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Novel Photochromic Compounds Responding to InGaN Diode Laser; Synthesis and Photochromic Behavior of Dibenzothiophenylcycloalkenes

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Abstract : 1, 2 - *bis*(3-Methylbenzo[b]thiophen-2-yl)cycloalkene derivatives **3a, 3b** and 1 - (2-methylbenzo[b]thiophen – 3 - yl) - 2 - (3 - methylbenzo[b]thiophen – 2 - yl)cyclohexene **9** were synthesized. The obtained compounds exhibited photochromic property and the absorption bands of the colored forms **4a**, **4b** and **10** centered between 360-440 nm thus possessing the sensitivity at the wavelength of the newly developed InGaN diode laser.

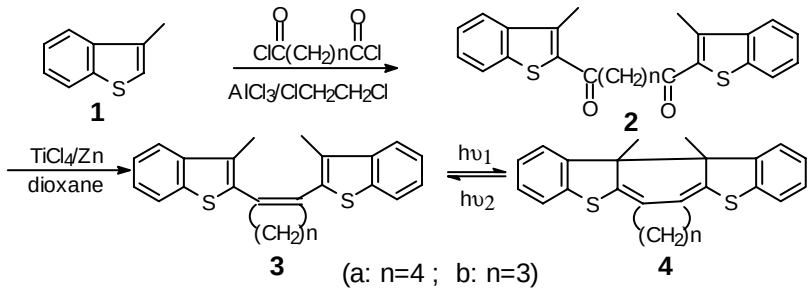
Keywords: 1,2-Diheteroarylcycloalkene, benzothiophene, photochromism.

In recent years, photochromic compounds have attracted increasing attention due to their potential application in optical data storage[1]. Among them, 1,2-diarylethenes constitute an important class owing to their bistationary states thermal stability and fatigue resistance[2]. Much efforts have been so far paid to synthesize the materials that absorb near-infrared light in order to achieve compatibility with conventional infrared diode laser ($\lambda \approx 0.8\,\mu$ m) used in compact disc system. Most of the closed forms of the reported synthesized diarylethenes have their absorption maxima above 560 nm and some have their absorption bands expanding up to infrared range. With the recent progress in laser technology, shorter wavelength laser sources have been developed fast. The InGaN diode laser, which emits between 400-440 nm is expected to be brought into commercial application in the near future[3-4]. Thus, replacing the conventional infrared diode laser with the new coming InGaN diode laser will increase the optical information density by nearly four times because the density of the optical data storage is proportional to $1/\lambda^2$ (where λ is the wavelength of the light used for writing and /or reading). The remaining challenges are to design and synthesize molecules which can undergo reversible photoreaction induced by blue light . With a view to exploring novel photochromic compounds, herein we report the synthesis and photochromic property of a new kind of photochromic dibenzothiophenylcycloalkenes which possess the sensitivity within the range between 400-440 nm wavelength.

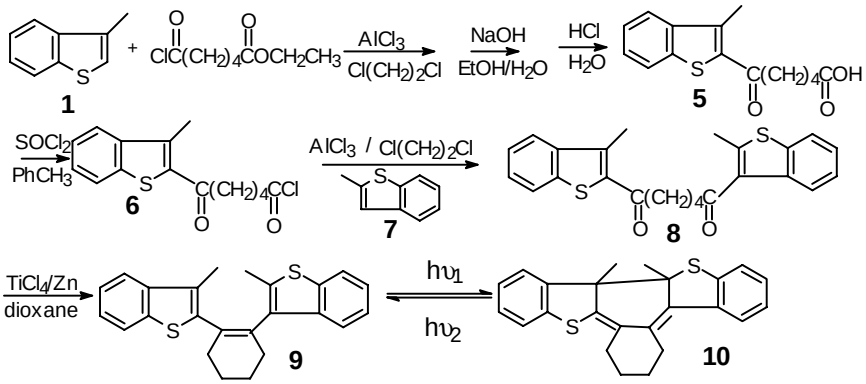
For the synthesis and photochromic reaction of compound **3a**, **3b** and **9**, the following reactions, as shown in **Scheme 1** and **Scheme 2**, represent the general

procedures:

