

Fullerene–Acene Chemistry: Diastereoselective Synthesis of a *cis,cis*-Tris[60]fullerene Adduct of 6,8,15,17-Tetraphenylheptacene

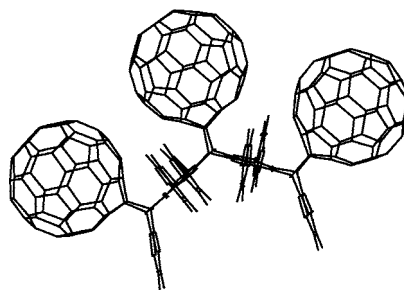
Glen P. Miller* and Jonathan Briggs

Department of Chemistry, University of New Hampshire,
Durham, New Hampshire 03824

gpm@cisunix.unh.edu

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ABSTRACT



A one-pot, diastereoselective synthesis of a *cis,cis*-tris[60]fullerene adduct of 6,8,15,17-tetraphenylheptacene has been demonstrated starting from [60]fullerene and 5,7,9,14,16,18-hexahydro-6,8,15,17-tetraphenylheptacene.

Numerous supramolecular assemblies involving electron-poor [60]fullerene and electron-rich arenes are known. The electron-rich arenes include hydroquinone,¹ cyclotrimeratrylene,² and calixarenes.³ In each case, weak π – π donor–acceptor interactions contribute to the supramolecular assembly, while fullerene–arene van der Waals interactions help to stabilize the resulting complex. Recently, we demonstrated^{4,5} the use of a different noncovalent interaction, namely, [60]fullerene–[60]fullerene π -stacking, during the diastereoselective syn addition of [60]fullerenes across 6,13-disubstituted pentacenes. Since [60]fullerene is a weak electron donor, π – π

donor–acceptor interactions cannot be invoked to explain the syn addition of [60]fullerenes across 6,13-disubstituted pentacenes. Instead, the [60]fullerene–[60]fullerene interactions are purely van der Waals (i.e., π -stacking) in nature. An X-ray crystal structure⁶ of the *cis*-bis[60]fullerene adduct of 6,13-diphenylpentacene, **1**, confirms the syn addition and the importance of van der Waals interactions in stabilizing this adduct.

In an effort to further exploit [60]fullerene–[60]fullerene π -stacking interactions for the assembly of interesting structures, we now report a highly diastereoselective synthesis of a *cis,cis*-tris[60]fullerene adduct of 6,8,15,17-tetraphenylheptacene, **2**. Compound **2** is prepared in one pot starting with [60]fullerene and 5,7,9,14,16,18-hexahydro-6,8,15,17-

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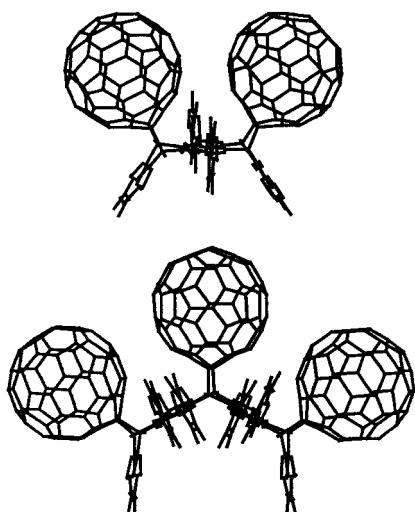
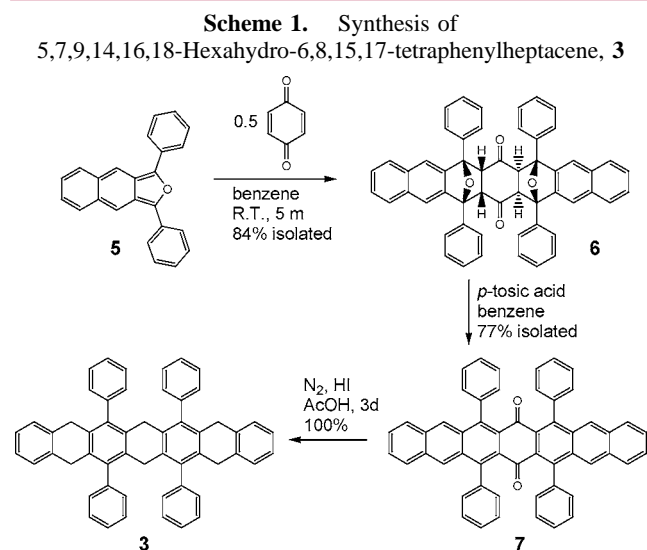


