Study on Photochromic Diarylethene with Phenolic Schiff Base: Preparation and Photochromism of Diarylethene with Benzoxazole

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Received March 16, 2004

A photochromic diarylethene with phenolic Schiff base **1a** can be easily transformed to photochromic diarylethene with benzoxazole **3a** in the conditions of base and phototrigger. Both of their photochromic properties are investigated. They show that the conversions of ring-open form to ring-closed form at photostationary equilibrium are ca. 20% and 10% for **3a** and **1a**, respectively, and the backconversions are in nearly quantitative yield for both compounds. They also show that the response time for photostationary equilibrium is ca. 0.5 and 5 min for **3a** and **1a**, respectively, in the solution. In addition, a general preparation of 2-arylbenzoxazole from phenolic Schiff base in the conditions of base and phototrigger is demonstrated by employing phenolic Schiff bases with different substituted groups as template, and other conditions (solvents, in the presence and absence of oxygen) for preparation of benzoxazole from phenolic Schiff base are explored as well.

Introduction

Control of physical properties of molecules by external stimulation has attracted great attention, not only in relation to biological supramolecular machines but also for the development of molecular switches and devices.[1−4] Photochromic compounds exhibit reversible variations in their physical characteristics when stimulated by light and are one of the best contenders for use in optelectronic devices and memory media.[5−8] Among the photochromic compounds, diarylethenes are regarded as the best candidates because of fatigue resistance and bistability.[9−11] The current research interest for photochromic diarylethenes is to develop molecular systems that integrate several switchable functions into a single molecule in order to miniaturize the components of machinery and electronics down to the molecular level.[12,13] The ultimate goal of miniaturization is to use molecular assemblies as memory, processing, and mechanical devices. To reach these goals, it is essential to transform molecular structures between two or more states in response to external signals such as photonic, chemical, electrochemical, or magnetic stimuli and to tailor readable output such as electronic or optical signals that reflect the molecular state. Herein we present for the first time the photochromism and formation of diarylethene with benzoxazole **3a**, which was produced from photochromic diarylethene with phenolic Schiff base **1a**.[14] The photochromic isomerizations of **1a** and **1b**, **3a** and **3b**, and the process of formation from **1a** to **3a** are described in Scheme 1.

Results and Discussion

The absorption spectral changes of **1a** in acetonitrile are shown in Figure 1. By irradiation with 254 nm light the absorption bands at 362 nm ($\epsilon_{max} = 1.12 \times 10^4$ M^{-1} cm^{-1}, in acetonitrile) and 260 nm ($\epsilon_{max} = 8.5 \times 10^3$ M^{-1} cm^{-1}, in acetonitrile) decrease along with the increase of two new absorption bands at 608 nm and 320 nm, which correspond to the ring-closed form **1b**. The photostationary equilibrium is achieved only after **1a** is irradiated for 5 min, and the conversion is ca. 10%. The original absorption spectrum is recovered completely upon irradiation ($\geq$510 nm) in acetonitrile. It indicates the ring-closed form (**1b**) can be reversed back to the open form (**1a**), and the backconversion is in nearly quantitative yield. It is worth noting that the absorption change of photoisomerization between the *cis* form and *trans* form of **1a** is not observed in this case.

Addition of NaOH (0.01 M in ethanol) to solution of **1a** produces a decrease of the band at 362 nm with a

