

Photochromism of Arylchromenes: Remarkable Modification of Absorption Properties and Lifetimes of *o*-Quinonoid Intermediates

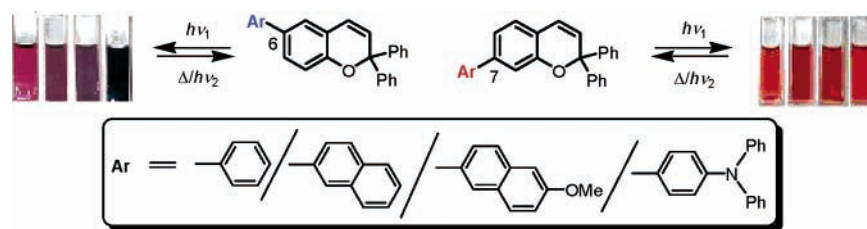
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ABSTRACT

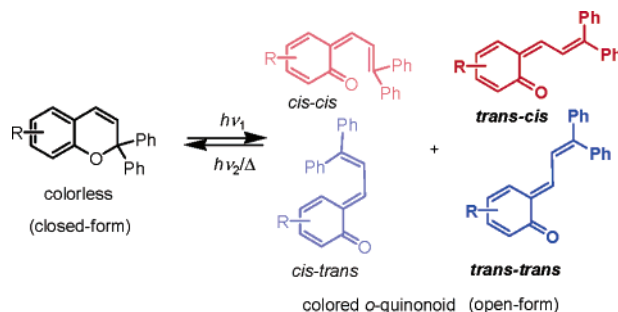


A significant π -conjugation in 6- and 7-arylchromenes manifests dramatically in the absorption properties of their photogenerated *o*-quinonoid intermediates. This in conjunction with facile synthesis via Suzuki coupling may render a myriad of photochromic arylchromenes with wide-ranging spectrokinetic properties readily accessible.

Design and synthesis of molecular systems that respond to photons as an external stimulus constitute an important endeavor in the development of organic photochromic materials, which have assumed significant contemporary interest due to their diverse applications in variable transmission glasses, high-density optical storage and switching, biological phenomena such as photomorphogenesis, vision process, etc., imaging devices and smart windows.¹ Among various photochromic systems known, the molecules that contain 2*H*-chromene unit, e.g., naphthopyrans and spiro-pyrans,² have proven to be of rich industrial value in the production of ophthalmic lenses.³

Mechanistically, photoirradiation of colorless pyrans (closed-forms) leads to the formation of colored *o*-quinonoid intermediates (open-forms) via heterolytic cleavage of the C(sp³)–O bond in their singlet-excited states (Scheme 1). The colored quinonoid intermediates may revert to the

Scheme 1



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starting colorless closed-forms either by heating or by irradiation with a visible light (Scheme 1).⁴ Unfortunately, simple derivatives of pyran such as benzopyrans exhibit photochromism only at low temperatures (263–173 K);⁵ reversion of the open forms to the closed forms is too fast in benzopyrans to preclude detection of the quinonoid intermediates at the room temperature. In order to modify the kinetic behavior of the photogenerated quinonoid intermediates and to develop photochromic materials with improved properties, various design strategies have been explored.⁶

In the course of our recent studies on helical pyrans⁷ that are photochromic, our attention was drawn toward indeno-fused benzopyrans **1–3** (Figure 1), whose photogenerated

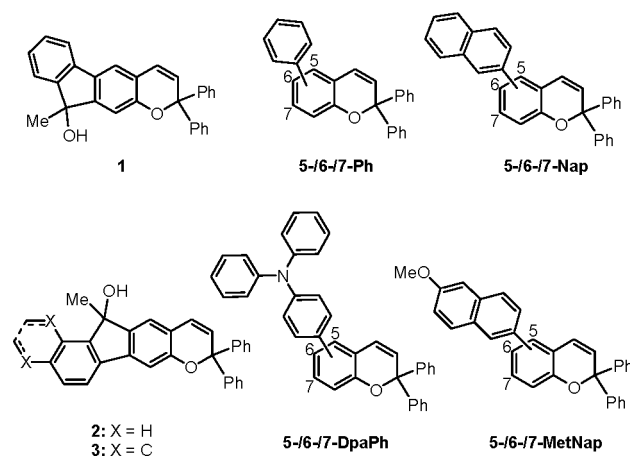


Figure 1. Structures of literature-reported indeno-fused chromenes and presently examined arylchromenes.

quinonoid intermediates were reported to exhibit remarkable variations in their absorption properties due to extended π -conjugation.⁸ Given that the two phenyl rings in biphenyls and the phenyl/naphthyl rings in α - and β -phenylnaphthalenes⁹ are not entirely orthogonal, and that there exists only a diminished conjugation between the two rings, we won-

dered as to how the mesomeric effects transmitted by the aryl substituents in 5-, 6-, and 7-arylbenzopyrans would influence the photochromic behavior. Indeed, we were inspired to investigate such effects based on the fact that a library of diversely substituted molecules can be readily accessed via Pd(0)-mediated Suzuki-coupling protocol.¹⁰ Herein, we demonstrate that substitution of the parent benzopyran nucleus with aryl rings (see **5–7**, Figure 1) leads to dramatic modification of the photochromism via extended π -conjugation.