Figure 1. *cis*-Bis[60]fullerene adduct of 6,13-diphenylpentacene, **1** (top), and *cis,cis*-tris[60]fullerene adduct of 6,8,15,17-tetraphenylheptacene, **2** (bottom).

tetraphenylheptacene, **3**. Compound **3** does not react with [60]fullerene but can be oxidized in situ to afford 6,8,15,17-tetraphenylheptacene **4**, which readily adds 3 equiv of [60]fullerene in a diastereoselective fashion.

Our synthesis of **3** utilizes 1,3-diphenylnaphtho[2,3-*c*]furan, **5**, an excellent diene for Diels–Alder chemistry. Lustrous red crystals of compound **5** were prepared using a modified Cava procedure⁷ and then reacted with 0.5 equiv of *p*-benzoquinone (Scheme 1). The double-Diels–Alder



addition is complete within a few minutes at room temperature and yields a single diastereomer of 6,17,8,15-diepoxy-

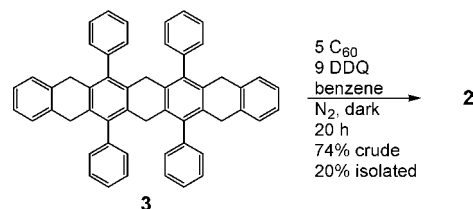
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6,8,15,17-tetraphenylheptacene-7,16-quinone, **6**. ¹H and ¹³C NMR spectra suggest that **6** forms via an endo,exo Diels–Alder sequence analogous to the carefully studied reaction between 1,3-diphenylisobenzofuran and *p*-benzoquinone.⁸ A double dehydration of **6** with *p*-tosic acid in benzene affords previously unknown 6,8,15,17-tetraphenylheptacene-7,16-quinone, **7**. Reduction of **7** with hydriodic acid in acetic acid gives compound **3** in quantitative yield.

Quantitative formation of **3** was an unexpected but welcome result. Similar reductive conditions have been utilized for over 100 years on smaller acene quinones and related systems. Thus, Liebermann showed⁹ that HI and red phosphorus would reduce 9,10-anthraquinone at elevated temperatures to form a mixture of anthrone, 9,10-dihydroanthracene, and anthracene. More recently, Harvey noted¹⁰ that mixtures of HI and acetic acid convert polycyclic aromatic quinones into their corresponding arenes or dihydroarenes in good to excellent yields. We expected the HI/AcOH reduction of **7** to produce either 7,16-dihydro-6,8,15,17-tetraphenylheptacene or 6,8,15,17-tetraphenylheptacene, **4**, but not the “over-reduced” **3**. Only a small number of other hydrogenated heptacenes are known for comparison to **3**. Hart observed¹¹ spontaneous isomerization of 5,9,14,18-tetrahydroheptacene into the thermodynamically preferred 5,8,15,18-tetrahydroheptacene. With its alternating benzenoid rings and intact terphenyl moieties, compound **3** persists indefinitely and can be considered a protected, stable version of acene **4**.

