

Controlled Photocyclization, Photodimerization, and Photoisomerization of Stilbazole Salts within Nafion Membranes

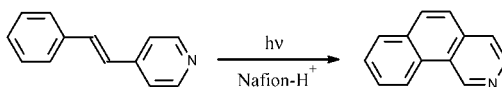
Xiao-Hong Li, Li-Zhu Wu,* Li-Ping Zhang, and Chen-Ho Tung*

Technical Institute of Physics and Chemistry, The Chinese Academy of Sciences,
Beijing 100101, China

chtung@ipc.ac.cn

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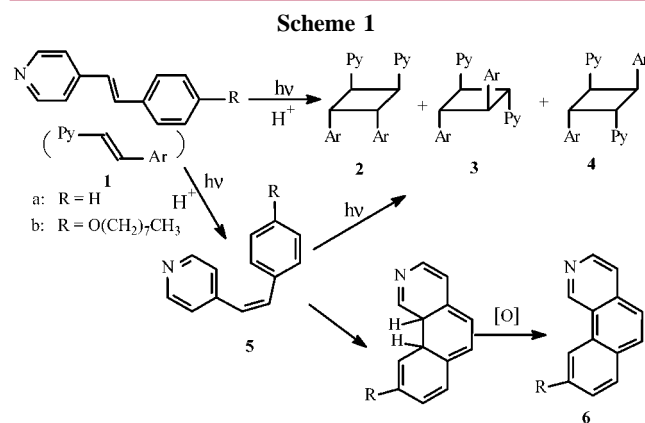
ABSTRACT



Water- and methanol-swollen Nafion membranes were used as microreactors to successfully control the photochemical reaction pathway of stilbazole derivatives. Of particular interest is the production of azaphenanthrene (the product not obtainable in homogeneous solution) in high yield under high bulk concentration.

Selectivity in organic phototransformations is one of the main topics of current interest. Of the various approaches, use of constrained and organized media as microreactors to control the reaction pathways has shown considerable promise.^{1,2} Nafion represents a unique family of polymers which consist of a perfluorinated backbone and short pendent chains terminated by sulfonic groups. When swollen in water, its structure resembles that of a reverse micelle. The hydrated sulfonic headgroups are clustered together in water-containing pockets of ca. 50 Å in diameter, which are interconnected by short channels (ca. 10 Å in diameter) within the perfluorocarbon matrix.^{3–5} This water-swollen Nafion can incorporate high concentrations of organic molecules and thus may act as microreactor to gain selectivity. In the present Letter we report an investigation on the photochemistry of the salts of *trans*-4-stilbazole (**1a**) and *trans*-1-(4-octyloxyphenyl)-2-(4-pyridyl)ethylene (**1b**) within Nafion mem-

branes. Stilbazole salt and its derivatives can, in principle, undergo a variety of photochemical reactions (Scheme 1),



including cyclization to azaphenanthrenes, dimerization to cyclobutanes, and *cis*–*trans* isomerization.^{6–10} Although the photodimerization and *cis*–*trans* photoisomerization have

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been extensively investigated,^{6–10} the photocyclization products have never been isolated. Furthermore, in the photodimerization the main product is the head-to-tail (h–t) dimer. Many efforts have been made to prepare the head-to-head (h–h) dimer.^{6–10} We found that one can use water- and methanol-swollen Nafion membranes as microreactors to direct the photochemical reaction selectively toward either the cyclization or the dimerization, and in the case of dimerization to increase the yield of the h–h dimer.