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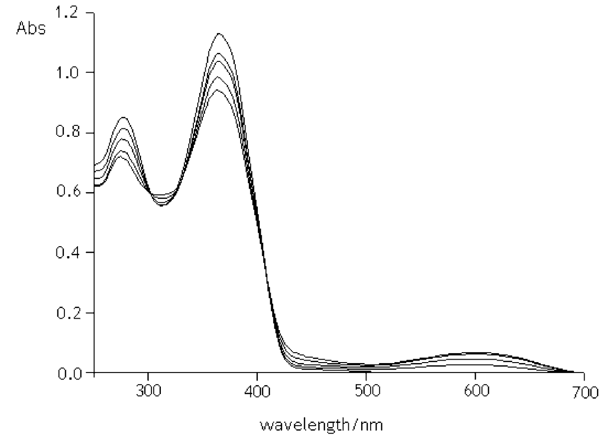
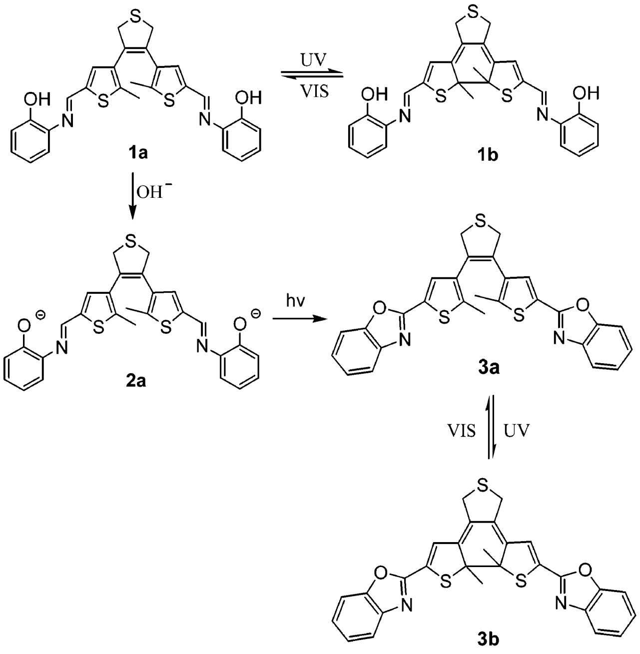


FIGURE 1. Absorption changes of **1a** (1.0×10^{-4} M, in CH_3CN) upon irradiation with 245 nm light.

SCHEME 1. Photoisomerization of 1a and 1b, 3a and 3b and Process of Formation of 3a from 1a



concomitant increase of two new ones at 412 nm ($\epsilon_{max} = 7.8 \times 10^3$ M^{-1} cm^{-1}, in acetonitrile) and 310 nm ($\epsilon_{max} = 8.6 \times 10^3$ M^{-1} cm^{-1}, in acetonitrile), respectively, which are attributed to **2a** (Figure 2). Comparing the longest absorption band of **2a** with that of **1a** finds the longest band of **2a** is red-shifted as much as 50 nm ($\Delta\lambda_{max} = 412 - 362$ nm), which results from deprotonation of phenol.

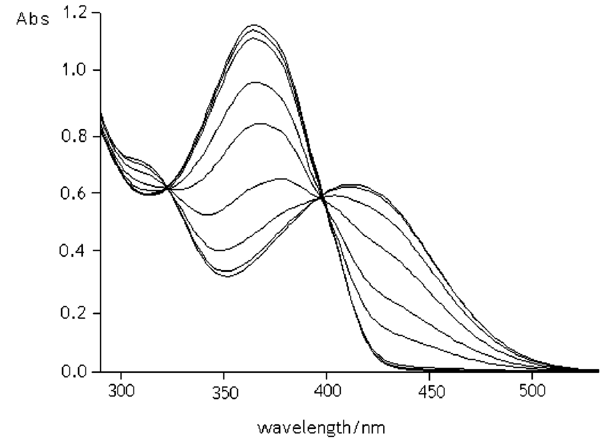


FIGURE 2. Absorption changes of **1a** (1.0×10^{-4} M, in CH_3CN) with addition of NaOH (1.0×10^{-2} M, in EtOH, 1, 5, 7, 10, 20, 30, 40, and 50 μL).

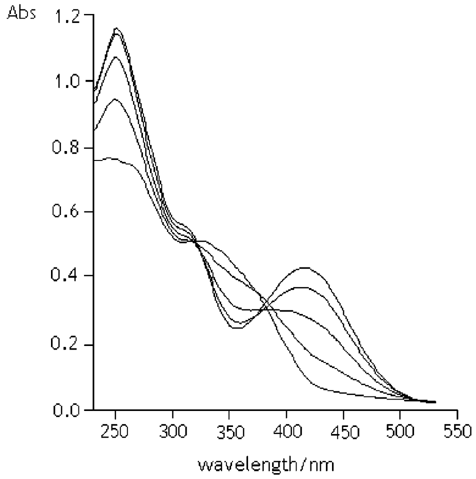


FIGURE 3. Absorption changes of **2a** (1.0×10^{-4} M, in CH_3CN) upon irradiation with 410 nm light.

