ORGANIC LETTERS
2006
Vol. 8, No. 21
4891−4894

Facile Synthesis, Fluorescence, and Photochromism of Novel Helical Pyrones and Chromenes

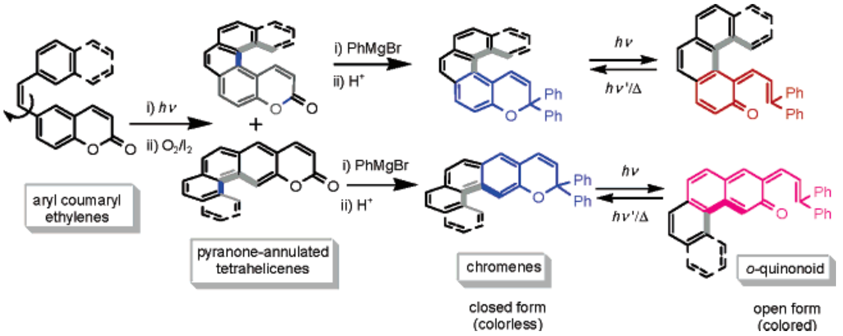
Jarugu Narasimha Moorthy,* Parthasarathy Venkatakrishnan, Sanchita Sengupta, and Mahiuddin Baidya

Department of Chemistry, Indian Institute of Technology, Kanpur 208016, India

moorthy@iitk.ac.in

Received August 3, 2006

ABSTRACT



Aryl coumaryl ethylenes undergo oxidative photocyclization readily to yield helical pyrone-annulated condensed aromatics. The pyrones are conveniently converted to the corresponding photochromic diphenylpyrans/chromenes. Both pyrones and chromenes exhibit helicity-dependent fluorescence efficiency and persistence, respectively.

Helicity is ubiquitous in nature and pervades every sphere of day-to-day life. Historically, helical structures have elicited tremendous interest as aesthetic marvels. However, remarkable applications of helicenes in the development of nonlinear optical materials,[1] liquid crystals,[2] chiroptical materials,[3] etc.[4] have unfolded only in recent years. Consequently, there is a sudden surge of interest in helices with unique properties and in the development of novel synthetic protocols to access them.[5] Among various routes for the synthesis of organic helical structures,[5,6] oxidative photocyclization of diarylethylenes continues to be most favored.[6c,7]

In our recent investigations aimed at exploring modification of the reactivity of stilbenes via 2-pyranone-annulation, we uncovered novel cis → trans isomerization of some derivatives in the solid state.[8] In a continuation of these studies, we reasoned that it should be possible to convert 2-pyranone-annulated phenyl aryl ethylenes into novel helical structures containing the basic benzopyrone, i.e., coumarin, moiety; coumarins are fantastic fluorophores and are widespread as dyes, DNA intercalators, biologically active

---

[1] (a) Verbiest, T.; Elshocht, S. V.; Kauranen, M.; Hellemans, L.; Snauwaert, J.; Nuckolls, C.; Katz, T. J.; Persoons, A. *Science* **1998**, *282*, 913. (b) Verbiest, T.; Sioncke, S.; Persoons, A.; Vyklický, L.; Katz, T. J. *Angew. Chem., Int. Ed.* **2002**, *41*, 3882.

[2] Nuckolls, C.; Katz, T. J. *J. Am. Chem. Soc.* **1998**, *120*, 9541.

[3] (a) Feringa, B. L.; van Delden, R. A.; ter Wiel, M. K. J. In *Molecular Switches*; Feringa, B. L., Ed.; Wiley-VCH: Weinheim, 2001; Chapter 5, p 123. (b) Feringa, B. L.; van Delden, R. A.; Koumura, N.; Geertsema, E. M. *Chem. Rev.* **2000**, *100*, 1789.

[4] (a) Meurer, K. P.; Vogtle, F. *Top. Curr. Chem.* **1985**, *127*, 1. (b) Rowan, A. E.; Nolte, R. J. M. *Angew. Chem., Int. Ed.* **1998**, *37*, 63. (c) Katz, T. J. *Angew. Chem., Int. Ed.* **2000**, *39*, 1921.

