Fluorescence Patterning using Photochemical Cycloaddition of Di-9,9'-anthracene Conjugates linked by Perethylsilyl Chains

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Dianthrylsilan es composed of two 9-anthryl groups and perethyloligosilane (n = 1, 2 or 3) chain units were prepared (A2S1, A2S2, and A2S3). Photochemical intramolecular cyclization reactions of these compounds were studied in solution and in PMMA spin coated film. In cyclohexane solution, the A2S n molecules gave one of three cycloadducts, depending on the chain length of the A2S n molecules. We also demonstrate the fabrication of fluorescent images using cycloaddition reactions in PMMA film.

Keywords: Patterning, Fluorescence image, Intramolecular Cycloaddition, Dianthrylsilane

1. Introduction

α,α-Diaryl oligosilanes have attracted much attentions because they exhibit interesting photochemical characteristics that are not found in their carbon chain analogs [1–7]. α,α-Di(3-pyrenyl)oligosilanes were reported to show excimer emission upon photoexcitation [4]. On the basis of 1H NMR chemical shift data, two pyrenyl groups were proposed to interact even in the ground state, and strong excimer emission was observed when the disilane unit acted as a linker [4]. Furthermore, in some cases, a charge transfer (CT) state of diaryloligosilanes is formed in addition to excimer formation [1–7].

Although the Si–Si bond is a single bond, it shows σ conjugation through σ orbital overlap. If a silane chain and two aromatic rings are connected, π orbitals of the aromatic rings can also conjugate with σ orbitals of the silane chain. In addition, the π orbitals of the two aromatic rings can spatially interact with each other directly in the excited state; this state is termed the excimeric state.

A detailed experimental and theoretical investigation of the conformation of the intramolecular interactions of 1,2-diphenyltetramethyldisilane has been reported [8]. According to that study, intramolecular interactions in the HOMO arise from interactions between the phenyl π orbital and the disilane σ orbital (σSiSi−π), and those in the LUMO originate between the phenyl π* orbital and the disilane π* orbital (π*SiSi−π*).

We studied the photochemical properties of compounds composed of two aryl groups connected by a dimethylsilane chain. Intramolecular interaction between the anthryl group and the disilane unit requires a perpendicular conformation between these two groups, since the overlap of the π orbital of the anthryl group with the σ orbital of the Si–Si chain is the origin of this interaction. We investigated this intramolecular interaction for A2S2, in which the disilane unit is substituted at the 9 position of the anthryl group, and found that steric hindrance between the disilane unit and the hydrogen atoms at the 1 and 8 positions of the anthracene was the primary driving force behind the intramolecular interaction. Excimer emissions are observed for diaryloligosilanes containing a short silane linker in both nonpolar and polar solvents. CT emissions are also observed in acetonitrile (a polar solvent) solutions of diaryloligosilanes that have longer linker units (n > 4). If two aromatic groups have different excitation energies, such as the 9-anthryl and 1-naphthyl groups, excitation energy will transfer more efficiently through the silane chain than through the carbon chain analogue [7].
Few studies of the photochemistry of diarylsilanes have been conducted compared to studies of their photophysical properties. The principle photochemical reaction of the simple silane chain is generally photodegradation of the silane chain; however, if aryl groups are attached to the silane chain, then photochemical addition between the two aryl groups becomes the main reaction. 1,1-Di(9-anthryl)-dimethylsilane is reported to produce unique [4 + 2] cycloadducts [2], which are very similar to the photochemical adducts produced from 1,2-di(9-anthryl)ethanes [9]. The long bond lengths of the Si-Si and Si-C bonds affect their reactivity in this reaction. In the present study, we investigated the photochemical cyclization reaction of 1, 1-di-(9-anthryl)dimethylsilane (A2S1), 1, 2-di-(9-anthryl)-tetramethyldisilane (A2S2), and 1, 3-di-(9-anthryl)-hexamethyltrisilane (A2S3). We also used this photochemical cyclization reaction to fabricate fluorescently patterned thin films.

2. Experimental

2.1. Photochemical reactions in solution.

Compounds A2S1, A2S2, and A2S3 were prepared as previously reported [2, 5, 6].

