J. Org. Chem. **1998,** *63,* 5857−5862

Regioselectivity in the Photocycloaddition of 9-Substituted Anthracenes Incorporated within Nafion Membranes

Chen-Ho Tung* and Jing-Qu Guan

Institute of Photographic Chemistry, Chinese Academy of Sciences, Beijing 100101, China

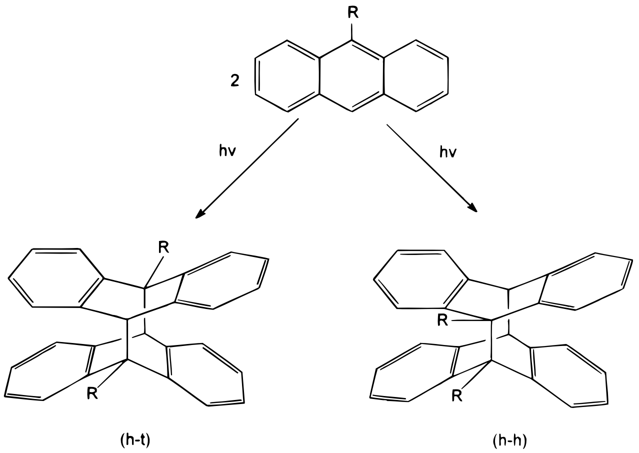
Received March 4, 1998

The photocycloaddition of five 9-substituted anthracenes [$AnCH_2N^+(CH_3)_3Br^-$ (**1**), $AnCH_2COO^-Na^+$ (**2**), $AnCH_2OH$ (**3**), $AnCOCH_3$ (**4**), and $AnCH_3$ (**5**), An = 9-anthryl] incorporated within Nafion membranes has been investigated. While irradiation of the above compounds in homogeneous solutions, and **5** in Nafion also, mainly gave rise to their head-to-tail (h−t) photocyclomers, photoirradiation of the samples of **1**−**4** incorporated within Nafion membranes almost exclusively resulted in the head-to-head (h−h) photocyclomers. Furthermore, the h−h photocyclomers are significantly more stable in Nafion membranes than in homogeneous solutions. These observations can be explained in terms of the preorientation of the substrate molecules in the inverse micelle-like clusters of Nafion.

Introduction

Photocylcoaddition of anthracene and its derivatives has been extensively investigated and is still of substantial interest.[1] Irradiation of 9-substituted anthracenes in organic solution typically results in cylcoaddition of the aromatic rings at the 9,10-positions to yield head-to-tail (h−t) cyclomers (Scheme 1), although evidence for the concomitant formation of thermally more labile head-to-head (h−h) cyclomers has been obtained in some instances.[1d] This regioselectivity was rationalized in terms of electrostatic and steric effects of the substituents, i.e., steric and/or electrostatic repulsions between the two 9-substituents are more severe in the transition state leading to the h−h cyclomer than that to the h−t cyclomer.[1a] To increase the synthetic yields of the h−h photocyclomers, a variety of approaches have been employed.[1−9] Two decades ago, Bouas-Laurent and co-workers investigated the cross-photocycloaddition between an anthracene substituted by an electron-releasing group (9-methoxyanthracene) and another anthracene bearing an electron-withdrawing substituent (9-cyanoanthracene) by irradiation of their 1:1 mixture in a nonpolar solvent.[2] The dipole−dipole interactions between the substituents leads to formation of the h−h cross-photocyclomer in high yield with no trace of the h−t isomer. De Schryver,[3] Bouas-Laurent,[1a] and others[4] used an aliphatic chain to link two anthracenes. Thus, the two terminal chromophores are forced to adopt a h−h geometry, and the photocycloaddition becomes chain-controlled. Recently, Ito and co-workers reported that irradiation of crystals of 9-anthracenecarboxylic acid exclusively results in h−h cyclomer, which is a topochemically expected product.[5a] Furthermore, they irradiated the double salts prepared from anthracene-9-propionic acid and 1,2-diamines in their solid state and successfully produced the h−h cyclomer of the substituted anthracene.[5b] Sakaki[6] and Tung[7] used calixarene as a template to synthesize the h−h cyclomers of 9-substituted anthracenes. Wolff[8] and Melo[9] reported that incorporating 9-substituted anthracenes into micelles and vesicles of surfactants can induce the anthracene rings in h−h orientation, thus increasing the yield of the h−h photo-

