

Photochemical Electrocyclization of the Indolinyphenylethenes Involving a C–N Bond Formation

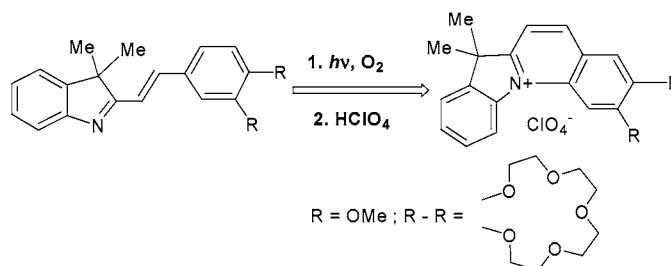
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ABSTRACT



A novel oxidative photodehydrocyclization of indolinyphenylethenes to a polycyclic heteroaromatic cation with good yields was described. Starting from the trans derivative, the phototransformation is a multistep process. The process includes two photochemical reactions and a trans–cis isomerization reaction, followed by an 1-aza-1,3,5-hexatrienic electrocyclic reaction involving the formation of a C–N bond. The cyclized product gives the stable heteroaromatic cations from hydride elimination with oxygen from air or iodine.

Conjugated diarylethylenes, the prototype of which is stilbene, are well-known for undergoing a photoreversible cyclization reaction leading to dihydrophenanthrenes.¹ Although in the presence of air, dihydrophenanthrene irreversibly converts to phenanthrene by hydrogen elimination with oxygen, it thermally returns to the initial stilbene in the absence of oxygen.^{1–3} When methyl groups are substituted at 2- and 6-positions of the phenyl rings, the compound undergoes a reversible photocyclization reaction even in the presence of air.^{4,5} When the aryl groups were replaced by furan, thiophen, or other heterocyclic rings, which have low

aromatic stabilization energies, the closed ring forms were thermally stable and did not return to the open-ring forms in the dark.^{6–8} Thermal irreversibility and fatigue resistance of the two photochemical forms are a prerequisite for applications of dihetarylethenes to optoelectronic devices such as memories and switches.⁹

The photochemical behavior reported for stilbenes in which one phenyl group is substituted by a heterocycle is not different from that of the parent carbocyclic compounds: trans–cis isomerization,^{9,10} [2 + 2]-photocycloaddition reaction,^{11–13} and hexatriene cyclization reaction^{14,15} that leads to polycyclic heterocycles after oxidative dehy-

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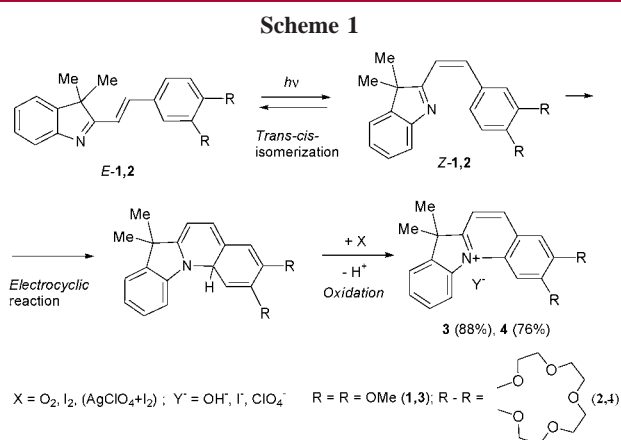
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drogenation. It is remarkable that an N-heteroatom in the ortho position of the double bond does not take part in the photocyclization; for example, 2-stilbazole leads to benzo-[f]quinoline.¹⁶

In this paper, we report the oxidative intramolecular photocyclization reaction of indolylphenylethenes **1** and **2** (Scheme 1). Compounds **1** and **2** were prepared by conden-



sation of 2,3,3-trimethylindolenine with substituted benzaldehydes in the presence of NaOMe in DMSO as has been described early.¹⁷ The thermodynamic trans isomers of indolylphenylethenes **1** and **2** were obtained as judged by the coupling constants of the olefinic protons (near 16.0 Hz).

