

## [2+2] Cyclodimers of 1-Cyanoacenaphthylene and Benzene

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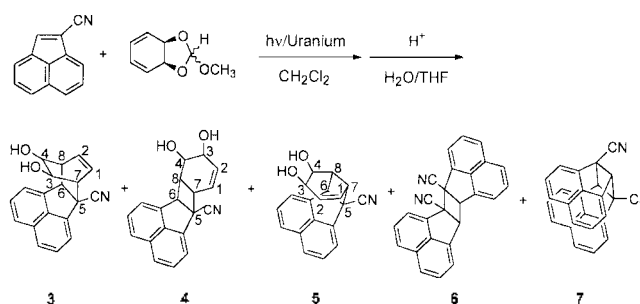
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The chemistry of the cyclodimers of different aromatic units has been studied rather limitedly due to their instability and some synthetic problems. The units of the cyclodimers reported thus far include benzene,<sup>1</sup> naphthalene,<sup>2-4</sup> anthracene,<sup>5,6</sup> furan<sup>3,6</sup> and phenanthrene.<sup>7</sup> Moreover, the properties of both *anti*- and *syn*-[2+2] cyclodimers have been rarely compared. In the studies on [2+2] dibenzenes, *syn*-[2+2] dibenzene was found to be kinetically more stable than *anti*-[2+2] dibenzene, although the latter was thermodynamically more stable than the former.<sup>1</sup> It was explained by the through-bond interaction between two 1,3-cyclohexadiene units through the cyclobutyl ring, and this was supported by photoelectron spectroscopy.<sup>8</sup> However, *syn*-[2+2] cyclodimer of 9-cyanophenanthrene and benzene was recently found to be kinetically less stable than *anti*-cyclodimer.<sup>7</sup> In this paper, we report the syntheses and properties of [2+2] cyclodimers (**1** and **2**) of 1-cyanoacenaphthylene (1-CA) and benzene.

The "masked 1,3,5-cyclohexatriene" strategy<sup>1,5</sup> was used in the synthesis of the cyclodimers. A dichloromethane (130 mL) solution of 1-CA<sup>9</sup> (3.11 g) and excess methyl orthoformate (9.40 g) of *cis*-3,5-cyclohexadiene-1,2-diol was irradiated at ambient temperature through a Uranium filter for 4 h (Scheme 1). After the hydrolysis with HCl, the resulting products were separated by silica gel chromatographies eluting with dichloromethane and ethyl acetate. The products isolated were **3** (14%), **4** (1%), **5** (4%), **6**<sup>10</sup> (16%) and **7**<sup>10</sup> (55%). The diol (**4** and **5**) was treated with excess DMF dimethyl acetal to give the corresponding dimethylformamide acetal, which was then treated with *N,N*-diisopropylethylamine (2.0 equivalents) and trifluoromethanesulfonic anhydride (1.0 equivalent).<sup>7</sup> The reaction mixture was subjected to a separation by a silica gel chromatography eluting with *n*-hexane and dichloromethane. The isolated yield of the two steps for the preparation of **2** was 44%. The preparation for **1** was conducted in a cold room (4 °C), and the isolated yield was 15%. The low yield in the synthesis of **1** was probably due to its thermal instability.

The mass spectrum for each of **3**, **4** and **5** in a CI mode indicated an 1 : 1 adduct of 1-CA and *cis*-3,5-cyclohexadiene-1,2-diol.<sup>11</sup> The regiochemistry of **3** was assigned particularly on the basis of the crosspeaks of H<sub>2</sub> (6.59 ppm) and H<sub>4</sub> (3.00 ppm) with H<sub>8</sub> (3.35 ppm) which also showed a cross-peak with H<sub>6</sub> (aliphatic proton near CN exhibiting doublet) in its COSY spectrum. The downfield shifted peaks of olefinic protons in its H NMR spectrum, compared with those of [4+2] cycloadducts of acenaphthylene and 1,3-cyclohex-

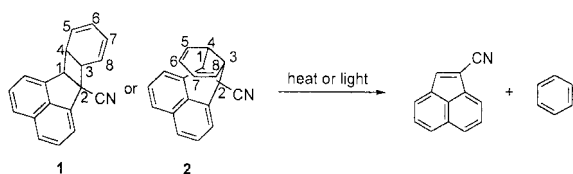


Scheme 1

tadiene,<sup>12</sup> suggested the *exo* orientation. The connectivities of **4** and **5** were assigned to be the [2+2] cycloadducts by considering strong interactions of the peak of H<sub>8</sub> with the peaks of H<sub>4</sub>, H<sub>6</sub> and H<sub>7</sub> in their COSY spectra and their expected chemical shifts. The NOESY spectrum of **5** exhibited the crosspeaks of H<sub>1</sub> and H<sub>4</sub> with aromatic protons, and this may imply the *syn* orientation. The upfield shifted peaks of olefinic protons of **5** compared to **4**, and the downfield shifted peaks of cyclobutyl protons of **5** compared to **4** are consistent with the interpretation.<sup>1</sup> The larger *J*<sub>1,4</sub> value of **2** (9.5 Hz) than **1** (4.4 Hz) as well as the upfield shifted peaks (5.24-5.10 ppm) of olefinic protons of **2** supports the interpretation.<sup>1,7,13</sup>

