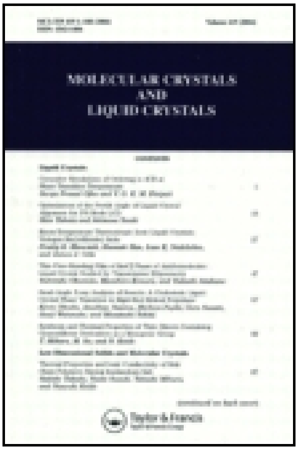

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Synthesis and Photochromic Behavior of 1,2-bis(1,3-dimethylindol-2-yl)cycloalkenes

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Synthesis and Photochromic Behavior of 1,2-bis(1,3-dimethylindol-2-yl)cycloalkenes

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Two novel 1,2-bis(1,3-dimethylindol-2-yl)cycloalkenes(**2**) were designed and synthesized by intramolecular coupling reaction using low-valance titanium as catalyst. Photochromic properties of these compounds were initially investigated. The results show that the thermal stability of colored form of **2** is much better than that of 1,2-bis(1-ethyl-2-methylindol-3-yl)cycloalkenes(**4**), and the absorption maximum of them is shorter than that of 1,2-bis(1-ethyl-2-methylindol-3-yl)cycloalkenes.

Keywords: synthesis; cycloalkene; photochromic; stability

INTRODUCTION

Over the last few years, organic photochromic compounds have increasingly attracted the attention and interest of chemists and engineers due to their potential applications in optical information storage[1,2]. Diarylethene derivatives are one kind of important photochromic compounds, which have the excellent properties of fatigue resistance and thermal stability. Upon irradiation with UV light,

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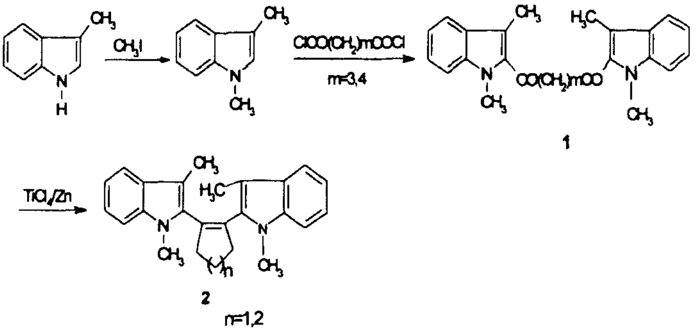
diarylethene derivatives (colorless form) undergo a cyclization reaction, and produce colored forms, possessing absorption in the visible region.The colored form can return reversibly to the starting material after exposure to visible light. In order to find out novel types of photochromic compounds, we designed and synthesized 1,2-diheterocycles cycloalkene derivatives by the intramolecular coupling method, which construct an efficient photochromic system. We herein report our preliminary results. The synthetic route is outlined as shown in scheme I.



SCHEME I. The synthetic route of compounds **2**

RESULTS AND DISCUSSION

Synthesis

Bis(1,3-dimethylindol-2-yl)alkane- α , ω -dione(**1**) was prepared by treatment of 1,3-dimethylindole with α , ω -bisacylate dichloride using boron trifluoride ethyl etherate as catalyst in room temperature.

The final products **2** was synthesized by the intramolecular coupling reaction of **1** in anhydrous dioxane using low-valence titanium as catalyst. General procedure for the preparation of 1,2-bis(1,3-dimethylindol-2-yl)cycloalkenes **2** is as follows. Titanium tetrachloride (9mmol) was added dropwise to stirred suspension of zinc powder (18mmol) in anhydrous dioxane(50ml) at -10 ℃ under dry argon nitrogen. The resulting dark mixure was heated under the refluxing about 1 hr, and a solution of **1** (3mmol) in dioxane was slowly added.

The reaction mixture was refluxed under stirring for 12hrs, cooled and poured into 10% aqueous potassium carbonate. The aqueous layer was extracted with ether (3 × 50ml), and the combined organic extracts were dried and evaporated to give a oil. The pure products **2a** and **2b** were available by column chromatography on silica gel using petroleum/chloroform as eluents. The physical chemistry data was collected in TABLE 1. The two compouds in TABLE 1 are novel, and were identified by ^{1}H NMR, MS.

TABLE 1 The physical chemistry data of compound **2**

Compd.	n	Formula	M.P.(℃)	Yield(%)
2a	2	$C_{26}H_{28}N_2$	186-188	16.3
2b	1	$C_{25}H_{26}N_2$	178-180	20.5

Photochromic Reaction

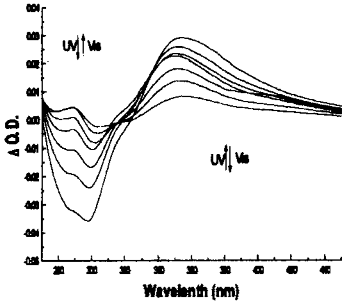


FIGURE 1. Typical absorption change of compound 2a in cyclohexane(3.3 × 10^{-5}mol/l)in the photostationary state under irradiation with 254nm light

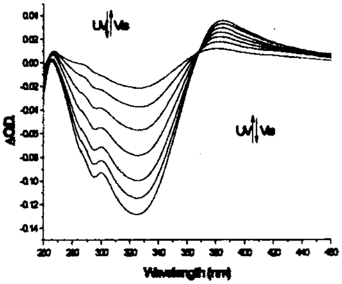
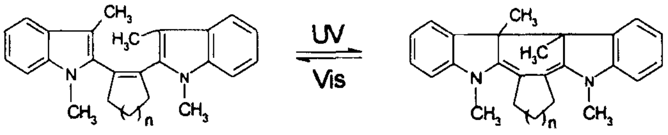


FIGURE 2 Absorption change of compound 2b in cyclohexane(3.3 × 10^{-5} mol/l)in the photostationary state under irradiation with 254nm light

Irradiation of the solution of **2a** with 254nm light led to the formation of a pale yellow solution and absorption maxima at 353nm is assigned to the closed isomer **3a**, which disappeared instantly on exposure to the light longer than 400nm as shown in FIGURE 1. Irradiation of the solution of **2b** with 254nm light led to the formation of a pale yellow solution too and absorption maxima at 387nm is assigned to the closed isomer **3b**,which disappeared instantly on exposure to the light longer than 400nm too as shown in FIGURE 2.

