

# A Novel Photochemical Cycloaddition of 1-Cyanonaphthalene to Substituted Pyridines

Masami Sakamoto,<sup>\*,†</sup> Tadao Yagi,<sup>†</sup> Takashi Mino,<sup>†</sup> Kentaro Yamaguchi,<sup>‡</sup> and Tsutomu Fujita<sup>†</sup>

Contribution from the Department of Materials Technology and Chemical Analysis Center, Faculty of Engineering, Chiba University, Yayoi-cho, Inage-ku, Chiba 263-8522, Japan

Received September 8, 1999. Revised Manuscript Received May 31, 2000

**Abstract:** The photochemical reaction of 1-cyanonaphthalene (1-CNNap) with substituted pyridine was studied. Irradiation of a benzene solution of 1-CNNap (0.02 M) in the presence of 3-cyano-2-methoxypyridine (0.02 M) gave a 1:1 adduct in 24% yield and the pyridine dimer in 56% yield, when the reaction conversion reached 32%. Photoaddition of 1-CNNap with 3-cyano-2-methoxy-6-methylpyridine, 3-cyano-4,6-dimethyl-2-methoxypyridine, or 3-cyano-2,6-dimethoxypyridine was also successful, and the corresponding adducts were isolated in 41%, 75%, and 98% yield, respectively. The structure was established by X-ray structural analysis. The postulated mechanism initiated by  $2\pi+2\pi$  photocycloaddition between the C3–C4 position of 1-CNNap and the C2–C3 position of the pyridine was supported by Frontier-MO calculations using the PM3 Hamiltonian contained within the MOPAC program. The naphthalene–pyridine adducts were stable at room temperature; however, pyrolysis of the adduct gave a 1,3-sigmatropic rearrangement product, quantitatively.

## Introduction

The photochemical reaction of aromatic compounds has received much attention from both the mechanistic and synthetic perspectives.<sup>1–4</sup> Especially, photochemical additions of hydrocarbon aromatics, such as naphthalene and anthracene derivatives, are well documented. It is well-known that the substituted naphthalene undergoes 4+4 cycloaddition leading to a  $4\pi+4\pi$  dimer;<sup>5–11</sup> however, the cycloaddition toward monocyclic aromatics is quite rare. Pac et al. reported the first example of the cycloaddition of 1-cyanonaphthalene to furan via a singlet exciplex, in which they isolated a  $4\pi+4\pi$  dimer.<sup>12,13</sup> Recently, Noh et al. reinvestigated the same photoreaction followed by low-temperature NMR spectroscopy, and found that two diastereomeric 4+4 dimers were formed.<sup>14</sup> This reaction system is the only reported photoreaction of naphthalene derivatives with monocyclic aromatics, to our best knowledge. We are interested in new aspects of the photochemical cycloaddition of aromatic compounds and application of the methodology to heteroaromatics.<sup>15</sup> Now we provide the first example of photo-cycloaddition of 1-cyanonaphthalene with substituted pyridines.

## Results and Discussion

A benzene solution of 1-cyanonaphthalene (1-CNNap) (0.02 M) in the presence of 3-cyano-2-methoxypyridine (**1a**, 0.02 M) was irradiated with a 313 nm line of a high-pressure mercury lamp.<sup>16</sup> Separation by chromatography on silica gel gave a 1:1 adduct **2a** (24%) accompanied by the pyridine dimer **3a** in 56% yield, when the reaction conversion reached 32% (Table 1). Photoaddition of 1-CNNap with other pyridines **1b–d** was also successful, and the corresponding adducts were isolated in moderate yields as shown in Table 1. In the case of entry 3 and 4, a pyridine dimer was not formed and adducts **2c,d** were obtained predominantly. When a Pyrex filtered light (>290 nm) was used for the photoreaction, the same results were obtained in terms of chemical yield and product distribution. Furthermore, when acetonitrile was used for the photoreaction as a solvent, the efficiency declined drastically. A nonpolar solvent is preferred for this cycloaddition.

