Dissymmetrical Photodimerization of Methyl 9-Anthroate

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(Received January 20, 1997; CL-970042)

Irradiation of methyl 9-anthroate through a Uranium filter gave the 1,4-10',9' and 1,4-9',10' cyclodimers as well as the 9,10-10',9' cyclodimer; this is the first example of intermolecular photodimerization involving the 1, 4, 9', and 10' positions of *meso*-substituted anthracenes. These dissymmetrical cyclodimers were found to be thermally more labile than the 9,10-10',9' cyclodimer.

The photochemistry of anthracenes is still of substantial interest.[1-3] Most *meso*-substituted anthracenes readily form photodimers upon irradiation. However, 9-phenylanthracene does not photodimerize. 9-*tert*-Butylanthracene undergoes the photochemical valence isomerization to 9-*tert*-butyl-9,10-(Dewar anthracene) isomer.[4] In all of the cases in which photodimerization of *meso*-substituted anthracene has been observed, the products are bridgehead-substituted dianthracenes formed by head-to-tail (HT) and/or head-to-head (HH) dimerizations. HT dimers are exclusively formed in most cases, but the concomitant formation of HH dimers has been observed in some instances such as the photoreaction of 9-methoxyanthracene.[5] To the best of our knowledge, no other intermolecular photodimerization mode of *meso*-substituted anthracene has been reported. We wish to report the first example of intermolecular photodimerization of *meso*-substituted anthracene involving the 1, 4, 9', and 10' positions of the anthracene rings as well as a preliminary study on the properties of the dissymmetrical cyclodimers.

A diethyl ether solution of **1** was irradiated through a Uranium glass filter (λ > 330 nm) with a 450 watt Hanovia medium-pressure mercury lamp. By consecutive filtration of the precipitates in dichloromethane and silica gel chromatography, three products were isolated. The R_f values of the products on silica gel TLC eluting with dichloromethane/hexane (v/v 4:1) are 0.75 (isolated yield based on the consumed **1**: 83.6%), 0.67 (8.2%), and 0.49 (2.1%), respectively.

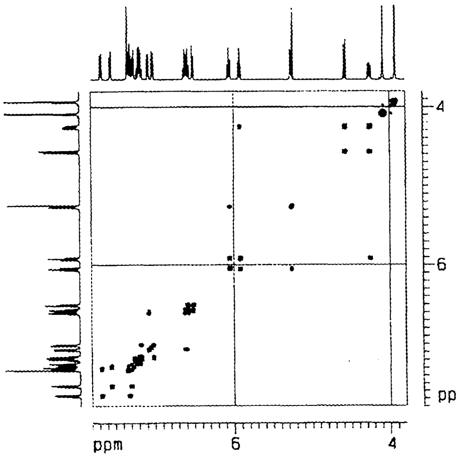


Figure 1. COSY spectrum of **3** in $CDCl_3$.

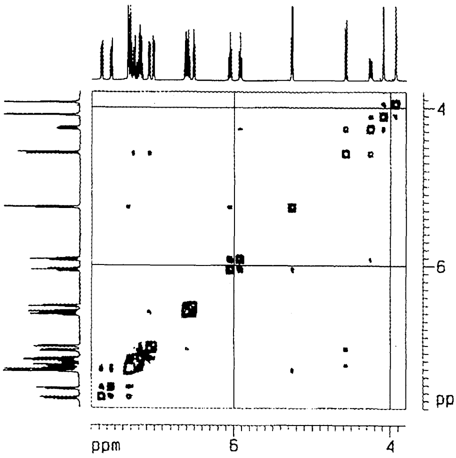
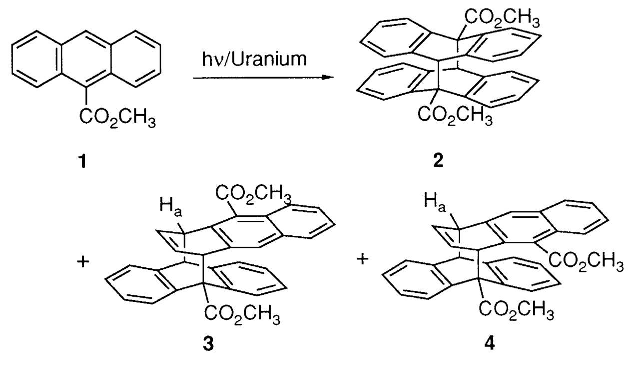


Figure 2. NOESY spectrum of **3** in $CDCl_3$.

The exclusive formation of 9,10-10',9' cyclodimer (**2**) in the irradiation of **1** has been reported previously.[6] The product with the R_f value of 0.75 was assigned to be **2** by the comparison of melting point and spectroscopic analyses (Scheme 1). Upon heating, the other products were quantitatively converted to **1**. Their mass spectra (FAB) exhibit the molecular ion peaks at m/z 473 (MH^+), which reveals that the products are 1:1 adducts of **1**. The UV spectrum for each cyclodimer exhibits a naphthalene pattern implying that the cycloaddition occurs through vertices 1 and 4 of one anthracene ring. This nature of the dimers was confirmed by ^1H NMR and COSY spectra (Figure 1). Different peaks for the two methyl groups, three bridgehead protons, and two olefinic protons in the ^1H NMR spectrum clearly indicate the connections between the 1,4 positions of one ring and the 9',10' positions of the other ring. Coupling patterns in the COSY spectrum, especially in the range of δ 4.2-6.1, confirmed the analyses. Since only two isomers bonding through the vertices 1 and 4 are possible, their structures were assigned by the polarity revealed by TLC and the chemical shift of bridgehead protons. Therefore, the compound with the R_f value of 0.67 and the chemical shift of δ 4.25 for H_a was assigned to be 1,4-10',9' cyclodimer (**3**), and the compound with the R_f value of 0.49 and the chemical shift of δ 4.15 for H_a to be 1,4-9',10' cyclodimer (**4**) (Scheme 1). This was confirmed by the NOESY spectrum of **3**, where aromatic protons show NOE with the bridgehead proton at δ 5.26 but not with H_a (Figure 2).[7]

