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Photodimerization of a *m*-Phenylenebis(arylmethanofullerene): The First Rigorous Proof for Photochemical Inter-Fullerene [2 + 2] Cycloaddition

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The functionalization of C_{60} offers a valuable tool for obtaining new materials with special physical and electronic features. The electron-accepting and -conducting properties of the fullerene cage can be utilized in different types of molecular devices.[1] An example is the use of processable fullerene derivatives in bulk heterojunction photovoltaic cells in which the fullerene functions as a continuous *n*-type semiconducting network.[2] For optimum electron transport, the fullerene cages have to be assembled in some sort of (linear) array. Therefore, we initiated a study of functionalized molecules containing two or more C_{60} units that can adopt conformations in which the fullerene cages are in close proximity. This type of smallest “oligomeric” C_{60} may serve as a model for more extended fullerene arrays and clarify certain aspects of the reported behavior of C_{60} in the solid state when exposed to light,[3] high pressure,[4] and reducing species.[5]

To date, several compounds incorporating two remote C_{60} units including compounds with general structure “C_{60}−spacer−C_{60}” have been reported.[6,7] We envisaged that an appropriate choice of spacer could lead to well-defined interactions between the two independent fullerene units. On the basis of molecular models we selected a *m*-phenylenebis(methanofullerene) with general structure R-C_{61}−(*1,3*-Ph)−C_{61}-R as a synthetic target, since conformational freedom allows the two fullerene cages to be in close contact.

To avoid solubility problems we prepared *m*-phenylenebis(arylmethanofullerene) **2b** carrying four solubilizing chains via a double Bamford−Stevens protocol[8] from bis-tosylhydrazone **1**[9] (Scheme 1). Reaction of **1** with sodium methoxide (1.96 equiv) in the presence of excess C_{60} (3.6 equiv) at 70−75 °C in 1,2-dichlorobenzene (ODCB)/pyridine afforded a complex isomeric mixture (36%) containing the expected bisfulleroid **2a**. Upon heating (ODCB, reflux) the isomeric mixture was cleanly converted into the highly soluble *m*-phenylenebis(arylmethanofullerene) **2b** in 94% yield.

In contrast to the thermal behavior of **2a**, prolonged irradiation of a deoxygenated solution of **2a** (150 W sodium flood lamp) in ODCB afforded a clean steady-state mixture consisting of **2b** (∼40%) and a new compound (∼60%) according to HPLC and TLC analysis. Irradiation of **2b** under identical conditions gave the same result, indicating that the new compound is formed from **2b**, not **2a**. The UV−vis characteristics of the new compound, obtained from HPLC diode array detection (Figure 1), lacked any resemblance with a (mono)1,2-substituted fullerene of the type present in **2b**. Especially the weak absorption bands in the 400−800 nm region were diagnostic for a fullerene bis-addition product. On the basis of detailed studies on the regiochemistry of 2-fold additions to C_{60} by Hirsch and co-workers,[10] we were able to unambiguously assign the UV−vis data to a *cis*-3 regioisomer, which is consistent with the formation of *photodimer* **2c** from **2b**. Structure **2c** is in full agreement with the predicted unique dimerization site for two specific (enantiotopic) *cis*-3 C=C bonds in each fullerene moiety of **2b**.[11] Since **2c** can be formed only as a “meso” dimer (with C_S symmetry), the asymmetry of the dimerization site does not lead to two isomeric products.

Photodimer **2c** was obtained in pure form (84% based on 60% conversion) after separation from **2b** using flash chromatography with a silica gel column and CS_2/toluene (90/10) as the eluent. The 500 MHz ^1H NMR spectrum of **2c** (Figure 2) recorded in CS_2 at 25 °C showed resonances for the bridging *m*-phenylene unit (8.50 (H_2), 7.74 (H_4, H_6), and 7.29 (H_5) ppm) shifted upfield with respect to **2b** (8.75 (H_2), 8.12 (H_4, H_6), and 7.65 (H_5) ppm). These shifts are probably caused by the effect of two rigidly interlocked fullerene cages in dimer **2c**.

