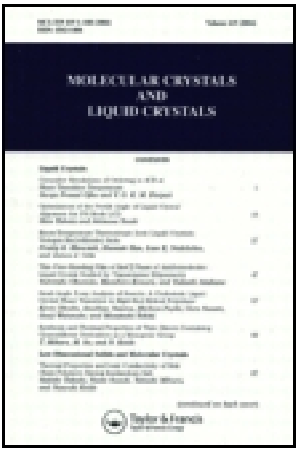

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Syntheses and Photochromic Behaviour of 1,2-Bis (1-Alkyl-2-Methylindol-3-Yl) Cycloalkene Derivatives

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SYNTHESES AND PHOTOCHROMIC BEHAVIOUR OF 1,2-BIS(1-ALKYL-2-METHYLINDOL-3-YL)CYCLOALKENE DERIVATIVES

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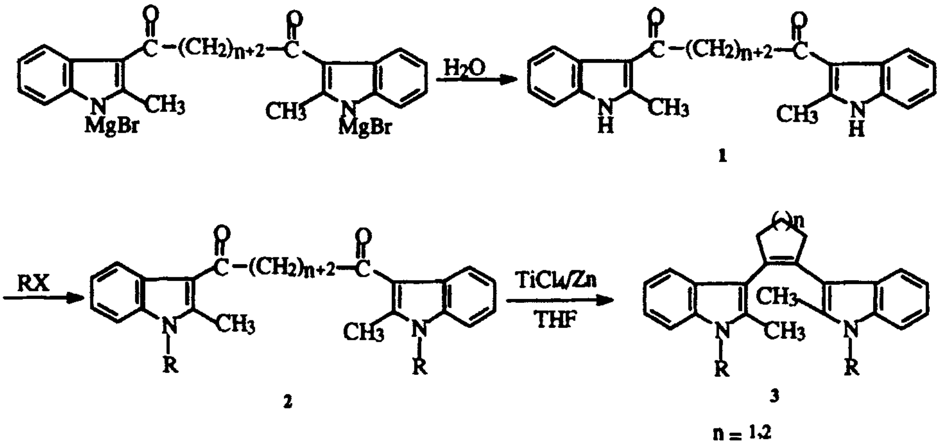
Abstract Six novel 1,2-bis(1-alkyl-2-methylindol-3-yl)cycloalkene derivatives were designed and synthesized by the intramolecular coupling reaction using low-valance titanium as catalyst. Photochromic properties of these compounds were initially investigated. The results show that the fatigue resistant properties of these compounds, the thermal stability and the absorption maxima of their photocyclization products are influenced by the ring size of cycloalkene and substituents on the heterocyclic rings.

INTRODUCTION

There have been considerable interests in the synthesis of photochromic compounds because of their theoretical aspects and potential use in optical data storage media. Among these compounds, 1,2-diarylethenes containing heterocyclic rings have promising properties for practical use[1-4]. The compounds undergo electrocyclic reactions to produce closed-ring forms which absorb light in the visible region. However, *cis-trans* isomerization can also occur, and is unfavorable for practical application since it competes with the cyclization[5]. To prohibit *cis-trans* isomerization, Irie *et al.* have developed photochromic 1,2-diheterocyclic substituents perflorocyclopentene derivatives[6] and 2,3-diheterocyclic substituents maleic anhydrides[4]. Recently, with a view to looking for novel types of photochromic compounds, we designed and synthesized 1,2-diheterocycles cycloalkene derivatives by the intramolecular coupling method, which can not undergo *cis-trans* isomerization and construct an efficient photochromic system. We herein report our preliminary results. The synthetic route is outlined as shown in Scheme I.



Scheme I

RESULTS AND DISCUSSION

1. Synthesis

Bis(2-methylindol-3-yl)alkane-α,ω-dione **1** was prepared by treatment of α,ω-bisacylate dichloride with 2-methyl indolyl magnesium bromide. Diketone **2** was subsequently obtained by alkylation of **1** in DMSO under an alkali condition. The final products **3** was synthesized by the intramolecular coupling reaction of **2** in anhydrous tetrahydrofuran using low-valence titanium as catalyst.

