

Creation of Concave-Shaped Conformation in Crystal Structures Using an Iminodicarbonyl Linker. An Application to Solid-State Intramolecular [4 + 4] Photocycloaddition Reactions of 2-Pyridone Derivatives

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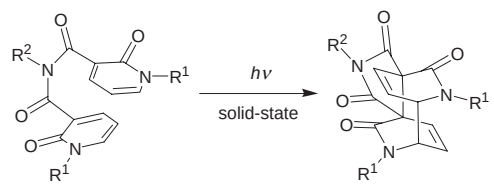
Single-crystal X-ray structures of 6 carboxamides possessing two units of 2-pyridone moieties connected with an iminodicarbonyl linker were examined to show the usefulness of this linker for the creation of concave-shaped conformation in crystal structures. In all cases, the carboxamides showed concave-shaped conformations in which two 2-pyridone moieties faced each other. Their solid-state [4 + 4] photocycloaddition was carried out, and their reactivity was considered based on geometrical parameters (distances, angles, and torsion angles) obtained from the single-crystal X-ray analysis.

Solid-state photochemistry[1] is advantageous over that in solution in terms of stereoselectivity, owing to the rigidity of the conformation of the reactants in the crystalline state. However, this rigidity of conformation is often problematic. If molecules to be reacted have incorrect conformations, it is difficult to adjust their conformations to reactive ones because of their immobility in the crystalline state. In order to carry out a photochemical reaction between two chromophores in the solid state, it is required to place them in a desirable location in which the distance between the chromophores should be within a certain range, and also their molecular orbitals should be well overlapped.[2] Therefore, in the case of intramolecular solid-state reaction between two reactive chromophores, it is essential to choose the proper linker that has a tendency to place the two linking chromophores in a concave-shape with the above-mentioned requirements. During the course of our study on an intramolecular photocycloaddition of aromatic compounds in the solid state, we found that an iminodicarbonyl group was a satisfactory linker for this purpose,[3] and achieved an absolute asymmetric synthesis in the solid-state [4 + 4] photocycloaddition of aromatic chain imides.[4] The two aromatic chromophores linked by an iminodicarbonyl linker are forced to face each other to create a concave-shaped conformation in the crystalline state. We have also shown the usefulness of this linker for the construction of aromatic foldamers.[5] In this paper, we further demonstrate the usefulness of this intriguing linker for creating concave-shaped conformations of aromatic compounds in the crystalline state. Intramolecular solid-state [4 + 4] photocycloadditions of 2-pyridone derivatives are employed to attest to the effectiveness of this linker to create such conformations as a further example.

Results and Discussion

Six 2-pyridone derivatives (**1a–f**) possessing two 2-pyridone moieties connected with an iminodicarbonyl linker were prepared to examine their conformations in the crystalline state. The effectiveness of an iminodicarbonyl linker for the creation of concave-shape conformations was evaluated by a single-crystal X-ray diffraction analysis and their reactivity in intramolecular photocycloaddition in the solid-state (Scheme 1, Table 1). Their single-crystal X-ray diffraction analysis showed that they adopted concave-shaped conformations in all cases. Their conformations were independent of the sub-



	R^1	R^2		R^1	R^2
1a :	Bn	*i*-Pr	**1d** :	Me	*i*-Pr
1b :	Bn	*n*-Bu	**1e** :	Me	*n*-Pr
1c :	Bn	Bn	**1f** :	Me	Bn

Scheme 1.