The structure of the adducts **2** was determined on the basis of spectral data. Finally, the structure of **2b** was established by X-ray structural analysis (Figure 1). For the structure of the pyridine dimer **3**, we already reported the photodimerization of 2-alkoxy-3-cyanopyridines, and the structure was confirmed by X-ray structural analysis.<sup>17</sup>

Figure 2 shows the UV spectra of 1-CNNap and pyridine **1a** in cyclohexane and the concentrations are  $1.0 \times 10^{-4}$  M, which indicates that 1-CNNap absorbs light quantum above 310 nm exclusively and pyridine **1** is not excited directly when a 313

<sup>†</sup> Department of Materials Technology.

<sup>‡</sup> Chemical Analysis Center.

(1) Bryce-Smith, D.; Gilbert, A. *Tetrahedron* **1976**, *32*, 1309.

(2) Gilbert, A. *Synthetic Organic Photochemistry*; Horspool, W. M., Ed.; Plenum: New York, 1984.

(3) McCullough, J. J. *Chem. Rev.* **1987**, *87*, 811.

(4) Sieburth, S. McN.; Cunard, N. T. *Tetrahedron* **1996**, *52*, 6251.

(5) Bradshaw, J. S.; Hammond, G. S. *J. Am. Chem. Soc.* **1963**, *85*, 3953.

(6) Teitei, T.; Wells, D.; Sasse, W. H. F. *Tetrahedron Lett.* **1974**, 367.

(7) Seliger, B. K.; Sterns, M. J. *Chem. Soc., Chem. Commun.* **1969**, 978.

(8) Becker, H.-D. *Adv. Photochem.* **1990**, *15*, 139.

(9) Becker, H.-D. *Chem. Rev.* **1993**, *93*, 145.

(10) Kaupp, G.; Teufel, E. *Chem. Ber.* **1980**, *113*, 3669.

(11) Becker, H.-D.; Langer, V. *J. Org. Chem.* **1993**, *58*, 4703.

(12) Pac, C.; Sugioka, T.; Sakurai, H. *Chem. Lett.* **1972**, 39.

(13) Mizuno, K.; Pac, C.; Sakurai, H. *J. Chem. Soc., Perkin Trans. 1* **1974**, 2360.

(14) Noh, T.; Kim, D. *Tetrahedron Lett.* **1996**, *52*, 9329.

(15) We recently reported a new photochemical reaction of a pyridine–furan system underwent 4+4 cycloaddition, subsequently followed by 2+2 photoaddition and a unique rearrangement, leading to cage products. Sakamoto, M.; Kinbara, A.; Yagi, T.; Takahashi, M.; Yamaguchi, K.; Mino, T.; Watanabe, S.; Fujita, T. *J. Chem. Soc., Perkin Trans. 1* **1999**, 171.

(16) A 313 nm line was isolated by using a solution filter of  $K_2CrO_4$  and  $Na_2CO_3$ ; see: Murov, S. L. *Handbook of Photochemistry*; Marcel Dekker: New York, 1973.

(17) Sakamoto, M.; Kimura, M.; Fujita, T.; Nishio, T.; Iida, I.; Watanabe, S. *J. Am. Chem. Soc.* **1991**, *113*, 5859.

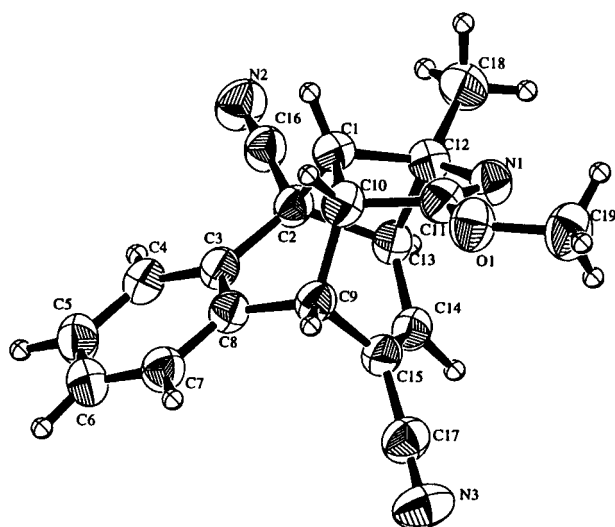
**Table 1.** Photoreaction of the 1-CNNap–Pyridine System

entry	pyridine	R <sup>1</sup>	R <sup>2</sup>	conv (%)	yield (%) <sup>a</sup>	
					2	3
1	<b>1a</b>	H	H	32	24	56
2	<b>1b</b>	H	Me	33	41 <sup>b</sup>	54
3	<b>1c</b>	Me	Me	36	75	0 <sup>c</sup>
4	<b>1d</b>	H	MeO	40	98	0

<sup>a</sup> A benzene solution of 0.02 M of 1-cyanonaphthalene and 0.02 M of pyridine **1** was irradiated with a high-pressure mercury lamp. The chemical yields were determined on the basis of consumed pyridine **1**.