Scheme 1. Photocycloaddition of 9-Substituted Anthracene



---

[1] (a) Bouas-Laurent, H.; Castellan, A.; Desvergne, J.-P. *Pure Appl. Chem.* **1980**, *52*, 2633. (b) Cowan, D. O.; Drisko, R. L. *Elements of Organic Photochemistry*; Plenum: New York, 1976; p 37. (c) Becker, H.-D. *Chem. Rev.* **1993**, *93*, 73. (d) Becker, H. D.; Langer, V.; Becker, H.-C. *J. Org. Chem.* **1993**, *58*, 6394. (e) Wolff, T.; Klaussner, B. *Adv. Colloid Interface Sci.* **1995**, *59*, 31. (f) Bouas-Laurent, H.; Desvergne, J.-P. In *Photochromism: Molecules and Systems*; Durr, H., Bouas-Laurent, H., Eds.; Elsevier: Amsterdam, 1990; Chapter 4, p 561. (g) Kaupp, G. In *Advances in Photochemistry*; Neckers, D. C., Volman, D. H., von Bunau, G., Eds.; John Wiley & Sons: New York, 1995; Vol. 19, p 119. (h) Mori, Y.; Horikoshi, Y.; Maeda, K. *Bull. Chem. Soc. Jpn.* **1996**, *69*, 1755. (i) Noh, T.; Lim, H. *Chem. Lett.* **1997**, 495.

[2] Castellan, A.; Lapouyade, R.; Bouas-Laurent, H.; Lallemand, J. Y. *Tetrahedron Lett.* **1975**, *29*, 2467.

[3] (a) De Schryver, F. C.; Boens, N.; Put, J. In *Advances in Photochemistry*; Pitts, J., Hammond, G. S., Gollnick, K., Eds.; Wiley: New York, 1979; Vol. 11, p 489. (b) De Schryver, F. C.; Boens, N.; Huybrechts, J.; Daemen, J.; De Brackeleire, M. *Pure Appl. Chem.* **1977**, *49*, 237.

[4] (a) Bergmark, W. R.; Jones, G., II; Th. Reinhardt, E.; Halpern, A. M. *J. Am. Chem. Soc.* **1978**, *100*, 6665. (b) Anderson, B. F.; Ferguson, J.; Morita, M.; Robertson, G. B. *J. Am. Chem. Soc.* **1979**, *101*, 1832.

[5] (a) Ito, Y.; Fujita, H. *J. Org. Chem.* **1996**, *61*, 5677. (b) Ito, Y.; Olovsson, G. *J. Chem. Soc., Perkin Trans. 1* **1997**, 127.

[6] Deng, G.; Sakaki, T.; Y, Kawahara, Shinkai, S. *Tetrahedron Lett.* **1992**, *33*, 2163.

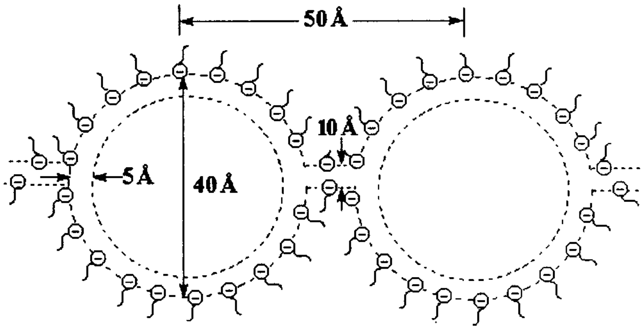
[7] Tung, C.-H.; Li, Y.; Wang, G.-Q.; Huang, Z.-T. *Photogr. Sci. Photochem.* **1995**, *13*, 151.

[8] (a) Wolff, T. *J. Photochem.* **1981**, *16*, 343. (b) Wolff, T.; Muller, N.; von Bunau, G. *J. Photochem.* **1983**, *22*, 71. (c) Wolff, T.; Muller, N. *J. Photochem.* **1983**, *23*, 131. (d) Schutz, A.; Wolff, T. *J. Photochem. Photobiol. A, Chem.* **1997**, *109*, 251.

[9] Moreno, M. J.; Lourtie, I. M. G.; Melo, E. *J. Phys. Chem.* **1996**, *100*, 18192.

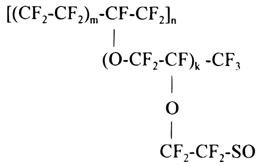
S0022-3263(98)00412-5 CCC: $15.00

Scheme 2. Schematic Representation of the Two-Phase Cluster-Network Model for Nafion Membrane



cyclomers. In the present study, we wish to report that photoirradiation of anthracene with a polar 9-substituent incorporated within Nafion membranes almost exclusively yields the h−h photocyclomers.

Nafion represents a novel and unique family of polymers that consists of a perfluorinated backbone and short pendant chains terminated by sulfonic groups:



$$[(CF_2\text{-}CF_2)_m\text{-}CF\text{-}CF_2]_n \; | \; (O\text{-}CF_2\text{-}CF)_k\text{-}CF_3 \; | \; O \; | \; CF_2\text{-}CF_2\text{-}SO_3H$$