Cyclohexane solutions of A2S1, A2S2, and A2S3 (5 mg in 200 ml) were introduced into Pyrex vessels pre-purged with argon (25 ml/min × 20 min). The solutions were irradiated using a 500 W Xe-lamp equipped with a U360 glass filter for 4 to 40 h. The reaction was followed by measuring the absorption spectrum of anthracene between 300–420 nm using a JASCO U-570 spectrophotometer. The photochemical products were identified from their 1H-NMR spectra (JEOL JMN-GSX400).

1H-NMR (CDCl3, TMS) of product of A2S1 (Type I): δ 6.60–7.90 (13H, m, Ar-H) 6.20 (1H, dd, Hα, J=9.8, 2.4 Hz) 5.82 (1H, dd, Hβ, J=9.9, 3.9 Hz) 3.96 (1H, d, H3, J=12 Hz) 4.31 (1H, d, H4, J=2.7Hz) 3.29 (1H, m, H4).

1H-NMR (CDCl3, TMS) of product of A2S2 (Type II): δ 7.70 (1H, d, Ar-H, J=7.2 Hz) 7.54 (1H, d, Ar-H, J=8.8 Hz) 7.25 (4H, m, Ar-H) 7.11 (1H, s, Ar-H ) 7.08 (2H, m, Ar-H) 6.97 (1H, d, J=7.0 Hz Ar-H) 6.69 (1H, d, Hβ, J=7.4 Hz) 6.52 (1H, t, Ar-H, J=7.4 Hz) 4.64 (1H, dd, Ar-H, J=7.6 Hz) 6.41 (1H, m, H3) 5.80 (1H, ddd, J=8.7, 7.2, 1.5 Hz, Hβ) 4.30 (1H, d, H1, J=10Hz) 4.16 (1H, ddd, J=10, 7.0, 1.5 Hz Hβ) 4.13 (1H, d, H1, J=7.0 Hz).

1H-NMR (CDCl3, TMS) of product of A2S3 (Type II): δ 7.73–7.77 (1H, m, Ar-H) 7.59–7.45 (1H, m, Ar-H) 7.31–7.37 (3H, m, Ar-H) 7.18–7.25 (2H, m, Ar-H) 7.12–7.15 (3H, m, Ar-H) 6.91–6.93 (1H, m, Ar-H) 6.79–6.81 (1H, m, Ar-H) 6.56–6.58 (2H, m, Ar-H) 6.20 (1H, ddd, H3, J=8.0, 6.8, 1.0Hz) 6.02 (1H, ddd, H4, J=8.6, 7.3, 1.2 Hz) 4.66 (1H, ddd, H4, J=7.5, 0.7Hz) 4.42 (1H, d, H1, J=11Hz) 4.19 (1H, m, Hβ).

2.2 Photochemical reaction of A2S1 and A2S3 in PMMA film.

A2Sn (4 mg) and 52 mg of PMMA were dissolved in CHCl3 (0.4 ml) and spin coated on a glass plate at 1500 rpm. The film was irradiated with light from a 150 W Xe-lamp passed through a photomask and glass filter (2.64 mW/cm²).

3. Results and Discussion

3.1. Photochemical cyclization in solution.

Irradiation of a dilute solution of A2S1 in cyclohexane (5×10⁻⁵ M) purged with argon at λ≥300 nm gave two intramolecular cyclization products. The reaction was followed by UV-Vis absorption, providing the spectra shown in Fig. 2a. A decrease in the intensity of the absorption band around 320–410 nm (characteristic of the anthracene moiety) and an increase in the intensity of the band around 270–320 nm were observed. The main product of this reaction is a [2+4] adduct that has cyclo-added structure at 1, 2 and 9', 10' positions of each anthracene moiety (Type I in Fig. 1). Formation of this adduct has been previously reported [2]. The increase in the 270–320 nm absorption band is believed to be due to the formation of a naphthyl moiety after the cyclization.
reaction. The second product formed is a [4+4] adduct (Type III in Fig. 1) $^1$H-NMR spectroscopy (see details in the $^1$H-NMR analysis section) indicated that the ratio of Type I: Type III is 2:1. These products could not be isolated because of their instability on silica gel.

Figure 2. Absorption spectral changes in A2S1, A2S2, and A2S3 (from top to bottom) upon irradiation at 365 nm.