The arylchromenes **5–7** were conveniently synthesized starting from arylphenols, which were, in turn, prepared in a facile manner by Suzuki coupling, see SI. Treatment of the arylphenols with 1,1-diphenylprop-2-yn-1-ol in the presence of PPTS (pyridinium *p*-toluenesulfonate) as a catalyst in 1,2-dichloroethane afforded the aryl-substituted chromenes **5–7** in respectable yields.

The X-ray crystal structure analyses carried out for **5-MetNap**, **6-Nap**, **6-DpaPh**, and **7-MetNap** show that the angle between the planes of the aryl and the chromene rings is maximum (ca. 42°) for **5-MetNap**, while it varies from 6 to 32° for 6- and 7-aryl analogues (Figure 2). The theoretical

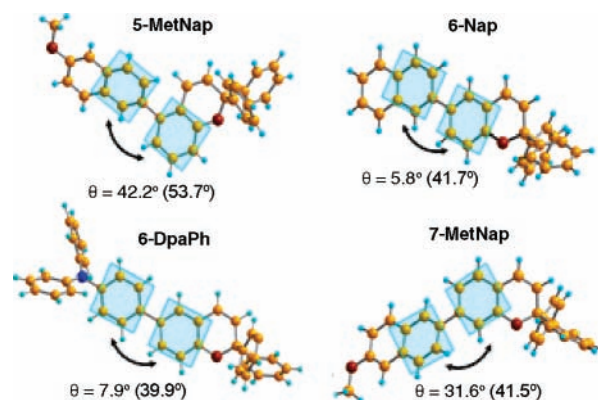


Figure 2. X-ray determined molecular structures of arylchromenes. Notice that the angle (θ /deg) between the planes of the benzene part of the chromene ring and the aryl ring is larger for 5-arylchromenes. The values in parentheses refer to the angles calculated for AM1-minimized structures.

AM1-calculated angles for the same molecules are relatively higher, cf. Figure 2. As mentioned earlier, it is known that the two phenyl rings in biphenyl are coplanar in the solid state, while they are neither orthogonal nor coplanar in the solution state.¹¹ Therefore, although the angles between the aryl rings as determined from X-ray studies as well as AM1 calculations are not necessarily applicable in the solution state, they are otherwise a useful guide to gauge qualitatively the inhibition of resonance in a closely related series. Based on the angle between the planes, the steric inhibition of

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resonance is expected a priori to be maximum for 5-substituted chromenes, while that in the case of 6- and 7-substituted analogues may parallel the trend observed for biphenyl or β -phenylnaphthalene. In line with this reasoning, the spectral attributes are found to be entirely different for the three differently substituted analogues, viz., **5-Nap**, **6-Nap**, and **7-Nap** (Figure 3 and Table 1). A similar trend in the

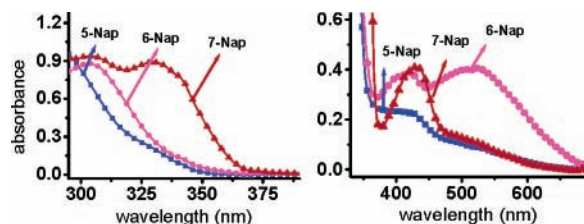


Figure 3. Absorption spectra of 5-, 6-, and 7-naphthylchromenes before (left) and after irradiation (right).

absorption profiles was uniformly observed for phenyl-, 6-methoxynaphthyl-, and *p*-diphenylaminophenyl-substituted chromenes **6** and **7**. The absorption properties of all arylchromenes are recorded in Table 1. One observes ca. 10^{-}