[5] Urbano, A. *Angew. Chem., Int. Ed.* **2003**, *42*, 3986.

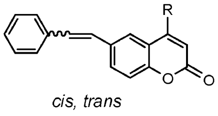
[6] (a) Liu, L.; Katz, T. J. *Tetrahedron Lett.* **1990**, *31*, 3983. (b) Carreno, M. C.; García-Cerrada, S.; Urbano, A. *J. Am. Chem. Soc.* **2001**, *123*, 7929. (c) Norsten, T. B.; Peters, A.; McDonald, R.; Wang, M.; Branda, N. R. *J. Am. Chem. Soc.* **2001**, *123*, 7447.

[7] For example, see: (a) Nakamura, Y.; Yamazaki, T.; Nishimura, J. *Org. Lett.* **2005**, *7*, 3259. (b) Wigglesworth, T. J.; Sud, D.; Norsten, T. B.; Lekhi, V. S.; Branda, N. R. *J. Am. Chem. Soc.* **2005**, *127*, 7272 (c) Kelly, T. R.; Sestelo, J. P.; Tellitu, I. *J. Org. Chem.* **1998**, *63*, 3655.

[8] (a) Moorthy, J. N.; Venkatakrishnan, P.; Savitha, G.; Weiss, R. G. *Photochem. Photobiol. Sci.* **2006**, DOI: 10.1039/b606027g.

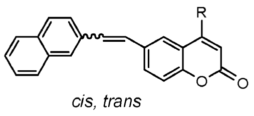
10.1021/ol0619260 CCC: $33.50

ingredients, etc. Further, we envisioned that the helical pyrones can be most conveniently transformed into chromenes, which are helical in nature; chromenes are well-known in the realm of photochromism and readily exhibit photoinduced color changes via heterolysis of the C−O bond in the singlet-excited state, which results in the formation of colored quinonoid intermediates.[9] Herein, we report facile and regioselective cyclization of coumarins **1** and **2** to 2-pyranone-annulated helical systems, which are subsequently transformed easily to the corresponding chromenes. It is shown that helical pyrones are novel fluorescent molecules and that the chromenes derived therefrom exhibit readily observable photochromism. Further, a remarkable influence of helicity on the fluorescence and photochromic properties is unraveled.