m = 5-15.3;
n = ca. 1000;
k = 1, 2, 3

When swollen in water, the structure of Nafion is believed to resemble that of an inverse micelle (Scheme 2).[10−12] The hydrated SO_3^- headgroups are clustered together in a water-containing pocket of ca. 40 Å in diameter, which are interconnected by short channels (ca. 10 Å in diameter) within the perfluorocarbon matrix. It has been established[13−15] that water-swollen Nafion can incorporate high concentrations of aromatic hydrocarbons and organic dyes, thus raising the possibility of obtaining high local concentration of organic molecules and inorganic cations. These optically transparent membrane systems are readily amenable to spectroscopic and photochemical investigations. Because of these attractive properties, this polymer has been utilized as a medium for photophysical and photochemical studies in recent years.[16−20] However, the use of Nafion to direct regioselectivity of a photochemical reaction has never been reported. When anthracene bearing an ionic or a polar substituent is incorporated within Nafion membranes, one might expect that their molecules would be arranged in such a way that the anthracene moiety is directed toward the hydrophobic phase of the polymer backbone with the polar substituent toward the water pool interface. This preorientation would favor the formation of h−h photocyclomer. We found that photoirradiation of **1**−**4** incorporated in Nafion indeed almost exclusively leads to the h−h photocyclomers. Furthermore, the h−h cyclomers incorporated in Nafion membranes are much more stable than in homogeneous solutions.

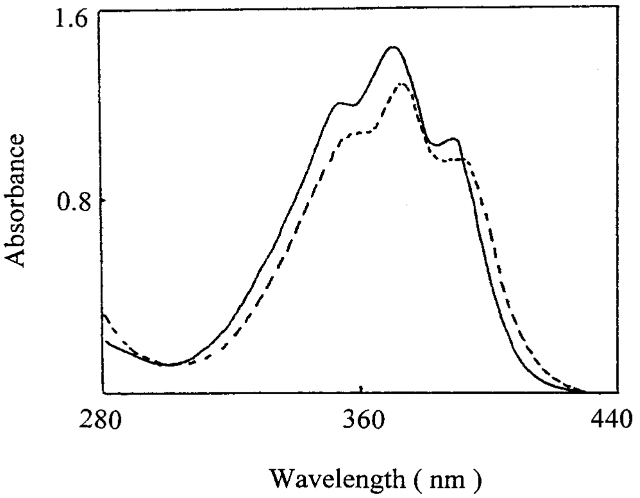


Figure 1. Absorption spectra of **1** in water-swollen Nafion (—) and in aqueous solution (···).

Table 1. Absorption and Emission Parameters of 1−5 in Nafion and in Aqueous Solution

compd	medium	λ_{abs}^{max} (nm)	ϵ (10^4 cm^{-1} M^{-1})	λ_{flu}^{max} (nm)
1	water	372	0.92	419.1
	nafion	370	0.90	417.5
2	water	362	0.93	412.5
	nafion	361	0.95	412.7
3	water	366	0.94	411.5
	nafion	362	0.94	410.0
4	water	384	1.16	428.1
	nafion	378	1.22	427.6
5	water			
	nafion	363	1.02	410.7

Results and Discussion

Incorporation and Spectral Properties of 1−5 in Nafion Membranes. The Nafion membranes used in the present study were in their sodium form (Nafion-Na$^+$). **1** is a positively charged aromatic compound. Due to hydrophobic and electrostatic interactions, **1** is easily adsorbed into Nafion by immersing the polymer in a well stirred aqueous solution of **1**. The solubility of **1** in Nafion-Na$^+$ can be rather high (ca. 0.07 M, calculated in its swollen form). Figure 1 shows the absorption spectrum of a Nafion sample after equilibration with a 2.03 $\times$ 10^{-4} M solution of **1** in water. Control experiments show that the absorption of Nafion membrane above 290 nm is negligibly weak. The maxima of the absorption spectrum of **1** in Nafion are at ca. 356, 370, and 391 nm. Compared with the spectrum in water (Figure 1), the spectrum in Nafion is slightly blue-shifted by ca. 2 nm (Table 1). Since the absorption of anthracene chromophore is of $\pi \rightarrow p^*$ transition character,[21] the blue-shift suggests that the environment around the molecules of **1** in Nafion is slightly less polar than that in water. Considering the hydrophobicity and the positive charge of **1**, it is likely

---

(10) Komoroski, R. A.; Mauritz, K. A. *J. Am. Chem. Soc.* **1978**, *100*, 7487.

(11) Lee, P. C.; Meisel, D. *J. Am. Chem. Soc.* **1980**, *102*, 5477.

(12) Sondheimer, S. J.; Bunce, N. J.; Fyfe, C. A. *J. Macromol. Sci., Rev. Macromol. Chem. Phys.* **1986**, *C26*, 353.

(13) Lee, P. C.; Meisel, D. *Photochem. Photobiol.* **1985**, *41*, 21.

(14) Szentirmay, M. N.; Prieto, N. E.; Martin, C. R. *J. Phys. Chem.* **1985**, *89*, 3017.

(15) Niu, E.-P.; Ghihhino, K. P.; Smith, T. A.; Mau, A. W.-H. *J. Lumin.* **1990**, *46*, 191.

(16) Niu, E.-P.; Mau, A. W.-H. *Aust. J. Chem.* **1991**, *44*, 695.