Table 1. Absorption Properties and Lifetime Data of Arylchromenes **5–7** and Their Respective Quinonoid Intermediates

substrate	absorption properties ^{a,b}		decay rates ^c k_1 and k_2 (s ⁻¹)
	before $h\nu$ (nm) (ϵ)	after $h\nu$ (nm)	
1		427, 524	0.160, 0.025 ^d
2		439, 505	0.120, 0.011 ^d
3		457, 538	0.091, 0.017 ^d
5-Ph	317 (br, 4026)	416 (br)	<i>e</i>
5-Nap	328 (sh, 4110)	426 (br)	<i>e</i>
5-MetNap	301 (sh, 13524)	436 (br)	<i>e</i>
5-DpaPh	313 (28435)	484	<i>e</i>
6-Ph	322 (br, 2669)	414 (br), 522 (br)	0.061, 0.0017
6-Nap	304 (30681)	422 (br), 526 (br)	0.024, 0.0054
6-MetNap	302 (33466)	415 (br), 543 (br)	0.040, <i>f</i>
6-DpaPh	322 (39944)	424, 564 (br)	0.072, 0.0108
7-Ph	325 (12740)	422, 530 (sh)	0.140, 0.0019
7-Nap	306 (16724) 330 (16784)	430, 528 (sh)	0.029, 0.0069
7-MetNap	332 (28072)	439, 528 (sh)	0.018, 0.0037
7-DpaPh	355 (33237)	474	0.105, 0.0075

^a Based on absorption spectra of chromenes **5–7** in dry toluene solutions (5×10^{-5} M). ^b br = broad and sh = shoulder. ^c Unless otherwise mentioned, the decays were monitored at 288 K after steady-state irradiation for 3–5 min. ^d From ref 8 at 298 K. ^e The decay kinetics were too fast. ^f The contribution of slow-decaying component was negligible.

40 nm variation in the absorption maximum, which attests to the fact that there exist varying degrees of mesomeric effect between aryl and chromene rings in **5–7**.

Under steady-state irradiation conditions at 283 K, the colorless solutions of all arylchromenes **5–7** in toluene (ca.

5×10^{-4} M) exhibited readily observable color changes, which varied from orange-yellow to blue. In Figure 3 are shown the absorption spectra of β -naphthyl-substituted chromenes **5–7** in toluene recorded immediately after irradiation at 350 nm for a brief period (30 s) at 283 K; extended duration of irradiation for ca. 6 min was found to have no effect on spectral features. A similar trend was observed for the photolysis of phenyl-, *p*-diphenylaminophenyl-, and 6-methoxynaphthyl-substituted chromenes **5–7**; see the Supporting Information. Interestingly, the irradiation of 6-arylchromenes led to a purple-to-blue color (λ_{\max} ca. 520–570 nm), while that of the 5- and 7-arylchromenes led to yellow-to-orange red color (λ_{\max} ca. 420–480 nm). The color due to the photogenerated intermediates was found to disappear thermally as well as photolytically with a long wavelength radiation. It is noteworthy that the transients of 6-arylchromenes display red-shifted absorption by ca. 50–100 nm relative to those of the transients of 5- and 7-substituted regioisomers. The substitution of a methoxy group in the naphthyl moiety appears to result only in a marginal red shift by 10–20 nm. The absorption properties of all the colored intermediates of arylchromenes **5–7** are given in Table 1.

The absorptions of the transients in the visible region are typical of *o*-quinone methide intermediates, which are formed by the heterolysis of precursor chromenes in their singlet-excited states (Scheme 1). Based on a comparison of the absorption spectral features to those reported in the literature,¹² we attribute the absorptions of the photogenerated transients in Figure 3 to their respective trans-cis and trans-trans *o*-quinone methide intermediates.¹³ In general, these two isomers are implicated as being responsible for the observed color (Scheme 1); the cis-cis isomer is known to decay quite readily, while the cis-trans isomer can only be formed with difficulty.

For thermal decay kinetics of the transient *o*-quinonoid intermediates, the solutions of 6- and 7-arylchromenes in toluene were irradiated at their λ_{\max} until the photostationary state (PSS) was reached. At this stage, the change in absorbance at the absorption maximum with time was monitored for all cases at 288 K; the duration of irradiation for the attainment of PSS was determined from coloration plots (see the Supporting Information). For all of the 5-substituted derivatives, the decays were too fast to be followed at 288 K. The decays for the transients of 6- and 7-arylchromenes followed a biexponential pattern (Figure 4).¹⁴ The rate constants for the decay of the photogenerated intermediates of 6- and 7-arylchromenes, extracted from biexponential fits, are collected in Table 1. For comparison, the rate constants reported for the transients of **1–3** are also

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(14) At a given temperature, 7-arylchromenes, upon photolysis, exhibited highest colorability; the intermediates derived from 7-arylchromenes were found to decay with virtually minimum absorbance as compared those of the 5- and 6-substituted analogues.

