

Novel Diarylethenes: N-Substituted-3, 4-bisheteroaryl-2, 5-dihydropyrrole

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Abstract: Novel diarylethene derivatives: N-substituted-3,4-bisheteroaryl-2,5-dihydropyrroles were synthesized through McMurry couple reaction with high yields. The photochromic properties and UV-Vis absorption spectra were studied. The maximal absorptions of their close forms were around at 406 nm or 446 nm, which related mainly with heteroaryl groups but not with substituted groups at nitrogen atom of dihydropyrrole. The absorption of their colored form could be matched with blue light laser.

Keywords: Diarylethene, 3, 4-bisheteroaryl-2, 5-dihydropyrrole, photochromism.

Diarylethene derivatives constitute an important class of photochromic compounds and often exhibit excellent photochromic properties, thermal and photochemical stability, very good fatigue resistance for photochemical reversibility¹. In recent years, concerning of synthesis, structure, photochromic properties and applications, diarylethenes has been widely studied¹⁻⁶.

In our previous papers, a series of diarylethenes were created⁵, such as bisarylcyclopentenes, bisarylcyclohexenes, bisaryldihydrothiophenes and bisaryldihydrofurans. In this paper, novel diarylethene derivatives: N-substituted-3, 4-bisheteroaryl-2, 5-dihydropyrroles were synthesized by McMurry reaction with high yield. The synthesis reaction was shown as below (**Scheme 1**). Melting points, ¹H-NMR and GC-MS of all compounds were identified.

Experimental

Melting points were recorded on X-4 melting point apparatus. ¹H-NMRs were recorded in CDCl₃ on Varian Germina-300 MHz spectrometer using TMS as internal standard. UV-Vis spectra were recorded on Hitachi U-3010 spectrometer at room temperature. MS was measured with a Trio-2000 GC-MS spectrometer.

General procedure: Zn dust (6 mmol) was added in small portions to TiCl₄ (3 mmol) in anhydrous THF (50 mL) with ice cooling under N₂ atmosphere. The mixture was heated to reflux for 1 h and then cooled. A solution of compounds **3** or **4** (1 mmol) in

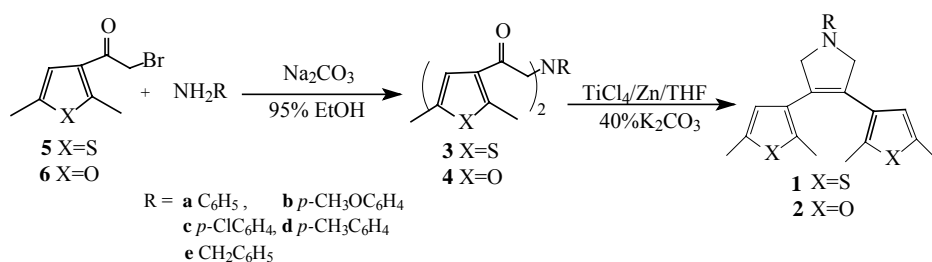
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anhydrous THF (50 mL) was added dropwise over a period of 8 h at room temperature. The reaction mixture was heated at reflux for 24 h and then cooled to room temperature, quenched with 40% K₂CO₃ solution (10 mL). The crude reaction product was extracted with chloroform (250 mL). The extract was dried (MgSO₄), filtered and concentrated in vacuum. The residue was purified by column chromatography on silica gel using ether/petroleum ether as eluent. The N-substituted-3, 4-bisheteroaryl-2, 5-dihydropyrrole (compounds **1** and compounds **2**) were obtained after evaporation of the solvent.

Results and Discussion

Photochromic reaction of N-substituted-3, 4-bisaryl-2, 5-dihydropyrrole is shown in **Scheme 2**.