cis, trans

1



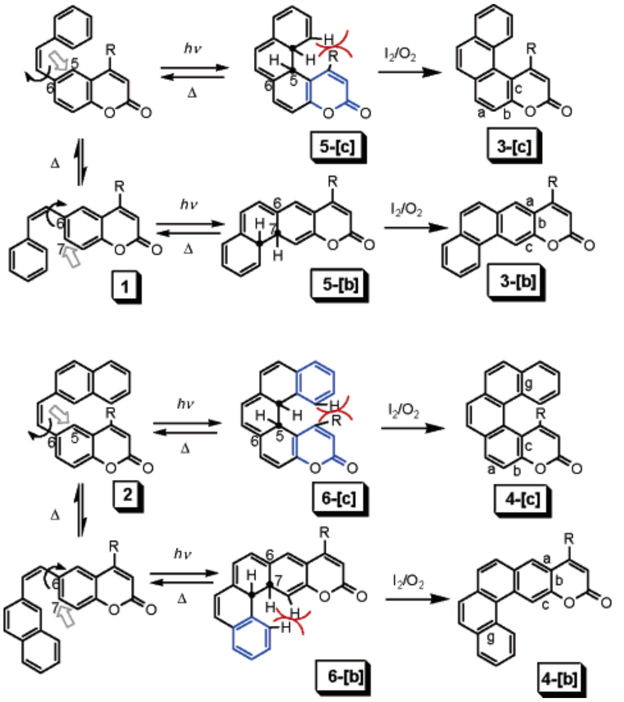
cis, trans

2

a : R = H
b : R = CH_3
c : R = Cl
d : R = OMe

The *cis* and *trans* mixtures of coumarins **1** and **2** were synthesized in 64−90% isolated yields from the Wittig reaction between the triphenylphosphonium salts of appropriately substituted 6-bromomethylcoumarins and benzaldehyde (for **1**) or 2-naphthaldehyde (for **2**). Photolysis (Luzchem photoreactor, $\lambda \simeq 350$ nm) of the solutions of *cis* isomers of **1** and **2** in benzene under N_2 atmosphere led to a readily observable color change, and the color in each case was found to disappear rapidly when kept in the dark; the color in the case of coumarins **1** varied from orange to violet, whereas it was red in coumarins **2**. The attendant color changes were monitored by electronic absorption spectroscopy; see Supporting Information. The transients responsible for the absorptions are attributed to the formation of dihydro (DH) intermediates **5** and **6**,[10] Scheme 1. Indeed, the formation of oxidation products in the presence of O_2 or added I_2 (vide infra) lends credence to this assignment.

Scheme 1



The photolyses of solutions of **1** and **2** as mixtures of *cis* and *trans* isomers ($\lambda \simeq 350$ nm) in the presence of I_2 led to the formation of electrocyclized aromatic products. The photolysis in each case was continued until the disappearance of the coumarin, as monitored by ^1H NMR spectroscopy (Table 1), and the photolysates were subjected to chromatographic techniques to isolate mixtures of regioisomeric pyrone-annulated phenanthrenes **3** and tetrahelicenes **4** (Scheme 1). The pure regioisomers were thoroughly characterized by IR, ^1H and ^{13}C NMR, and mass spectroscopic techniques (Supporting Information). As given in Table 1, the isolated yields of 2-pyrone-annulated aromatic products were >90% except for the chloro-substituted coumarins **1c** (73%) and **2c** (65%). Remarkably, the cyclizations were found to occur with a noticeable regioselectivity, as revealed by 400 MHz ^1H NMR spectroscopy of the mixtures of regioisomeric cyclization products. Whereas coumarins **1** exhibited preference for cyclization at position 5 of the coumarin leading to 2-pyranone-annulated phenanthrenes **3**-[c], coumarins **2,** with the exception of **2a**, underwent cyclization selectively at position 7 yielding pyran-2-one-annulated tetrahelicenes **4**-[b]; cf. Scheme 1. In coumarins **1**, the selectivity for cyclization ranged from 69% to 89%, whereas it was 53−90% in coumarins **2** (Table 1). The observed regioselectivities in oxidative cyclizations can, in principle, be reconciled from a composite of steric and electronic interactions.[11,12] Although energies of transition states that lead to the two regioisomers, as calculated from

Table 1. Results of Oxidative Photocyclizations of **1** and **2**[a]

substrate	duration of irradiation (h)	concn (M)	relative ratios of cyclized products[b] [c]:[b]	isolated yield (%)
1a	15	2×10^{-4}	89:11	92
1b	36	8×10^{-5}	69:31	95
1c	36	5×10^{-4}	72:28	73
1d	36	2×10^{-4}	78:22	92
2a	24	2×10^{-4}	47:53	94
2b	24	4×10^{-4}	25:75	92
2c	36	1×10^{-4}	10:90	65
2d	36	4×10^{-4}	29:71	93

[a] Photolyses were carried out in Pyrex flasks containing solutions of **1** or **2** in benzene (ca. 10^{-4} to 10^{-5} M) in the presence of iodine (0.5 equiv); $\lambda \simeq 350$ nm. [b] From ^1H NMR analyses; [b] and [c] refer to the faces of annulation (see text).

---

(9) (a) Gemert B. V. In *Organic Photochromic and Thermochromic Compounds*; Crano, J. C., Guglielmetti, R., Eds.; Plenum Press: New York, 1999; Vol. 1, Chapter 3. For a recent example, see: (b) Zhao, W.; Carreira, E. M. *Org. Lett.* **2006**, *8*, 99.