Because acenes larger than pentacene are known to degrade via photooxidation¹² and photodimerization¹³ reactions, we sought to prepare and react heptacene **4** in situ. Thus, compound **3** was heated in benzene along with excess 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) and [60]fullerene (Scheme 2). After rinsing with ethanol to

Scheme 2. Synthesis of *cis,cis*-Tris[60]fullerene Adduct of 6,8,15,17-Tetraphenylheptacene, **2**



remove hydroquinone byproduct and excess DDQ, trisadduct **2** was obtained in 74% crude yield based on mass balance and ¹H NMR integration. A ¹H NMR spectrum of the crude

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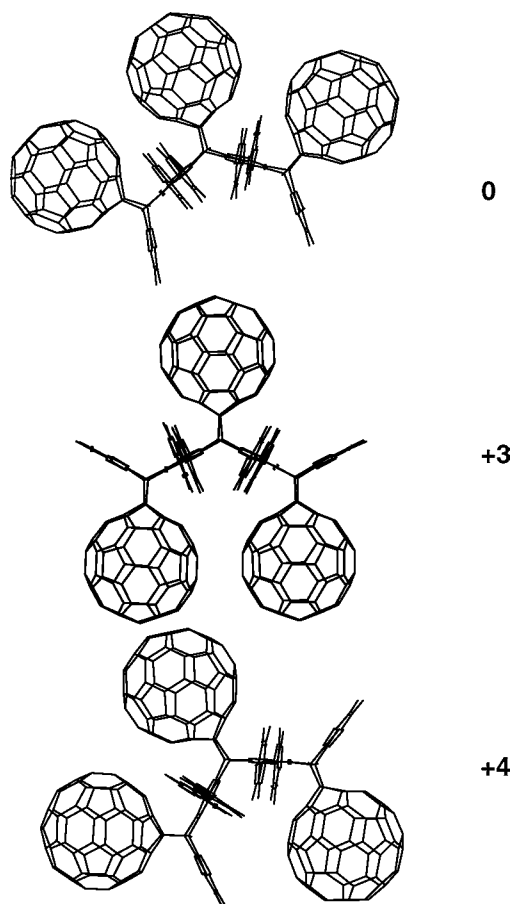


Figure 2. Relative MM2 strain energies (kcal/mol) for C_{2v} symmetric *cis,cis*-trisadduct **2** (top), C_{2v} symmetric *trans,trans*-trisadduct **8** (middle), and C_s symmetric *cis,trans*-trisadduct **9** (bottom).

reaction mixture reveals a reasonably clean transformation to trisadduct **2**. Minor byproduct signals are observed and appear to be consistent with oligomerization reactions in which, for example, a single [60]fullerene bridges two acenes.

As expected, a ^{13}C NMR spectrum indicated the presence of excess [60]fullerene in the crude reaction mixture. Isolating trisadduct **2** from the excess [60]fullerene proved to be difficult. TLC analyses indicate that trisadduct **2** and [60]fullerene have nearly identical retention behaviors on silica under all solvent conditions tested. Consequently, silica column chromatography is complicated by coelution of [60]fullerene and **2**. Compound **2** was eventually obtained pure,¹⁴ albeit in a modest 20% isolated yield, via successive runs on a flash silica column with neat CS_2 as the eluant.

In principle, three tris[60]fullerene adducts can form (Figure 2) upon reacting [60]fullerene with 6,8,15,17-tetra-

phenylheptacene. These are C_{2v} symmetric *cis,cis*-trisadduct **2**, C_{2v} symmetric *trans,trans*-trisadduct **8** and C_s symmetric *cis,trans*-trisadduct **9**. The reaction is highly diastereoselective for only one of these compounds. A ^1H NMR spectrum of the pure product reveals a molecule with C_{2v} symmetry, thereby eliminating compound **9** from consideration. Thus, two methine singlets integrating for 4 and 2 protons are observed at 5.69 and 5.80 ppm, respectively, confirming three [60]fullerene cycloadditions and two planes of symmetry. The only other ^1H NMR signals attributable to the heptacene backbone are a single set of AA'MM' signals at 7.45 and 7.53 ppm. These can only correspond to the two equivalent, terminal benzene rings of the heptacene backbone. Consequently, 3 equiv of [60]fullerene must cycloadd across the (C5,C18), (C7,C16), and (C9,C14) carbons of heptacene **4**.