<sup>b</sup> The structure of **2b** was established by X-ray crystallographic analysis.

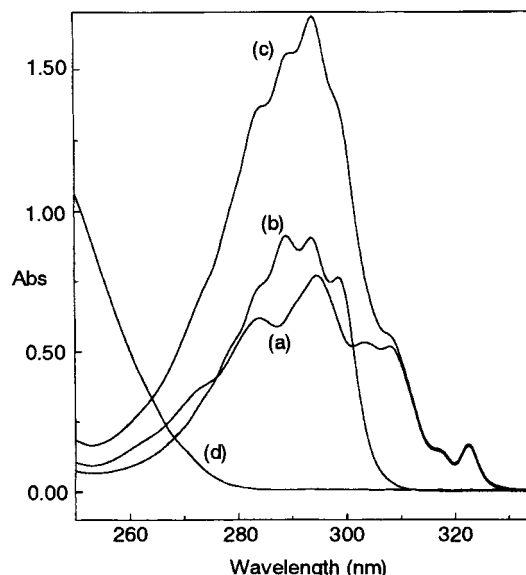
<sup>c</sup> Transpositional isomer, 3-cyano-2,4-dimethyl-6-methoxypyridine, was also obtained in 8% yield.

**Figure 1.** ORTEP drawing of **2b**.

nm line was used for the photoreaction. The ground state of the mixture does not form any complexes detectable by UV spectroscopy.

It is reported that the photochemical cycloaddition of 1-CNNap with furan involves a singlet exciplex leading to the 4+4 adduct.<sup>12–14</sup> Furthermore, the formation of an excimer is well-known in the photodimerization of naphthalene derivatives. In the fluorescence spectra of the mixture of an equimolar amount of 1-CNNap and pyridine **1a**, only emissions derived from 1-CNNap and pyridine **1a** were observed without any new emissions. This result indicates that the addition of excited 1-CNNap with pyridine may proceed directly without the formation of exciplex.

When a 313 nm line was used for the photoreaction, >95% of photons were absorbed by 1-CNNap, and pyridine **1** could not be excited directly under these photoreaction conditions; however, the pyridine dimers **3a** and **3b** were obtained in entries 1 and 2. In entries 3 and 4, the corresponding pyridine dimers were not formed, because these pyridines **1c** and **1d** did not dimerize even by direct photolysis.<sup>17</sup> Irradiation of a benzene

**Figure 2.** UV spectra of 1-CNNap and pyridine **1a** in cyclohexane at 20 °C. All spectra were measured at the concentration of  $1.0 \times 10^{-4}$  M: (a) 1-CNNap, (b) pyridine **1a**, (c) 1-CNNap and **1a**, and (d) the adduct **2a**.

solution of **1c** gave only a transpositional isomer, and **1d** was inert toward the photolysis. In entries 1 and 2, the dimerization of the pyridine should be promoted by energy transfer from the excited state of 1-CNNap when a 313 nm line was used for excitation.

The intermolecular photoreaction should be influenced by the concentration of the substrate. When a benzene solution of 1-CNNap and **1a** at a concentration under 0.01 M was used, the cycloaddition was quite inefficient. Irradiation of a solution of higher concentration of 1-CNNap (0.05 M) and **1a** (0.02 M) resulted in the formation of the naphthalene dimer with a decline in the chemical yields of the pyridine dimer and even the naphthalene–pyridine adduct **2a**. A 0.02 M concentration each of 1-CNNap and **1** is the best condition to lead to the 1:1 adduct.