The *trans*-isomer (**1a**) of stilbazole was used as the starting material throughout the present study. For the photolysis in aqueous solution, this starting material was dissolved in 1 N HCl. The solution was degassed with nitrogen and irradiated with a 500-W high-pressure mercury lamp. After irradiation, the solution was neutralized with 1 N NaOH and extracted with CH₂Cl₂. The products were analyzed by HPLC and separated by column chromatography on silica gel with ethyl ether as the eluting solvent. The main products were the *cis*-isomer **5a** and the photodimers **3a** and **4a** (Scheme 1). The structures proposed for the photodimers rests mainly on their ¹H NMR spectra, which are in close agreement with those reported in the literature.^{6–11} Furthermore, in the mass spectra the fragment ions from the h–t dimer (**4a**) involve the monomer unit and those from the h–h dimer (**3a**) involve stilbene and dipyrindylethylene moieties in addition to the monomer unit.¹¹ Table 1 shows the product distribution for

Table 1. Product Distribution in the Photochemical Reaction of **1a** and **1b** in Aqueous Hydrochloric Acid Solution and within Nafion Membranes

media	product (%) ^a					h–h/ h–t	cyclomer/ dimers
	2	3	4	5	6		
1a HCl solution	0	5	60	35	0	1.0:12	0
1a H ₂ O-swollen Nafion							
<i>n</i> = 70	16	0	77	7	0	1.0:4.8	0
<i>n</i> = 2	14	0	73	0	13	1.0:5.2	1.0/6.8
<i>n</i> = 1	8	0	45	0	47	1.0:5.6	1.0/1.1
<i>n</i> = 0.25	6	0	30	0	64	1.0:5.0	1.8/1.0
1a methanol-swollen Nafion							
<i>n</i> = 70	13	0	82	5	0	1.0:6.3	0
<i>n</i> = 0.25	5	0	25	8	62	1.0:5.0	2.0/1.0
1b HCl solution	75	2	1	22	0	77:1.0	0
1b water-swollen Nafion	28	18	44	10	0	1.0:1.0	0
<i>n</i> = 70							
methanol-swollen Nafion	23	13	57	7	0	1.0:1.6	0
<i>n</i> = 70							

^a Error was estimated to be 2%.

irradiation of $a3 \times 10^{-4}$ M aqueous solution of **1a**. The ratio of the *cis*-isomer **5a** to the photodimers was found to be dependent on the concentration of **1a**, with high concentration favoring the formation of the photodimers. The main photodimer was the *syn* h–t isomer (**4a**), although a small amount of the *anti* h–h isomer (**3a**) was produced (**3a:4a** =

1:12). No *syn* h–h dimer (**2a**) was detected. This regioselectivity is obviously due to the minimization of the like-charge repulsion. Since it has been well documented that *cis*-stilbene can undergo photocyclization to give phenanthrene in the presence of oxygen,¹² originally we expected that the generated *cis*-isomer **5a** might photocyclize to dihydroazaphenanthrene which then is oxidized to azaphenanthrene (**6a**, Scheme 1) during the product isolation. However, upon prolonged irradiation of the diluted solution (1×10^{-5} M) of **1a**, we could not detect any trace of **6a**. We attribute the absence of **6a** formation to the fast *cis*–*trans* isomerization and/or dimerization of the excited state of **5a**.

The Nafion membranes used for the reaction media were the water- or methanol-swollen acid form (Nafion-H⁺). **1a** was easily adsorbed into Nafion by immersing the polymer in its well-stirred solution in water or methanol. In these membranes **1a** exists in the stilbazolium salt form where the counterion is the sulfonate of Nafion. The solubility of **1a** in Nafion-H⁺ can be rather high (ca. 0.1 mol/g Nafion, calculated in its swollen form). By changing the ratio of the substrate to Nafion membranes, we could prepare the samples with any loading in the region of 0–0.1 mol of **1a** in each gram of Nafion. Using the parameters of Nafion membrane reported in the literature,^{5,13} the occupancy number (*n*, the number of the substrate molecules contained in each water cluster of Nafion) of the samples was calculated and is given in Table 1. Photoirradiation was carried out in a Pyrex reactor with a 500-W high-pressure mercury lamp as the light source. Prior to irradiation, the samples were degassed with nitrogen for 15 min. The photochemical reaction was monitored by UV absorption spectroscopy. Generally, after 5 h of photolysis the conversion of the starting material was close to 100%. After irradiation, the excess acids of Nafion-H⁺ membranes were neutralized with a 1 N NaOH aqueous solution, and then the products were extracted with methanol. The products could be quantitatively extracted, and the material balance was generally near 100%. The product distribution within Nafion membranes is dramatically altered compared with that in aqueous solution (Table 1). First, it was found that the product distribution is remarkably dependent on the substrate loading. At high loading (*n* = 70), **1a** mainly undergoes photodimerization, although a small amount of the *cis*-isomer **5a** was detected. The ratio of the isomerization product **5a** to the dimers is changed from 1.0:1.8 in aqueous solution to 1.0:13 in water-swollen Nafion and 1.0:19 in methanol-swollen Nafion. Furthermore, in the photodimerization the yield of the h–h dimer **2a** was