Scheme 1



Scheme 2



2a: yield 61.5 (%), m.p.164-166℃. IR (ν /cm-1): 3051 (w), 2922 (w), 1665 (m), 1644 (s), 755 (m), 727 (m). ^{1}HNMR (ppm, $CDCl_3$): 1.88-1.90 (m, 4H, $2CH_2$), 2.77 (s, 6H, 2CH3), 3.02 (t, 4H, $2CH_2$), 7.40-7.90 (m, 8H, Ar-H). GC-MS (m/z): 406 (M^+, 4.98), 176 (15.88), 175 (100), 147 (53.38). **2b**: yield 63.7 (%). m.p. 168-170℃. IR (v/cm^{-1}): 3045 (w), 2943 (w), 1650 (s), 1209. (s), 760 (s), 728 (m). ^{1}HNMR (ppm, $CDCl_3$): 2.26 (p, 2H, CH_2, J=6.93Hz), 2.79 (s, 6H, $2CH_3$), 3.12 (t, 4H, $2CH_2$, J=6.93Hz), 7.43-7.89 (m, 8H, Ar-H). GC-MS (m/z): 392 (M^+, 11.19), 245 (16.08), 176 (14.16), 175 (100), 147 (49.65) . **8:** 0.65g, yield 32 (%). m.p. 99-101℃. IR（v/cm）: 3056 (w), 2931 (w), 2862 (w), 1658 (s), 1645 (s), 1183 (s), 764 (s), 731 (s); ^{1}HNMR (ppm, $CDCl_3$): 1.86-1.95 (m, 4H, $2CH_2$), 2.78 (s, 6H, $2CH_3$), 3.0-3.1 (m, 4H, $2CH_2$), 7.3-8.2 (m, 8H, Ar-H); GC-MS (m/z): 406 (M^+, 1.55), 259 (1.30), 176 (19.43), 175 (100), 147 (41.36). **3a**: yield 40 (%), m.p. 147-149℃, IR (v/cm): 2935.3 (w), 2904.1 (w), 1434.26 (m), 749.9 (s), 725.7 (s). ^{1}HNMR (ppm, $CDCl_3$): 1.93-1.96 (m, 4H, $2CH_2$), 2.18 (s, 6H, $2CH_3$), 2.55 (m, 4H, $2CH_2$), 7.2-7.7 (m, 8H, Ar-H); GC-MS (m/z): 375 ($M+1^+$, 28.23), 374 (M^+, 100), 344 (20.97), 147 (41.33). **3b**: yield 10 (%), m.p.129-131℃, IR (v/cm) : 3051.2 (w), 2943.6 (w), 2906 (m), 2841.4 (m), 1434.4 (m), 752.2 (s), 726.7 (s). ^{1}HNMR (ppm, $CDCl_3$): 1.93 (s, 6H, $2CH_3$), 2.20 (p, 2H, CH_2, J=7.5Hz), 3.05 (t, 4H, $2CH_2$, J=7.5Hz), 7.3-7.8 (m, 8H, Ar-H); GC-MS (m/z): 361 ($M+1^+$, 25.80), 360 (M^+, 100), 345 (21.00), 147 (31.80) **9**: yield 17 (%), m.p.120-122℃, IR (v/cm): 2953 (w), 2904 (w), 1434 (m), 757 (s), 725 (s).

^{1}HNMR (ppm, $CDCl_3$): 1.95 (m, 4H, $2CH_2$), 2.12 (s, 3H, CH_3), 2.35 (s, 3H, CH_3), 2.55 (m, 4H, $2CH_2$), 7.15-7.68 (m, 8H, Ar-H); GC-MS (m/z): 375 ($M+1^+$, 29.95), 374 (M^+, 100), 359 (44.27), 344 (35.42), 147 (43.23).

Figure 1. Absorption spectra change of **3a** (3.29×10^{-5} mol/L in cyclohexane) upon irradiation with UV (λ = 254 nm) and visible light. Inset: monitored between 340-460nm.

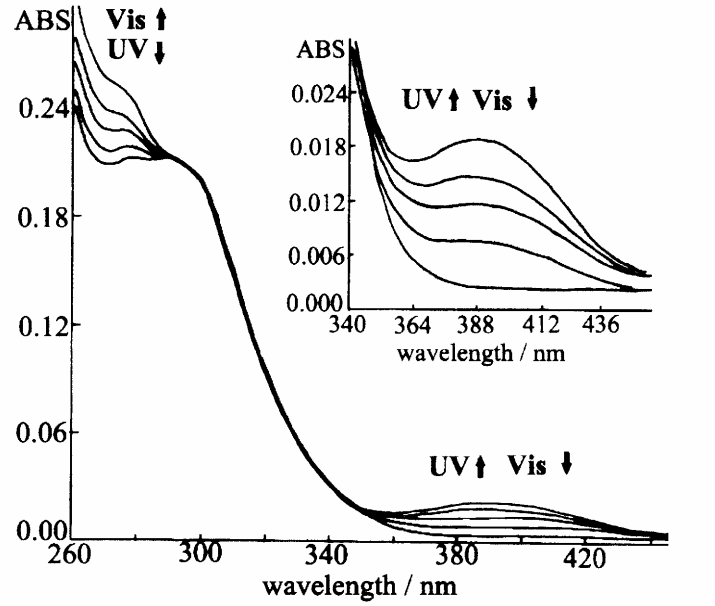


Table 1. The absorption data of compounds

compound	**3a**	**4a**	**3b**	**4b**	**9**	**10**
λmax(nm)	232	397	232	390	232	410
ε ($cm^{-1}.mol^{-1}.L$)	24070		157800		35580	

In our preliminary experiment, compound **3a**, **3b** and **9** exhibited a typical photochromic behavior. On irradiation with UV light (9w, λ =254 nm), the colorless **3a**, **3b** and **9** underwent photochromic reaction to afford the colored forms **4a**, **4b** and **10** in cyclohexane according to the Woodward-Hoffmann rule; The colored forms can also bleach and return to the initial colorless forms by exposure to visible light. **Figure 1** shows the absorption spectral change of a cyclohexane solution of **3a** before and after irradiation at 254 nm. The absorption maxima of **3a**, **3b** and **9** and their closed forms **4a**, **4b**, **10** in cyclohexane are collected in **Table 1**. The colored forms **4a**, **4b** and **10** have their absorption bands centered between 360-440 nm thus possessing the sensitivity at the wavelength range emitted by InGaN diode laser.

Compound **4a**, **4b** and **10** showed good thermal stability in the dark. Their absorption spectra and optical density at 60℃ in tetralin remained substantially constant for more than 10 hrs. The detailed studies on the photochromic properties of these compounds will be published elsewhere.

Acknowledgments

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