For the formation of 1-CNNap–pyridine adduct **2**, a mechanism is postulated in which  $2\pi+2\pi$  photocycloaddition is initiated between the C3–C4 position of 1-CNNap and the C2–C3 position of the pyridine **1**. The cyclobutane adduct **4** converted to cyclooctatriene **5** by a ring expansion, which was subsequently followed by a secondary photochemical  $2\pi+2\pi$  photocycloaddition leading to **2**. The direct rearrangement from **4** to **2** is also possible. We tried to detect the reaction intermediate directly by low-temperature photolysis followed by NMR spectroscopy.<sup>18</sup> When a toluene solution of 1-CNNap and **1a** in a NMR tube was irradiated at  $-50$  °C, no peaks derived from 1-CNNap–pyridine cycloadduct were observed. Photolysis at  $-30$  °C showed peaks owing to only the adduct **2a**, and no intermediate such as the cyclobutane **4** or the cyclooctatriene **5** could be detected by NMR spectroscopy.

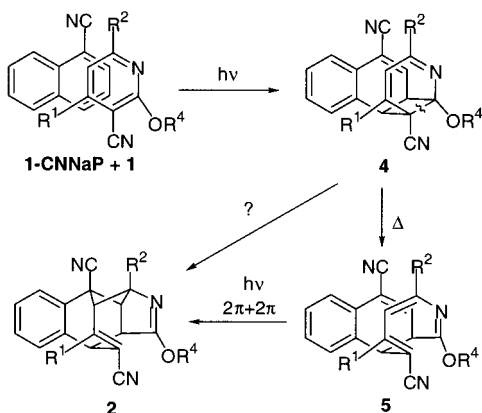
The regioselectivity and stereoselectivity in many singlet photoadditions can be explained by orbital interactions.<sup>19,20</sup> In this naphthalene–pyridine system, the initially promoted  $2\pi+2\pi$  photocycloaddition was supported by Frontier-MO calculations using the PM3 Hamiltonian contained within the MOPAC

(18) Recently, direct determination of the 1-CNNap–furan adduct by low-temperature NMR spectroscopy has been reported. See ref 13.

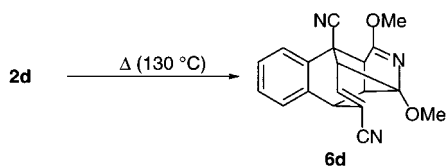
(19) Yang, N. C.; Gan, H.; Kim, S. S.; Masnovi, J. M. *Tetrahedron Lett.* **1990**, *31*, 3825.

(20) Somekawa, K.; Okuhira, H.; Sendayama, M.; Suishu, T.; Shimo, T. *J. Org. Chem.* **1992**, *57*, 5708.

## Scheme 1



## Scheme 2



program.<sup>21</sup> The orbital energies and coefficients of the singlet excited state for 1-CNNap (HSOMO  $-3.64012$  eV and LSOMO  $-6.58521$  eV) and those of the ground state of pyridine **1a** (LUMO  $-0.85026$  eV and HOMO  $-9.78493$  eV) were obtained. The energy gap ( $\Delta E$ ) between HSOMO and LUMO is smaller than that between LSOMO and HOMO, and this frontier orbital interaction also supports our assumption that an initial bond formation between the C3–C4 positions of 1-CNNap and the C2–C3 positions of pyridine occurs and leads to **4**.

Gilbert et al. reported the photochemical addition of 2-cyanoanisole with vinyl ether leading to 2+2 adduct, subsequently followed by ring-opening to cyclooctatriene.<sup>22</sup> The cyclooctatriene cyclizes to a secondary photoproduct, a bicyclo[4.2.0]octa-2,7-diene structure, upon irradiation. Furthermore, Wagner et al. reported the intramolecular cycloaddition of a benzene ring with an alkenyl group, and obtained cyclooctatriene and the secondary photoproducts.<sup>23</sup> The reversibility of the photochemical reaction and the thermal conversion between cyclooctatriene and the bicyclo[4.2.0]octa-2,7-diene were confirmed. In the present 1-CNNap–pyridine system, the secondary photoproduct is completely different from their reactions, however; compound **2** similarly has a cyclobutane ring attached with an alkenyl group. The thermal and photochemical reactions of **2** were tried to obtain further supporting information on the reaction.