General procedure for the preparation of 1,2-bis(1-alkyl-2-methylindol-3-yl)-cycloalkenes **3** is as follows. Titanium tetrachloride (4 mmol) was added dropwise to a stirred suspension of zinc powder (8 mmol) in anhydrous tetrahydronfuran (100 mL) at -10°C under dry argon. The resulting dark mixture was warmed to room temperature for 2 hrs, and solution of **2** (8 mmol) in THF was added. The reaction mixture was refluxed under stirring for 24 hrs, cooled and poured into 10% aqueous potassium carbonate. The aqueous layer was extracted with ether (3.x 40 mL), and the combined organic extracts were dried and evaporated to give a yellow oil. The pure products **3a-f** were available by column chromatograph on silica gel using petroleum/ethyl acetate as eluents.

TABLE 1 Preparation of 1,2-bis(1-alkyl-2-methylindol-3-yl)cycloalkenes **3**.

Comp.	n	R	Formula	M.P.(°C)	Yield(%)
3a	2	C_2H_5	$C_{28}H_{32}N_2$	196–198	26
3b	2	CH_2Ph	$C_{38}H_{36}N_2$	272–274	23
3c	2	$C_{16}H_{33}$	$C_{56}H_{88}N_2$	< 30	44
3d	1	C_2H_5	$C_{27}H_{30}N_2$	182 – 184	42
3e	1	CH_2Ph	$C_{37}H_{34}N_2$	174 – 176	35
3f	1	$C_{16}H_{33}$	$C_{55}H_{86}N_2$	32 – 34	65

All the compounds in Table 1 are novel, and were identified by ^1H NMR, MS-FAB and elemental analyses. The detailed spectra data will be published elsewhere.

2. Photochromic Reaction

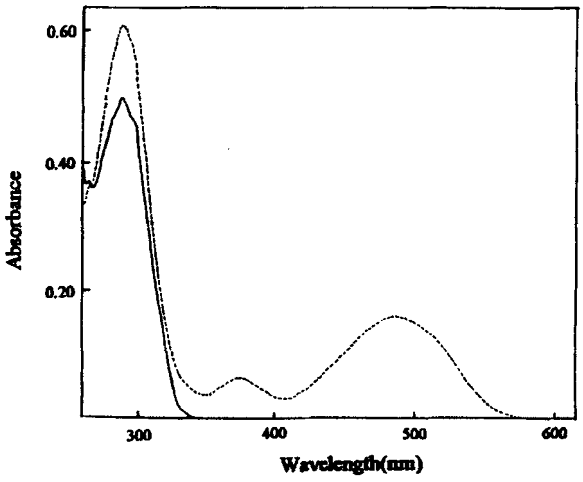
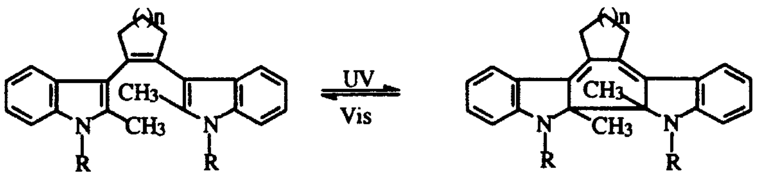


FIGURE. 1 Absorption spectra of **3a** (1.3×10^{-5} mol/L)(—) and in the photostationary state under irradiation with 254 nm light (----).

Title compounds exhibit good photochromic properties either in solution or in poly-matrixes. When a solution of **3** in common organic solvents such as cyclohexene, benzene and alcohol, was irradiated by UV light, it became red. The reverse process could also take place by exposure to visible light and the color bleached.

Figure 1 shows the absorption spectra change of a cyclohexane solution of **3a** before and after photoirradiation with 254 nm light. Irradiation of the solution with 254 nm light led to the formation of a red solution and absorption maxima at 484 nm and 374 nm due to the generation of the closed isomer **4a**, which disappeared instantly on exposure to the light longer than 400 nm. In the ^{1}H NMR spectrum, when **3** was irradiated with UV light, it caused the 2-methyl proton of heterocycles to shift upfield which confirmed that the ring-closed form is produced as following equation. The absorption maxima are listed in Table 2.



3 **4**

TABLE 2 Absorption maxima of **4** in cyclohexane (~ 10^{-4} mol/L).