The irradiation of an acetonitrile solution of compounds **1** and **2** at 365 or 313 nm leads to a photostationary states of trans and cis isomers (Scheme 1). The absorption spectrum of the *cis*-**2** was calculated by applying Fischer's method¹⁸ using the corresponding spectra of the trans isomer and the spectra of photostationary states obtained upon irradiation with 365 and 313 nm light (Figure 1). The quantum yields of the trans-to-cis and cis-to-trans photoisomerization reactions of **2** at 365 nm were calculated to be 0.43 and 0.31, respectively. Filtered light from a DRK-120 high-pressure mercury lamp was employed in quantum yield determination experiments. Individual lines of this lamp (313 and 365 nm) were isolated with the use of glass filters. Our experiments showed that (*E*)-/(*Z*)-**1** and (*E*)-/(*Z*)-**2** are sufficiently stable in dark.

The irradiation of the acetonitrile solution of compounds **1** and **2** with the unfiltered output of a 120 W high-pressure Hg arc lamp and simultaneous bubbling of air for 16 min

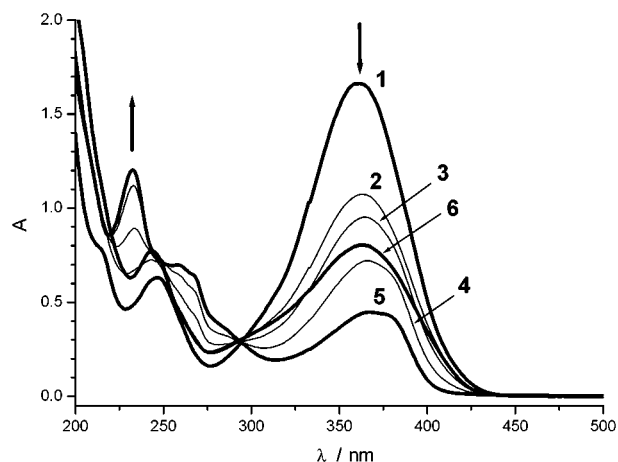


Figure 1. Spectral changes during the photolysis of an acetonitrile solution of **2**. [**2**] = 0.04 mM, irradiation with a high-pressure Hg-lamp (DRK-120, 120W), under air, for periods of 0 min (**1**), 1 min (**2**), 4 min (**3**), 8 min (**4**), and 16 min (**5**). (**6**) UV-visible absorption spectrum of (*Z*)-**2** (0.04 mM), calculated by Fischer's method.¹⁸

results in the appearance of novel photoproducts **3** and **4** (Figure 1). After the evaporation of acetonitrile, the products were isolated by crystallization from MeOH with small addition of HClO₄ as the perchlorate.

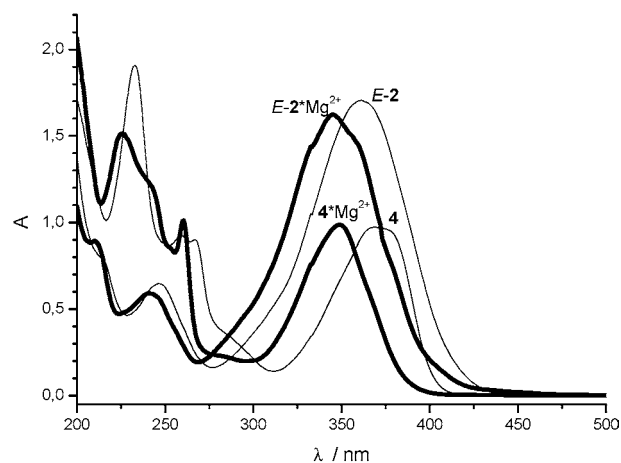


Figure 2. UV-visible absorption spectra of (*E*)-**2** (0.04 mM), **4** (0.04 mM) in acetonitrile and a 0.01 M acetonitrile solution of Mg(ClO₄)₂ ((*E*)-**2***Mg²⁺ and **4***Mg²⁺).

The NMR analysis of the reaction mixture showed the disappearance of the olefinic protons (H-a, H-b) and a large deshielding of the aromatic part as the result of the electron depletion of the aromatic rings by the nitrogen cation. The obtained NMR spectra indicated the formation of heteroaromatic cations **3** and **4** (Scheme 1). We propose that the reaction formation of **3** and **4** is a multistep process. The first step of the photochemical reaction is the formation of cis-trans mixture (Figure 1). The second step is an intramo-

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lecular photocyclization through the formation of a C–N bond. The primary product of the photocyclization has not been detected but has been trapped by hydride elimination with oxygen (Figure 1). Figure 3 demonstrates the decrease