(10) (a) Muszkat, K. A. *Top. Curr. Chem.* **1980**, *88*, 89. (b) Laarhoven, W. H. In *Photochromism, Molecules and Systems*; Durr, H., Bouas-Laurent, H., Eds.; Elsevier: Amsterdam, 1990; p 270. (c) Irie, M. *Chem. Rev.* **2000**, *100*, 1685.

semiempirical calculations, may shed light on the regioselectivity, it has been pointed out recently that the regioselectivities are determined by relative rates of ring opening, sigmatropic rearrangements of the DH-intermediates as well as their rates of oxidation.[13] All of these processes are susceptible to variation in structure, solvent, temperature, concentration, reactivity of the oxidant, etc. to cause any generalizations as to the regioselectivities less meaningful.

As the helicity in the cyclization products of the naphthalene derivatives **2** was expected to be substantial, we specifically examined the X-ray crystal structures of the photocyclization products of **2a** and **2b**. That these molecular systems are indeed helical is evident from their X-ray determined structures shown in Figure 1. From the angle between the mean planes constructed for the terminal aromatic rings of these pyrones, it can be readily discerned that the helicity in the case of [c]-face-annulated pyrones, i.e., **4a**-[c] and **4b**-[c], is higher (ca. 44°−45°) than those of the [b]-face annulated analogues (ca. 26°), i.e., **4a**-[b] and **4b**-[b]. It is noteworthy that the substituent at the fourth position of the pyrone ring as in **4b**-[c] does not result in any perceptible difference in the helicity as compared to **4a**-[c]. In the absence of structural studies on pyrone-annulated phenathrenes **3a**-[b] and **3a**-[c], it is logical to believe that the helicity in the case of **3a**-[c], which may be considered equivalent to a tetrahelicene, should be comparable or more than that in the case of [b]-face-annulated tetrahelicenes, namely, **4a**-[b]. Of course, the [b]-face-annulated phenanthrenes **3a**-[b] must be planar.

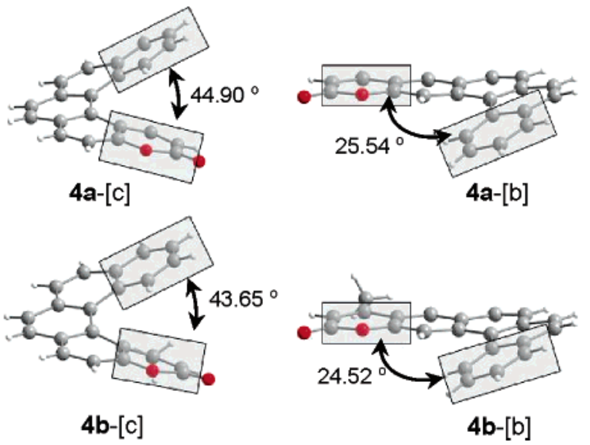


Figure 1. X-ray determined structures of 2-pyrone-annulated tetrahelicenes **4a**-[c], **4a**-[b], **4b**-[c], and **4b**-[b].

In light of these structural insights, it was interesting to inquire into the dependence of fluorescence efficiencies on the helicity. As mentioned at the outset, the pyrone-annulation imparts fluorescence property to the aromatic systems. As expected, the pyrones **3** and **4** were found to exhibit high emission intensities at as low concentrations as 10^{-5} to 10^{-6} M. While the absorption in all cases tapers off at ca. 400 nm, the pyrones were found to exhibit blue emission in the range of 400−550 nm. In Figure 2 are shown the fluorescence spectra recorded typically for **4a**-[c] and **4a**-[b]. It is noteworthy that the [b]-face-annulated phenanthrene and tetrahelicene, i.e., **3a**-[b] and **4a**-[b], exhibit 20 nm shift in their structured emission maxima relative to those of the [c]-face annulated analogues, i.e., **3a**-[c] and **4a**-[c]. Their fluorescence efficiencies were determined in a nonpolar cyclohexane and a polar protic methanol solvents using 9,-10-diphenylanthracene as a standard.