Figure 1 shows the UV spectrum of the adduct of **2a**, which indicates **2a** absorbs lower wavelength light. When an acetonitrile solution of the isolated adduct **2d** was irradiated with 254 nm line with a low-pressure mercury lamp, a yellowish solution possessing  $\lambda_{\text{max}}$  at 390 nm was obtained, but prolonged irradiation produced polymeric materials. This yellow compound was unstable at room temperature and gradually changed to colorless unidentified materials. Because of the low conversion, the structural determination of the labile material could not be performed; however, there is a possibility of its being a cyclooctatriene structure **5d** from the UV spectrum.

The naphthalene–pyridine adduct **2** was stable at room temperature; however, when **2d** was heated above the melting

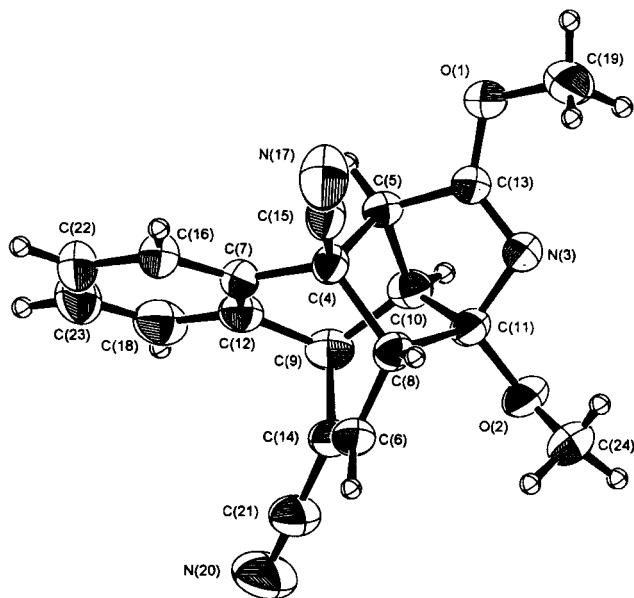


Figure 3. ORTEP drawing of **6d**.

point ( $>130$  °C), a new colorless compound **6d** was obtained quantitatively (Scheme 2). The structure was established by X-ray structural analysis and the ORTEP diagram is shown in Figure 3. The formation was reasonably explained in terms of 1,3-sigmatropic rearrangement. The release of energy of the highly strained cage compound with a cyclobutane ring resulted in efficient sigmatropic transformation to **6d**.

In conclusion, we have provided the first example of the photochemical cycloaddition of a naphthalene–pyridine system. When 2-CNNap, 1- and 2-naphthalenecarboxylic acid methyl esters, and 1,4-dicyanonaphthalene were used instead of 1-CNNap, the photoaddition did not take place. We are now continuing investigations to explore the limitations of this unique cycloaddition and to elucidate the reaction mechanism.

## Experimental Section

**General Methods.** NMR spectra were recorded on  $\text{CDCl}_3$  solutions on a JEOL GSX-400 and Bruker-300, respectively, for  $^1\text{H}$ - and  $^{13}\text{C}$  NMR spectroscopy unless otherwise noted. Chemical shifts are reported in parts per million (ppm) relative to TMS as internal standards. Elemental analyses were made using a Perkin-Elmer-240 instrument. Ultraviolet (UV) spectra were determined with a JASCO model V-570 UV/VIS/NIR spectrophotometer. IR spectra were recorded on a JASCO FT/IR-230 spectrometer as KBr disks, unless otherwise noted. Eikohsya 500-W high-pressure and 100-W low-pressure mercury lamps were used as the irradiation source.

**Preparation of Substituted 2-Alkoxy-3-cyanopyridines 1a–d.** These pyridines were obtained by alkylation of the corresponding pyridones according to the literature method.<sup>15</sup>