(17) Mohan, H.; Iyer, R. M. *J. Chem. Soc., Faraday Trans.* **1992**, *88*, 41.

(18) Mika, A. M.; Lorenz, K.; Azczuek, A. *J. Membr. Sci.* **1989**, *41*, 163.

(19) Priydarsini, K. I.; Mohan, H.; Mittall, J. P. *J. Photochem. Photobiol. A: Chem.* **1993**, *69*, 345.

(20) (a) Tung, C.-H.; Guan, J.-Q. *J. Org. Chem.* **1996**, *61*, 9417. (b) Tung, C.-H.; Guan, J.-Q. *Chin. J. Chem.* **1996**, *14*, 541.

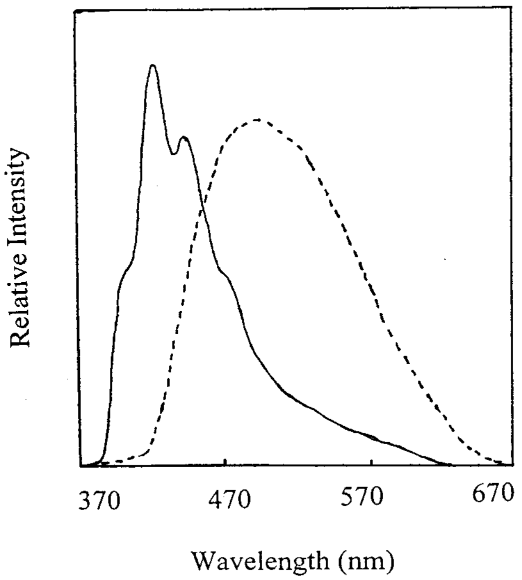


Figure 2. Emission spectra of **1** in Nafion: [**1**] = 0.004 M (—); [**1**] = 0.07 M (···). Excitation wavelength: 350 nm.

that the molecules of **1** are located in the fluorocarbon/water interface of the membrane. This allows electrostatic interactions with the sulfonate headgroups as well as interactions with the hydrophobic domain of Nafion.

The fluorescence spectra of two Nafion samples adsorbing **1** are given in Figure 2. The concentrations of **1** in the samples are ca. 0.07 and 0.004 M, respectively. By using the parameters reported in the literature,[20,22] we could calculate the average occupancy numbers (the number of substrate molecules contained in each water cluster of Nafion) of the samples for the high and low concentrations of **1** to be 6.2 and 0.35, respectively. While the sample with **1** in low concentration exhibits the structure fluorescence characteristics of anthracene monomer[22,23] with maxima at 402, 419, and 442 nm, the one with **1** in high concentration shows excimer emission with maxium at 484 nm. To get information on the interaction between the molecules of **1** in ground state, the excitation spectra for the monomer and excimer fluorescence were measured and given in Figure 3. While the excitation spectrum of the monomer emission is analogous to the absorption spectrum of **1**, the excitation spectrum for the excimer emission is broad and evidently red-shifted. This suggests the existence of preassociation of the anthracene chromorphores within Nafion prior to excitation.

In contrast, the adsorption behavior of **2**, a molecule bearing an anionic substituent, into Nafion membranes is completely different from that for **1**. When the membrane sample is immersed in the desired aqueous solution of **2** and reaches equilibration, the concentration of **2** in the membrane is almost the same as that in the bulk solution, as determined by UV. The inhibition of **2** from adsorption to the membrane is obviously due to the electrostatic repulsion between the anions of **2** and the sulfonate headgroups of Nafion. However, we could successfully incorporate **2** into water-swollen Nafion by soaking the membranes in an aqueous salt solution of **2**. Figure 4 shows the absorption spectrum of **2** in Nafion as a function of NaCl concentration in the bulk solution. The concentration of **2** in Nafion can reach ca. 0.029 M. Obviously, in the presence of the salt, the negative charge of the sulfonate headgroups is shielded by the added