Upon heating, the [2+2] cyclodimers were quantitatively dissociated into their unit components (Scheme 2). Kinetic analyses for the thermolysis in DMF were conducted by UV spectroscopy (Table 1).<sup>14</sup> The free energy of activation for **1** (22.78 kcal/mol) was lower than that for **2** (28.08 kcal/mol), which suggests that *syn*-[2+2] cyclodimer is kinetically more stable than its corresponding *anti*-[2+2] cyclodimer. Half-life times for the thermoreversion of **1** and **2** at 80 °C were estimated to be 0.36 min and 4.3 h, respectively. These mean that the through-bond interaction between 1,3-cyclohexadiene unit and acenaphthylene unit of the cyclodimers was effective, which is similar to the case of [2+2] dibenzenes.<sup>1,8</sup>

Upon irradiation through a Pyrex filter, the cyclodimers were quantitatively dissociated into their unit components (Scheme 2). The efficiencies for their photodissociation of **1** and **2** at 300 nm measured by ferrioxalate actinometry<sup>7,15</sup> were 0.65 and 0.77. Thermodynamically unstable **2** seemed to be photodecomposed faster than **1**. When irradiated at 300 nm, 1-CA emission was observed (Figure 1) in addition to a very weak fluorescence of the cyclodimers (less than 5% compared to 1-CA emission). This suggests that high exothermicity in the photoreversion allows the production of the

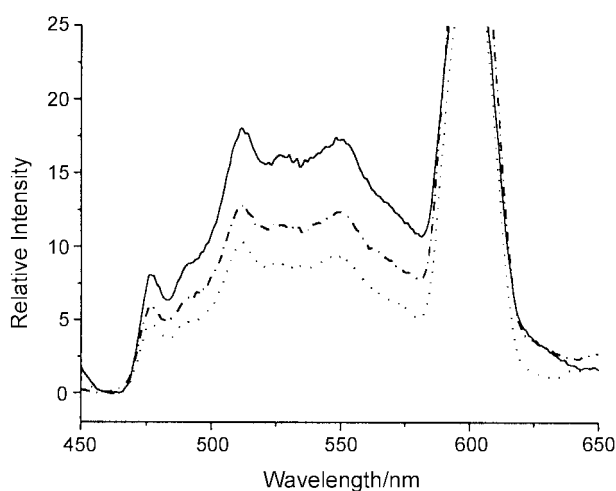


Scheme 2

**Table 1.** Free Energy of Activation for Thermoreversion and Quantum Yields for Photoreversion

	1	2
$\Delta G^\ddagger$ (kcal/mol) <sup>a</sup>	22.78 ± 1.28	28.08 ± 1.35
$\Phi_{\text{dec}}^b$	0.65 ± 0.05	0.77 ± 0.10
$\Phi_{\text{dec}}^{*b}$	0.50 ± 0.07	0.71 ± 0.02

<sup>a</sup>At 298.15 K in DMF. <sup>b</sup>Obtained in cyclohexane from at least three independent determinations.

**Figure 1.** Emission spectra of 1-CA (—), **1** (···) and **2** (---) in cyclohexane when irradiated at 300 nm.

excited state 1-CA.<sup>5,7</sup> The efficiency for the formation of the excited 1-CA was estimated by the comparison with the emissions from 1-CA to be 0.50 and 0.71. The quantum yields of adiabaticity in the photodissociation are much higher than that (0.40 ± 0.02) of *syn*-[2+2] cyclodimer of 2-cyanonaphthalene and benzene.<sup>4</sup> Since the internal energies of **1** and **2** are expected to be smaller than that of *syn*-[2+2] cyclodimer of 2-cyanonaphthalene and benzene by considering the resonance energies of their unit components, the higher adiabaticity for the photodissociation of **1** and **2** is due to the lower excited state energies of 1-CA.

A detailed comparison with some derivatives of the cyclodimers is under investigation in our laboratory.

