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Communications

Chemistry of [4+4] Anthracenes-Furan Cyclodimers

Taehee Noh*, Heejun Lim, and Daekyun Kim

Department of Chemistry Education, Seoul National University, Seoul 151-742, Korea

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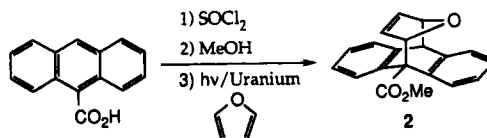
In addition to the important role of dimer formation upon deactivation from excited states, cyclodimers of aromatic compounds have interesting physical and chemical properties because of their unique topology and high internal energy. Much progress has been made on the studies of the unusual chemical and physical properties of these cyclodimers, especially of the arene-benzene cyclodimers. Adiabatic photodissociation has been reported in some anthracene-benzene dimers,^{1,2} naphthalene-benzene dimers,³ and anthracene-naphthalene dimers.⁴ Chemiluminescence was also observed from the thermoreversion of several substituted anthracene-benzene dimers.⁵ The photoelectron spectra of some benzene dimers have been taken and analyzed by through-bond interaction.⁶ However, systematic studies on their chemistry have been rather limited due to poor synthetic yields, instability of target compounds, and/or purification problems.

Since benzene itself does not add photochemically to anthracene, indirect synthetic method utilizing 1,3-cyclohexadiene derivatives has been employed.^{1,2} In order to synthesize cyclodimers efficiently and study their properties, synthetic methods using direct irradiation might be desirable. Since the resonance energy of furan is 17.2 kcal/mole,⁷ it is expected that photocycloaddition by direct irradiation might work. Indeed, it has been reported that [4+4] cyclodimers of furan with 9-cyanoanthracene (**1**),⁸ 1-cyanonaphthalene and 2-cyanonaphthalene⁹ were produced upon irradiation. In this communication, we wish to report the synthesis of the [4+4] cyclodimer (**2**) of methyl 9-anthroate and furan and a detailed study of thermal and photochemical dissociations of **1** and **2**.

Compound **1** was prepared as previously reported.⁸ In order to synthesize **2**, methyl 9-anthroate was prepared from the corresponding carboxylic acid (Scheme 1). Treatment of

9-anthracenecarboxylic acid with thionyl chloride, followed by the addition of methanol, gave the methyl ester in 99.5% yield. A solution of methyl 9-anthroate (486.8 mg, 2.060 mmol) containing a large excess of furan (40 mL) was irradiated with a 450 watt Hanovia medium-pressure mercury lamp through a Uranium glass filter at ambient temperature for 3 hours. The reaction mixture was separated by a silica gel (70-230 mesh) chromatography, eluting with n-hexane-dichloromethane mixtures of increasing polarity. Compound **2** was isolated in 35.5% yield¹⁰ and methyl 9-anthroate (3.5 mg, 0.7%) was recovered. The other isolated products (32%) were the cyclodimers of methyl 9-anthroate as indicated by the data of thermolysis and preliminary spectroscopic analyses. The regiochemistry and stereochemistry of the cyclodimers are currently under investigation.

The structure of **2** was determined by studying the mass spectroscopic data and by UV, NMR, and IR analyses. The mass spectrum (EI) of **2** had weak molecular ion peak (*m/e* 304) but intense fragment peaks at *m/e* 236 and 68, indicating a facile dissociation into methyl 9-anthroate and furan. The UV spectrum of **2** showed similar absorption maxima to that of the [4+4] cyclodimer of methyl 9-anthroate and benzene indicating the presence of the 9,10-dihydroanthracene chromophore.¹¹ The ¹H NMR peaks of **2** are similar to those of **1** except the peak of the methoxycarbonyl protons at 4.01 ppm.

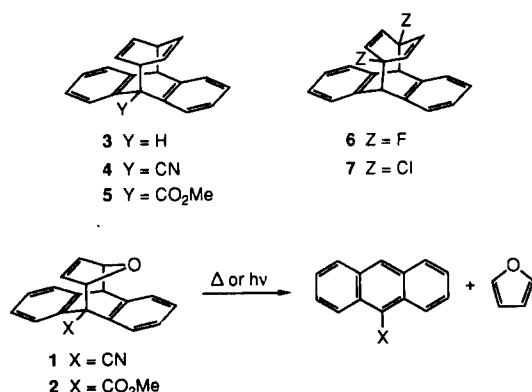


Scheme 1. Synthetic route of the cyclodimer **2**.