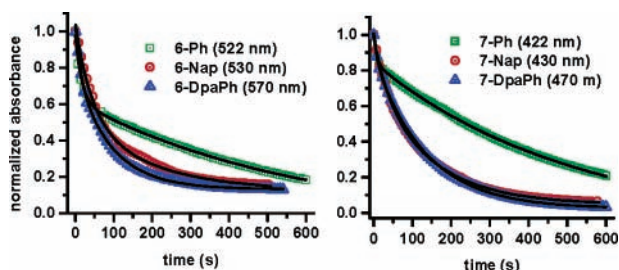


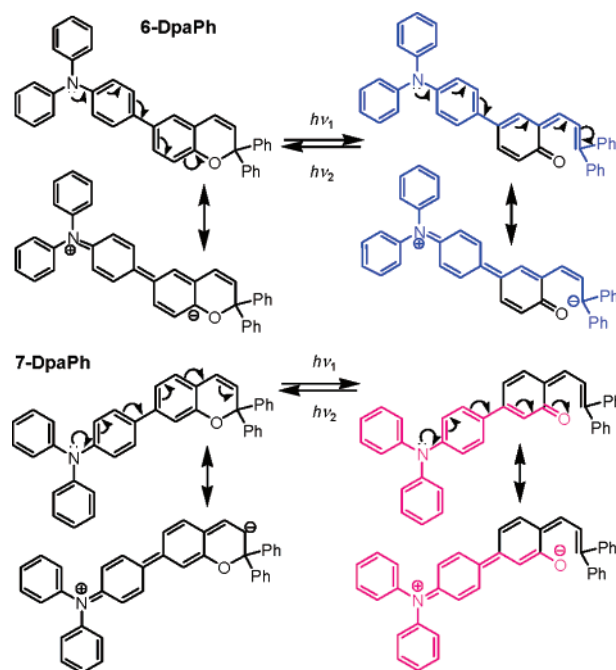
Figure 4. Comparative picture of the thermal normalized decay profiles of the photogenerated *o*-quinonoid intermediates of 6- (left) and 7-arylchromenes (right). The wavelengths at which the decays were monitored are given in parentheses.

given in Table 1. We attribute fast- and the slow-decaying transients to trans-*cis* and trans-*trans* isomers (cf. Scheme 1), respectively, in analogy to the previous assignments for the transients of **1–3**.⁸ It is known that different isomer distributions may be produced depending on the irradiation technique and that the relative thermal stabilities of the isomers as well as their propensities to interconvert may cause the biexponential character of fading more significant or less relevant.¹⁵ Otherwise, a perusal of the data in Table 1 reveals that transients of 6- and 7-arylchromenes exhibit spectrokinetic properties that parallel those of **1–3**.

Let us now consider the absorption properties of the transients of 6- and 7-arylchromenes in particular. It can be readily gleaned from the data in Table 1 and from Figure 3 that the absorption maximum in the case of 6-arylchromenes is blue-shifted as compared to that of the 7-arylchromenes, but the former yield quinonoid intermediates with more extended conjugation and, hence, red-shifted absorption maximum as compared to those of the latter. These differences should be reconciled from the way the electronic effects are transmitted from the aryl ring to the chromene and quinonoid moiety. In Scheme 2 are shown the mesomeric structures for **DpaPh** derivatives of 6- and 7-chromenes as representative cases and also for their respective quinonoid intermediates. It can be seen from the resonance structures that there exists more extended mesomeric effect in the case of *o*-quinonoid intermediates of 6-arylchromenes as compared to those of the 7-aryl analogues.

It is compelling to compare the absorptions of the transients of *fused* **1–3** with those of the corresponding *free* arylchromenes **6-Ph**, **7-Ph**, and **7-Nap**, respectively. The absorption maxima for the intermediates of the latter parallel very closely to those reported for the transients of **1–3**, cf. Table 1, which attests to the fact that the *simple* aryl analogues are as good as their *synthetically tedious* cyclic counterparts. Clearly, there exists considerable π -conjugation between the aryl ring and the chromene nucleus in 6- and 7-arylchromenes. That the absorption properties can indeed

Scheme 2



be modulated by a variation of the substitution pattern (position 6 or 7) as well the substituents is evident from the results observed for 6- and 7-arylchromenes; while the transients of 7-arylchromenes exhibit orange-red color, those of 6-aryl analogues exhibit blue color (see Table 1 and Figure 3).

In summary, we have shown that a variety of simple arylchromenes can be easily synthesized via a Suzuki-coupling protocol and that they exhibit photochromism in a manner that parallels the trends reported for more complex indeno-fused chromenes. In accordance with X-ray crystallographic analyses of **5-MetNap**, **6-Nap**, **6-DpaPh**, and **7-MetNap**, the aryl substituents at positions 5, 6, and 7 exert varying degrees of mesomeric effects to modify the absorption properties of chromenes and their photogenerated quinonoid intermediates. The facile synthesis via Suzuki coupling should render a myriad of photochromic arylchromenes with wide ranging spectrokinetic properties readily accessible.

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Supporting Information Available: Experimental procedures, spectral data (UV and NMR), crystal data and structure refinement details, and AM1 output files. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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