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Synthesis and photochromic properties of a dithiazolylindole

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ABSTRACT

A novel photochromic 2,3-dithiazolylindole has been synthesized and its photochromic properties was elucidated. This compound showed reversible photochromism both in solution and in a crystal with no spontaneous bleaching under dark conditions. The photocyclization quantum yield of the dithiazolylindole was as high as 83% in hexane, suggesting the photoreactive conformation was stabilized through intramolecular interactions. X-ray crystal structure analysis revealed that the dithiazolylindole adopted the photoreactive conformation with quasi-C_2 symmetry around the hexatriene moiety in the crystalline state. This conformation was assisted by presumed intramolecular CH/N hydrogen bonding between the central *N*-methylindole and the side-chain thiazolyl units in combination with steric interactions between methyl groups at the reactive center carbons. The suggestion of intramolecular hydrogen bonding in solution was also supported by a ^{1}H NMR variable temperature study.

1. Introduction

Photochromic molecules undergo a reversible color change, which originates from their structural change upon light irradiation [1–6]. Photochromic molecules can be employed to modulate various physicochemical properties upon light irradiation and they have received remarkable attention for their potential applications to various photoswitches and optical memory systems. Among the classes of photochromic compounds diarylethenes with heterocyclic aryl groups are the most interesting because of their specific properties such as high thermal stability of the colored state, fatigue resistance, and high photochromic reactivity even in solid state [7]. Diarylethenes are known to have several conformations because of the rotational isomerization around single bonds between the side aryl groups and the central ethene unit. Since the photocyclization reaction to the cyclohexadiene form proceeds only from the C_2 symmetrical conformation of hexatriene form, the photocyclization quantum yields of most diarylethenes have been reported to be about 50% or less [7a,b]. Therefore, the control of ground state geometry has been a subject of considerable interest in this field [8]. Recently, photochromic triangular terarylenes have been reported to show similar photochromic reactions to those of diarylethenes [9,10]. Unlike the diarylethenes, terarylenes and related molecules can be designed to have various types of intramolecular interactions between the central and both of the side aryl units and some of these systems exhibited considerably high photocyclization quantum yields [11]. In the present study, we report on a highly reactive photochromic terarylene molecule exhibiting a photocyclization quantum yield as high as 83%, and its ground state conformation is efficiently stabilized in the photoreactive quasi-C_2 symmetric conformation around the hexatriene moiety by intramolecular H-bonding and steric interactions.

2. Material and methods

2.1. Methods

^{1}H NMR spectra were recorded on a JEOL AL-300 spectrometer (300 MHz). Separative HPLC was performed on a HITACHI LaChrom ELITE HPLC system and a JASCO LC-2000 Plus system. Mass spectra were measured with a mass spectrometer JEOL JMS-T100LC AccuTOF. Absorption spectra in solution were studied with JASCO V-550 and V-670 spectrophotometers with a temperature control unit. Photoirradiation was carried out using an USHIO 500 W ultra-high-pressure mercury lamp. Monochromic light was obtained by passing the light through a monochromator (Shimazu SPG-120S, 120 mm, $f = 3.5$). Absorption spectra in the single-crystalline phase were measured using an Olympus BX-51 polarizing microscope connected with a Hamamatsu PMA-11 photodetector with an optical fiber. Polarizer and analyzer were set in parallel to each other. X-ray crystallographic analyses were carried out with a Rigaku R-AXIS RAPID/s Imaging Plate diffractometer with Mo Kα radiation at 296 K.

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2.2. Experimental

2,3-Dithiazolylindole **1a** was synthesized according to Scheme 1.

2.2.1. Synthesis of 3-bromo-2-iodo-1-methyl-1H-indole *(3)*

To a solution of 3-bromo-2-iodo-1-(phenylsulfonyl)-1H-indole [12] (**2**, 1.0 g, 2.2 mmol) in DMF (8 mL) was added NaH (2.0 g, 50.0 mmol) at 0 °C under argon, and the reaction mixture was stirred at room temperature for 0.5 h. Methyl iodide (0.4 mL, 6.3 mmol) was then added to the stirred reaction mixture, and the mixture was stirred at room temperature for 15 h. Water was added to the resulting reaction mixture, and the water phase was extracted with Et_2O. The combined organic phase was dried with anhydrous magnesium sulfate, filtered, and concentrated. Silica gel column chromatography (hexane/ethyl acetate 10:1) afforded compound **3** (0.53 g, 1.6 mmol, 73%) as an off-white solid.

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.53–7.50 (dd, 1H), 7.33–7.30 (d, 1H), 7.23–7.10 (m, 2H), 3.82 (s, 3H); mp 56–58 °C.

2.2.2. Synthesis of 2,3-bis(5-methyl-2-phenylthiazol-4-yl)-1-methyl-1H-indole *(1a)*

A mixture of **3** (0.14 g, 0.4 mmol), 5-methyl-2-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) thiazole (**4**, 0.29 g, 1.0 mmol), $Pd(OAc)_2$ (9 mg, 0.04 mmol), tri(*o*-tolyl)phosphine (24 mg, 0.08 mmol), and K_2CO_3 (0.67 g 4.8 mmol) in a 100-mL four-necked flask was flushed with nitrogen for 10 min. A solution of DMF (25 mL) was added using a syringe and the mixture was heated at 100 °C for 15 h under nitrogen. The cooled reaction mixture was extracted with ether and the organic layer was dried with anhydrous magnesium sulfate, filtered, and concentrated. Silica gel column chromatography (hexane/ethyl acetate 9:1) and normal phase HPLC (hexane/ethyl acetate 49:1) afforded compound **1a** (6 mg, 0.013 mmol, 3%) as a white solid.