Published on the web June 6, 2005; DOI 10.1246/bcsj.78.1127

Table 1. Crystallographic Data of Compounds **1a**–**1f** and **2a**

	1a	**1b**	**1c**	**1d**	**1e**	**1f**	**2a**
Formula	$C_{29}H_{27}N_3O_4$	$C_{30}H_{29}N_3O_4$	$C_{33}H_{27}N_3O_4$	$C_{17}H_{19}N_3O_4$	$C_{17}H_{19}N_3O_4$	$C_{21}H_{19}N_3O_4$	$C_{29}H_{27}N_3O_4$
F. W.	481.55	495.58	529.59	329.35	329.35	377.40	481.55
Crystal system	tetragonal	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
Space group	$P4_12_12$	$P2_1/a$	$P2_1/a$	$C2/c$	$P2_1/n$	$P2_1/c$	$P2_1/a$
a/Å	17.168 (3)	18.771 (1)	18.708 (2)	27.354 (4)	27.851 (3)	9.268 (2)	15.935 (4)
b/Å	17.168 (3)	22.567 (2)	22.823 (2)	13.567 (1)	13.0681 (8)	20.502 (4)	23.222 (4)
c/Å	8.467 (2)	12.440 (3)	12.858 (1)	16.434 (2)	16.030 (2)	10.258 (2)	14.534 (3)
β/deg	90.000	99.92 (1)	100.378 (8)	125.401 (9)	122.219 (8)	110.507 (3)	114.21 (2)
V/Å^3	2495.6 (8)	5190 (1)	5400.0 (9)	4971 (1)	4936.0 (9)	1825.5 (6)	4904 (1)
Z	4	8	8	12	12	4	8
radiation	Mo Kα	Cu Kα	Cu Kα	Cu Kα	Cu Kα	Mo Kα	Cu Kα
T/K	273	298	298	298	298	173	298
$R(F)$	0.0437	0.0626	0.0555	0.0642	0.0525	0.0402	0.0569

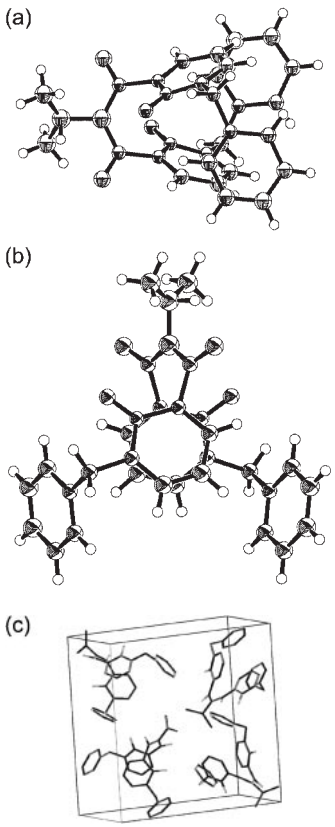
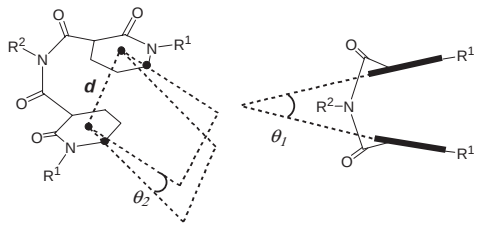


Fig. 1. ORTEP diagrams of a side view (a) and a top view (b), and packing diagram (c) of **1a**.

stituents at the imide and 2-pyridone's nitrogen atoms. The X-ray structure of **1a** is shown in Fig. 1 as an example. In its structure, the two 2-pyridone rings take the trans, syn-relation. It is known that two 2-pyridone moieties prefer to orient in an anti-parallel manner due to dipole–dipole interaction between the two pyridone carbonyls.[6] Its packing diagram shows that the molecule has curled so as to have a compact conformation. Intermolecularly, no stacking was observed. Table 2 gives the geometrical parameters, the distance (d) between the centroids of two 2-pyridone rings, the angle (θ_1) created with the two 2-pyridone ring planes, and the torsion angle (θ_2) between the two 2-pyridone ring planes, obtained from their single-crystal

Table 2. Geometrical Parameters (d, θ_1, and θ_2) and Photochemical Reactivity of 2-Pyridone Derivatives in Solid-State[a)]



	d/Å	θ_1/°	θ_2/°	$\theta_1+\theta_2$	Time/h	Conv./%
1a	3.66	36.9	21.1	58.0	7	≥99
1b[b)]	3.76	41.3	25.1	66.4	36	31
1c[b)]	3.80	42.1	26.7	68.8	96	76
1d[b)]	3.66	37.7	24.9	62.6	8	≥99
1e[c)]	3.73	38.2	27.2	65.4	8	95
1f	3.71	39.1	26.7	65.8	30	96

a) Reaction was carried out at ca. 23 °C. b) Parameters are given as average values of those of two independent molecules in the unit cell. c) Parameters are given as average values of those of three independent molecules in the unit cell.