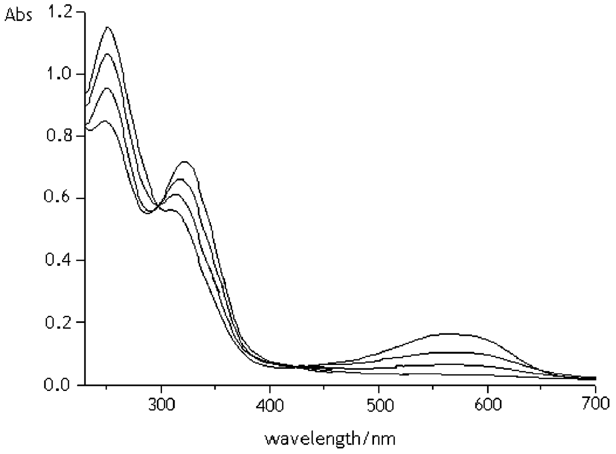


FIGURE 4. Absorption changes of **2a** (1.0×10^{-4} M, in CH_3CN) upon irradiation with 313 nm light.

Irradiation of **2a** with 410 nm light gives an unexpected absorption spectrum, which is shown in Figure 3. The new appeared absorption band at 322 nm is blue-shifted as much as 90 nm ($\Delta\lambda_{max} = 412 - 322$ nm) compared with the longest band of **2a** at 412 nm. By all appearances, this new band does not correspond to the closed form of **2a** since the absorption band is usually red-shifted when the ring-open form of a photochromic compound changes to the ring-closed form. When 313 nm light is employed to irradiate the above solution, however, the expected absorption spectroscopy is obtained, as shown in Figure 4. It is found that a new absorption band at 564 nm increases along with decrease of band at 322 nm. Comparing the longest band of **2a** before and after irradiation finds a large red-shift of 152 nm ($\Delta\lambda = 564 - 412$ nm). Such a large bathochromic shift is usually attributed to the ring-closed form of a photochromic compound. The photobleaching (Figure 5) also shows that

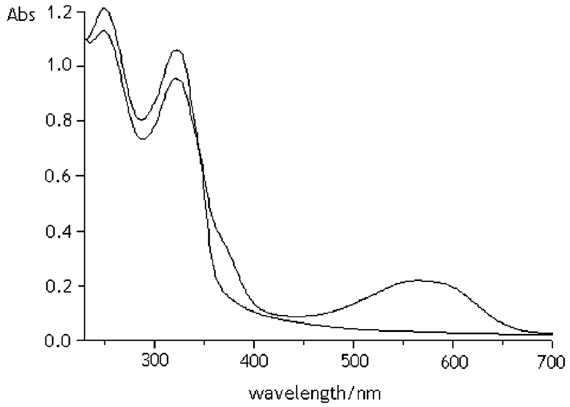
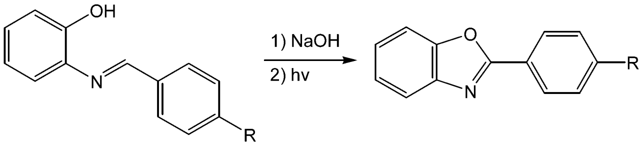


FIGURE 5. Photochromic bleaching of the band at 564 nm with 560 nm light.

SCHEME 2. Preparation of 2-Arylbenzoxazoles from Derived Phenolic Schiff Bases



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a = H, b = CH_3, c = OCH_3, d = Cl, e = NO_2

the band at 412 nm does not increase when the band at 564 nm decreases and only the band at 322 nm increases in that case. All results indicate that the band at 322 nm can be attributed to a new chemical species that is from **2a** by irradiation with 410 nm light.

Further investigation confirms that the band at 564 nm has close relations with the band at 322 nm. When the solution is irradiated with 313 nm light, the band at 564 nm appears and increases with decrease of the band at 322 nm. Conversely the band at 322 nm increases with decrease of band at 564 nm when above solution is bleached with 560 nm light. What is more, no significant photodegradation is detected when coloration and bleaching of the solution as above is repeated for 10 times. The photostationary equilibrium is achieved very quickly (0.5 min for the above solution) and the conversion is ca. 20%.

