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Articles

The Reaction of Fullerene C_{60} with Phthalazine: The Mechanochemical Solid-State Reaction Yielding a New C_{60} Dimer versus the Liquid-Phase Reaction Affording an Open-Cage Fullerene

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The reaction of fullerene C_{60} with phthalazine was studied both in solution and in the solid state using the high-speed vibration-milling technique. The reaction in solution gave open-cage fullerene derivative **1** in 44% yield by a one-pot reaction. In contrast, the solid-state reaction afforded dimeric derivative **2** as the sole product. Dimeric derivative **2** was found to undergo intramolecular [2 + 2] cycloaddtion between the two C_{60} cages located in close proximity to give a new C_{60} dimer **6** in quantitative yield. The structures of these new derivatives of C_{60} were determined by spectroscopic methods, and the electrochemical behavior of **2** and **6** was also studied.

Introduction

It is commonly understood that organic reactions are best conducted in a homogeneous solution. However, organic reactions without any solvent have attracted much recent interest from the perspective of environment-benignity to avoid waste materials.[1] Actually, various organic reactions have been shown to take place in the solid state when a mortar and pestle is used without solvents.[2] In these examples, essentially the same reactions are reported to occur regardless of the presence or absence of solvent.

"Mechanochemistry" is the chemistry involving the solid-state reactions caused by mechanical energy.[3] The simplest method of mechanochemistry is the use of mortar and pestle, while ball milling is suitable when a prolonged reaction time is required.[4] We, however, have used the so-called high-speed vibration milling (HSVM) for solid-state reactions with relatively small amounts of reactants.[5,6] By using this technique, which utilizes the high-speed vibration of a metal capsule containing a

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(1) (a) Anastas, P. T.; Williamson, T. C. In *Green Chemistry, Designing Chemistry for the Environment*; Anastas, P. T., Williamson, T. C., Eds.; Americal Chemical Society: Washington, DC, 1996; pp 1−17. (b) Metzger, J. O. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 2975−2978.

(2) For example, see: (a) Toda, F. *Acc. Chem. Res.* **1995**, *28*, 480−486. (b) Toda, F. *Synlett* **1993**, 303−312.

(3) (a) Heinicke, G. *Tribochemistry*; Hanser: Munich, 1984. (b) Boldyrev, V. V. *Solid State Ionics* **1993**, *63*, 537−543. (c) Gilman, J. J. *Science* **1996**, *274*, 65−65. (d) Braun, T. *Fullerene Sci. Technol.* **1997**, *5*, 1291−1311. (e) Fernández-Bertran, J. F. *Pure Appl. Chem.* **1999**, *71*, 581−586.

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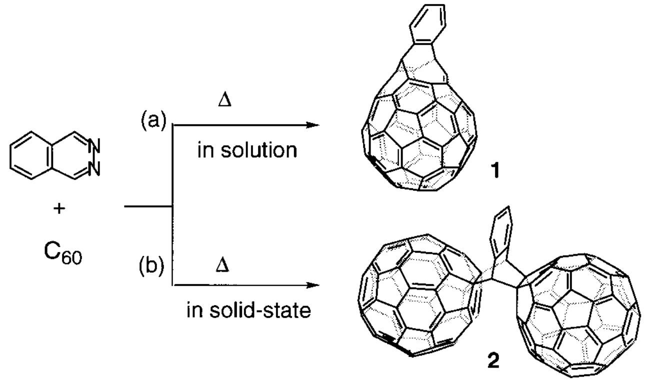
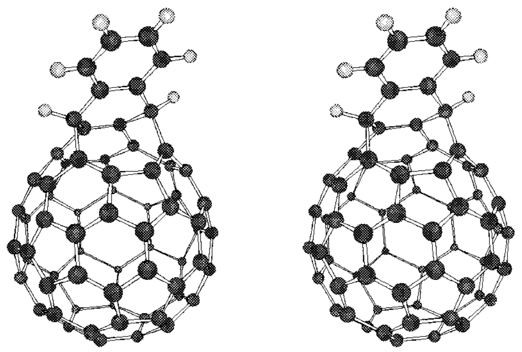
10.1021/jo010496i CCC: $20.00

Scheme 1





Structure of **1** (stereoview) optimized by HF/3-21G.

milling ball, the local pressure is expected to reach the range of 10 000−20 000 bar,[7] and some reactions totally differ from those in the liquid phase under such extreme conditions.