X-ray diffraction analysis. They are in the range of 3.66–3.80 Å (d), 36.9–42.1° (θ_1), and 21.1–27.2° (θ_2). These values indicate that two 2-pyridone moieties are reasonably overlapped, and should be photo-reactive in a [4 + 4] cycloaddition mode in the solid state.[4] It is known that 2-pyridone derivatives undergo a photochemical [4 + 4] cycloaddition reaction,[7] which is an efficient and direct method to prepare eight-membered carbocyclic rings, such as the carbocyclic skeleton of Taxol.[8] However, examples of solid-state photoreaction of 2-pyridones were limited. Some examples reported intramolecular 1,4-electrocyclizations.[9] Their intermolecular [4 + 4] photodimerizations have been found in inclusion complexes,[10] and very few show intermolecular reactions without the aid of host molecules.[11] If the solid-state intramolecular [4 + 4] photocycloadditions of **1a**–**1f** occur efficiently, it proves that an iminodicarbonyl is an eminent linker for creating a concave-shape in the crystalline state.

Prior to their solid-state photochemical reactions, their photocycloadditions were carried out in benzene irradiated with a

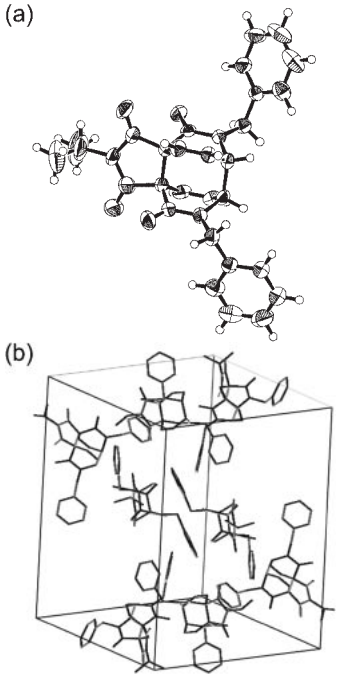


Fig. 2. ORTEP diagram (a) and packing diagram (b) of **2a**.

high-pressure mercury lamp through a Pyrex filter. In all cases, the corresponding [4 + 4] photocycloadducts were obtained in an almost quantitative yield. The stereochemistry of [4 + 4] photocycloadducts was unequivocally determined to be trans, syn by the single-crystal X-ray diffraction analysis of **2a** (Fig. 2). The trans stereochemistry was reported in the intramolecular photocycloadditions of 2-pyridone derivatives in solution,[12] which was interpreted in terms of a dipole–dipole interaction between the two pyridone carbonyls.

A solid-state photochemical reaction was carried out on a finely ground sample of 2-pyridone derivatives placed between two slide glasses. The irradiation of **1a–f** with a high-pressure mercury lamp in the solid state at ca. 23 °C afforded the corresponding [4 + 4] adducts **2a–f**, which were the same products as those obtained in their solution photochemistry. The geometrical parameters indicate that the larger their values become, less reactivity is observed. Compounds **1b** ($d = 3.76$ Å) and **1c** ($d = 3.80$ Å) with relatively large values of d required a longer irradiation time for the reaction. Even after irradiation for 36 and 96 h, the conversion for **1b** and **1c** was 31 and 76%, respectively. These compounds also have larger values of θ_1 and θ_2 (**1b**: $\theta_1 + \theta_2 = 66.4°$, **1c**: $\theta_1 + \theta_2 = 68.8°$) than those of the others. In contrast, other 2-pyridone derivatives gave conversions from 95% to almost quantitative after 7–30 h irradiation. They have values of 3.66–3.71 Å and 58.0–65.8° for d and $(\theta_1 + \theta_2)$, respectively. The conformation of **1a** was reflected in the stereochemistry of the cycloadduct **2a**, which suggested that cycloaddition occurred in a stereoselective way.