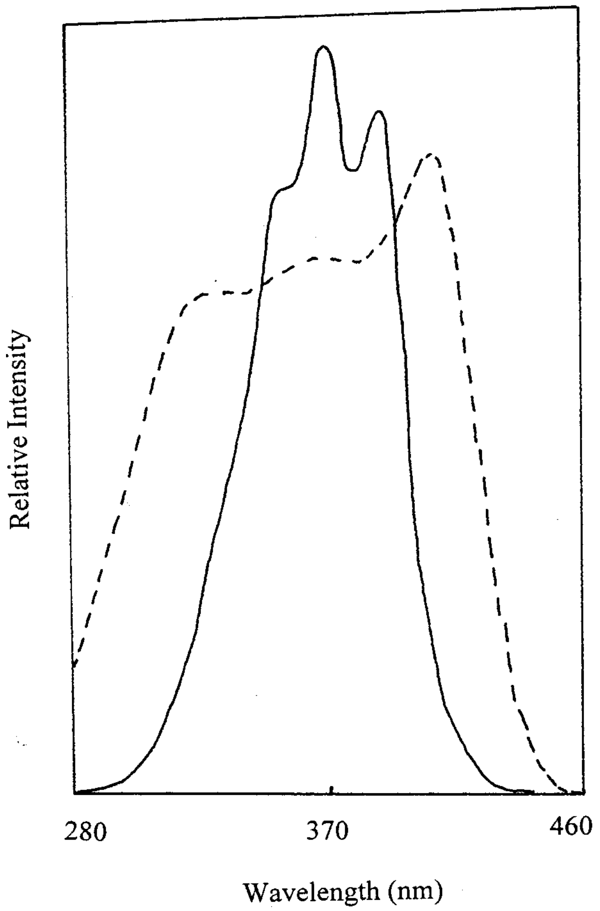


Figure 3. Excitation spectra for the monomer (—, [**1**] = 0.004 M, λ_{em} = 419 nm) and the excimer (- - -, [**1**] = 0.07 M, λ_{em} = 484 nm) fluorescence of **1** incorporated in Nafion membranes.

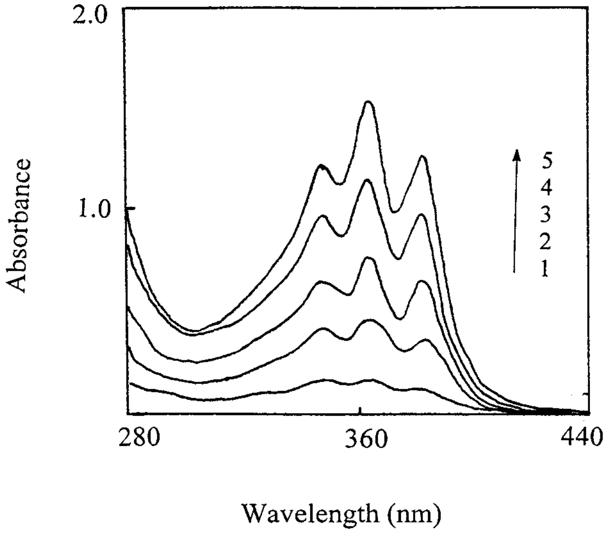


Figure 4. Absorption spectra of **2** in Nafion as a function of [NaCl] in the bulk solution. The concentration of **2** in bulk solution is 2.7×10^{-4} M. The time of immersing the membrane in solution is 1.5 h. The concentrations of NaCl for the spectra 1, 2, 3, 4, and 5 are 0, 5.0×10^{-5}, 5.0×10^{-4}, 5.0×10^{-3}, and 0.02 M, respectively.

---

(21) Turro, N. J. *Modern Molecular Photochemistry*; Benjamin: London, 1978.

(22) Gierke, T. D.; Munn, G. E.; Wilson, F. C. *J. Polym. Sci., Polym. Phys. Ed.* **1981**, *19*, 1687.

(23) Birks, J. B. *Photophysics of Aromatic Molecules*; Wiley: London, 1970.

Table 2. Chemical Shifts (ppm, $CDCl_3$) of the Bridgehead Protons and h−t/h−h Ratios of the Photocyclomers of 1−5

	chemical shifts of bridged protons		ratios of h−t to h−h		
compd	δ_{h-t}	δ_{h-h}	EtOEt	$CDCl_3$	Nafion
1	4.37	4.50	90:10	92:8	0:100
2	4.80	5.16	83:17	100: 0	7:93
3	4.55	4.80	84:16	90:10	6:94
4	5.77	5.63	100:0	94:6	6:94
5	3.97	4.58	93:7	99:1	92:8

sodium ions. It was found that **2** can be easily removed from the Nafion membrane just by washing the sample in distilled water. As in the case of **1**, the absorption spectrum of **2** incorporated in Nafion is slightly blue-shifted by ca. 1 nm. The spectral parameters for absorption and fluorescence are listed in Table 1. Because of the hydrophobicity of the antharcene moiety and the charged carboxyl group, it is expected that the solubilization site of **2** may be in the fluorocarbon/water interface. The anthracene moiety is localized in the fluorocarbon domain, whereas the substituent is toward the electrical double layer of the reverse micelle of Nafion and interacts with the counterions in the water pool.

Water-insoluble **3**−**5** were incorporated into water-swollen Nafion by immersing the membrane samples in water containing the solid substrates. To prepare the samples with high concentration of the substrate, the mixture has to be continuously stirred for a long time. Although the solubilities of these compounds in water are low, their concentrations in Nafion-Na^+ can be rather high (ca. 0.087 M for **3**, 0.045 M for **4**, and 0.059 M for **5**). The absorption spectra for compounds **3** and **4** in Nafion are slightly blue-shifted compared with that in water by 4−6 nm (Table 1). Considering the insolubility of these compounds in water, it is proposed that in water-swollen Nafion these molecules are primarily solubilized in the hydrophobic perfluorocarbon backbone region. By analogy with the studies on nonpolar pyrene and anthracene in Nafion by Mau and co-workers,[16,24] the solubilization site may be close to the fluorocarbon/water interface.