FIGURE 1 and 2 show that compounds **2a** and **2b** exhibit good photochromic properties in solution. The photochromic reactions are shown in SCHEME II.

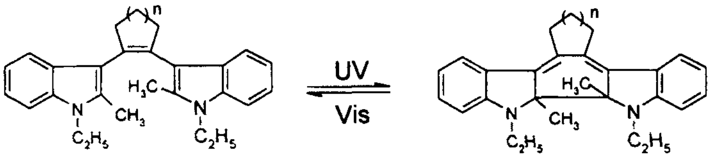


2 **3**

a: n=2 **b**: n=1

SCHEME II Photochromic reaction of **2** and their colored forms **3**

The studies of photochromic behaviors of 1,2-bis(1-ethyl-2-methylindol-3-yl)cycloalkenes **4** have been published in 1997. The photochoromism of them are shown as SCHEME III.



4 **5**

a: n=2 **b**: n=1

SCHEME III Photochromic reaction of **4** and their colored forms **5**

The absorption maxima of **3a** and **3b** was compared with that of **5a** and **5b** (see TABLE 2).It can be found that the absorption maxima of colored form of 1,2-bis(1,3-dimethylindol-2-yl)cycloalkenes is much shorter than that of 1,2-bis(1-ethyl-2-methylindol-3-yl)cycloalkenes.

TABLE 2 The absorption maxima for **3a**, **3b**, **5a** and **5b**

Compd.	**3a**	**3b**	**5a**	**5b**
λ max/nm	353	387	484	488

The large difference is mainly caused by a large π - π conjugation in the colored form **5** and p- π conjugation including in the colored form **3**. The absorption maxima of the colored form **5** shift to a little longer wavelength as decreasing the ring size from a six to five-member ring of alkene. It implied that the ring size probably affects the planarity in the closed-ring forms . When the ring size is small, the resulting rigid structure favors to keep planarity of the cyclohexadiene molecular framework and to increase the π -conjugation thus leading to a little bathchromic shift.

<u>Thermal Stability of the Closed-Ring Forms</u>

The thermal stability of the photogenerated closed-ring forms **3** have been examined at room temperature and at 60℃ respectively as shown in FIGURE 3 and 4.

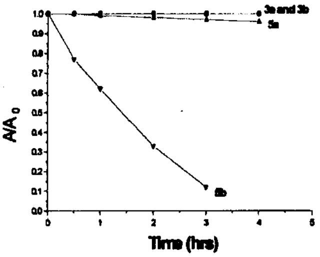


Figure 3 The thermal stability of **3a**, **3b**, **5a** and **5b** at 23℃ in dark

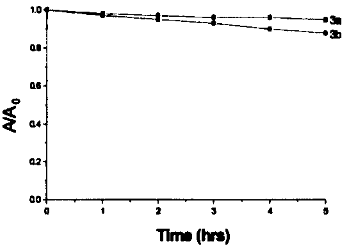


FIGURE 4 The thermal stability of **3a** and **3b** at 60℃ in dark

FIGURE 3 illustrates the comparison of the thermal stability of **3a**, **3b** with **5a** and **5b** at room temperature in the dark. The value of A/A₀ was plotted against storage time, where A₀ is the initial absorption of the closed forms, and A is the absorption after stored for different time interval at room temperature. As seen in figure 3, the photogenerated closed forms **3a** and **3b** are thermal stable and their optical density have no change during the period of 4 hours. While **5a** and **5b** are thermally unstable at room temperature. From figure 4, it can be found that **3a** and **3b** are considerately stable even at 60℃.

Based on the above discussion, we conclude that the thermal stability of **3** is much better than that of **5**. According to literature[3], the thermal stability of the ring-closed form of diarylethene derivatives depends on the aromatic stabilization energy of the heterocyclic groups; when the aromatic stabilization energy is large in the course of ring-opening reaction, the thermal stability of the closed-ring form is not good. Looking the ring-opening form **2** in SCHEME2, the stereohindrance between N-substituent and methylene substituent of the cycloalkene makes the molecular framework of **2** to be largely twisted. So that the indole ring and the cycloalkene can not form a conjugation system, which decrease the aromatic stabilization energy of the indole ring. In contrast, there is no stereohindrance between methylene group of cycloalkene with N-substituent of indole ring, thus the indol ring and the cycloalkene could be coplanar in certain degree. Therefore the indole ring could conjugate with the cycloalkene, and then increase the aromatic stabilization energy of indole ring.

ACKNOWLEDGEMENTS

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References

[1] R.C. Bertelson, in G.H. Brown (Ed.), *Photochromism,* Wiley-Interscience, New York, 1971.

[2] H. Durr, H. Bouas-Laurent, Photochromism. *Molecules and Systems,* Elsevier, Amsterdam, 1990.

[3] Z.N. Huang, S. Jin, Y.F. Ming, M.G. Fan, *Mol. Cryst. Liq. Cryst.,* 1997, **Vol. 297,** PP.99–106.