In sharp contrast to the unsubstituted C_{60} photodimer (C_{120})[7d] and structural analogues,[7a,c,e] **2c** displayed reasonable solubility in common fullerene solvents (toluene, ODCB, CS_2). Hence, a ^{13}C NMR spectrum in CS_2 was obtained without much difficulty (Figure 3). As compared to **2b**, photodimer **2c** showed four signals for fullerene-sp^3 carbon atoms (δ 79.65, 74.71 (cyclopropyl) and δ 76.00, 73.14 (cyclobutyl)) and a total of 53 fullerene-sp^2 carbons (of a possible 56) which is in full agreement with its C_S symmetry.

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(11) The *cis*-3 position as unique dimerization site in **2b** was predicted from Darling molecular models and computer-generated molecular models using Hyperchem, version 5.1. A preliminary modeling study suggests that it is hard to design other spacers (apart from *m*-phenylene) in which two parallel C=C bonds (from different C_{60} fragments) can cyclodimerize without the introduction of a substantial amount of strain in the product.

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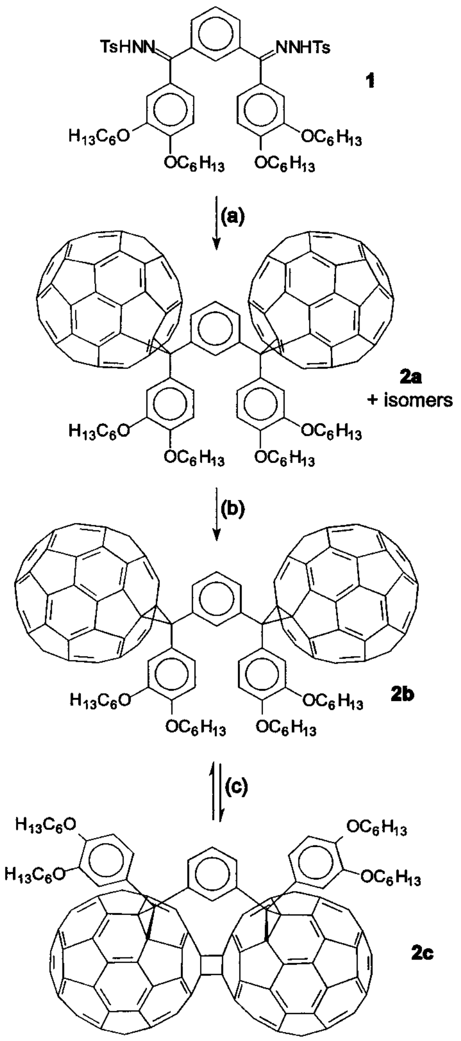
Scheme 1. Synthesis of *m*-Phenylenebis(arylmethanofullerene) **2b** and Photodimerization Process **2b**→**2c**[a]



[a] Reagents and conditions: (a) NaOMe, pyridine/ODCB, C_{60}, 70−75 °C. (b) ODCB, Δ. (c) ODCB, hν, 17 °C.

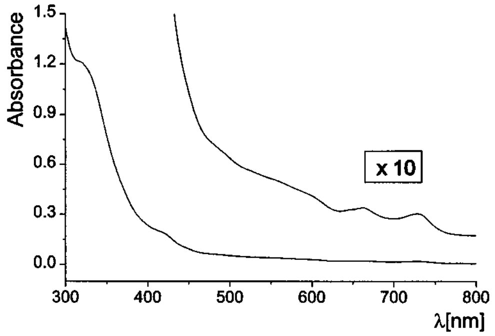


Figure 1. UV−vis spectrum of photodimer **2c** in toluene.

