

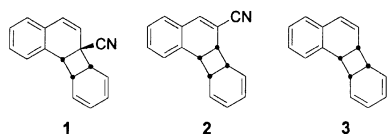
***syn*-[2+2] Cyclodimers of 2-Cyanonaphthalene and Benzene**

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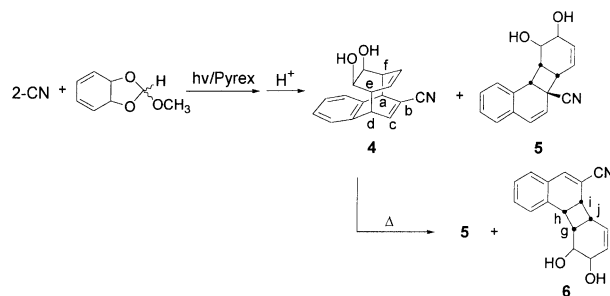
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The chemistry of arenes-arenes cyclodimers has been a subject of considerable interest due to their novel properties as well as their theoretical significance. Although the cyclodimers of several arene units have been synthesized,¹⁻⁶ substituent effect on their properties was extensively studied only for bridgehead-substituted [4+4] anthracene-benzene cyclodimers. Electron withdrawing groups substituted at 9,10-positions of the anthracene portion facilitate thermal dissociation and decrease the efficiency of adiabatic photodissociation.⁴ Electron withdrawing groups substituted at 1,4-positions of the benzene portion also facilitate thermal dissociation, but make the cyclodimer nonchemiluminescent.^{4,5} In this communication, we report the synthesis of *syn*-[2+2] cyclodimers (**1**, **2**) of 2-cyanonaphthalene (2-CN) and benzene, and compare their properties with those of *syn*-[2+2] naphthalene-benzene cyclodimer (**3**).



Adducts **4** and **5** were obtained from irradiation of 2-CN (0.078 M) and methyl orthoformate (0.42 M) through Pyrex filter at ambient temperature followed by hydrolysis with HCl (Scheme 1).⁷ The resulting mixture was not separated completely by conventional purification methods. The isolated yield of **5** by silica gel chromatography was 15% based on consumed 2-CN. Adduct **4** was partially separated by recrystallization from dichloromethane/*n*-hexane in 7% yield. Heating **4** at 101 °C for 30 min yielded **5** and **6**,⁷ which were isolated by silica gel chromatography in 57% and 35% yields, respectively. Among the two possible modes of the rearrangement, the conversion to **5** was preferred. A similar result was previously reported with *exo*-[4+4] adduct of 2-CN and 1,3-cyclohexadiene (CHD),⁸ which may be explained by the stabilizing effect of cyano group on the C-bond-forming for the rearrangement.

Four aromatic proton peaks in ¹H NMR spectrum of **4** indicated that the product is resulted from the addition to the substituted ring of 2-CN. Four intense peaks at 45-48 ppm in ¹³C NMR spectrum, three olefinic proton peaks in ¹H NMR spectrum, and strong couplings between H-a (3.93 ppm) and H-f (3.26 ppm), and between H-d (3.90 ppm) and H-e (3.20 ppm) in COSY spectrum suggest the [4+4] structure. The spectroscopic data of **5** are similar to those of *syn*-[2+2] adduct of 2-CN and CHD.⁸ The formation of **5** in the Cope rearrangement of **4** also supports the *syn*-[2+2] structure of **5**. The regiochemistry of **6** was determined by strong cou-



Scheme 1

plings of H-j with H-g, H-i, and H-k in its COSY spectrum. The large coupling constant (9.8 Hz) between H-h (4.22 ppm) and H-g (3.02 ppm) suggest the structure to be a *syn*-[2+2] form.

Diols **5** and **6** were converted to their DMF acetals by treating with excess DMF dimethyl acetal under anhydrous conditions. The crude acetals were treated with trifluoromethanesulfonic anhydride and diisopropylethylamine at room temperature.¹ The isolated yields of **1** and **2** were 64% and 30%, respectively.⁹

Upon heating, **1** and **2** were dissociated into 2-CN and benzene. Kinetic analyses were conducted by UV spectroscopy (Table 1). We have not observed any solvent effect in the thermolysis of **3** to indicate that the dissociation mechanism does not involve polar transition state but biradical transition state. The activation enthalpy for **1** in DMF was found to be 2.0 kcal/mole lower than that for **3**. Half-life times for **1** and **3** at 70 °C were estimated to be 32 min and 16 h, respectively. On the other hand, the activation enthalpy for **2** (half-life time = 39 h) is higher than that for **3**. Since biradical A has two resonance forms in which the aromatic sextet of the adjacent ring remains intact while biradical B has only one (Scheme 2), the cleavage of bond-a is expected to be favored in the thermolysis of *syn*-[2+2] cyclodimers. The effect of 1-cyano functionalization (S₁) of the biradical A in the case of **1** is reasonable, considering that additional

Table 1. Activation parameters for the thermoreversion of *syn*-[2+2] naphthalenes-benzene cyclodimers

	1 ^a	2 ^a	3 ^a	3 ^b
<i>E_a</i> (kcal/mole)	25.5 ± 0.7	29.6 ± 0.3	27.5 ± 0.8	28.2 ± 0.2
Δ <i>H</i> [‡] (kcal/mole)	24.9 ± 0.7	29.0 ± 0.3	26.9 ± 0.8	27.6 ± 0.2
Δ <i>S</i> [‡] (eu)	-2.0 ± 4.4	1.4 ± 2.1	-2.7 ± 5.0	-1.6 ± 2.1
Δ <i>G</i> [‡] (kcal/mole)	25.5 ± 2.0	28.6 ± 0.9	27.8 ± 2.3	28.1 ± 0.8

^aIn DMF at 298.15 K. ^bIn cyclohexane-d₁₂ at 298.15 K. Taken from ref 2a.