Photochemical Reactions of 1−5 in Nafion Membranes. The photocycloaddition of **3**−**5** in organic solution and in solid states has been extensively investigated,[1a−b,8] while the photochemical reaction of **1** and **2** has never been reported. Irradiation of the solutions of **1**−**5** in organic solvents through Pyrex at ambient temperature generally leads to formation of the h−t cyclomers. However, in some instances, the h−h photocyclomers were also obtained as minor products (Table 2). The h−h and h−t cyclomers could be distinguished by HPLC. The ratios of h−t to h−h cyclomers for **1**−**5** photogenerated in ether and in $CDCl_3$ are listed in Table 2. For all the substrates, the yields of the photocyclomers are close to 100% on the basis of the consumption of the starting materials. The structure proposed for the products of **3**−**5** as the $[4\pi + 4\pi]$ cyclomers rests mainly on their ^1H NMR spectra, which are in close agreement with those reported in the literature.[1] The structure determination of the photocyclomers for **1** and **2** is based on both the ^1H NMR and ^{13}C NMR spectra. The spectral details of all of the cyclomers are given in the Experimental Section. The assignment of the h−t and the h−h photocyclomers relies on the chemical shifts of bridgehead protons in their ^1H NMR spectra. It has been established[1,5a] that the chemical shifts of bridgehead protons for h−h cyclomers appear at lower regions compared with those for the corresponding h−t cyclomers. However, it was found that the bridgehead methine protons of the h−h cyclomer of **4** resonate at higher field than that of the h−t cyclomer because the bridgehead proton of the h−t cyclomer is deshielded by the adjacent carbonyl group. The chemical shifts of the bridgehead protons in the h−t and h−h cyclomers of **1**−**5** are summerized in Table 2.

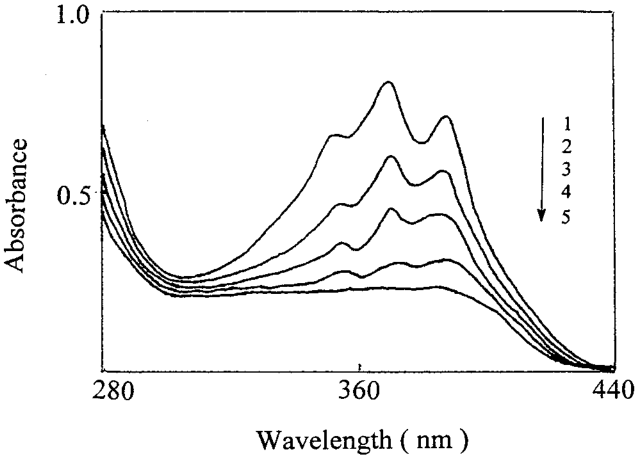


Figure 5. Absorption spectra of **1** in Nafion membranes as a function of irradiation time: 1, 10 min; 2, 20 min; 3, 50 min; 4, 80 min; 5, 120 min.

In contrast, irradiation of **1**−**4** incorporated within Nafion membranes almost exclusively results in the formation of the h−h cyclomers. On the other hand, under identical conditions, such a regioselectivity for the photocycloaddition of **5** was not observed. The Nafion membranes adsorbing the substrate were photoirradiated at ambient temperature through Pyrex. The photocycloaddition was followed by UV absorption. Figure 5 shows an example for **1**. Generally, after 2 h of irradiation, the conversion was near 100%. Similar conversion was obtained in ether after the same period of photoirradiation. The products were extracted from the Nafion membranes by methanol and analyzed by HPLC and ^1H NMR spectroscopy. The mass balance was greater than 90%, suggesting that any unidentified products must be minor. The ratios of h−t to h−h cyclomers are given in Table 2. The almost exclusive formation of the h−h cyclomers for **1**−**4** incorporated in Nafion is evidently attributed to preorientation of substrate molecules in the inverse micelle-like structure of Nafion. As described in the above section, the substrate molecules are located in the fluorocarbon/water interface of the Nafion membrane. Because of the hydrophobicity of the anthracene moiety and the charged or polar nature of the substituent for **1**−**4**, the anthracene chromorphore should reside in the fluorocarbon domain, while the substituent is anchored among the sulfonate headgroups of Nafion. Thus, the molecular plain would tend to be perpendicular to the interface of the water cluster, and the substituent is directed toward the water pool. Consequently, the photocycloaddition of two neighbored anthracene molecules favors the formation of h−h cyclomers. Since the non-polar reference substrate **5** lacks such a preorientation

---

(24) Blatt, E.; Launikonis, A.; Mau, A. W.-H.; Sasse, W. H. F. *Aust. J. Chem.* **1987**, *40*, 1.

in Nafion membranes, the enhancement of h−h cyclomer formation is not observed.