It is known that an amide unit prefers to take the *cis* conformation,[13] and that the folded conformations of aromatic amide oligomers are more stable than those of aliphatic amides.[14] Since an iminodicarbonyl linker can be considered as a sequential combination of two amide units, 2-pyridone derivatives **1** might have a tendency to form a concave-shaped folding conformation. It is also known that some aromatic amides with bulky substituents have a fairly stable atropisomeric conformation.[15] Therefore, 2-pyridone derivatives **1** can also be considered to be a combination of two units of atropisomeric amides. These tendencies seem to be a unique characteristic of the iminodicarbonyl linker, which is advantageous over other linkers. Some examples showed that linkers with the length of three atoms, similar to the length of iminodicarbonyl, such as propano[16] and 2-azapropano,[17] were ineffective to place the two linking aromatic rings facing each other in their crystalline state.

The present results show that an iminodicarbonyl is a useful linker for the creation of a concave-shape in aromatic crystal engineering, though the stereochemistry of the cycloadducts obtained in the solid-state photochemical reactions is the same as that observed in reactions occurring in solution.

Experimental

General. Common commercial reagents were used as received from commercial suppliers without further purification. IR spectra were measured on KBr pellets. UV–vis absorption spectra are reported in λ_{max} and ε_{max}. ^{1}H and ^{13}C NMR spectra were obtained in $CDCl_3$. Chemical shifts are reported in delta (δ) units, parts per million (ppm) relative to TMS as an internal standard. Coupling constants J are in Hz. A certain amount of solvent molecules or water was included in several compounds upon crystallization. This was taken into account in calculations of elemental analysis. Unless otherwise noted, each spectrum was measured at room temperature.

Materials. 1,1′-Dibenzyl-3,3′-(*N*-isopropyliminodicarbonyl)-di-2-pyridone (**1a**): 2-Hydroxynicotinic acid (3.00 g, 21.6 mmol) was added to a water–methanol (7:1) solution (40 mL) of KOH (85%, 2.86 g, 43.4 mmol). Then, benzyl bromide (5.20 mL, 43.7 mmol) was added to this solution. After being refluxed for 6.5 h, additional KOH (85%, 1.30 g, 19.7 mmol) was added to this solution and refluxed further (2 h). After cooling to room temperature, the solution was evaporated to half of the volume and acidified with an aqueous 10% HCl solution (25 mL). The yellow precipitate was collected by vacuum filtration and dried to give 1-benzyl-2-oxo-1,2-dihydropyridine-3-carboxylic acid (yield 4.59 g, 93%).

Thionyl chloride (2.06 mL, 28.4 mmol) was added to the carboxylic acid (1.30 g, 5.68 mmol) in dry toluene (30 mL). After the solution was heated at 80 °C for 21 h with stirring, excess thionyl chloride and toluene were evaporated. Isopropylamine (0.265 mL, 3.11 mmol), triethylamine (0.790 mL, 5.69 mmol), and dry toluene (40 mL) were added to the mixture, and then the solution was refluxed for two days with stirring. After cooling to room temperature, the solution was washed with a saturated aqueous solution of $NaHCO_3$, and then with an aqueous 1 mol/L HCl solution. The separated organic phase was dried over $MgSO_4$, filtered, and evaporated. The residue was purified by silica-gel column chromatography with hexane/ethyl acetate (3:2) as the eluent. Further purification by recrystallization from hexane/chloroform gave **1a** as yellow crystals (0.390 g, 28%). In a similar way as for **1a**, other carboxamides **1b–1f** were prepared in 49, 58, 29, 28, and 37% yields, respectively.