The MALDI-TOF-MS data for **2c** showed the expected molecular ion with most intense peak at $m/z = 2097.0$ (M + 1) (calculated for $^{12}C_{163}(^{13}C)H_{64}O_4$ (M + 1): $m/z = 2097.5$).

Control experiments showed that the photodimerization process **2b**→**2c** is significantly retarded by molecular oxygen, implying a mechanism involving the (methano)fullerene triplet excited state. A similar effect was reported for the photopolymerization process in thin solid films of C_{60}.[3a] Furthermore we observed complete cycloreversion of **2c** to **2b** within 15 min in refluxing ODCB which is quite similar to the behavior reported for C_{120}[7d] and higher C_{60} oligomers,[12] which revert to C_{60} upon heating.

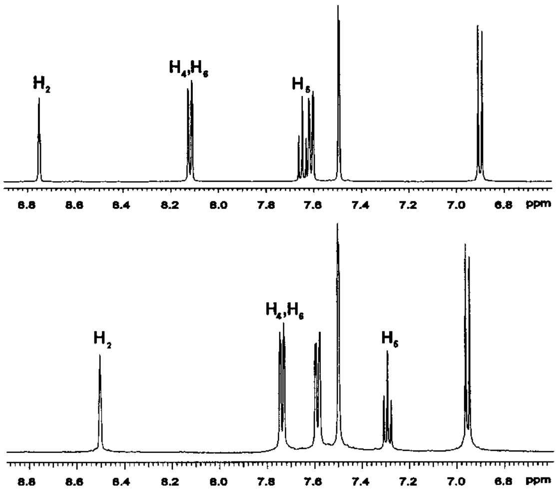


Figure 2. ^1H NMR spectra of **2b** (top) and **2c** (bottom) recorded in CS_2 at 25 °C.

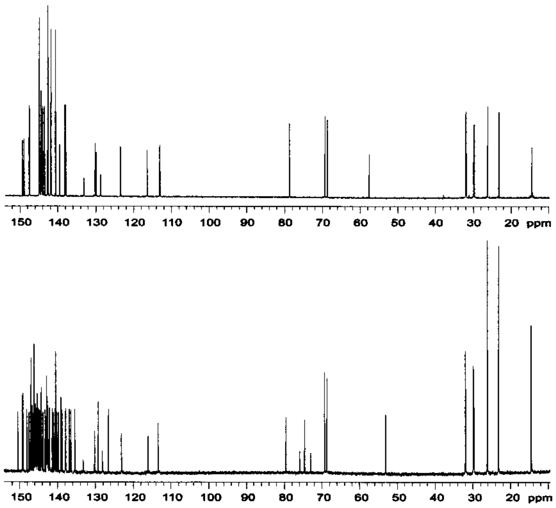


Figure 3. ^{13}C NMR spectra of **2b** (top) and **2c** (bottom) recorded in CS_2 at 25 °C.

The three different fullerenes **2a**, **2b**, and **2c** displayed identical behavior when solutions in ODCB were irradiated for 44 h at 20 °C. In all cases mixtures of **2c**/**2b** of fairly identical composition (58/42 from **2a**, 61/39 from **2b**, and 61/39 from **2c**) were obtained. This confirms the reversibility of the photodimerization process **2b**→**2c**.

The synthesis of **2c** represents the first example of a controlled [2 + 2] cycloaddition process of fullerenes. It adds clear proof to long-standing proposals on structures and mechanisms involved in solid-state photo- and pressure-polymerized C_{60}. Since [2 + 2] cycloaddition (e.g., the interconversion **2b**→**2c**) will ultimately influence the performance of devices in which the fullerene phase plays a role as electron-accepting/transporting medium, the presence of parallel oriented C=C bonds in the contact area between adjacent C_{60} moieties has to be taken into account in the design of fullerene arrays.

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Supporting Information Available: Synthetic procedures and characterization data for compounds **1**, **2a**, **2b,** and **2c** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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