We also investigated the photocyclization reactions of A2S2 and A2S3 and compared their behavior with that of A2S1. A2S2 was irradiated and its products were identified in a manner similar to that described for A2S1. The UV-Vis absorption spectrum of the product is shown in Fig. 2b. The intensity of the absorption band characteristic of the anthracene moiety around 320-410 nm decreased, while the intensity of the band around 270-320 nm increased. The primary product was deduced to be a [4+4] adduct that has cyclo-added structure at 1, 4 and 9',10' positions of anthracenes (Type II in Fig. 1).

Formation of this type of adduct has been reported for the 9,9'-anthracene conjugate containing a -Si(Me)$_2$-O-Si(Me)$_2$- linker unit [9]. The increased intensity of the absorption band around 270-320 nm is likely due to formation of a naphthyl moiety following cyclization. For A2S2, the formation of the absorption band around 270-320 nm was weak and the band is broad, due to the low concentration of the Type II product. The second product is a [4+4] adduct that has a cyclo-added structure at 9, 10 and 9', 10' of anthracenes (Type III in Fig. 1). This type of addition has been reported for many anthracene conjugates, for example, 1, 2-(9, 9'-dianthryl)ethane [9–11]. The Type I: Type III products ratio of A2S2 was determined to be 8:1.

Irradiation at $\lambda \geq 300$ nm of a dilute solution of A2S3 in cyclohexane (5×10$^{-5}$ M) purged with argon gave two intramolecular cyclization products. As shown in Fig. 2c, a decrease in the intensity of an absorption band characteristic of the anthracene moiety, at 320-410 nm, and an increase in the absorbance band around 270-320 nm, were observed. The products were [4+4] adducts that had cyclo-added structures at 1, 4 and 9', 10' positions, and at 9, 10 and 9', 10' of anthracenes (Type II and III, respectively, in Fig. 1). In case of A2S3, the Type I: Type III ratio was determined to be 0.9:1.

The relative rates of cyclization of A2S1, A2S2, and A2S3 were compared. Although single adducts were not formed in each case, the reaction was faster with compounds having a shorter linker chain (see Fig. 3).

3.2 $^1$H-NMR analysis

The structures of the products were identified by $^1$H-NMR. Three types of photocycloadduct products were expected (Type I–III in Fig. 1). The structures of these products can be identified from the signals of the $^1$H's attached to the carbon atoms engaged in the cyclization. The relationship between the dihedral angle and the coupling constant for vicinal protons is known as the vicinal Karplus correlation [12].
The $^1$H signals of product A2S1 were at $\delta=3.29$ (1H, m, H$^a$), 3.96 (1H, d, $J=12$Hz, H$^f$), 4.31 (1H, d, $J=2.7$Hz, H$^b$), 5.82 (1H, dd, $J=9.9$, 3.9 Hz, H$^e$), 6.2 (1H, dd, $J=9.8$, 2.4 Hz, H$^d$). These signals were assigned to H$^a$ to H$^d$ of a Type I product. Because the $^1$H coupling constants have correlations with the dihedral angles, it was concluded that ($J$(H$^{b-c}$)=3.9Hz corresponds to a dihedral angle of 45°, $J$(H$^{f-e}$)=2.7Hz to a dihedral angle of 60°, and $J$(H$^{d-c}$)=12Hz to a dihedral angle of 0°). These angles are characteristic of the structure of Type I adducts.

In addition, a signal at $\delta=4.7$ (2H, s, H$^f$) was observed. This is characteristic of the structure of a Type III adduct. Integration of the signal intensities indicated that the product was a mixture of Type I:Type III = 2:1.

As mentioned above, the signals of the products of A2S2 were assigned to a mixture of Type II and Type III adducts. The coupling constants of $J$(H$^{b-c}$)=10Hz (dihedral angle=0°), $J$(H$^{b-c}$)=7.2Hz and $J$(H$^{f-e}$)=7.0Hz (dihedral angle=10°) are characteristic of the structure of Type II adducts. ($\delta=4.13$ (1H, d, $J=7.0$Hz, H$^d$), 4.16 (1H, ddd, $J=10$, 7.0, 1.5Hz, H$^b$), 4.30 (1H, d, $J=10$Hz, H$^f$), 5.8 (1H, ddd, $J=8.7$, 7.2, 1.5Hz, H$^e$), 6.4 (1H, m, H$^c$)). Comparison of the signals of Type III at $\delta=4.7$ (2H, s, H$^f$) with the signals of Type II indicates that the ratio of Type II:Type III is 8:1.0.