Stabilization of h−h Photocyclomers by Incorporation in Nafion Membranes. It has been established that the h−h photocyclomers of 9-substituted anthracenes generally are thermally more labile (regenerating the starting materials) compared with the corresponding h−t cyclomers.[1] This instability of the h−h cyclomers is one of the reasons why their production was rarely observed. Thus, we have examined the stability of the h−h cyclomers of **1**−**4** in Nafion. The Nafion samples adsorbing **1**−**4** were irradiated thoroughly as described above so that all of the starting material was converted into h−h (major) and h−t (minor) cyclomers. These samples were stored in the dark at room temperature, and the regenerated starting materials were checked at intervals by quick UV measurements. It was found that the h−h cyclomers of **1**, **2**, and **4** generated in Nafion underwent no decomposition over a period of 2 weeks. On the other hand, 8% of the cyclomer of **3** formed in the Nafion sample decomposed within 10 days. However, when these h−h cyclomers were extracted into methanol, they decomposed within 1 day on storage in the dark at room temperature, regenerating the starting materials. Thus, the h−h cyclomers were stabilized by confining them in Nafion membranes. This stabilization probably is one of the reasons for the enhanced formation of the h−h cyclomers in the photochemical reaction of **1**−**4** in Nafion membranes.

Conclusions

Anthracene bearing an ionic or a polar 9-substituent can be incorporated in water-swollen Nafion membranes in high concentration. The anthracene moiety is most likely located in the perfluorocarbon backbone region and the molecular plan is perpendicular to the interface of the aqueous cluster, while the charged or polar substituent is anchored among the sulfonate headgroups of the membrane. Irradiation of such preorienated 9-substituted anthracene resulted in almost exclusive formation of the h−h cyclomer, which is hardly produced in homogeneous solution. The Nafion membranes also stabilized the h−h cyclomers. Thus, Nafion membranes provides a useful medium for controlling the regioselectivity in the photocycloaddition of substituted anthracenes.

Experimental Section

Materials. Nafion membranes 117 with an equivalent weight of 1100 and thickness of 0.0175 cm were a product of Du Pont and were kindly donated by Drs. A. W.−H. Mau and L. M. Dai of CSIRO, Division of Molecular Science. Prior to use, the membranes were cleaned by boiling in concentrated nitric acid for 4 h and then thoroughly washed with distilled water and finally immersed in water for 24 h. The membranes in sodium form (Nafion-Na^+) were obtained by immersing the pretreated Nafion-H^+ membranes in 1 M NaOH aqueous solution. Excess base was then removed by stirring the samples in water. Doubly distilled water was used throughout this work. All the solvents were of analytical grade.

(9-Anthrylmethyl)trimethylammonium bromide, **1**, was synthesized by the following procedure: A mixture of 9-methylanthracene (0.5 g, 0.026 mol) and *N*-bromosuccinimide (0.46 g, 0.026 mol) in CCl_4 solution (12 mL) was refluxed for 4 h. After filtration, the filtrate solution was saturated by trimethylamine gas while the mixture was kept vigorously stirred. Yellow product was precipitated gradually from the solution. This precipitate was recrystallized from methanol-acetone mixture solution giving pure **1**: mp 202−204 °C dec; MS *m/z* 239 (M^+); ^1H NMR ($CDCl_3$, ppm) 3.47 (s, 9H), 6.02 (s, 2H), 7.44−7.51 (m, 2H), 7.65−7.73 (m, 2H), 7.96−8.03 (m, 2H), 8.53 (s, 1H), 8.80−8.90 (m, 2H).

Sodium 9-anthrylacetate, **2**, was synthesized by Grignard reaction of (9-anthrylmethyl)magnesium bromide with carbon dioxide. An ether solution of 9-anthrylmethyl bromide (0.37 g, 0.0136 mol, prepared as mentioned above) was dropped into a mixture of magnesium powder (0.33 g, 0.0137 mol) and diethyl ether while the mixture was vigorously stirred. After being stirred at room temperature for 40 min, the mixture solution was refluxed for 2 h and then saturated with a dried carbon dioxide gas and refluxed for another 1 h. After evaporation of ether, an appropriate amount of water was dropped and the 9-anthrylacetic acid was precipitated. Neutralization of 9-anthrylacetic acid with NaOH gave compound **2**: ^1H NMR ($CDCl_3$, ppm) 8.58 (s, 1H), 8.30 (d, 2H), 8.11 (d, 2H), 7.52−7.57 (m, 4H), 4.65 (s, 2H). Compounds **3**−**5** were Aldrich products and used without further purification.

Preparation of Nafion Samples. The Nafion membrane samples (3.0 cm × 0.8 cm × 0.0175 cm) were immersed in an aqueous solution of the substrate, and the solution was kept continuously stirred. At certain intervals, the samples were taken out from the solution to obtain the desired concentration of the substrate. In the preparation of the samples incorporating **3**−**5**, the aqueous solutions contained the solid substrates. To prepare the sample adsorbing **2** with high concentration, the Nafion membranes were immersed in an aqueous salt solution of **2**. The amount of uptake of the substrate by Nafion was determined by the UV absorption.