1,1′-Dibenzyl-3,3′-(*N*-isopropyliminodicarbonyl)di-2-pyridone (1a): mp 211–213 °C. IR (KBr) 2971 (br), 1655 (s), 1584 (s), 1548 (s), 1270 (m) cm^{-1}. UV–vis (CH_3CN) λ_{max} (ε), 243 (7300), 283 (3500), 341 (9300) nm. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.42 (dd, $J = 7.5$, 2.2 Hz, 2H), 7.35–7.34 (m, 6H),

7.29–7.27 (m, 4H), 7.14–7.13 (m, 2H), 5.60 (t, $J = 6.9$ Hz, 2H), 5.04 (m7, $J = 6.9$ Hz, 1H), 4.91 (s, 4H), 1.51 (d, $J = 6.7$ Hz, 6H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 169.4 (s), 159.2 (s), 141.5 (d), 140.1 (d), 135.2 (s), 129.0 (d), 128.9 (d), 128.4 (d), 105.2 (d), 52.5 (t), 49.4 (d), 20.5 (q). MS (EI) m/z 481 [M^+]. Anal. Calcd for $C_{29}H_{27}N_3O_4$: C, 72.33; H, 5.65; N, 8.73%. Found: C, 72.01; H, 5.63; N, 8.66%.

1,1′-Dibenzyl-3,3′-(*N*-butyliminodicarbonyl)di-2-pyridone (1b): mp 167–169 °C (yellow crystals). ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.49 (dd, $J = 7.1$, 2.2 Hz, 2H), 7.37–7.26 (m, 10H), 7.16 (dd, $J = 6.9$, 2.1 Hz, 2H), 5.62 (t, $J = 6.7$ Hz, 2H), 4.92 (s, 4H), 3.98 (br, 2H), 1.76 (m, $J = 7.6$ Hz, 2H), 1.42 (m6, $J = 7.3$ Hz, 2H), 0.94 (t, $J = 7.3$ Hz, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 169.4 (s), 159.3 (s), 141.7 (d), 140.1 (d), 135.3 (s), 129.0 (d), 128.9 (d), 128.4 (d), 128.3 (s), 105.3 (d), 52.5 (t), 45.3 (t), 30.6 (t), 20.3 (t), 13.9 (q). MS (EI) m/z 495 [M^+]. Anal. Calcd for $C_{30}H_{29}N_3O_4$: C, 72.71; H, 5.90; N, 8.48%. Found: C, 72.61; H, 5.87; N, 8.39%.

1,1′-Dibenzyl-3,3′-(*N*-benzyliminodicarbonyl)di-2-pyridone (1c): mp. 169–171 °C (yellow crystals). IR (KBr) 3067 (m), 3031 (m), 1656 (s), 1582 (s), 1549 (s), 1244 (s) cm^{-1}. UV–vis (CH_3CN) λ_{max} (ε), 257 (3200), 285 (2500), 343 (10000) nm. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.54 (td, $J = 7.1$, 2.1 Hz, 4H), 7.35–7.17 (m, 13H), 7.14 (dd, $J = 5.9$, 2.2 Hz, 2H), 5.66 (t, $J = 6.9$ Hz, 2H), 5.20 (s, 2H), 4.91 (s, 4H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 169.3 (s), 159.2 (s), 142.1 (d), 140.3 (d), 137.5 (s), 135.3 (s), 128.8 (d), 128.3 (d), 128.2 (d), 127.9 (d), 127.7 (s), 126.8 (d), 105.2 (d), 52.4 (t), 48.6 (t). MS (EI) m/z 529 [M^+]. Anal. Calcd for $C_{33}H_{27}N_3O_4$: C, 74.84; H, 5.14; N, 7.93%. Found: C, 74.84; H, 5.10; N, 7.87%.

1,1′-Dimethyl-3,3′-(*N*-isopropyliminodicarbonyl)di-2-pyridone (1d): mp. 220–222 °C (yellow crystals). IR (KBr) 2976 (w), 1657 (s), 1590 (s), 1549 (s), 1268 (s) cm^{-1}. UV–vis (CH_3CN) λ_{max} (ε), 252 (2700), 282 (2700), 340 (10000), 374 (4700) nm. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.75 (dd, $J = 7.3$, 2.1 Hz, 2H), 7.24 (dd, $J = 6.6$, 2.3 Hz, 2H), 6.04 (t, $J = 6.9$ Hz, 2H), 4.98 (m7, $J = 6.9$ Hz, 1H), 3.41 (s, 6H), 1.52 (d, $J = 6.7$ Hz, 6H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 169.3 (s), 159.8 (s), 141.5 (d), 141.3 (d), 128.6 (s), 104.9 (d), 49.5 (d), 37.9 (q), 20.3 (q). MS (EI) m/z 329 [M^+]. Anal. Calcd for $C_{17}H_{19}N_3O_4$: C, 62.00; H, 5.81; N, 12.76%. Found: C, 61.73; H, 5.80; N, 12.71%.