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- 3**: <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, 300 MHz)  $\delta$  7.89 (1H, d, 8.1 Hz), 7.83-7.61 (4H, m), 7.53 (1H, d, 6.9 Hz), 6.59 (dd, 7.6, 6.8 Hz, H<sub>2</sub>), 6.48 (dd, 7.9, 6.5 Hz, H<sub>1</sub>), 4.48 (d, 5.3 Hz, -OH), 4.43 (d, 5.4 Hz, -OH), 4.01 (d, 4.0 Hz, H<sub>6</sub>), 3.50 (m, H<sub>7</sub>), 3.35 (m, H<sub>8</sub>), 3.00 (m, H<sub>4</sub>), 2.96 (m, H<sub>3</sub>); HRMS (CI<sup>+</sup>) calcd for C<sub>19</sub>H<sub>16</sub>O<sub>2</sub>N (MH<sup>+</sup>) *m/z* 290.1182, found 290.1185. **4**: <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz)  $\delta$  7.82-7.75 (2H, m), 7.61-7.55 (3H, m), 7.40 (1H, d, 6.9 Hz), 6.27-6.18 (m, H<sub>1</sub>, H<sub>2</sub>), 4.53 (bs, H<sub>3</sub>), 4.28 (broad d, 4.2 Hz, H<sub>4</sub>, H<sub>6</sub>), 3.20 (ddd, 8.2, 4.2, 0.7 Hz, H<sub>7</sub>), 2.61 (ddd, 8.2, 6.3, 4.2 Hz, H<sub>8</sub>), 2.27 (2H, bs, -OH); HRMS (CI<sup>+</sup>) calcd for C<sub>19</sub>H<sub>16</sub>O<sub>2</sub>N (MH<sup>+</sup>) *m/z* 290.1182, found 290.1178. **5**: <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, 300 MHz)  $\delta$  7.81-7.73 (2H, m), 7.59-7.49 (3H, m), 7.38 (1H, d, 6.9 Hz), 5.63 (dd, 10.0, 3.6 Hz, H<sub>1</sub>), 5.46 (ddd, 10.0, 4.9, 1.9 Hz, H<sub>2</sub>), 4.90 (d, 10.0 Hz, H<sub>6</sub>), 4.44 (d, 5.3 Hz, -OH), 4.20 (d, 5.0 Hz, -OH), 3.92 (m, 10.0 Hz, H<sub>7</sub>), 3.25 (ddd, 10.0, 10.0, 7.5 Hz, H<sub>8</sub>), 3.05 (m, H<sub>3</sub>), 2.72 (m, H<sub>4</sub>); HRMS (CI<sup>+</sup>) calcd for C<sub>19</sub>H<sub>16</sub>O<sub>2</sub>N (MH<sup>+</sup>) *m/z* 290.1182, found 290.1181.
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- 1**: <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz)  $\delta$  7.78-7.74 (2H, m), 7.60-7.50 (3H, m), 7.37 (1H, m), 6.17 (dd, 9.6, 5.3 Hz, H<sub>8</sub>), 6.03-5.85 (m, H<sub>5</sub>, H<sub>6</sub>, H<sub>7</sub>), 4.56 (d, 4.4 Hz, H<sub>1</sub>), 3.39 (dd, 11.2, 5.3 Hz, H<sub>3</sub>), 3.03 (m, H<sub>4</sub>); UV (cyclohexane)  $\lambda_{\text{max}}$  ( $\epsilon$ ) 293 (9100) nm; HRMS (FAB<sup>-</sup>) calcd for C<sub>19</sub>H<sub>14</sub>N (MH<sup>-</sup>) *m/z* 256.1127, found 256.1113. **2**: <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz)  $\delta$  7.73 (1H, d, 8.2 Hz), 7.70 (1H, d, 8.2 Hz), 7.67-7.46 (2H, m), 7.34 (1H, dd, 7.0, 0.5 Hz), 7.16 (1H, d, 6.9 Hz), 5.24-5.10 (m, H<sub>5</sub>, H<sub>6</sub>, H<sub>7</sub>, H<sub>8</sub>), 5.02 (d, 9.5 Hz, H<sub>1</sub>), 4.21 (dd, 13.5, 4.7 Hz, H<sub>3</sub>), 4.02 (dddd, *J* = 13.5, 9.6, 4.5, 1.3 Hz, H<sub>4</sub>); <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz)  $\delta$  141.1, 140.7, 139.6, 131.7, 127.8, 127.7, 124.9, 124.4, 123.7, 122.6, 121.6, 121.4, 121.3, 109.5, 58.7, 51.6, 41.8, 34.3; UV (cyclohexane)  $\lambda_{\text{max}}$  ( $\epsilon$ ) 290 (9590) nm; HRMS (FAB<sup>+</sup>) calcd for C<sub>19</sub>H<sub>12</sub>N (M-1) *m/z* 254.0971, found 254.0976.
- The temperature ranges of the kinetic studies were 20-40 °C for **1** and 79-139 °C for **2**. **1**:  $\ln k = 26.75 - 10660/T$ . **2**:  $\ln k = 32.85 - 15140/T$ .
- The optical density of the samples was adjusted to be less than 0.20 at 300 nm. In the case of **1**, the temperature was maintained at 7-10 °C.