A total of 63 ^{13}C NMR signals are expected for either **2** or **8**. These include 32 signals for the terminal [60]fullerene moieties, 17 signals for the central [60]fullerene moiety, 8 signals for the heptacene backbone, and 6 signals for the phenyl substituents (slowly rotating, vide infra). A ^{13}C NMR spectrum of pure product reveals four unique sp^3 carbons. These are assigned to the two unique methine carbons on the heptacene backbone (52.2 and 55.1 ppm) and two unique quaternary carbons on the [60]fullerene skeletons (72.1 and 72.5 ppm). A total of 53 distinct ^{13}C signals are observed in the sp^2 region between 125 and 156 ppm, whereas 59 signals are expected. A close examination of this congested region indicates several shoulders alongside discernible signals, indicating instances of coincidental overlap.

MM2 calculations have proven to be a valuable and convenient tool for comparing diastereomeric bis[60]fullerene adducts of 6,13-disubstituted pentacenes.⁶ They fare far better in this regard than either AM1 or PM3 semiempirical calculations,¹⁵ presumably because the latter do not consider van der Waals forces. Compared to **8** and **9**, compound **2** maximizes [60]fullerene–[60]fullerene π -stacking interactions and is predicted by MM2 calculations to be the thermodynamically preferred isomer (Figure 2).

Further evidence for formation of a *cis,cis* structure (i.e., **2**) comes from a careful examination of the ^1H NMR spectrum for the pure product. As in the case of *cis*-bisadduct **1**,^{4,5} five separate phenyl ^1H NMR signals are observed, indicating slow rotation of the phenyl groups on the NMR time scale. One set of ortho protons gives rise to a quasi-doublet at 6.86 ppm and is considerably shielded compared

(14) NMR data for **2**: ^1H NMR ($\text{CS}_2/\text{CDCl}_3$) δ 5.69 (s, 4H), 5.80 (s, 2H), 6.84–6.87 (m, 4H), 7.05–7.09 (m, 4H), 7.32–7.37 (m, 4H), 7.41–7.47 (m, 8H), 7.49–7.56 (m, 8H); ^{13}C NMR ($\text{CS}_2/\text{CDCl}_3$) δ 52.16, 55.09, 72.12, 72.47, 125.55, 127.24, 127.58, 128.20, 128.42, 128.70, 129.19, 129.90, 136.20, 136.59, 136.72, 136.86, 138.82, 138.84, 139.57, 139.79, 139.83, 141.35, 141.48, 141.57, 141.81, 141.82, 141.85, 141.88, 141.94, 142.32, 142.35, 142.40, 142.41, 142.44, 142.48, 142.54, 142.76, 144.42, 144.46, 144.50, 145.06, 145.10, 145.12, 145.18, 145.22, 145.44, 145.45, 145.95, 145.98, 146.00, 146.22, 146.26, 146.27, 147.30, 147.32, 154.96, 155.46.

(15) MM2 calculations correctly predict that *cis*-bis[60]fullerene adduct **1** is preferred to the corresponding *trans* isomer. Moreover, the 3.08 Å (atoms of closest contact) and 9.84 Å (fullerene centroid-to-centroid) distances between adjacent [60]fullerenes predicted by MM2 are remarkably close to the 3.065 and 9.805 Å distances observed in the X-ray structure of **1**. AM1 and PM3 calculations place the atoms of closest contact on adjacent [60]fullerenes ~ 4.2 Å apart and the fullerene centroid-to-centroid distance at ~ 10.9 Å. See ref 3 for more details.

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to the other set of ortho protons that give rise to a quasi-doublet at 7.46 ppm. Likewise, a quasi-triplet at 7.07 ppm corresponds to a set of shielded meta protons. We assign the shielded ortho and meta ^1H signals, respectively, to those protons on **2** that are syn to the [60]fullerene moieties (Figure 3). These protons are shielded due to secondary anisotropic

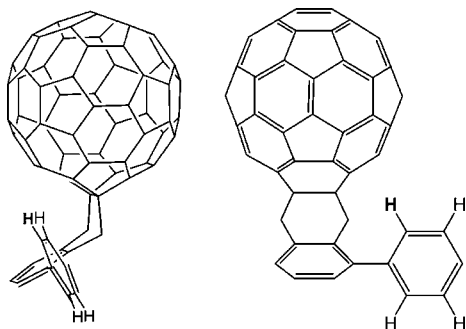


Figure 3. Two views of a partial [60]fullerene-acene structure with ortho and meta phenyl protons shown. The syn-ortho protons (in boldface above) on **1**, **2**, **10**, and **11** are approximately 3 Å removed from a [60]fullerene cage.