In fact, we have found that the reaction of fullerene C_{60} with potassium or sodium cyanide selectively gives the [2 + 2] cyclodimer C_{120} under HSVM conditions,[6] while the same reaction in solution only affords the cyanated C_{60} derivatives.[8] As another example, the reaction of C_{60} with pentacene in solution only gives the 1:1 cycloadduct,[9,10] while the same reaction under HSVM conditions can afford the C_{60}−pentacene 2:1 adduct.[9]

Here, we report another example in which the reaction takes a totally different course depending on the reaction phase, that is, the reaction of C_{60} with a nitrogen-containing condensed aromatic compound, phthalazine (2,3-diazanaphthalene). A new fullerene dimer with two C_{60} cages incorporated in a bicyclic framework is formed under the mechanochemical solid-state reaction conditions, while a new derivative of the open-cage fullerene is obtained by the liquid-phase reaction by a one-pot reaction.

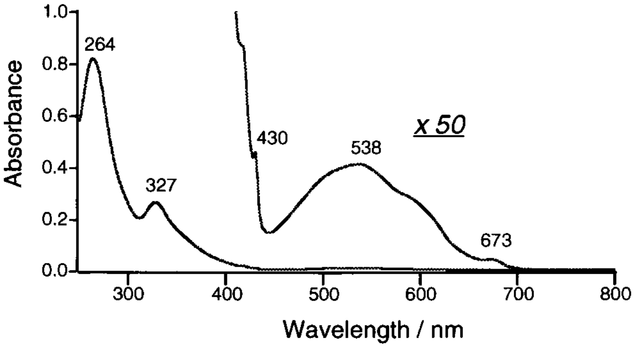


Figure 1. UV−vis spectrum of open-cage fullerene **1** in $CHCl_3$ (6.62×10^{-5} M).

Results and Discussion

When the reaction of C_{60} with 1 equiv of phthalazine was carried out in a solution of 1-chloronaphthalene at 255 °C for 1 h and the products were separated by flash chromatography, a dark brown solid **1**, which exhibited a *m/z* 822 (M^-) peak upon atmospheric-pressure chemical-ionization mass spectroscopy (APCI MS), was isolated in 44% yield together with 23% recovered C_{60}. Based on the molecular-ion peak of the mass spectrum, the product **1** appeared to be formed by the addition of phthalazine to C_{60} with a loss of 1 equiv of nitrogen. The ^{1}H NMR spectrum of **1** showed a singlet at δ 7.20 and AA′BB′ multiplets at δ 7.71 and 7.54, corresponding to a bridgehead proton and aromatic protons, respectively. The ^{13}C NMR spectrum exhibited only one signal (δ 49.14) in the sp^3 carbon region and 35 signals in the sp^2 carbon region (δ 151.62−127.31), suggesting the presence of C_s symmetry in **1** (Scheme 1a). The color of a solution of this material in chloroform is purple, and the UV−vis spectrum has a maximum absorption at 538 nm, closely resembling the spectrum of C_{60} as shown in Figure 1. These results clearly indicate that the 60 original fullerene carbons remain in an sp^2-hybridized form in a π-conjugated system. On the basis of these findings, the structure of **1** was determined as the benzo derivative of the open-cage fullerene: the compound without benzo-annelation had been originally prepared by Rubin and coworkers through multistep synthesis.[11,12] It is to be noted that such a compound, with its quite complicated structure, was formed by a simple one-pot reaction in the present work.