^{1}H NMR (300 MHz, CD_2Cl_2): δ 8.00–7.97 (d, J = 7.5 Hz, 2H), 7.96–7.93 (d, J = 7.5 Hz, 2H), 7.79–7.76 (d, J = 7.8 Hz, 1H), 7.49–7.41 (m, 7H), 7.36–7.31 (t, J = 7.8 Hz, 1H), 7.21–7.15 (t, J = 7.8 Hz, 1H), 3.85 (s, 3H), 2.02 (s, 3H), 1.98 (s, 3H). ^{13}C NMR(75 MHz, $CDCl_3$/TMS): δ 164.92, 164.11, 147.87, 144.30, 138.08, 135.01, 134.61, 134.15, 132.34, 130.31, 129.83, 129.52, 129.35, 129.22, 127.73, 126.62, 126.47, 124.14, 122.98, 121.13, 121.05, 120.34, 119.79, 110.91, 110.59, 109.91, 31.50, 12.216.; dp 120 °C.

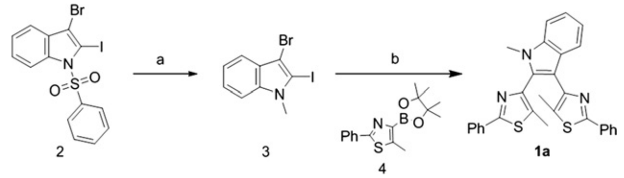
EI HRMS (m/z) $[M]^+$ calcd. for $C_{29}H_{23}N_3S_2$ (M^+): 477.1333; Found (M^+): 477.1332.

1b : ^{1}H NMR (300 MHz, CD_2Cl_2): δ 7.97 (m, 4H), 7.62 (d, 1H), 7.45 (m, 6H), 7.23 (t, 1H), 7.12 (t, 1H), 3.88 (s, 3H), 2.61 (s, 6H).

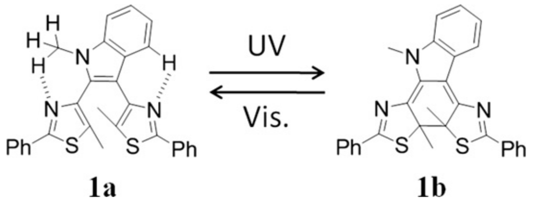
3. Results and discussion

3.1. Molecular design of new photochromic terarylene

2,3-Bis(2-phenyl-5-methylthiazol-3-yl)-1-methylindole, **1a** was designed as illustrated in Scheme 2, in which the photoreactive conformation is potentially stabilized by intramolecular hydrogen bonding between the central and the side aryl groups. In addition, the CH-π interactions between the methyl groups at the reactive carbon atoms and the aryl groups also seem to stabilize the photoreactive conformation of C_2 symmetry around the hexatriene moiety. Similar conformational control with the intramolecular hydrogen bonding has been employed in foldamer chemistry [13]. Steric repulsion between methyl groups in the thiazole units and the 1-methylindole unit is also expected to contribute partly to the relative stabilization of the reactive conformation.



Scheme 1. Synthetic route for compound **1**.



Scheme 2. Photochromic reactions of terarylene **1**.

3.2. Photochromism

As shown in Fig. 1, **1a** exhibited an absorption band between 250 and 400 nm before irradiation, while a new absorption band appeared between 550 and 800 nm after the irradiation with UV light (λ = 313 nm).

Since isosbestic points were observed, this spectral change is attributed to the two-component photochromic reaction comparable to those observed in diarylethene and terarylene derivatives. A proposed reaction scheme is also presented in Scheme 2. The colored solution was bleached completely after visible light irradiation with light of a wavelength longer than 500 nm.

The colored ring-closed compound, **1b**, formed after the UV-light irradiation was isolated by normal-phase HPLC, which showed the same mass-number of **1a**. The chemical structure of **1b** was confirmed by ^{1}H NMR spectroscopy. The values of λ_{max} and ε of **1a** and **1b** are summarized in Table 1. After UV light irradiation for a long period (ca. 2 h), small amount of unknown by-products were observed in the HPLC chart and the isosbestic point in Fig. 1 showed slight shift indicating side-reactions. The conversion ratio from **1a** to **1b** at their quasi-stationary states achieved under the continuous irradiation with UV light (λ = 313 nm) was about 97%, which may include about 2–3% of a probable error. The cyclization quantum yield of **1a** in hexane was determined to be $\Phi_{oc} = 0.83$ using 4,5-bis(5-methyl-2-phenylthiazol-4-yl)-2-phenylthiazole as a reference compound [11a]. This value seems to be significantly high in comparison with previously reported values for diarylethenes and is similar to that of a compound recently reported by Yokoyama and coworkers [11c].

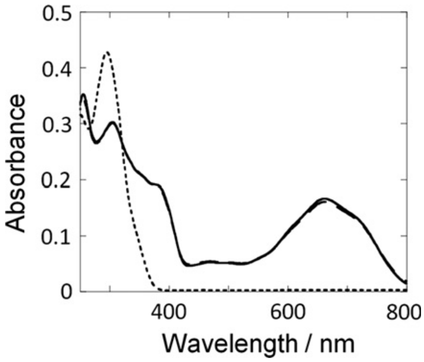


Fig. 1. Absorption spectral changes of **1** in hexane: open-form a (dotted line), closed-form b (solid line) and photostationary state under irradiation with 313 nm light (dashed line). The concentration of 1 was 1.3 × 10^{-5} M.