Scheme 1 The synthesis reaction of N-substituted-3, 4-bisheteroaryl-2, 5-dihydropyrrole



Scheme 2 photochromic reaction of compounds **1** and **2**

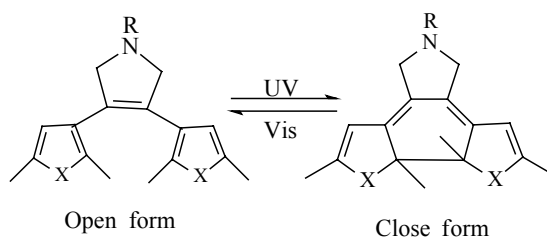


Figure 1 Absorption spectra of **1c**, open form (—) and close form (⋯) in acetonitrile

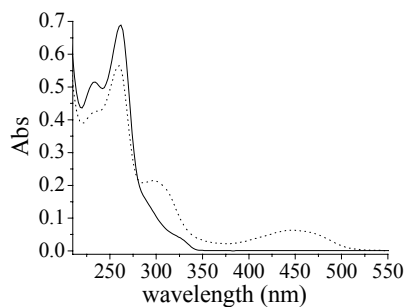


Figure 1 shows UV-Vis absorption spectra of open form and close form of compound **1c**. When **1c** was irradiated with UV light, a new absorption band appears at 446 nm in acetonitrile which is attributed to the absorption of its close form.

Absorption spectra data of compounds **1a-e** and **2a-c** and their close form were summarized in **Table 1**. The substituted groups **R** had no remarkable effect on the absorption spectra of close form, since they did not conjugate very well with cyclohexadiene unit. But when R is benzyl (**1e**), the peak value of close form is 436 nm with about 10 nm blue shift comparing with which of **1a-d**. Because π -electron system of phenyl and cyclohexadiene are separated by methylene group of benzyl, it is indicated that the π -electron system of phenyl may have some interaction with cyclohexadiene unit through p-electron pair of nitrogen and methylene group in dihydropyrrole unit. The absorption coefficients (ϵ) were quite large of **1a-e** and **2a-c**. Red shift was observed in absorption spectra of close form when acetonitrile is replaced by cyclohexane as solvent. It was indicated that the excited state of close form was π - π^* transition⁷. There was remarkable effect on maximum absorption when thienyl was replaced by furyl group. The maximum absorption of close forms of **1a-e** were around 446 nm while which of **2a-c** were shifted to 406 nm in acetonitrile. Because oxygen has larger electronegativity than sulfur, the close form of compounds **1** can be polarized easier than the close form of compounds **2** in excited state. It was to say that heteroaryl groups at 3, 4 positions of dihydropyrroles would affect basically on the maximum absorption wavelength of close form of N-substituted-3, 4-bisheteroaryl-2, 5-dihydropyrroles.

Conclusion

We have synthesized a novel type of diarylethene derivatives. These compounds might be matched with blue light laser and used in high density optical storage. Their absorption spectra of close forms were affected remarkably by heteroaryl groups of dihydropyrroles.

Table 1 absorption spectra data of compounds **1a-e** and **2a-c**

	R	λ_{\max} (open) (ϵ) ^a acetonitrile	λ_{\max} (open) (ϵ) cyclohexane	λ_{\max} (close) acetonitrile	λ_{\max} (close) cyclohexane
1a	C ₆ H ₅	252 (3.1)	250(3.5)	446	448
1b	<i>p</i> -OCH ₃ C ₆ H ₄	248 (3.1)	240(3.3)	446	450
1c	<i>p</i> -ClC ₆ H ₄	234 (2.6)	236(3.0)	446	448
		262 (3.5)	260(3.9)		
1d	<i>p</i> -CH ₃ C ₆ H ₄	252 (3.5)	252(3.7)	444	448
1e	CH ₂ C ₆ H ₅	230 (2.1)	232(2.1)	436	438
2a	C ₆ H ₅	252 (1.7)	250(1.9)	406	408
2b	<i>p</i> -OCH ₃ C ₆ H ₄	250 (2.2)	250(2.5)	406	408
2c	<i>p</i> -ClC ₆ H ₄	262 (1.9)	260(2.0)	406	408

a: λ_{\max} (nm), ϵ ($\times 10^4 \text{cm}^{-1}\text{M}^{-1}$)

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