[9]

Table 1. Lifetimes (τ) for the Colored Open Form of Benzopyran **4** Collected at 390 and 520 nm in Acetonitrile (MeCN), Methylcyclohexane (MCH), and Ethanol (EtOH) Solutions

solvent	τ (μs) (390 nm)	τ (μs) (520 nm)
MeCN	650	650
MeCN (degassed)	640	660
EtOH	640	640
MCH	915	925

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Supporting Information Available. Experimental procedures. This material is available free of charge via the Internet at http://pubs.acs.org.

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