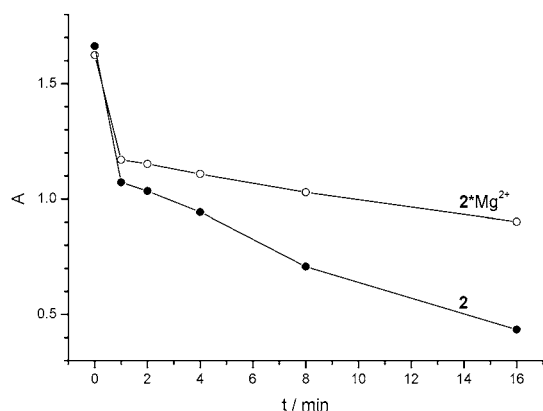


Figure 3. Dependence of absorption of **2** (0.04 mM) (at 360 nm) and **2**·Mg²⁺ (0.04 mM) (at 345 nm) on time of irradiation with a high-pressure Hg-lamp and under air.

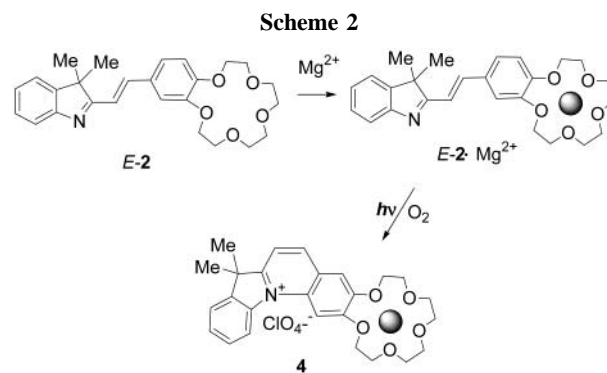
of intensity of the ligand **2** absorption long-wavelength band upon the irradiation with full light. The substantial decrease of absorption intensity during the first minute corresponds to the reaction of trans–cis isomerization, which occurs with high quantum yield. Slower changes of absorption intensity were observed during the oxidative photocyclization.

The chemical yields of the cyclic products **3** and **4** are rather high (see Scheme 1). The photocyclization took place faster when I₂ or a mixture of I₂ and AgClO₄ was used as an oxidizing agent. In this case, the heteroaromatic cations formed with I[−] and ClO₄[−] as counterions accordingly.

Compound **2** is a typical chromo-fluoro probe for alkali and alkaline-earth cations¹⁹ in which the ionophore is the electron-donating group in the first electronic transition. As we have discovered the photoreactivity of this probe, it was tempting to study the influence of the complex formation process through the crown ether fragment of **2** on the course of the photocyclization reaction (Scheme 2).

The addition of Mg(ClO₄)₂ to the acetonitrile solution of **2** causes the hypsochromic shift of the long-wavelength band, indicating the formation of complex **2**·Mg²⁺ (Figure 2). The irradiation of the complex with the full light of the lamp, in

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the presence of oxygen, results in the formation of complexed cyclic product **4**·Mg²⁺. The UV spectrum of **4**·Mg²⁺ is hypsochromically shifted in comparison with UV spectrum of free ligand **4** (Figure 2).

These hypsochromic shifts, upon cation complexation, show that the first electronic transition of **2** and **4** has a charge-transfer character from the benzocrown group to indolenine extremity, which is reduced by the presence of the cation in the crown in **2**·Mg²⁺ and **4**·Mg²⁺.

From the data in Figure 2, it was possible to compare the changes of absorption intensity for compound **2** and its complex (**2**·Mg²⁺) during the phototransformation. One can conclude that formation of product **4** occurs more slowly in the presence of Mg²⁺ cations. The observed phenomena is probably due to the complex formation process preventing the hydride elimination from the cyclic intermediate.

Thus, the novel phototransformation of indolinyphenylethenes **1** and **2** into the heteroaromatic cations **3** and **4** was described. The process includes the electrocyclic reaction through the formation of a C–N bond. The observed photocyclization has possible preparative value, especially in view of the comparative inaccessibility of heteroaromatic cations by normal chemical synthesis. The changes in UV spectrum observed upon the complex formation of compound **4** with Mg²⁺ cations point out the optical sensitivity of novel crown-containing heteroaromatic cation to the presence of metal cations in solution.

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Supporting Information Available: Experimental procedures and data for compounds **1**–**4**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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