In contrast, when C_{60} was allowed to react with 4 equiv of phthalazine under mechanochemical solid-state conditions using the HSVM technique for 1 h, no indications of the formation of **1** were observed but a totally different product with a much larger molecular weight was formed as indicated by the HPLC analysis (toluene/Buckyprep column). By heating this reaction mixture as a solid at 200 °C for 2 h, the amount of this new product, which was separated by preparative HPLC (1,2-dichlorobenzene/5PBB column) to give a dark brown solid, was found to increase. The amount of the recovered C_{60} was 66%, and the isolated yield of the newly formed product **2**,

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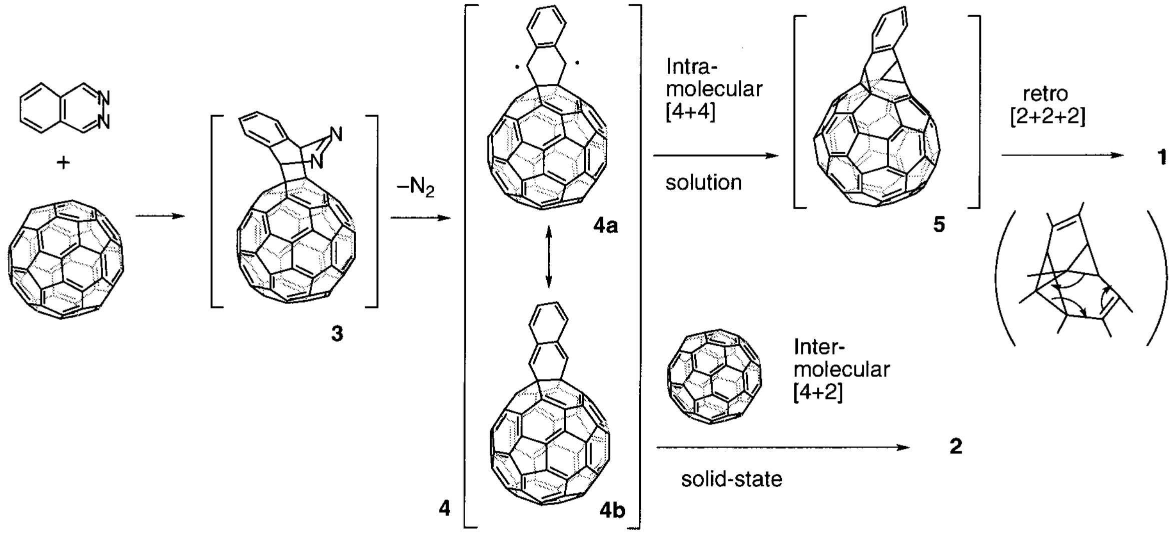
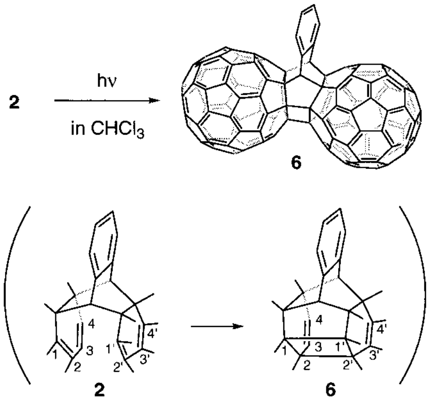
Scheme 2



which exhibited a molecular ion peak at m/z 1542 (M^-) upon APCI MS, was found to be 14%. Formation of no other product was observed. From its molecular weight, **2** apparently has a molecular formula of $C_{128}H_6$, which corresponds to the sum of the molecular formulas of **1** and C_{60} and suggests that **2** has some dimeric structure. As will be described below, the ^1H and ^{13}C NMR data suggest that compound **2** has a structure with two C_{60} cages incorporated in a bicyclic framework (Scheme 1b). The ^1H NMR spectrum showed a singlet at δ 6.09 and AA′BB′ multiplets at δ 8.03 and 7.82 corresponding to a bridgehead proton and aromatic protons, respectively. The ^{13}C NMR spectrum exhibited two signals (δ 71.56 and 58.63) in the sp^3 carbon region and a total of 34 signals in the sp^2 carbon region (δ 157.03−126.45), suggesting the presence of C_{2v} symmetry in **2**. The color of the solution was brown, and the UV−vis spectrum showed a typical absorption pattern for the C_{60} monoadduct at the 6−6 junction bond.