(11) **2a**: ¹H NMR (CDCl₃, ppm) 8.30 (d, 4H), 7.18 (m, 14H), 4.57 (d, 2H), 4.59 (d, 2H); MS *m/z* 364 (M⁺ + 2), 362 (M⁺), 182, 181, 180. **4a**: ¹H NMR (CDCl₃, ppm) 8.27 (d, 4H), 7.17 (m, 14H), 4.57 (m, 2H), 4.60 (m, 2H); MS *m/z* 364 (M⁺ + 2), 362 (M⁺), 182, 181, 180. **2b**: ¹H NMR (CDCl₃, ppm) 8.42 (d, 4H), 7.06 (d, 4H), 6.97 (d, 4H), 6.73 (d, 4H), 4.42 (d, 2H), 4.37 (d, 2H), 3.89 (t, 4H), 1.76 (t, 4H), 1.3 (m, 20H), 0.9 (t, 6H); MS *m/z* 619 (M⁺ + 1), 618 (M⁺), 436, 309, 180. **3b**: ¹H NMR (CDCl₃, ppm) 8.4 (d, 4H), 7.22 (m, 8H), 6.91 (d, 4H), 3.97 (t, 4H), 3.71 (t, 2H), 3.54 (t, 2H), 1.76 (t, 4H), 1.3 (m, 20H), 0.9 (t, 6H); MS *m/z* 619 (M⁺ + 1), 436, 309, 180. **4b**: ¹H NMR (CDCl₃, ppm) 8.4 (d, 4H), 7.22 (d, 4H), 6.96 (d, 4H), 6.74 (d, 4H), 4.46 (d, 2H), 4.50 (d, 2H), 3.84 (t, 4H), 1.76 (t, 4H), 1.3 (m, 20H), 0.9 (t, 6H); MS *m/z* 619 (M⁺ + 1), 309.

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increased. The ratio of the h–h to h–t dimers was increased from 1.0:12 in aqueous solution to 1.0:4.8 in Nafion. These observations can be interpreted in terms of the location and preorientation of **1a** molecules in Nafion membranes. Considering the hydrophobicity and the positive charge of the substrate, it is likely that the molecules of **1a** are located in the fluorocarbon/water (or fluorocarbon/methanol) interface of the membrane. The phenyl group of **1a** should reside in the fluorocarbon phase, while the pyridyl group is anchored among the sulfonated groups at the interface of the water pool. Evidently, the viscous environment at the fluorocarbon/water interface prevents **1a** from undergoing *cis*–*trans* photoisomerization, and the photodimerization of the two neighboring stilbazolium ions favors the formation of the h–h dimer. Second, for the sample with small occupancy numbers, a great amount of the photocyclization product¹⁴ **6a** was produced upon irradiation (Table 1). At the occupancy numbers of less than 0.5 substrate molecules in each water cluster, azaphenanthrene was the main product of the photochemical reaction. The occurrence of the photocyclization is attributed to the compartmentalization and viscosity effects of Nafion. At low loading, the probability of finding two substrate molecules in one water cluster is small. Thus, the photodimerization is prohibited. The high viscosity at the fluorocarbon/water interface prevents the excited state of the *cis*-isomer **5a** from isomerization to the *trans*-isomer. Although the high viscosity also reduces the rate of **5a** formation, once formed, **5a** can undergo photocyclization. Therefore, cyclization becomes the main photochemical decay path of the excited state of **5a**. The formation of azaphenanthrene in water- and methanol-swollen Nafion membranes is of significance. In many cases a molecule may undergo both intramolecular and intermolecular reactions. The rate of the latter is dependent on the concentration of the substrate, while that of the former is not. Hence, high substrate concentrations favor intermolecular reaction while intramolecular reaction proceeds in good chemical yield only at low concentrations. Furthermore, there are some examples for which even at low concentrations the intramolecular reaction products cannot be produced (for example, in solution at the concentrations as low as 1×10^{-5} M, the photocyclization of **1a** was not observed). In general, the intramolecular reaction has to be performed at substrate concentrations as low as 1×10^{-5} M. In previous studies^{15,16} we reported an approach to synthesize intramolecular products in high yields under high substrate concentrations. Our approach involves microporous solids or low-density polyethylene films as microreactors for intramolecular reaction. In each microreactor only one substrate molecule is loaded. Thus, intermolecular reactions are hindered and