Comp.	n	R	λmax/nm
4a	2	C_2H_5	484
4b	2	CH_2Ph	478
4c	2	$C_{16}H_{33}$	486
4d	1	C_2H_5	488
4e	1	CH_2Ph	482
4f	1	$C_{16}H_{33}$	490

Table 2 summarizes the absorption maxima of the colored forms **4a-4f**. From the Table 2, it can be found that the absorption maxima of colored form of 1,2-bis(1-alkyl-2-methylindol-3-yl)cycloalkene derivatives shift to a little longer wavelength upon decreasing the ring size from a six to five-membered ring of alkene. It implies that the ring size probably affects the planarity and π-conjugation in the closed-ring forms **4**. When the ring size is small, the resulting rigid structure favors to keep planarity of the cyclohexadiene molecular framework and to maintain the π-conjugation thus leading to a little bathochromic shift. When a 2-butene structural unit instead of cycloalkene is present, the absorption maximum of the closed-ring form will shift to the shorter wavelength. For example, 2,3-bis(1,2-dimethylindol-3-yl)-2-butene affords absorption maximum of its colored form at 470 nm upon irradiation with UV light[5].

3. Thermal Stability of the Closed-Ring Forms

Thermal stability of the photogenerated closed-ring forms **4** was examined at room temperature. The experiments showed that the thermal stability of **4** depends on two facts: (1) the ring size of cycloalkene moiety, and (2) the substituent attached to the N-atom of indole ring.

Figure 2 illustrates the thermal stability of **4a, 4c, 4d** and **4f** at room temperature in the dark. The value of $A/A_0 \times 100$ was plotted against storage time, where A_0 is the initial absorbance of the closed forms, and A is the absorbance after varied hours at room temperature. As seen in Figure 2A, the photogenerated closed form **4c** is relatively stable and maintaince of the absorption intensity almost constant within first 4 hours, while **4d** and **4f** having five-membered ring structure units are thermally unstable and gradually revert to **3d** and **3f**. Obviously, the strain of the five-membered ring combined with the cyclohexadiene molecular framework results in the thermal unstability of the colored form of **3**. In addition, the bulky substituent group attached to N-atom of indole ring is believed to prohibit the thermal disrotatory ring-opening reaction of **4** and increase the thermal stability of the corresponding closed-ring form. The closed-ring forms **4a** and **4c** with six-membered alkene ring moiety show that after 48 hrs, 97% of **4c** remains unchanged in contrast to **4a** which is only 63% (shown in

Figure 2B). According to literature[7], 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 less. The indole ring has appropriate aromatic stabilization energy, which makes the closed-ring forms of 1,2-bis(1-alkyl-2-methylindol-3-yl)cycloalkene derivatives thermally unstable at elevated

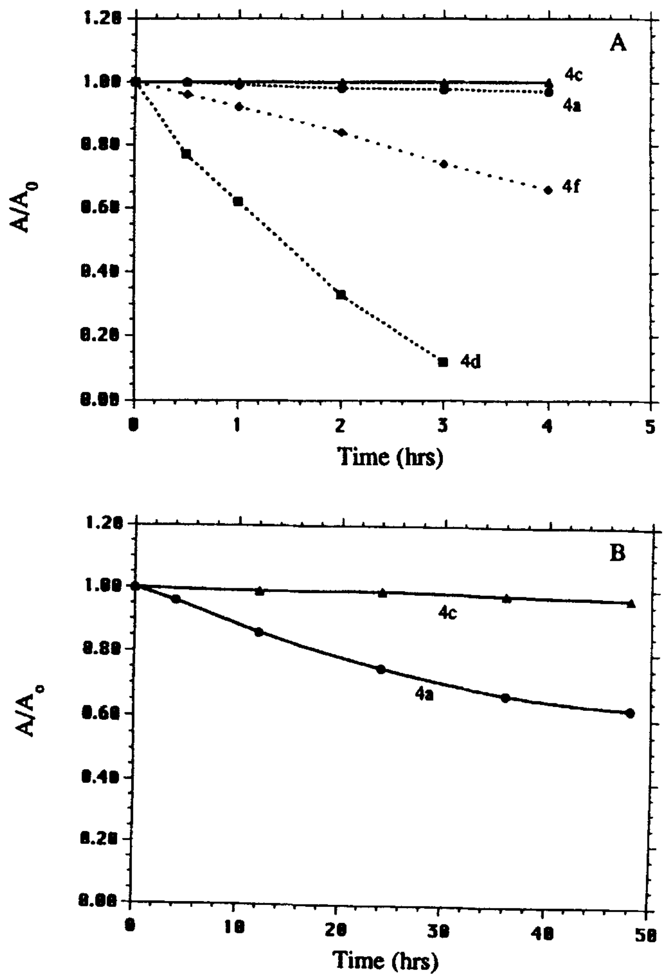


FIGURE. 2 The thermal stability of 4 in cyclohexane at room temperature (25°C) in dark. A, duration within 4 hrs.; B, duration prolonged to 48 hrs.

temperature. Therefore, it is expected that if the indole ring of 1,2-bis(1-alkyl-2-methylindol-3-yl)cycloalkenes were replaced by benzothiophene, thiophene and selenophene,, which have low aromatic stabilization energy, the thermal stability of the colored forms of 1,2-diheterocyclocles cycloalkenes would be improved.

