Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

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Version of record first published: 24 Sep 2006

Mol. Cryst. and Liq. Cryst., 2000, Vol. 345, pp. 33-38
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A novel kind of photochromic compounds, the derivatives of 1-(3-Methylbenzo[b]thiophen-2-yl)-2-(2-methylindol-3-yl)cyclo-alkene was successfully synthesized. The absorption bands of the closed-forms of these compounds centered at 440 nm thus possessing the sensitivity within the wavelength range of InGaN blue laser.

Keywords: 1; 2-diheteroarylcycloalkenes; benzothiophen; indole; photochromism; InGaN blue laser

INTRODUCTION

There have been considerable interests in the synthesis of photochromic compounds due to their potential application in optical-data storage [1]. Among these compounds, 1,2-diarylethenes constitute an important class because of their thermal stability and fatigue resistance [2]. Generally, after irradiation with UV light, this kind of compounds will lead to the eletrocyclic reactions to produce their closed forms which absorb light in the visible region. The closed-forms can be bleached and

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return to their original open-forms when irradiated with visible light. Up to now, from the viewpoint of applications, much efforts have been paid to synthesize the compounds which 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 longer than 560 nm. 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 blue laser will increase the optical information density by nearly four times. The remaining challenges are to design and synthesize the molecules which can undergo reversible photoreaction induced by blue light, however,few studies on this issue have been reported[5]. In the present work, we successfully synthesized a novel kind of photochromic compounds, the unsymmetrically substituted 1,2-diheteroarylcycloalkene derivatives, 1-(3-Methylbenzo[b]thiophen-2-yl)-2-(2-methylindol-3-yl)cycloalkene **6** Upon irradiation with UV light (λ = 254nm), compounds **6** underwent eletrocyclic reactions to produce their closed-ring forms **7** ,which could be bleached to return their original open-forms **6** when irradiated with blue light.

EXPERIMENT

NMR, MS and IR data were obtained with Varian Gemini 300 NMR, TRIO 2000 MS and Bio-Rad Win-IR Spectroscopicmeter respectively.

The thermal stability of compounds **7** were monitored on Hitachi 557 Double Wavelength Double Beam Spectrophotometer by following the decay of the visible absorbency maximum of the closed-form in the dark after UV-irradiation (1min., λ =254nm, 9W mercury lamp).

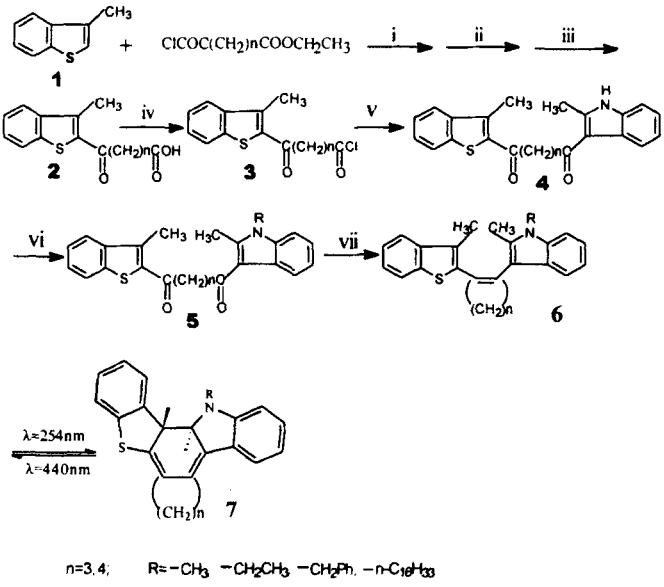
The Preparation of Compound **6** was described elsewhere [6]. The

related data were collected in TABLE 1.

TABLE 1. The Melting Point And Yields of Compound **6**

Compd	n	R	m.p.(℃)	yield %
6a	4	-Me	162-165	55
6b	4	-Et	125-127	43
6c	4	$-CH_2Ph$	161-163	27
6d	4	$-C_{16}H_{33}$	114-116	21
6e	3	-Me	184-186	34
6f	3	-Et	126-128	32
6g	3	$-CH_2Ph$	129-131	28