(14) **6a**: ¹H NMR (CDCl₃, ppm), 8.8 (d, 2H), 8.0 (m, 2H), 7.7–7.8 (m, 5H). MS *m/z* 179 (M⁺), 151, 152.

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intramolecular reactions can occur without competition. Since the concentration of the microreactor is high, the intramolecular products can be synthesized in high yields under high substrate concentrations. The production of azaphenanthrene within Nafion membranes reported in the present work is another example of such an approach. For the sample of **1a** in water-swollen Nafion membranes, the occupancy number of 0.5 corresponds to 6×10^{-4} mol of the substrate in each gram of Nafion (the concentration of the water cluster is ca. 1.2×10^{-3} mol/g Nafion),^{5,13} or 9.6 mol of the substrate in each liter of Nafion (the density of water-swollen Nafion is ca. 1.61 kg/L).^{5,13} Thus, even when the bulk concentration is as high as 9.7 M, the main product is azaphenanthrene.

As mentioned above, in the photodimerization of **1a** within Nafion membranes the yield of the h–h dimer was evidently increased compared with that in aqueous solution, because of the preorientation of the substrate molecules at the fluorocarbon/water interface. However, the products were still dominated by the h–t dimer. Thus, we incorporated an octyloxy group into the stilbazole moiety to synthesize **1b** and expected that the hydrophobic hydrocarbon chain would increase the extent of preorientation of the substrate molecules at the fluorocarbon/water interface by insertion into the fluorocarbon phase of Nafion. In sharp contrast with **1a**, photoirradiation of **1b** in aqueous hydrochloric acid solution at concentrations above 4.2×10^{-5} M mainly gave the *syn* h–h dimer **2b** in addition to a small amount of the *cis*-isomer **5b** (Table 1). This observation originates from the formation of micelles. We have demonstrated by surface tension measurements that the alkylated stilbazole salt **1b** as a surfactant forms micelles with a critical micelle concentration (CMC) of ca. 4.2×10^{-5} M in a 1 N HCl solution. In micelles **1b** molecules are preorientated in such a way that the alkyl chains are located in the hydrophobic core while the cationic chromophores are directed to the water interface. Consequently, the photodimerization of two neighboring stilbazolium ions favors the formation of the h–h dimer. When **1b** was incorporated into water- or methanol-swollen Nafion membranes, the yield of the h–h dimer was indeed increased compared with that of **1a**. The ratio of the h–h to h–t dimers in water-swollen Nafion was increased from 1.0:4.8 for **1a** to 1.0:1.0 for **1b**. These observations suggest that the extent of preorientation of **1b** at the fluorocarbon/water interface is much better than that of **1a**, but not as perfect as in its micelles.

The above results demonstrate that water- or methanol-swollen Nafion membranes can act as microreactors to control the pathways of the photochemical reactions of stilbazole salts.

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