Dissymmetrical dimerization might be rationalized by slower rate of closure between the positions 9,10 and 10',9' due to steric effects. It is well known that ground-state geometry of the anthracene ring and methoxycarbonyl group deviates from planarity because of the spatial demands of 1,8-hydrogens and the methoxycarbonyl group.[6] However, it is interesting to note that the intermolecular dissymmetrical dimerization rather than a



Scheme 1.

photochemical valence isomerization to Dewar anthracene occurs for **1** with the spatially demanding substituent. This dimerization mode through the vertices 1 and 4 of the anthracene ring has been reported in the intramolecular photodimerization of non-conjugatively linked bichromophoric anthracenes[8] and the intermolecular photodimerization of some laterally substituted anthracenes such as 2,6-didecyloxyanthracene,[9] 1-acetylanthracene, and methyl 1-anthroate.[10] However, the present mode of intermolecular photodimerization of *meso*-substituted anthracene is unprecedented, although it has been extensively studied.[1]

The thermolytic behavior of **2**, **3**, and **4** in degassed solution was studied. Kinetic analyses for the thermolysis at the temperature range of 79-138 °C in DMF were performed by UV spectroscopy. The thermal decomposition into **1** was found to be first order as expected. The half-life times of **2**, **3**, and **4** at 100 °C are estimated to be 42.7, 3.2, and 1.9 h, respectively. The activation parameters, obtained from transition state theory, are shown in Table 1. The activation enthalpies for the thermolysis of **3** and **4** were found to be quite similar. These values are lower than that of **2** by about 2.6 kcal/mole. This kinetic instability may be explained by the resonance energy of the aromatic units of the cyclodimers. When **2** with four benzene rings is converted to **1** with two anthracene rings, about 24 kcal/mole of resonance energy is gained.[11] In the conversion of **3** to **1**, about 35 kcal/mole of resonance energy is gained. The large positive activation entropies indicate the biradical mechanism for the dissociation.

Extension of the dissymmetrical photodimerization of *meso*-substituted anthracenes and studies of the properties of the energy-rich cyclodimers are under investigation in our laboratories.

Table 1. The activation parameters for the thermolysis of the anthracene dimers[a]

	E_a, kcal/mole	$\Delta H^{\ddagger}$, kcal/mole	$\Delta S^{\ddagger}$, eu	$\Delta G^{\ddagger}$, kcal/mole
2	36.0(±0.4)	35.4(±0.4)	11.5(±1.4)	32.0(±0.4)
3	33.4(±0.2)	32.9(±0.2)	9.8(±0.6)	29.9(±0.2)
4	33.4(±0.4)	32.8(±0.4)	10.7(±1.5)	29.6(±0.4)

[a] In DMF, at 298.15 K.

This research was financially supported by Korean Ministry of Education through Research Fund (BSRI-96-3448) and Korea Science and Engineering Foundation (951-0301-031-2).

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7 Satisfactory spectroscopic data were obtained for **2**, **3**, and **4**. Selected data for **3** and **4** are as follows. **3**: mp 143-144 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.93 (s, 3H), 4.09 (s, 3H), 4.25 (ddd, J = 10.7, 7.2, 0.8 Hz, 1H), 4.57 (d, J = 10.7 Hz, 1H), 5.26 (d, J = 6.2 Hz, 1H), 5.92 (ddd, J = 7.7, 7.7, 1.0 Hz, 1H), 6.05 (ddd, J = 7.8, 7.8, 1.0 Hz, 1H), 6.51 (dd, J = 7.5, 1.2 Hz, 1H), 6.56-6.63 (m, 2H), 7.02 (dd, J = 7.2, 1.4 Hz, 1H), 7.07 (dd, J = 7.2, 1.5 Hz, 1H), 7.15-7.21 (m, 2H), 7.25-7.34 (m, 4H), 7.55 (dd, J = 7.4, 1.3 Hz, 1H), 7.67 (dd, J = 8.0, 1.1 Hz, 1H); IR ($CHCl_3$) 3020, 2950, 1713, 1240 cm^{-1}; UV (λ_{max} in DMF, ε) 265 (10400) 330 (1200); MS (FAB) m/z 473 (MH^+), 236, 185 (100). **4**: mp 144.5-145.5 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.92 (s, 3H), 4.11 (s, 3H), 4.15 (ddd, J = 10.8, 6.9, 1.4 Hz, 1H), 4.55 (d, J = 10.8 Hz, 1H), 5.34 (dd, J = 7.2, 1.2 Hz, 1H), 5.99 (ddd, J = 7.7, 7.7, 1.3 Hz, 1H), 6.04 (ddd, J = 7.5, 7.5, 1.3 Hz, 1H), 6.60-6.65 (m, 2H), 6.78-6.83 (m, 2H), 6.94 (dd, J = 7.4, 1.4 Hz, 1H), 7.15-7.22 (m, 3H), 7.26 (dd, J = 7.1, 1.5 Hz, 1H), 7.29-7.33 (m, 2H), 7.53-7.55 (m, 1H), 7.57-7.59 (m, 1H); IR ($CHCl_3$) 3017, 2990, 1726, 1200 cm^{-1}; UV (λ_{max} in DMF, ε) 266 (8700) 315 (930) 330 (830); MS (FAB) m/z 473 (MH^+), 236, 185 (100).

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