**General Procedure for the Photochemical Reaction of 1-CNNap in the presence of 2-Alkoxy-3-cyanopyridine 1a–d.** A benzene solution containing 1-CNNap (0.02 M) and 2-alkoxy-3-cyanopyridines **1** (0.02 M) was deaerated by bubbling argon for 15 min and was irradiated by Pyrex filtered light with a 500-W high-pressure mercury lamp at  $15$ – $20$  °C. When a 313 nm line was used for irradiation, the line was isolated by the use of a filter solution of  $\text{K}_2\text{CrO}_4$  and  $\text{Na}_2\text{CO}_3$ .<sup>16</sup> After irradiation, the solvent was removed in vacuo and the residual mixture was subjected to chromatography on silica gel (eluant: mixture of *n*-hexane and ethyl acetate). The crystalline photoproducts were recrystallized from a mixture of chloroform and hexane. The structures of **2a–d** were determined on the basis of elemental analysis and the spectral data. Furthermore, the structure of **2b** was established by X-ray crystallographic analysis. The structures of **3a,b** and 3-cyano-2,4-dimethyl-6-methoxypyridine were determined by direct comparison with authentic sample.<sup>15,17</sup>

(21) Stewart, J. J. P. *J. Comput. Chem.* **1989**, *10*, 221.

(22) Gilbert, A.; Heath, P. *Tetrahedron Lett.* **1987**, *28*, 5909.

(23) Wagner, P. J.; Sakamoto, M.; Madkour, A. E. *J. Am. Chem. Soc.* **1992**, *114*, 7298.

**1,9-Dicyano-4-methoxy-11,12-benzo-5-azatetracyclo[5.5.0.0<sup>2,6</sup>.0<sup>3,10</sup>]dodeca-4,8-diene (2a).** Mp 160 °C dec; IR (CHCl<sub>3</sub>) 1630, 2210, 2236 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 3.20 (dd, *J* = 6.5 and 9.4 Hz, 1H, 3-CH), 3.54 (ddd, *J* = 4.3, 6.0 and 9.2 Hz, 1H, 2-CH), 3.88 (dd, *J* = 1.2 and 6.0 Hz, 1H, 10-CH), 3.97 (s, 3H, 4-OCH<sub>3</sub>), 4.04 (ddd, *J* = 4.4, 7.2 and 8.9 Hz, 1H, 7-CH), 5.02 (dd, *J* = 6.0 and 7.2 Hz, 1H, 6-CH), 6.14 (dd, *J* = 1.2 and 8.9 Hz, 1H, 8-CH), 7.27–7.33 (m, 1H, aromatic), 7.40–7.44 (m, 2H, aromatic), 7.62–7.64 (m, 1H, aromatic); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 38.1 (s, 1-C), 44.6 (d, 10-C), 47.6 (d, 3-C), 50.5 (d, 2-C), 52.0 (d, 7-C), 56.7 (q, 4-OCH<sub>3</sub>), 65.7 (d, 6-C), 118.0 (s, 9-C), 121.5 (s, CN), 122.4 (s, CN), 127.0 (d, aromatic), 127.8 (d, aromatic), 128.8 (s, 11-C), 129.6 (d, aromatic), 130.3 (d, aromatic), 135.7 (s, 12-C), 140.0 (d, 8-C), 180.1 (s, 4-C); HR-MS(FAB) calcd for C<sub>18</sub>H<sub>14</sub>N<sub>3</sub>O (MH<sup>+</sup>) 288.1137, found *m/z* 288.1137; elemental analysis calcd for C<sub>18</sub>H<sub>13</sub>N<sub>3</sub>O C 75.25, H 4.56, N 14.63, found C 75.19, H 4.73, N 14.52.