The formation of these different products, depending on the reaction conditions, can be explained as shown in Scheme 2. First, in both cases, a [4 + 2] cycloaddition of C_{60} with phthalazine takes place to produce adduct **3**, which after nitrogen extrusion gives a common intermediate of the orthoquinodimethane type, **4** (**4a** ↔ **4b**). Then, in solution at high temperature, the intermediate **4**, which is isolated from the unchanged C_{60} by solvation, undergoes the formal intramolecular [4 + 4] cycloaddition, possibly via a radical mechanism, to give the intermediate **5** with a rather strained structure. The two cyclopropane rings in **5** then open up in a retro [2 + 2 + 2] manner to furnish the benzo derivative of the open-cage fullerene **1**. In support of the present mechanism, the ab initio calculations at the HF/3-21G level show that the HOMO of intermediate **4** is highly localized at the orthoquinodimethane moiety. The relative energies calculated for **4** and **5** are 29.2 and 34.1 kcal/mol higher than **1**, respectively, thus favoring the ready transformation to **1**. In contrast, in the solid state where abundant C_{60} molecules are present in place of solvent molecules, the conjugated diene unit of intermediate **4** is trapped by another C_{60} molecule in a [4 + 2] fashion to give the C_{60} dimer **2**, with the two cages incorporated in a bicyclic framework.

Scheme 3



The dimer **2** has a structural characteristic in which the two C_{60} cages are rigidly fixed in a face-to-face position in close proximity. The distance between the closest carbons in the facing six-membered rings is 3.193 Å in the optimized structure at the HF/3-21G level. Although this compound is stable in the solid state at temperatures as high as 200 °C, it was found to undergo a gradual transformation into its isomer **6** in a solution of $CHCl_3$ upon irradiation with visible light (or by heating in 1,2-dichlorobenzene) (Scheme 3). This transformation can be followed by UV−vis spectra having isosbestic points, as shown in Figure 2. The newly formed compound, which was obtained in a quantitative yield,

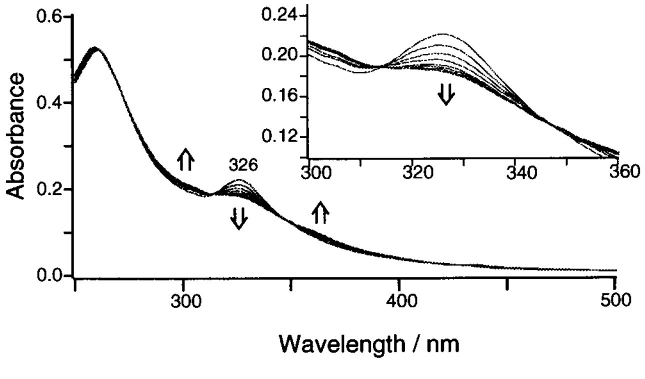


Figure 2. Change in the UV−vis spectrum during irradiation with visible light of a solution of **2** in $CHCl_3$ (3.37×10^{-5} M).

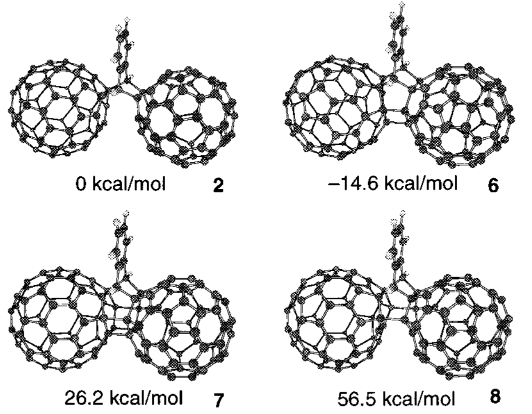
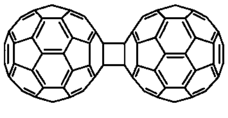


Figure 3. Optimized structures of **2** and its intramolecular cycloadducts **6**, **7**, and **8** by HF/3-21G and the relative energies with reference to **2**.