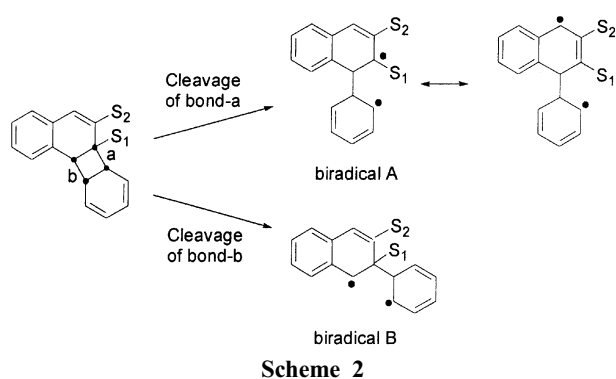


Table 2. Quantum yields for the photoreversion of *syn*-[2+2] naphthalenes-benzene cyclodimers in cyclohexane

	1 ^a	2 ^a	3
Φ	0.59 ± 0.02	0.52 ± 0.01	0.59 ± 0.05 ^a
Φ*	0.40 ± 0.02	0.51 ± 0.04	0.63 ± 0.01 ^b

^aThe average of three separate determinations. ^bTaken from ref 3.

resonance can be drawn. 1-Cyano substitution increases the unpaired electron withdrawal substantially. On the other hand, 2-cyano functionalization (S₂) results in large destabilization by inductive effect, as observed in *m*-cyano functionalization of benzyl radical.¹⁰

Adiabatic photodissociation was observed in the irradiation of **1** and **2**. The measured^{1,6} quantum yields in addition to those of **3**³ are summarized in Table 2. We have found that the quantum yields of photodissociation were similar regardless of the substituent, but the efficiency for the formation of the excited naphthalenes decreased by 2-cyano functionalization. This may mean that slight change by cyano substitution influences energy surfaces around the pericyclic minimum to result less efficient adiabaticity, as observed in [4+4] anthracene-benzene cyclodimers.^{4,5}

Theoretical elaboration is needed to account for the observations. Synthesis of several derivatives by using low-temperature irradiation⁸ to result in the addition to unsubstituted ring of 2-CN is also under investigation in our laboratory.

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7. **4**: mp 137-138 °C (CH₂Cl₂/*n*-hexane); ¹H NMR (300 MHz, CDCl₃) δ 7.29-7.13 (5H, m), 6.26 (1H, dd), 6.16 (1H, dd), 3.93 (1H, dd), 3.90 (1H, dd), 3.66 (2H, broad s), 3.26 (1H, ddd), 3.20 (1H, ddd), 2.37 (1H, broad s), 2.31 (1H, broad s); MS (CI) 266, 248, 154 (100), 112, 95; HRMS (CI) calcd for C₁₇H₁₅O₂N 266.1181, observed 266.1185. **5**: mp 165-167 °C (CH₂Cl₂/*n*-hexane); ¹H NMR (500MHz, CDCl₃) δ 7.27 (2H, m), 7.08 (2H, dd), 6.55 (1H, d), 6.15 (1H, ddd), 5.90 (1H, dd), 5.53 (1H, dd), 4.41 (1H, d), 4.06 (1H, dd), 4.02 (1H, ddd), 3.91 (1H, dd), 2.93 (1H, ddd), 2.17 (1H, s), 1.43 (1H, s); MS (CI) 266, 248, 182, 154 (100), 95; HRMS (CI) calcd for C₁₇H₁₅O₂N 266.1181, observed 266.1182. **6**: mp 192-193 °C (CH₂Cl₂/*n*-hexane); ¹H NMR (500 MHz, CDCl₃) δ 7.31 (1H, ddd), 7.22 (1H, ddd), 7.10 (1H, d), 7.07 (1H, d), 7.02 (1H, d), 6.11 (1H, dd), 6.08 (1H, dd), 4.22 (1H, dd), 3.94 (1H, broad s), 3.86 (1H, ddd), 3.78 (1H, m), 3.73 (1H, m), 3.02 (1H, m), 2.03 (1H, s), 1.46 (1H, d); MS (CI) 266 (100), 248, 230, 154, 95; HRMS (CI) calcd for C₁₇H₁₅O₂N 266.1181, observed 266.1185.
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9. **1**: mp 103.5-104.5 °C (CH₂Cl₂/*n*-hexane); ¹H NMR (300 MHz, CDCl₃) δ 7.20 (2H, m), 7.07 (1H, m), 6.94 (1H, m), 6.53 (1H, d), 5.89 (1H, dd), 5.76 (1H, d), 5.57 (1H, ddd), 5.42 (1H, dd), 5.08 (1H, dd), 4.55 (1H, d), 4.06 (1H, dd), 3.62 (1H, m); MS (FAB) 230 (M-1), 154 (100), 136. **2**: mp 119-120 °C (CH₂Cl₂/*n*-hexane); ¹H NMR (300 MHz, CDCl₃) δ 7.26 (1H, dd), 7.17 (1H, dd), 7.08 (1H, d), 7.08 (1H, s), 6.91 (1H, d), 5.84 (1H, dd), 5.57 (2H, m), 5.03 (1H, dd), 4.37 (1H, dd), 3.82 (1H, m), 3.72 (2H, m); MS (CI) 232, 154 (100), 79.
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