**1,9-Dicyano-4-methoxy-6-methyl-11,12-benzo-5-azatetracyclo[5.5.0.0<sup>2,6</sup>.0<sup>3,10</sup>]dodeca-4,8-diene (2b).** Mp 205 °C dec; IR (CHCl<sub>3</sub>) 1630, 2203, 2235 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 2.04 (s, 3H, 6-CH<sub>3</sub>), 3.20 (dd, *J* = 4.6 and 9.2 Hz, 1H, 2-CH), 3.27 (dd, *J* = 6.5 and 9.2 Hz, 1H, 3-CH), 3.74 (dd, *J* = 4.6 and 8.7 Hz, 1H, 7-CH), 3.88 (dd, *J* = 1.2 and 6.5 Hz, 1H, 10-CH), 3.94 (s, 3H, 4-OCH<sub>3</sub>), 6.21 (dd, *J* = 1.2 and 8.7 Hz, 1H, 8-CH), 7.26–7.31 (m, 1H, aromatic), 7.33–7.45 (m, 2H, aromatic), 7.6–7.7 (m, 1H, aromatic); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 25.0 (q, CH<sub>3</sub>), 36.3 (s, 1-C), 44.2 (d, 10-C), 49.3 (d, 3-C), 53.4 (d, 2-C), 56.5 (d, 7-C), 56.7 (q, 4-OCH<sub>3</sub>), 73.7 (s, 6-C), 117.7 (s, 9-C), 121.1 (s, CN), 121.8 (s, CN), 126.3 (d, aromatic), 127.6 (d, aromatic), 128.5 (d, aromatic), 129.0 (d, aromatic), 129.8 (s, 11-C), 135.2 (s, 12-C), 140.5 (d, 8-C), 176.8 (s, 4-C); HR-MS(FAB) calcd for C<sub>19</sub>H<sub>16</sub>N<sub>3</sub>O (MH<sup>+</sup>) 302.1293, found *m/z* 302.1302; elemental analysis calcd for C<sub>19</sub>H<sub>15</sub>N<sub>3</sub>O C, 75.73, H 5.02, N 13.94, found C 75.70, H 5.17, N 13.84.

**X-ray Crystallographic Analysis of 2b.** Colorless prismatic crystal of C<sub>19</sub>H<sub>15</sub>N<sub>3</sub>O, monoclinic space group *P*2<sub>1</sub>/*n*, *a* = 7.549(6) Å, *b* = 19.16(2) Å, *c* = 10.84(1) Å, β = 99.84(9)°, *V* = 1544.83 Å<sup>3</sup>, *Z* = 4, ρ = 1.296 g/cm<sup>3</sup>, μ(Mo Kα) = 7.11 cm<sup>-1</sup>. The structure was solved by the direct method and refined by the method of full-matrix least-squares, where the final *R* and *R*<sub>w</sub> were 0.062 and 0.063 for 2256 reflections.

**1,9-Dicyano-4-methoxy-6,8-dimethyl-11,12-benzo-5-azatetracyclo[5.5.0.0<sup>2,6</sup>.0<sup>3,10</sup>]dodeca-4,8-diene (2c).** Mp 178 °C dec; IR (CHCl<sub>3</sub>) 1628, 2216, 2236 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 1.91 (s, 3H, 6-CH<sub>3</sub>), 2.04 (s, 3H, 8-CH<sub>3</sub>), 3.18 (dd, *J* = 4.4 and 9.2 Hz, 1H, 2-CH), 3.22 (dd, *J* = 6.0 and 9.2 Hz, 1H, 3-CH), 3.57 (d, *J* = 4.4 Hz, 1H, 7-CH), 3.82 (d, *J* = 6.0 Hz, 1H, 10-CH), 3.92 (s, 3H, 4-OCH<sub>3</sub>), 7.27–7.31 (m, 1H, aromatic), 7.36–7.43 (m, 2H, aromatic), 7.68–7.70 (m, 1H, aromatic); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 25.4 (q, CH<sub>3</sub>), 25.5 (q, CH<sub>3</sub>), 36.2 (s, 1-C), 43.4

(d, 10-C), 49.1 (d, 3-C), 53.6 (d, 2-C), 61.5 (d, 7-C), 56.8 (q, 4-OCH<sub>3</sub>), 73.7 (s, 6-C), 113.7 (s, 9-C), 117.6 (s, CN), 122.1 (s, CN), 126.1 (d, aromatic), 127.3 (d, aromatic), 128.6 (d, aromatic), 128.7 (d, aromatic), 129.7 (s, 11-C), 136.0 (s, 12-C), 151.4 (d, 8-C), 177.3 (s, 4-C); HR-MS(FAB) calcd for C<sub>20</sub>H<sub>18</sub>N<sub>3</sub>O (MH<sup>+</sup>) 316.1450, found *m/z* 316.1438; elemental analysis calcd for C<sub>20</sub>H<sub>17</sub>N<sub>3</sub>O<sub>2</sub> C 76.17, H 5.43, N 13.32, found C 76.18, H 5.61, N 13.21.