Table 1. Activation Parameters for the Thermoreversion of the Cyclodimers of Anthracenes

	1 ^a	3 ^b	4 ^c	5 ^c
E_a (kcal/mole)	29.6±0.5			28.0±0.2
ΔH^\ddagger (kcal/mole)	29.0±0.5	33.0±0.9		27.4±0.2
ΔS^\ddagger (eu)	1.0±1.6	16.4±2.4		8.3±0.7
ΔG^\ddagger (kcal/mole)	28.7±0.5		21.5±0.0	

^aIn DMF at 298.15 K. ^bTaken from ref 1b, in octane. ^cTaken from ref 12, in DMF.



The thermolytic behavior of **1** and **2** in degassed solution was studied. The thermolysis of **1** quantitatively yielded 9-cyanoanthracene, while the thermolysis of **2** produced methyl 9-anthoate with unidentified products (less than 10% in ¹H NMR). Kinetic analyses of the thermolysis of **1** in the temperature range of 78.9–99.7 °C in *N,N*-dimethylformamide were performed by UV spectroscopy. Kinetic analysis of the initial decomposition (6% conversion) of **2** at 99.6 °C was also performed. The thermal decomposition of the cyclodimers into the parent arenes was found to be first order as can be expected for this type of unimolecular dissociation. The activation parameters, obtained from transition state theory, are shown in Table 1. We have found that the activation enthalpy for **1** is about 29 kcal/mole. High activation enthalpy and positive activation entropy indicate that the thermolysis of **1** proceeds in a biradical mechanism.¹ The rate constant for the thermal decomposition of **2** at 99.6 °C in *N,N*-dimethylformamide was found to be $2.75 \times 10^6 \text{ sec}^{-1}$. The half-life times for the thermal decomposition of **1** and **2** at 99.6 °C were estimated to be 1.5 and 70.1 hours, respectively. Compared to the results for the derivatives of anthracene-benzene dimer (**4** and **5**), **1** and **2** are kinetically more stable as expected from the resonance energy of furan. Cyclodimer **1** with the cyano group was found to be kinetically more unstable than **2**, which had been also observed in the thermolysis of anthracene-benzene dimer^{5,11} and the isomerization of quadricyclane to norbornadiene.¹²

Irradiation of the solution of **1** (0.11 M) in CDCl₃ through a Vycor filter for about 15 minutes yielded 14% of 9-cyanoanthracene and 86% of 9-cyanoanthracene cyclodimer (secondary product) based on the consumed **1**. 9-Cyanoanthracene was exclusively formed when irradiated at the concentration of $\sim 10^{-5}$ M. Similar results were obtained at the irradiation of **2**. In order to study the nature of the electronic state of substituted anthracenes formed in the photolysis, emission spectra for **1** and **2** ($\sim 10^{-5}$ M) were taken.

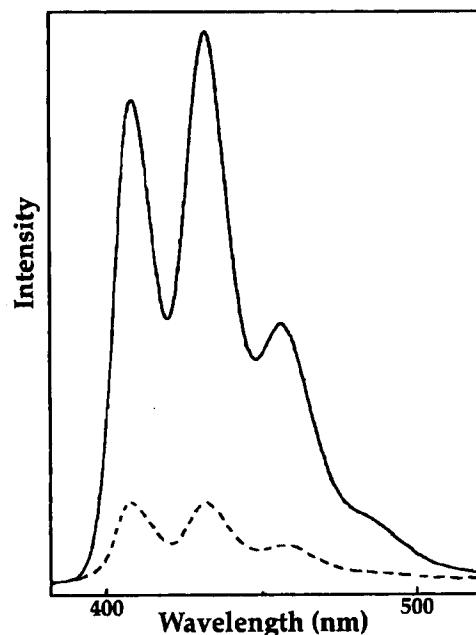


Figure 1. Emission spectra of **1** (dotted line) and 9-cyanoanthracene (solid line) in cyclohexane. These emission spectra are observed by the irradiation of UV light at 280 nm with same absorbance at that wavelength.

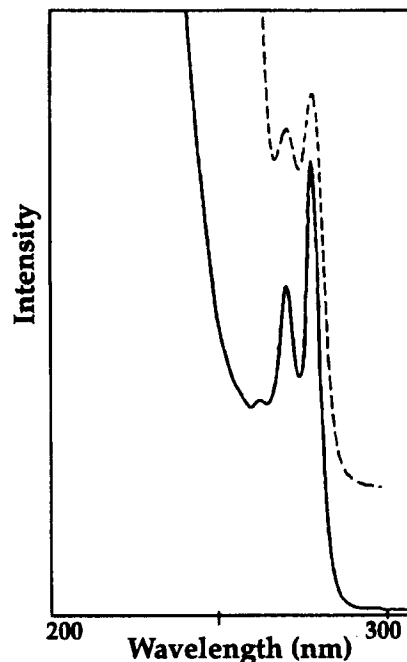


Figure 2. UV spectrum (solid line) and excitation spectrum (dotted line, $\lambda_{em}=400 \text{ nm}$) of **1**.