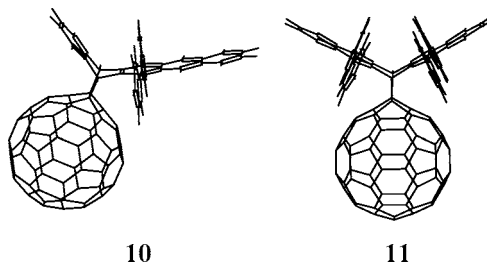
fields created by π -bonds on the [60]fullerene surface. The syn-ortho protons on **2** sit almost directly above and approximately 3 Å removed from two 6–5 bonds, one on each of two flanking [60]fullerene moieties. Each 6–5 bond is one bond removed from a quaternary carbon and is formally part of a benzene ring substructure on the corresponding [60]fullerene surface.

Although relatively few [60]fullerene-acene compounds with appropriately positioned phenyl substituents are known, [60]fullerene shielding of syn phenyl and especially syn-ortho protons is a common feature of those available for comparison. The syn-ortho protons on compounds **1**, **10**, and **11** all exhibit substantial upfield shifts relative to their anti-ortho proton counterparts (Table 1). The shielding of syn-ortho protons on **10** and **11** indicates that two [60]fullerene moieties are not required. However, the extent of shielding is greater when a syn-ortho proton is syn to two [60]fullerene moieties as in **1** and **2**. This is perhaps best gauged by comparing the chemical shift difference between syn-ortho and anti-ortho protons for each molecule ($\Delta\delta_o$ values, Table 1). Thus, compounds **1** and **2** with two [60]fullerenes surrounding each syn-ortho proton have $\Delta\delta_o$ values that are roughly twice those of compounds **10** and **11**. Considerable

Table 1. ^1H NMR Chemical Shifts (δ) for Syn-Ortho and Anti-Ortho Protons on [60]Fullerene-Acene Compounds^a

compd	syn δ_o	anti δ_o	$\Delta\delta_o$ (anti δ_o – syn δ_o)
1	7.09	7.65	0.56
2	6.86	7.46	0.60
10	7.32	7.61	0.29
11	7.01	7.38	0.37

^a All spectra were recorded in CS_2 - CDCl_3 solvent.



additional work would be required to quantify the relationship. Given the small number of molecules impacted, this may not be reasonable. Qualitatively, however, we can expect significant shielding of all syn-ortho protons on related [60]fullerene-acene adducts. To this end, the ^1H NMR spectrum of the tris[60]fullerene product is consistent with *cis,cis*-**2** but not *trans,trans*-**8**. Thus, both sets of ortho protons on **8** are subject to [60]fullerene shielding and the corresponding $\Delta\delta_o$ value should be substantially less than that observed for **1**. Instead, the $\Delta\delta_o$ value for **2** is modestly larger than that observed for **1**, consistent with a structure bearing one and only one set of shielded syn-ortho protons.

In summary, a diastereoselective synthesis of a *cis,cis*-tris[60]fullerene adduct of 6,8,15,17-tetraphenylheptacene, **2**, has been demonstrated starting with [60]fullerene and 5,7,9,14,16,18-hexahydro-6,8,15,17-tetraphenylheptacene. The assignment of a *cis,cis* stereochemistry for **2** is based upon previous results for structurally similar compounds, MM2 calculations, and a careful analysis of NMR data. The successful synthesis of **2** suggests that [60]fullerene-[60]fullerene π -stacking should be added to the synthetic chemist's list of noncovalent interactions that can drive the assembly of interesting structures.

Supporting Information Available: ^1H and ^{13}C NMR spectra for compounds **2**, **3**, **5–7**, **10**, and **11**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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