displayed the same *m*/*z* value (1542) as **2** in the APCI MS. In the ^{1}H NMR spectrum, the signal for the bridgehead proton split into two signals at δ 5.87 and 5.11, and the signals for the aromatic protons changed into complex multiplets centered at δ 7.7. The ^{13}C NMR spectrum exhibited six signals (δ 79.64, 70.84, 70.18, 69.79, 68.42, and 55.16) in the sp^3 carbon region and 62 signals in the sp^2 carbon region (δ 155.06−125.66). These NMR data suggest that compound **6** has C_s symmetry and has new intramolecular [2 + 2] bonds connecting the two closely located C_{60} cages; that is, compound **6** is an "intramolecular photodimer".

To compare the relative stabilities, ab initio calculations at the HF/3-21G level were conducted for the possible "intramolecular photodimers" such as **7** ([2 + 2] at 1,2- and 3,4-positions) and **8** ([4 + 4] at 1,4-positions) in addition to **2** and **6** (Figure 3). It was found that the relative energy of **6** is lower than that of **2** by 14.6 kcal/mol, while those of **7** and **8** are higher than that of **2** by 26.2 and 56.5 kcal/mol, respectively. This result is in good agreement with the observed selective formation of **6**. Reflecting its considerable stability, the "photodimer" **6** did not undergo any appreciable bond cleavage upon heating to 200 °C. This is in sharp contrast to the complete cycloreversion observed for the fullerene dimer C_{120} (**9**)[6] and its analogue **10**.[13]



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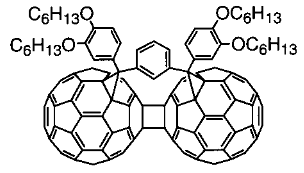

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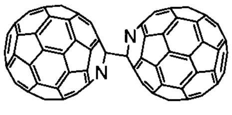

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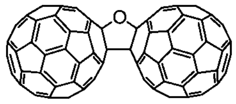

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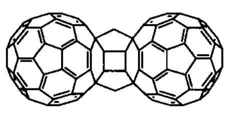

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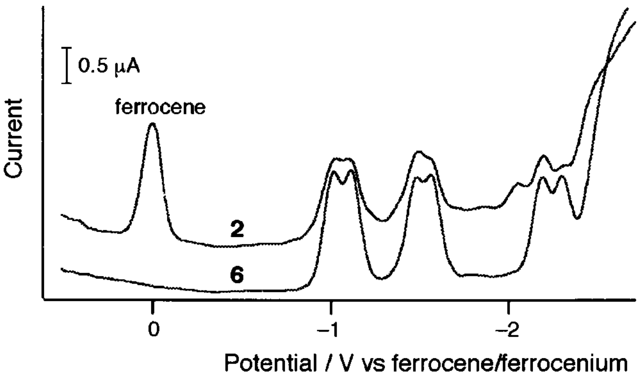

Figure 4. DPV charts of **2** and **6** in 1,2-dichlorobenzene-benzonitrile (1:1) (supporting electrolyte, 0.05 M Bu_4NBF_4; scan rate, 0.02 V s^{-1}).

The redox behaviors of dimeric fullerenes are of particular interest from the viewpoint of the electronic interaction between the fullerene cages. For the azafullerene dimer **11**,[14] oxa-bridged dimer **12**,[15] and bismethylenebridged dimer **13**,[16] the electrochemical reduction takes place stepwise on each fullerene cage, but not upon the two cages at the same time, because of the mutual recognition of the two cages. In contrast, the simplest dimer **9** undergoes cleavage of the central [2 + 2] bonds right after the first one-electron reduction, as observed by cyclic voltammetry (CV) and differential pulse voltammetry (DPV).[6] When we conducted the cyclic voltammetry on dimer **2**, we found that each of the two reduction waves appeared as two barely separated waves, indicating that the reduction takes place stepwise on each fullerene cage: the electronic interaction between the two cages is present, although the extent of this interaction is quite small. When compound **6** was examined by cyclic voltammetry, the voltammogram was found to be exactly the same as that of **2**, as clearly shown by the comparison of the differential pulse voltammograms (**2**, −1.03, −1.09, −1.49, −1.55, −2.20, −2.31 V; **6**, −1.02, −1.11, −1.48, −1.56, −2.20, −2.30 V vs ferrocene/ferrocenium; Figure 4). This implies that the [2 + 2] bond in **6** is readily cleaved upon the first reduction to give the radical anion (or dianion) of **2** and that further reduction successively takes place on this species. Thus, the [2 + 2] bond in **6** was shown to be quite weak toward one-electron reduction, as in the case of dimer **9**.