Upon photoexcitation of **1** at 280 nm in cyclohexane, the only emission observed was attributed to 9-cyanoanthracene fluorescence (Figure 1). This was confirmed by the excitation spectrum of **1** (Figure 2) which possesses a peak shape similar to the UV spectrum of **1**. Although fluorescence emission of **2** was observed, adiabatic photodissociation (monomer fluorescence) was also observed for **2** (Figure 3). These results suggest that the high exothermicity

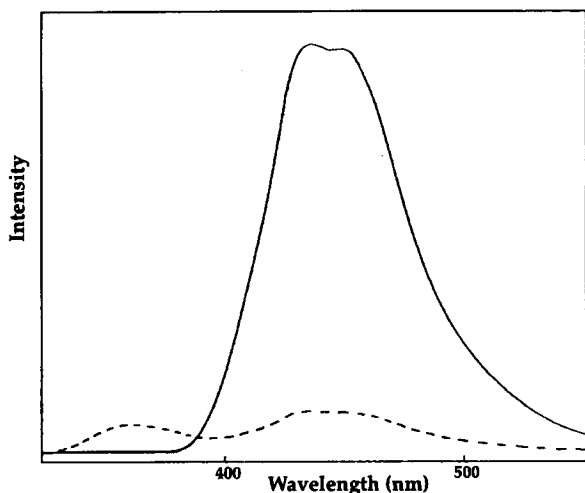


Figure 3. Emission spectra of **2** (dotted line) and methyl 9-anthroate (solid line) in cyclohexane. These emission spectra are observed by the irradiation of UV light at 280 nm with same absorbance at that wavelength.

Table 2. Quantum yields of the Photoreversion of the Cyclodimers of Anthracenes

	1 ^a	2 ^a	3 ^b	6 ^c	7 ^c
Φ_{An}	0.45±0.02	0.33±0.05	0.86±0.06		
Φ_{An^*}	0.15±0.00	0.12±0.02 ^d	0.80±0.08	0.69	0.39

^a The average of two separate determinations in cyclohexane.

^b Taken from ref 1b, in methanol. ^c Taken from ref 2, in hexane.

^d Fluorescence emission of the adduct (λ_{max} =360 nm) was also observed.

in the conversion of **1** and **2** to their unit components distorts the normal energy surfaces to tilt the excited state surface and thus to allow the production of the excited state anthracene.¹³ The efficiency of photolysis of **1** and **2** in degassed solution was determined with the quantitative photodissociation of anti-benzene dimer¹⁴ and the formation of excited anthracenes from **1** and **2** monitored with a JASCO spectrofluorometer (Table 2).¹ Quantum yields of photodissociation and quantum yields of adiabaticity are found to be lower than those of anthracenes-benzenes cyclodimers **6** and **7**,² but higher than those of anthracenes-cyclohexa-1,3-dienes cyclodimers.¹⁵ This may be due to internal energy of the adducts, which is related to the resonance energy of the unit component. It is noteworthy that a compound which can be prepared by a direct irradiation shows such a high efficiency of adiabaticity, which was only observed in the case of anthracene-naphthalene dimers.⁴

The potential chemiluminescent cycloreversion in solid states and thermoreversion and photoreversion of other energy-rich cyclodimers with the unit component of furan are under investigation.

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- 2**: mp 179-180 °C; ¹H NMR (200 MHz, CDCl₃) δ 7.24 (4H, m, aromatic H), 7.05 (3H, m, aromatic H), 6.81 (1H, m, aromatic H), 5.88 (1H, dd, $J=15.3$, 5.8 Hz, olefinic H), 5.86 (1H, dd, $J=13.1$, 5.8 Hz, olefinic H), 5.16 (1H, d, $J=1.7$ Hz, O-CH-C-CO₂Me), 4.63 (1H, dd, $J=6.6$, 1.6 Hz, O-CH-C=C), 4.08 (1H, d, $J=6.6$ Hz, Ar-CH), 4.02 (3H, s, -CO₂CH₃); IR (CHCl₃) 3075, 3040, 3010, 2955, 1725, 1470, 1455, 1435, 1315, 1245, 1205, 1160, 1130, 1100, 1035 cm⁻¹; UV (Cyclohexane) λ_{nm} (ϵ) 279.8 (1873), 272.0 (1352), 264.4 (901), 224.6 (7422); UV (DMF) λ_{nm} (ϵ) 280.0 (1714), 272.0 (1332); MS (EI⁺) m/e 304 (M⁺, very weak), 236 (100), 205, 177, 176, 151, 68.
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