Photoirradiation and Product Analysis. Photoirradiation of **1**−**5** in homogeneous solutions ($CDCl_3$ and diethyl ether) or in Nafion membranes was carried out in a Pyrex reactor. Prior to irradiation, the samples were degassed with nitrogen for 15 min. A 500-W high-pressure mercury lamp was used as the light source. The photocycloaddition process was monitored by UV absorption spectroscopy. The photocyclomers were precipitated from the solutions and isolated by filtration. For Nafion samples, after irradiation the membrane was extracted with methanol. The h−h and h−t cyclomers were separated by using a Varian VISTA HPLC with a Lickrosob RP 18 column, and methanol/water (95/5) was used as the eluting solvent. Of particular interest was the ratio of h−t to h−h cyclomers, which was determined both by HPLC measurement and the ^1H NMR spectroscopy of the product mixture. The ratio obtained by these two methods were consistent with each other.

h−t cyclomer of 1: mp 237 °C dec; ^1H NMR ($CDCl_3$, ppm) 6.63−6.93 (16 H, m), 4.37 (2 H, s), 3.75(4H, s), 3.41 (18 H, s); ^{13}C NMR (DMSO-d_6, ppm) 143.37, 142.08, 129.46, 127.52, 125.52, 125.16, 58.94, 56.27, 52.89, 48.09; $^1J_{CH}$ for bridgehead carbon and proton is 128 Hz, $^3J_{CH}$ for bridgehead carbon and methylene proton in the substituent is 17.3 Hz. Anal. Calcd for $C_{36}H_{40}N_2Br_2$: C, 65.45; H, 6.06; N, 4.24; Br, 24.24. Found: C, 65.78; H, 6.07; N, 4.24; Br, 24.25. **h−h cyclomer of 1:** ^1H NMR ($CDCl_3$, ppm) 6.58−7.07 (16 H, m), 4.50 (2 H, s), 3.76 (4 H, s), 3.41 (18 H, s). **h−t cyclomer of 2:** mp 268 °C dec; ^1H NMR ($CDCl_3$, ppm) 6.78−7.10 (16 H, m), 4.80 (2 H, s), 3.87 (4 H, s); ^{13}C NMR (DMSO-d_6, ppm) 176.43, 143.96, 142.85, 130.50, 129.46, 127.29, 125.09, 62.37, 58.25, 52.90; $^1J_{CH}$ for bridgehead carbon and proton is 133 Hz, $^3J_{CH}$ for bridgehead carbon and methylene proton in the substituent is 15.7 Hz. Anal. Calcd. for $C_{32}H_{22}O_4Na_2$: C, 74.42; H, 4.26. Found: C, 74.33; H, 4.28. **h−h cyclomer of 2:** ^1H NMR ($CDCl_3$, ppm) 6.82−7.15 (16 H, m), 5.16 (2 H, s), 3.89 (4 H, s). **h−t cyclomer of 2 in acid form:** ^1H NMR ($CDCl_3$, ppm) 6.73−7.00 (16H, m), 4.80 (2H, s), 3.77 (4H, s). **h−h cyclomer of 2 in acid form:** ^1H NMR ($CDCl_3$, ppm) 6.77−7.12 (16H, m), 5.15(2H, s), 3.79(4H, s). **h−t cyclomer of 3:** ^1H NMR ($CDCl_3$, ppm) 6.88−7.13 (16 H, m), 4.55 (2 H, s), 4.91 (4H, s). **h−h cyclomer of 3:** ^1H NMR ($CDCl_3$, ppm) 6.70−7.20 (16 H, m), 4.80 (2 H, s), 4.91 (4 H, s). **h−t cyclomer of 4:** ^1H NMR ($CDCl_3$, ppm) 6.49−6.87 (16 H, m), 5.77 (2 H, s), 2.63 (6 H, s). **h−h cyclomer of 4:** ^1H NMR ($CDCl_3$, ppm) 6.51−6.99 (16 H, m), 5.63 (2 H, s), 2.64 (6 H, s). **h−t cyclomer of 5:** ^1H NMR

(DMSO-d_6, ppm) 6.77−7.22 (16 H, m), 3.97 (2 H, s), 2.09 (6 H, s). **h−h cyclomer of 5:** ^{1}H NMR (DMSO-d_6, ppm) 6.70−7.32 (16 H, s), 4.58 (2 H, s), 1.92 (6 H, s).

Acknowledgment. We thank the National Science Foundation of China and the Bureau for Basic Research, Chinese Academy of Sciences, for financial supports. Thanks are also due to Drs. A. W.-H. Mau and L. M. Dai of CSIRO, Division of Molecular Science, for the donation of Nafion 117 membranes.

JO980412E