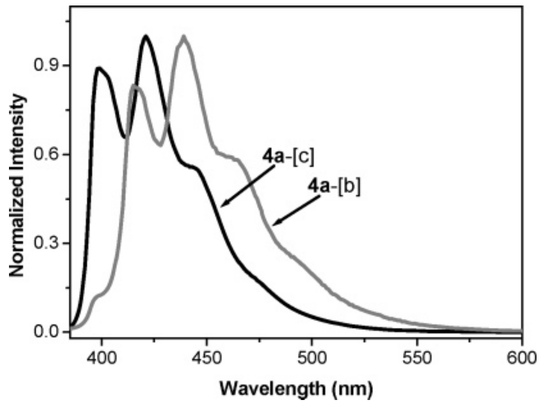


Figure 2. Normalized emission spectra for **4a**-[c] and **4a**-[b]. The spectra were recorded for $\lambda_{exc} = 366$ nm.

Table 2. Photophysical Properties of Helical Pyrones **3** and **4**

		emission[a] λ_{max} (nm)		quantum yield,[b] Φ_f	
substrate	abs λ_{max} (nm)	C_6H_{12}	MeOH	C_6H_{12}	MeOH
3a-[c]	380	410	430	0.08	0.06
3a-[b]	400	423	452	0.04	0.03
4a-[c]	360	421	450	0.14	0.10
4a-[b]	390	438	475	0.03	0.03

[a] $\lambda_{exc} = 366$ nm. [b] Error ± 10%

As given in Table 2, the quantum yields were found to be as high as 0.14.[14] Quite remarkably, they are higher for molecules with higher helicity. In both polar methanol and nonpolar cyclohexane solvents, one observes a ca. 2- to 4-fold increase in the quantum yields for **3a**-[c] and **4a**-[c] as compared to their regioisomers **3a**-[b] and **4a**-[b]. The

---

[11] Zimmerman, T. J.; Muller, T. J. *Eur. J. Org. Chem.* **2002**, 2269.

[12] (a) Laarhoven, W. H.; Cuppen, Th. J. H. M.; Nivard, R. J. F. *Tetrahedron* **1970**, *26*, 4865. (b) Muzkat, K. A.; Seger, G.; Sharafi-Ozeri, S. *J. Chem. Soc., Faraday Trans. 2* **1975**, 1529.

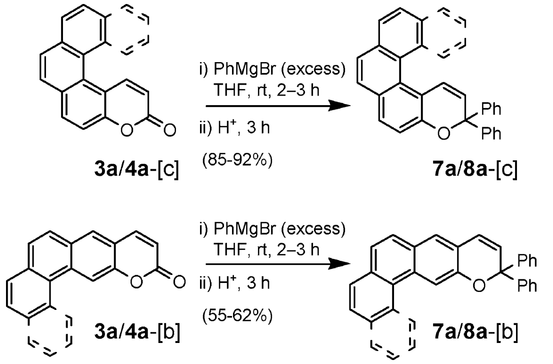
[13] Lewis, F. D.; Kalgutkar, R. S.; Yang, J.-S. *J. Am. Chem. Soc.* **2001**, *123*, 3878.

[14] For fluorescence studies of azahelicenes, see: Bazzini, C.; Brovelli, S.; Caronna, T.; Gambarotti, C.; Giannone, M.; Macchi, P.; Meinardi, F.; Mele, A.; Panzeri, W.; Recupero, F.; Sironi, A.; Tubino, R. *Eur. J. Org. Chem.* **2005**, 1247.

reason as to why the molecules with higher helicity exhibit higher efficiency is intriguing. Such a remarkable dependence of fluorescence efficiency on helicity is, to the best of our knowledge, heretofore unknown.