1,1′-Dimethyl-3,3′-(*N*-propyliminodicarbonyl)di-2-pyridone (1e): mp. 190–191 °C (yellow crystals). IR (KBr) 2960 (w), 1657 (s), 1585 (m), 1546 (s), 1082 (m), 768 (m) cm^{-1}. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.79 (dd, $J = 7.0$, 2.2 Hz, 2H), 7.24 (dd, $J = 6.6$, 2.1 Hz, 2H), 6.06 (t, $J = 7.1$ Hz, 2H), 3.96 (br, 2H), 3.41 (s, 6H), 1.78 (m6, $J = 7.7$ Hz, 2H), 0.99 (t, $J = 7.3$ Hz, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 169.3 (s), 159.9 (s), 141.9 (d), 141.4 (d), 128.0 (s), 105.0 (d), 46.9 (t), 38.0 (q), 21.9 (t), 11.5 (q). MS (EI) m/z 329 [M^+]. Anal. Calcd for $C_{17}H_{19}N_3O_4$: C, 62.00; H, 5.81; N, 12.76%. Found: C, 61.94; H, 5.77; N, 12.73%.

1,1′-Dimethyl-3,3′-(*N*-benzyliminodicarbonyl)di-2-pyridone (1f): mp. 206–208 °C (yellow crystals). IR (KBr) 3063 (w), 1693 (m), 1656 (s), 1593 (s), 1549 (s), 1295 (m) cm^{-1}. UV–vis (CH_3CN) λ_{max} (ε), 252 (4500), 282 (4200), 341 (10000), 372 (6000) nm. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.77 (dd, $J = 7.1$, 2.2 Hz, 2H), 7.54 (d, $J = 7.4$ Hz, 2H), 7.39–7.18 (m, 5H), 6.02 (t, $J = 6.9$ Hz, 2H), 5.19 (s, 2H), 3.36 (s, 6H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 169.1 (s), 159.7 (s), 142.2 (d), 141.8 (d), 137.5 (s), 128.2 (d), 127.8 (d), 127.3 (s), 126.7 (d), 104.9 (d), 48.4 (t), 37.9 (q). MS (EI) m/z 377 [M^+]. Anal. Calcd for $C_{21}H_{19}N_3O_4$: C, 66.83; H, 8.07; N, 11.13%. Found: C, 66.51; H, 5.07; N, 11.07%.

Photocycloaddition in Solid-State. Ground crystals of **1a** (0.020 g, 0.042 mmol) were placed between two glass plates. The sandwiched sample was placed in a transparent polyethylene bag. UV irradiation was carried out externally on this sample with a 400 W high-pressure mercury lamp through a Pyrex filter for 6 h at ca. 23 °C in a water bath. Without purification, **2a** was obtained as a pure product in quantitative yield. The cycloadduct **2a** was recrystallized from hexane/ethyl acetate to give colorless crystals. In a similar way as for **2a**, other [4 + 4] photocycloadducts **2b**–**2h** were obtained. The irradiation time and their yields are given in Table 2.