The product of A2S3 was also a mixture of Type II and Type III adducts. The signals of the Type II product were ($\delta=4.19$ (1H, m, H$^b$), 4.42 (1H, d, $J=1$Hz, H$^b$), 4.66 (1H, dd, $J=7.5$, 0.7Hz, H$^f$), 6.02 (1H, ddd, $J=8.6$, 7.3, 1.2Hz, H$^c$), 6.20 (1H, ddd, $J=8.0$, 6.8, 1.0Hz, H$^d$). $J$(H$^{b-c}$)=11Hz for (dihedral angle=0°), $J$(H$^{b-c}$)=7.2Hz and $J$(H$^{f-e}$)=7.0Hz (dihedral angle=30°)). The signals of the Type III product ($\delta=4.7$ (2H, s, H$^f$)) compared to the Type II product indicated a ratio of Type II:Type III of 0.9:1.0.

Irradiation of the photoprodut of A2S1 at 290±10 nm recovered the initial material, indicating that this reaction is reversible, as shown in Fig. 4.

![Figure 3. Relative rate of the cycloaddition reaction of A2S$n$ (n = 1, 2, and 3).](image)

![Figure 4. Spectral change in the absorption of the photoprodut of A2S1 during irradiation at 290 ± 10 nm.](image)

3.3 Investigation of the ground state structure by MM2 calculations

For a better understand of the cycloaddition reaction, the ground state conformations of A2S$n$ were investigated by MM2 calculations, as shown in Fig. 4. The conformers shown in Fig. 5 are in their ground state (stable) conformation, those are taking nearest structure to the each cyclization product for the compounds n = 1, 2 and 3.

![Figure 5. Optimized structure of A2S$n$ (n = 1, 2, and 3) by MM2 calculations.](image)
In the structures of A2S1 and A2S2, two anthryl groups are not in sandwich-like conformations, so the 9, 10 and 9', 10' positions are distant from each other, thereby reducing steric hindrance. Following excitation, rotation of the Si-C or Si-Si bond leads to cyclization. The longer bond lengths of Si-C ($r = 1.89$ Å) and Si-Si ($r = 2.35$ Å) compared to the C-C bond ($r = 1.54$ Å) enables them to form characteristic adducts. The extremely slow reactivity of A2S3 is explained by the increased number of conformers, and as a result, a decrease in the population of the conformer capable of undergoing cyclization.

3.4 Patterning of PMMA film

The patterning of fluorescent images on PMMA film using cyclization reactions of A2S1 and A2S3 were examined. Using a 150 W Xe-lamp and irradiating through a photomask provided the image shown in Fig 6. The UV-vis absorption spectrum was used to follow the progression of the reaction in the film (Fig. 7). Following irradiation, the fluorescence was quenched by a photochemical cyclization reaction, and brilliant blue fluorescence was observed by irradiating with a 4 W hand-held UV-lamp (365 nm).

![Figure 6. Photomask (left) and fluorescence image fabricated by a PMMA film containing A2S1 cast on a glass plate (right).](image)

After spin coating, anthracene conjugate molecules are likely to adopt an extended conformation, making intramolecular cycloaddition difficult for A2S3. However, this reaction occurred more efficiently with A2S3 than with A2S1: the reaction took about 44 min with A2S1, as shown in Fig. 7, but it was 3 times faster with A2S3. We therefore expect that cycloaddition in A2S3 is occurred intermolecularly. In the case of A2S1, it is not concluded from the available experimental data if the reaction is occurred intra- or inter-molecularly.

When the absorption spectra indicated that the reaction had gone to completion, the sample was irradiated at 290 nm with a 150 W Xe-lamp. However, no reversible reaction is observed, indicating that the reaction in the film is not as clean as that in cyclohexane, and that degradation reactions must have occurred.

![Figure 7. Absorption spectral changes of the PMMA thin film containing A2S1. The region below 280 nm could not be measured due to the glass plate.](image)

4. Conclusion

We have investigated the photochemical intramolecular cyclization reaction of 1, $n$-(9, 9'-dianthryl)permethyloligosilanes ($n = 1, 2$, and 3, A2S$n$) in cyclohexane. A2S$n$ gives three types of cycloadducts. We also succeeded in fabricating fluorescent image patterns on PMMA thin film by using intramolecular cycloaddition reactions of A2S$n$.

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