The pyrones can be readily converted to chromenes that are photochromic. The reaction of pyrones **3a**-[b], **3a**-[c], **4a**-[c], and **4a**-[b], representative cases, with excess PhMgBr followed by dehydration led to diphenylpyrans (chromenes) in 55−92% isolated yields as shown in Scheme 2.[15] A brief exposure (20−30 s) of the solutions of helical chromenes **7** and **8** in dry benzene (ca. 10^{-3} M) to UV radiation ($\lambda \simeq 350$ nm) under a N_2 gas atmosphere led to instantaneous color change. The UV−vis absorption spectral changes for the photolyzed solutions of chromenes **7** and **8** before and after irradiation at −20 °C are shown in Figure 3. The species responsible for color are attributed to the *o*-quinonoid intermediates as shown in Scheme 3. Whereas the absorptions due to the quinonoid intermediates in the case of chromenes **7a**-[c], **8a**-[c], and **8a**-[b] were found to be longer lived as monitored from UV−vis absorption spectroscopy, the transient in the case of **7a**-[b] was found to be very short-lived. Following a brief irradiation (30 s) of the solutions in toluene, the decay rate constants for the intermediates derived from **7a**-[c], **8a**-[c], and **8a**-[b] were determined at 295 K to be 0.080, 0.066, and 0.129 s^{-1}, respectively. The intermediate in the case of **7a**-[b] was too short-lived; see Supporting Information for details. The relatively longer lifetimes of the intermediates derived from chromenes **8a**-[b] and **8a**-[c], as compared to those derived from **7a**-[b] and **7a**-[c], attest to the unique role of helicity in influencing the lifetimes.

Scheme 2



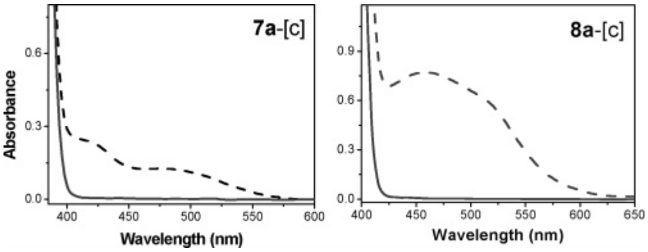
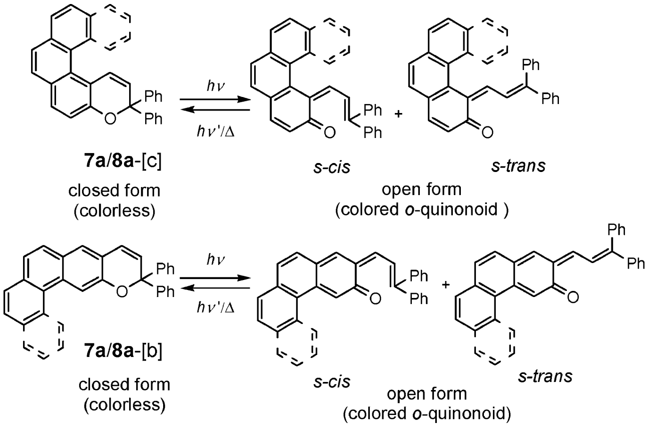


Figure 3. UV−vis absorption spectra for **7a**-[c] and **8a**-[c] before (—) and after (- - -) photoirradiation.

Scheme 3



In conclusion, we have shown that oxidative photocyclization of aryl coumaryl ethylenes is a facile protocol to access regioisomeric helical pyrones. The helicity of the pyrones is unequivocally established by X-ray crystal structure determinations. The pyran-2-one-annulated phenanthrenes and tetrahelicenes are found to exhibit fluorescence efficiencies that are remarkably dependent on the magnitude of helicity. We have shown that helical pyrones can be conveniently transformed into photochromic chromenes. In these cases, the persistence of color upon photolysis is found to depend on the helicity. The helicity-dependent fluorescence efficiency and persistence of quinonoid intermediates generated via heterolysis of chromenes bring out the importance of structural attributes on physical properties.

Acknowledgment. J.N.M. is thankful to DST, India for funding and P.V. to CSIR for a research fellowship.

Supporting Information Available: Experimental procedures, spectral data (UV, fluorescence, and NMR), X-ray structure determination details and CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

OL0619260

---

(15) Cottam, J.; Livingstone, R. *J. Chem. Soc.* **1965**, 6646.