RESULTS AND DISCUSSION



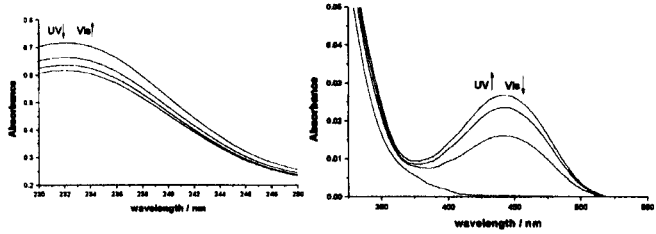
i: $AlCl_3$ / $ClCH_2CH_2Cl$; ii: NaOH / $CH_3CH_2OH.H_2O$; iii: HCl, H_2O

iv: $SOCl_2$ / $PhCH_3$; v: 2-methylindolyl magnesium bromide/ether

vi: R_2SO_4 or RBr/NaOH.H_2O,$(CH_3)_2CO$ vii: $TiCl_4$/Zn, dioxane

SCHEME 1 represents the general procedure for the synthesis and photochromism of **6** and **7**.

The absorption maximum of compound **6** centered at 232 nm. Upon irradiation with UV light (λ = 254 nm), compound **6** underwent photoperycyclic reaction to form compound **7** which absorbed at 440nm. In compound **6**, the indole ring, the cycloalkene ring and the benzothiophene ring are not co-planar, thus there does not exist conjugation among them. While in compound **7**, the three moieties of the molecules are nearly co-planar, and the conjugation can occur among the three moieties to a certain degree. Consequently, the absorption maximum of **7** is centered at blue light region.



UV-region Visible-region

FIGURE 1. The absorption spectral changes of **6a** after UV irradiation (8.79×10^{-6}mol.L^{-1}, solvent: cyclohexane)

For example, **6a** was irradiated with UV light to form closed form **7a**. The λ max at 232 nm was decreased, while the absorption in the blue light region (λ max = 440 nm) was increased, finally getting a photostationary state. While **7a** was irradiated with 450nm light , the process was reversed(see FIGURE 1). These results indicate that this kind of compounds possess excellent photochromic properties.The colored form would be compatible with the newly developed InGaN diode laser.

The thermal stability of the colored form **7** in dark was measured by following the decay of the absorption maximum at 440 nm at 60℃.

The effects of substituents attached to the N-atom of indole ring on the thermal stability of compound **7** were examined. The results are shown in FIGURE 2. It indicated that bulky substituent group on the N-atom of indole ring prohibits the thermal disrotatory ring-opening reaction of **7** and increase the thermal stability of closed-ring form. The absorption of the closed-ring form **7d** remained 88% after 10 hours, while for **7a**, only 35% remained.

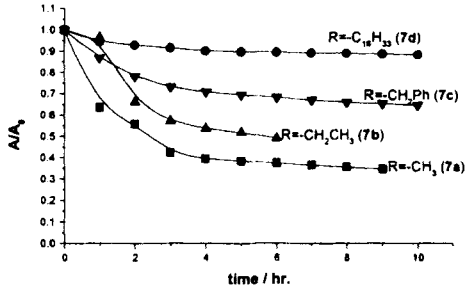


FIGURE 2 . The thermal stability of compound **7** at 60℃ (n = 2) (monitored at 440 nm, in the solution of teralin)

The thermal stability of the closed forms of 1-(3-methylbenzo[b]thiophen-2-yl)-2-(2-methylindol-3-yl)cycloalkene with that of 1,2-bis(3-methylbenzo[b]thiophen-2-yl)cycloalkene derivatives which we reported earlier [5], we found that the former was less stable than the latter. The phenomenon is explained by the difference of the aromatic stabilization energy between indole and benzothiophene[7].

CONCLUSION

1-(3-Methylbenzo[b]thiophen-2-yl)-2-(2-methylindol-3-yl)cycloalkene derivatives were succesfully synthezised by the intramolecular coupling of the corresponding diketones. The obtained compounds exhibited

photochromic property and the absorption bands of the colored forms **7** centered at 440 nm and possess the sensitivity within the wavelength range of InGaN blue laser. The thermal stability of the colored forms are influenced by the substituents attached to the nitrogen atom of the indole ring. Bulky substituent prohibits the thermal disrotatory reaction of the closed form thus increase its thermal stability.

ACKNOWLEDGEMENTS: This work was supported by National Natural Science Foundation of China (No. 29702009), National Principal Project (G1999033005), Guangxi Youth Science Foundation (No. 9515004) and Education Committee of Guangxi Zhuang Autonomous Region.

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