Conclusion

The [4 + 2] cycloaddition is one of the best-studied reactions of fullerene C_{60}. The present study has demonstrated that this cycloaddition can afford C_{60} derivatives with novel structural features when immediate follow-up reactions are involved. Particularly noteworthy is that the reaction with phthalazine takes a totally different course depending on the reaction phase. The solution-phase thermal reaction affords, in one pot, a derivative of an open-cage fullerene (**1**), that would otherwise require a synthetic route involving multistep reactions. In contrast, the solid-state reaction gives rise to a derivative with two C_{60} cages rigidly fixed in close

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proximity in a bicyclic framework (**2**). This geometrical characteristic is well reflected in a facile and quantitative transformation of this bicyclic compound into the intramolecular [2 + 2] photodimer **6** by irradiation with visible light. Since the newly formed [2 + 2] bonds can be electroreductively cleaved, this bonding system can thus serve as a prototype of a molecular switch based on fullerene arrays.

Experimental Section

General Methods. ^{1}H and ^{13}C NMR spectra were recorded at 300 and 75 MHz, respectively, in CS_2−acetone-d_6 (7:1). The solid-state reactions were performed using a high-speed vibration mill that consisted of a capsule and a milling ball made of stainless steel.[6b] The capsule containing the milling ball was fixed in a vibration arm, which was shaken vigorously at a rate of 3500 cycles per minute.

HPLC analysis was conducted using a Cosmosil Buckyprep column (4.6 × 250 mm) with toluene as an eluent for analytical purpose and a Cosmosil 5PBB column (10 × 250 mm) with 1,2-dichlorobenzene (ODCB) as an eluent for preparative purpose, detected at 326 nm. Cyclic voltammetry and differential pulse voltammetry were conducted using a three-electrode cell with a glassy carbon working electrode, a platinum wire counter electrode, and a Ag/0.01 M $AgNO_3$ reference electrode. The potentials were corrected against ferrocene used as an internal standard added after each measurement. All calculations were performed with the Gaussian 98 program.[17]

Fullerene C_{60} was commercial material (>99.5%) purchased from Term Co. Phthalazine was purchased from Aldrich Co.

Open-Cage Fullerene 1. A solution of C_{60} (31 mg, 0.043 mmol) and phthalazine (5.6 mg, 0.043 mmol) in 1-chloronaphthalene (2.0 mL) was heated at 255 °C for 1 h. Ether (40 mL) was added to the reaction mixture to give precipitates, which were collected by centrifugation and washed by ether (40 mL × 2). The residual brown powder was dissolved in CS_2 (1.5 mL) and subjected to flash chromatography over silica gel eluted with hexane−CS_2 (1:1) to give unchanged C_{60} (6.4 mg, 23%) followed by open-cage fullerene **1** (14.2 mg, 44%) as a brown powder. **1**: mp >300 °C; ^{1}H NMR δ 7.71 (AA′BB′, 1H), 7.54 (AA′BB′, 1H), 7.20 (s, 1H); ^{13}C NMR δ 151.62, 149.97, 146.23, 145.95, 145.71, 145.12, 145.08, 144.97, 144.69, 144.65, 144.62, 144.50, 144.46, 144.44, 144.41, 144.23, 144.00, 143.78, 143.49, 141.76, 141.43, 141.31, 141.11, 140.98, 140.01, 139.56, 139.42, 137.38, 137.15, 134.84, 134.75, 133.46, 129.53, 128.81, 127.31, 49.14; UV−vis ($CHCl_3$) λ_{max} (log ϵ) 264 (5.09), 327 (4.60), 430 (3.1), 538 (3.1), 673 (2.1); MS (-APCI) m/z 822 (M^-); HRMS (+FAB) calcd for $C_{68}H_6$ 822.0470, found 822.0478.