Next we turn our attention to figure out the molecular structure of the new chemical species produced from irradiation of **2a** with 410 nm light. ^{1}H NMR data shows that the protons (OH, CH=N) of **1a** appearing at 8.62 and 7.15 ppm, respectively, in the ^{1}H NMR spectrum disappeared in the ^{1}H NMR spectra of new chemical species. Moreover, the protons of new chemical species in the thiophene ring and benzene ring shift downfield as much as 0.72 and 0.69 ppm, respectively, by comparison with that of **1a**. In addition, the mass spectroscopy shows the relative abundance of molecular ion (m/z = 512) of the new chemical species is 100%. All indicate that the new chemical species produced from **2a** is diarylethene with benzoxazole **3a**, whose structure is shown in Scheme 1.

To confirm the molecular structure of **3a** and to test the general preparation method above, phenolic Schiff bases with different substituted group (Scheme 2) are prepared and employed as template. Comparing the ^{1}H NMR and MS data of 2-arylbenzoxazoles **5** with that of a known model compounds finds data of both ^{1}H NMR and MS of **5** are in agreement with that found in the literature.[15] It indicates that 2-arylbenzoxazoles **5** can be produced directly from phenolic Schiff bases derived (**4**) in good yields (63−78%) in the conditions of base (NaOH) and phototrigger (Hg high-pressure lamp, 500 W) in acetonitrile. It is known[16−19] that benzoxazole ring moieties are often found in compounds that exhibit biological activities, including antitumor, antimicrobial, and antiviral propterties. There are two general methods for synthesizing 2-substituted benzoxazoles. One is the coupling of 2-aminophenols with carboxylic acid derivatives, which either is catalyzed by strong acids[20] or requires microwave conditions.[21] The other is the oxidative cyclization of phenolic Schiff bases derived from the condensation of 2-aminophenols and aldehydes. In the latter reactions, various oxidants such as DDQ,[22] Mn(Oac)$_3$,[23] PhI(Oac)$_2$,[24] $Th^+ClO_4^-$,[25] and O_2 with activated carbon (Darco KB)[15] are used. The preparation of 2-arylbenzozaxoles from phenolic Schiff bases derived in the condition of base and phototrigger has, as far as we know, not been reported before. The investigation of photophysical property of 2-benzyl benzoxazole shows that the absorption band of 2-benzyl benzoxazole (λ_{max} = 304 nm, in acetonitrile) is blue-shifted as much as 46 nm ($\Delta\lambda_{max}$ = 350 − 304 nm) by comparison with phenolic Schiff base (λ_{max} = 350 nm, in acetonitrile). This result is similar to that above, in which as much as 40 nm ($\Delta\lambda_{max}$ = 362 − 322 nm) blue-shift is observed when **1a** is converted to **3a** in acetonitrile.

To explore the conversion of phenolic Schiff bases into 2-arylbenzoxazoles, the following tests are carried out. First, the solution of **1a** without adding NaOH base is tested by irradiation with 313 nm light. It is found that only the band of ring-closed form (**1b**) is detected as shown in Figure 1. It indicates that **1a** cannot be converted to **3a** in this case. Second, when a solution of **2a** (obtained from **1a** by addition of 1 equiv of NaOH solution till the absorption intensity does not change) is kept in darkness at room temperature for 24 h, no remarkable change is detected by UV absorption, indicating **2a** cannot be converted to **3a** without phototrigger. Third, irradiating the solution of **2a** with 313 nm light in the presence and absence of O_2, respectively, gives results that are the same. Last, different solvents (dichoromethan, toluene) and different substrates are employed and similar results are obtained. All indicate that both base and phototrigger play a key role in preparation

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of 2-arylbenzoxazoles directly from derived phenolic Schiff bases.

Conclusions

In summary, photochromic diarylethene with phenolic Schiff base converted to photochromic diarylethene with benzoxazole has been demonstrated. A general method for preparation of 2-arylbenzoxazoles from derived phenolic Schiff bases is also presented. Both base and phototrigger play a key role in the conversion of phenolic Schiff bases into 2-arylbenzoxazoles. Photochromic properties show that diarylethene derivative **3a** has an advantage over diarylethene derivative **1a** in the conversion of ring-open form to ring-closed form and response time to reach photostationary equilibrium.

Acknowledgment. We are grateful to the National Science Foundation of China (NO 60337020 and NO 60277001) and the National Principal Research Project “973” (G 1999033005) for financial support.

Supporting Information Available: ^{1}H NMR and MS data for compounds **1a**, **3a**, and **5a**−**d** and ^{1}H NMR spectroscopy of compounds **1a**, **3a**, and **5a**−**d**. This material is available free of charge via the Internet at http://pubs.acs.org.

JO049565U