3,11-Dibenzyl-7-isopropyl-3,7,11-triazatetracyclo[7.2.2.2.^{2,5}-0^{5,9}]pentadeca-12,14-diene-4,6,8,10-tetrone (2a): mp 158–160 °C. IR (KBr) 2979 (w), 1784 (m), 1714 (s), 1676 (s), 1454 (m), 1370 (s), 1264 (s) cm^{-1}. UV–vis (CH_3CN) λ_{max} (ε), 258 (160) nm. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.33–7.26 (m, 6H), 7.14–7.12 (m, 4H), 6.36 (d, $J = 7.7$ Hz, 2H), 6.26 (ddd, $J = 8.1$, 4.7, 2.2 Hz, 2H), 5.06 (d, $J = 15$ Hz, 2H), 4.56 (m7, $J = 7.0$ Hz, 1H), 4.09 (m, 2H), 3.67 (d, $J = 15$ Hz, 2H), 1.53 (d, $J = 7.0$ Hz, 3H), 1.50 (d, $J = 7.0$ Hz, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 172.6 (s), 168.2 (s), 135.1 (s), 133.6 (d), 132.1 (d), 128.9 (d), 128.2 (d), 61.9 (s), 57.9 (d), 50.5 (t), 45.4 (d), 19.4 (q), 19.0 (q). MS (EI) m/z 481 [M^+]. Anal. Calcd for $C_{29}H_{27}N_3O_4$: C, 72.33; H, 5.65; N, 8.73%. Found: C, 72.23; H, 5.63; N, 8.64%.

3,11-Dibenzyl-7-butyl-3,7,11-triazatetracyclo[7.2.2.2.^{2,5}0^{5,9}]-pentadeca-12,14-diene-4,6,8,10-tetrone (2b): ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.34–7.13 (m, 10H), 6.39 (d, $J = 8.2$ Hz, 2H), 6.28 (m, 2H), 5.10 (d, $J = 15$ Hz, 2H), 4.09 (m, 2H), 3.75 (dt, $J = 13$, 7.0 Hz, 1H), 3.69–3.65 (m, 3H), 1.76–1.66 (m, 2H), 1.42 (sext, $J = 7.3$ Hz, 2H), 0.97 (t, $J = 7.3$ Hz, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 172.7 (s), 168.2 (s), 135.1 (s), 133.7 (d), 132.1 (d), 129.0 (d), 128.2 (d), 128.2 (d), 62.4 (s), 57.8 (d), 50.6 (t), 39.9 (t), 29.6 (t), 19.8 (t), 13.7 (q). MS (EI) m/z 495 [M^+]. Anal. Calcd for $C_{30}H_{29}N_3O_4$: C, 72.71; H, 5.90; N, 8.48%. Found: C, 72.42; H, 5.87; N, 8.34%.

3,7,11-Tribenzyl-3,7,11-triazatetracyclo[7.2.2.2.^{2,5}0^{5,9}]pentadeca-12,14-diene-4,6,8,10-tetrone (2c): mp. 160–162 °C. IR (KBr) 3061 (w), 1787 (m), 1717 (s), 1672 (s), 1398 (m), 1245 (m) cm^{-1}. UV–vis (CH_3CN) λ_{max} (ε), 259 (970) nm. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.44 (d, $J = 7.3$ Hz, 2H), 7.37–7.26 (m, 9H), 7.12 (dd, $J = 7.7$, 1.7 Hz, 4H), 6.37 (d, $J = 8.0$ Hz, 2H), 6.28 (ddd, $J = 8.1$, 4.7, 2.1 Hz, 2H), 5.10 (d, $J = 15$ Hz, 2H), 4.94 (d, $J = 15$ Hz, 1H), 4.82 (d, $J = 15$ Hz, 1H), 4.08 (m, 2H), 3.65 (d, $J = 15$ Hz, 2H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 172.4 (s), 168.0 (s), 135.0 (s), 134.7 (s), 133.7 (d), 131.9 (d), 129.0 (d), 128.8 (d), 128.2 (d), 128.1 (d), 127.9 (d), 62.5 (s), 57.7 (d), 50.5 (t), 43.5 (t). MS (EI) m/z 530 [MH^+]. Anal. Calcd for $C_{33}H_{27}N_3O_4$: C, 74.84; H, 5.14; N, 7.93%. Found: C, 74.76; H, 5.09; N, 7.88%.