Dimeric Compound 2. A mixture of C_{60} (36 mg, 0.050 mmol) and phthalazine (27.4 mg, 0.21 mmol) was vigorously shaken together with a milling ball in a stainless steel capsule for 1 h by the use of a high-speed vibration mill under an atmosphere of nitrogen. The reaction mixture was further heated at 200 °C for 2 h and then dissolved in 4 mL of ODCB to give a dark brown solution, which was separated by HPLC (a Cosmosil 5PBB column/ODCB) to give unchanged C_{60} (22 mg, 61%) and dimeric compound **2** (5.4 mg, 14%) as brown powder: mp >300 °C; ^{1}H NMR δ 8.03 (AA′BB′, 1H), 7.82 (AA′BB′, 1H), 6.09 (s, 1H); ^{13}C NMR δ 157.03, 154.67, 148.13, 147.04, 146.90, 146.77, 146.68, 146.59, 146.03, 146.00, 145.98, 145.83, 145.64, 145.28, 145.18, 144.96, 144.46, 143.98, 143.14, 143.09, 142.74, 142.40, 142.27, 142.18, 142.11, 142.00, 141.31, 141.00, 140.60, 140.53, 136.23, 129.43, 129.18, 126.45, 71.56, 58.63; UV−vis ($CHCl_3$) λ_{max} (log ϵ) 259 (5.19), 327 (4.81), 420sh (3.9), 546sh (3.3), 712 (2.5); MS (-APCI) m/z 1542 (M^-).

Dimeric Compound 6. A solution of dimeric compound **2** in $CHCl_3$ (3×10^{-5} M) was irradiated by a 275 W incandescent lamp from a distance of 25 cm. The reaction was monitored by UV−vis spectrometry and HPLC analysis (a Buckyprep column/toluene). After irradiation for 1 h, the reaction was complete. In another experiment, a solution of **2** (4.4 mg, 0.0029 mmol) in ODCB (12 mL) was heated at 50 °C for 3 h. Removal of the solvent gave a dark brown residue, which was washed with pentane (40 mL × 4) to give dimeric compound **6** (4.4 mg, 100%) as a brown powder: mp > 300 °C; ^{1}H NMR δ 7.87−7.57 (m, 4H), 5.87 (s, 1H), 5.11 (s, 1H); ^{13}C NMR δ 155.06, 150.41, 149.91, 149.34, 149.26, 148.79, 148.65, 148.16, 147.90, 147.81, 147.42, 147.33, 147.13, 147.09, 147.02, 146.90, 146.57, 146.48, 146.43, 146.16, 146.00, 145.78, 145.57, 145.53, 145.52, 145.48, 145.46, 145.26, 145.16, 145.14, 144.97, 144.40, 144.25, 144.06, 144.01, 143.94, 143.84, 143.82, 143.75, 143.46, 143.26, 143.24, 143.14, 143.05, 142.98, 142.75, 142.66, 142.50, 142.17, 141.13, 140.82, 140.66, 139.58, 138.63, 133.68, 133.29, 133.12, 130.93, 130.06, 129.29, 128.09, 125.66, 79.64, 70.84, 70.18, 69.79, 68.42, 55.16; UV−vis ($CHCl_3$) λ_{max} (log ϵ) 261 (5.18),433 (3.8), 638 (2.7), 700 (2.2); MS (-APCI) m/z 1542 (M^-).

Acknowledgment. We are grateful to the Japan Society for the Promotion of Science (RFTF97R11601) for financial support.

Supporting Information Available: ^{1}H NMR and ^{13}C NMR spectra for the compounds **1**, **2**, and **6**. This material is available free of charge via the Internet at http://pubs.acs.org.

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