**1,9-Dicyano-4,7-dimethoxy-11,12-benzo-5-azatetracyclo[5.5.0.0<sup>2,6</sup>.0<sup>3,10</sup>]dodeca-4,8-diene (2d).** Mp 131 °C dec; IR (CHCl<sub>3</sub>) 1628, 2220, 2239 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 3.35 (dd, *J* = 6.8 and 9.5 Hz, 1H, 3-CH), 3.48 (dd, *J* = 5.4, and 9.5 Hz, 1H, 2-CH), 3.53 (s, 3H, 6-OCH<sub>3</sub>), 3.86 (dd, *J* = 1.2 and 6.8 Hz, 1H, 10-CH), 3.95 (s, 3H, 4-OCH<sub>3</sub>), 3.95 (dd, *J* = 5.4 and 8.2 Hz, 1H, 7-CH), 6.45 (dd, *J* = 1.2 and 8.2 Hz, 1H, 8-CH), 7.27–7.33 (m, 1H, aromatic), 7.38–7.46 (m, 2H, aromatic), 7.72–7.74 (m, 1H, aromatic); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 38.6 (s, 1-C), 43.8 (d, 10-C), 49.7 (d, 3-C), 52.1 (d, 2-C), 52.3 (d, 7-C), 57.0 (q, 4-OCH<sub>3</sub>), 57.4 (q, OMe), 104.6 (d, 6-C), 117.8 (s, 9-C), 120.8 (s, CN), 121.7 (s, CN), 126.7 (d, aromatic), 128.1 (d, aromatic), 128.9 (s, 11-C), 129.4 (d, aromatic), 130.1 (d, aromatic), 135.4 (s, 12-C), 140.2 (d, 8-C), 176.6 (s, 4-C); elemental analysis calcd for C<sub>19</sub>H<sub>15</sub>N<sub>3</sub>O<sub>2</sub> C 71.91, H 4.76, N 13.24, found C 71.97, H 4.45, N 13.14.

**Pyrolysis of 2d.** When the adduct **2d** in a sealed tube purged by argon was heated at 130 °C for 15 min, 1,3-sigmatropic rearrangement product, 1,8-dicyano-3,5-dimethoxy-11,12-benzo-4-azatetracyclo[5.3.2.0<sup>1,7</sup>.0<sup>5,10</sup>]dodeca-3,8-diene (**6d**), was obtained quantitatively. Spectral data for **6d**: mp 175–176 °C; IR (KBr) 1633, 2213 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 2.44 (d, *J* = 2.2 Hz, 1H, 2-CH), 2.98 (ddd, *J* = 2.2, 2.9, and 8.0 Hz, 1H, 6-CH), 3.38 (dd, *J* = 2.9 and 7.6 Hz, 1H, 10-CH), 3.45 (s, 3H, 5-OCH<sub>3</sub>), 3.74 (dd, *J* = 1.4 and 8.0 Hz, 1H, 7-CH), 3.97 (s, 3H, 3-OCH<sub>3</sub>), 6.33 (dd, *J* = 1.4 and 7.6 Hz, 1H, 9-CH), 7.31–7.36 (m, 3H, aromatic), 7.59 (m, 1H, aromatic); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 44.1, 48.8, 53.2, 53.5, 53.8, 55.5, 56.6, 77.2, 105.3, 116.6, 118.4, 125.6, 126.4, 127.8, 128.7, 133.9, 138.3, 139.8, 171.7; elemental analysis calcd for C<sub>19</sub>H<sub>15</sub>N<sub>3</sub>O<sub>2</sub> C 71.91, H 4.76, N 13.24, found C 71.78, H 4.81, N 13.09.

**X-ray Crystallographic Analysis of 6d.** Colorless prismatic crystal of C<sub>18</sub>H<sub>15</sub>N<sub>3</sub>O<sub>2</sub>, triclinic space group *P*2<sub>1</sub>/*a*, *a* = 17.674(4) Å, *b* = 9.099(3) Å, *c* = 10.579(3) Å, β = 107.16(2)°, *V* = 1625.5(7) Å<sup>3</sup>, *Z* = 4, ρ = 1.296 g/cm<sup>3</sup>, μ(Cu Kα) = 7.00 cm<sup>-1</sup>. The structure was solved by the direct method and refined by the method of full-matrix least-squares, where the final *R* and *R*<sub>w</sub> were 0.047 and 0.063 for 2534 reflections.

JA993260T