3,11-Dimethyl-7-isopropyl-3,7,11-triazatetracyclo[7.2.2.2.^{2,5}-0^{5,9}]pentadeca-12,14-diene-4,6,8,10-tetrone (2d): mp. 170 °C. IR (KBr) 2988 (w), 1784 (w), 1719 (s), 1673 (s), 1458 (w), 1399 (m), 1265 (m) cm^{-1}. UV–vis (CH_3CN) λ_{max} (ε), 258 (540) nm. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 6.62–6.56 (m, 2H), 6.36 (dd, $J = 8.7$, 0.8 Hz, 2H), 4.53 (m7, $J = 7.0$ Hz, 1H), 4.23 (m, 2H), 2.89 (s, 6H), 1.50 (d, $J = 7.0$ Hz, 3H), 1.48 (d, $J = 7.1$ Hz, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 172.6 (s), 168.0 (s), 132.8 (d), 132.0 (d), 62.0 (s), 61.3 (d), 45.2 (d), 35.3 (q), 19.2 (q), 18.9 (q). MS (EI) m/z 329 [M^+]. Anal. Calcd for

$C_{17}H_{19}N_3O_4$: C, 62.00; H, 5.81; N, 12.76%. Found: C, 61.73; H, 5.69; N, 12.83%.

3,11-Dimethyl-7-propyl-3,7,11-triazatetracyclo[7.2.2.2.^{2,5}0^{5,9}]-pentadeca-12,14-diene-4,6,8,10-tetrone (2e): ^{1}H NMR ($CDCl_3$, 500 MHz) δ 6.63–6.57 (m, 2H), 6.37 (dd, $J = 8.5$, 0.9 Hz, 2H), 4.24 (m, 2H), 3.70 (dt, $J = 13.1$, 7.1 Hz, 1H), 3.61 (dt, $J = 13.1$, 7.1 Hz, 1H), 2.90 (s, 6H), 1.73 (m6, $J = 7.4$ Hz, 2H), 0.97 (t, $J = 7.3$ Hz, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 172.8 (s), 168.0 (s), 132.6 (d), 132.4 (d), 62.6 (s), 61.5 (d), 41.5 (t), 35.6 (q), 20.9 (t), 11.0 (q). Anal. Calcd for $C_{17}H_{19}N_3O_4$: C, 62.00; H, 5.81; N, 12.76%. Found: C, 61.71; H, 5.78; N, 12.71%.

3,11-Dimethyl-7-benzyl-3,7,11-triazatetracyclo[7.2.2.2.^{2,5}0^{5,9}]-pentadeca-12,14-diene-4,6,8,10-tetrone (2f): mp. 177–179 °C. IR (KBr) 3067 (w), 1790 (m), 1718 (s), 1662 (s), 1395 (m) cm^{-1}. UV–vis (CH_3CN) λ_{max} (ε), 258 (650) nm. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.40–7.25 (m, 5H), 6.61–6.56 (m, 2H), 6.34 (d, $J = 7.9$ Hz, 2H), 4.91 (d, $J = 15$ Hz, 1H), 4.79 (d, $J = 15$ Hz, 1H), 4.22 (m, 2H), 2.88 (s, 6H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 172.4 (s), 167.8 (s), 134.7 (s), 132.6 (d), 132.2 (d), 128.8 (d), 127.9 (d), 127.6 (d), 62.7 (s), 61.4 (d), 43.3 (t), 35.6 (q). MS (EI) m/z 377 [MH$^+$]. Anal. Calcd for $C_{21}H_{19}N_3O_4$: C, 66.83; H, 5.07; N, 11.13%. Found: C, 66.52; H, 5.09; N, 11.12%.

X-ray Crystallography. An X-ray crystallographic analysis was undertaken using a Rigaku AFC7S four-circle diffractometer (for **1b**, **1c**, **1d**, **1e**, and **2a**) or Bruker Samrt1000 CCD diffractometer (for **1a** and **1f**). The crystals were mounted on glass fibers. A structure solution was carried out with the programs SIR 97 (Altomare et al., 1999) or SHELXS 97 (Sheldrick, 1997). For refining the structures, performing a structure analysis, and producing crystallographic illustrations, the program TEXSAN (Rigaku/MSC, 1998) was used. In all of the structures, H atoms were included at their calculated positions. Other details are described in CIF files for each compound.

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