4. Fatigue Resistance

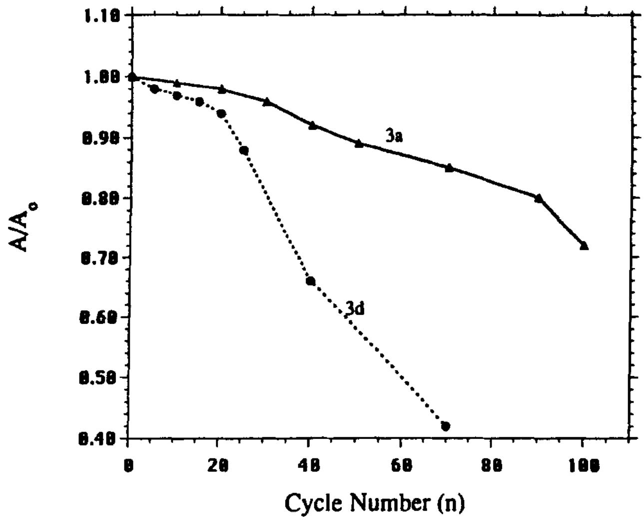


FIGURE 3 Fatigue resistant properties of **3a** and **3d** in cyclohexane.

A comparison of the fatigue resistant property for **3a** versus **3d** in cyclohexene is shown in Figure 3. The absorption intensity of the closed-ring form was plotted against colored and bleached cycle numbers. Cyclohexane solutions of the compound **3a** and **3d** (conc, ~10^{-4} mol/L, in a rectangular quartz cell with light pass length of 1 cm) were irradiated alternatively with UV 254 nm light for 30s and visible light (longer than 400 nm) for 2 min in the presence of air. The irradiation time was long enough for the compounds to convert to the photostationary state and to make the photobleached process complete. As seen in Figure 3, the fatigue resistance of 1,2-diindolylcycloalkenes is remarkably affected by the ring size of cycloalkene unit. The absorption intensity of the closed-ring form of **3a** at 484 nm decreases to 80% of the first cycle after more than 90 times coloration/decoloration cycles. In contrast, for **3d** with five-membered ring structure moiety, the absorbance of the closed-ring form decreases to 80% of the first cycle after not more than 40 times cycles. In this case, the difference of the fatigue properties between **3a** and **3d** is solely produced by the ring size of cycloalkenes since **3a** and **3d** own the identical substituents at the cycloalkene double bond. We believe that the ring strain of five-membered alkene ring structure unit results in the low fatigue resistant property of **3d.**

SUMMARY

Disubstituted-1,2-cycloalkene derivatives with substituted indole rings were synthesized. These compounds showed photochromic properties. The difference in the absorption maxima, thermal stability and fatigue resistance among the closed ring forms, which are the colored compounds generating from 1,2-bis(1-alkyl-2-methylindol-3-yl)cycloalkenes with different size of cycloalkenes and different substituents in indole rings were interpreted by ring strains and steric effect of substituents.

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REFERENCES

1. M. Irie and M. Mohri, J. Org. Chem., 53, 803 (1988).
2. K. Uchida, Y. Nakayama and M. Irie, Bull. Chem. Soc. Jpn., 63, 1311 (1990).
3. Y. Nakayama, K. Hayashi and M. Irie, J. Org. Chem, 55, 2592 (1990).
4. Y. Nakayama, K. Hayashi and M. Irie, Bull. Chem. Soc. Jpn., 64, 789 (1991).
5. G. B. Fan, Y. F. Ming and M. G. Fan, Youji Huaxue (Chinese J. of Org. Chem.), 14, 599 (1994).
6. M. Hanazawa, R. Sumiya, Y. Horikawa and M. Irie, J. Chem. Soc. Chem. Commun., 206 (1992).