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Probing the spatial requirements for [60]fullerene–[60]fullerene π-stacking and the *syn* addition of [60]fullerenes across acenes☆

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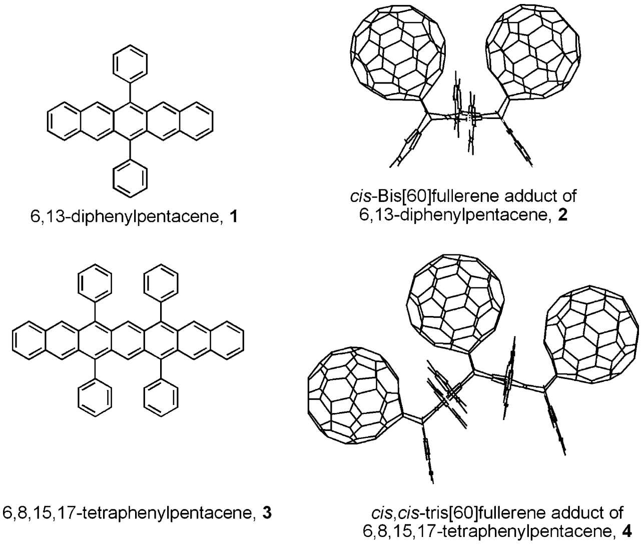
Abstract—The reaction between 2 equiv of [60]fullerene and 6,8,15,17-tetraphenylheptacene-7,16-quinone leads to both *cis* and *trans*-bis[60]fullerene adducts. This result contrasts sharply with the highly diastereoselective *syn* additions of [60]fullerenes across 6,13-diphenylpentacene and 6,8,15,17-tetraphenylheptacene. The importance of spatially dependent [60]fullerene–[60]fullerene π-stacking interactions in promoting a *syn* addition of [60]fullerenes is discussed.

1. Introduction

Recently, we reported[1–3] the highly diastereoselective *syn* addition of [60]fullerenes across several acenes including 6,13-diphenylpentacene and 6,8,15,17-tetraphenylheptacene. Thus, 2 equiv of [60]fullerene cycloadd across 6,13-diphenylpentacene, **1**, to produce *cis*-bis[60]fullerene adduct **2**[1,2] and 3 equiv of [60]fullerene cycloadd across 6,8,15,17-tetraphenylheptacene, **3**, to produce *cis*, *cis*-tris[60]fullerene adduct, **4** (Fig. 1).[3] Diastereoselective *syn* additions of [60]fullerene are observed for reactions that are run under both kinetically controlled (i.e., irreversible) and thermodynamically controlled (i.e., reversible) conditions.[2] We have hypothesized[2–4] that the diastereoselectivity arises from favorable van der Waals interactions (i.e., π-stacking) between adjacent [60]fullerene moieties on **2** and **4**. These interactions presumably lower the corresponding *syn* transition state and *syn* ground-state energies. While a limited number of experimental and computational data support this proposal,[2,4] there has been no attempt to exploit the spatial requirements of π-stacking in order to directly probe the link between [60]fullerene–[60]fullerene π-stacking and the *syn* addition of [60]fullerenes. In the present study, the synthesis of 6,8,15,17-tetraphenylheptacene-7,16-quinone, **5**, is described as is its Diels–Alder reactivity with [60]fullerene. Quinone **5** was chosen because its Diels–Alder reactive sites are too far removed from one another to accommodate [60]fullerene–[60]fullerene π-stacking. If [60]fullerene–[60]fullerene π-stacking is responsible for the *syn* addition of [60]fullerenes across **1** and **3**, then [60]fullerenes should add with reduced diastereoselectivity across **5**.



6,13-diphenylpentacene, **1**

cis-Bis[60]fullerene adduct of 6,13-diphenylpentacene, **2**

6,8,15,17-tetraphenylpentacene, **3**

cis,*cis*-tris[60]fullerene adduct of 6,8,15,17-tetraphenylpentacene, **4**

Figure 1. Structures of acenes and [60]fullerene–acene adducts.

Keywords: [60]Fullerene; Diels–Alder; Acene quinone; Heptacene quinone; *syn* Addition.

☆ Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2003.11.010.

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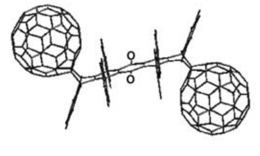

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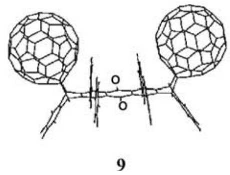

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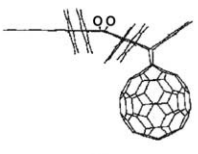

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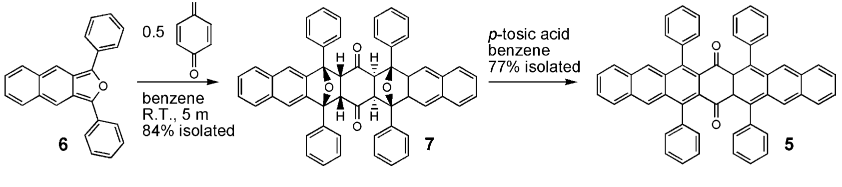
2. Results

Quinone **5** is prepared in two steps from 1,3-diphenylnaphtho[2,3-*c*]furan, **6**, and *p*-benzoquinone (Scheme 1). Compound **6** is prepared using a modified Cava[5] procedure. The double Diels–Alder reaction between **6** and *p*-benzoquinone proceeds in an *endo*, *exo* sequence[6] to afford 6,8,15,17-tetraphenyl-6,17:8,15-dioxido-6,6a,7,7a,8,15,15a,16,16a,17-decahydro-7,16-heptacene quinone, **7**, in 84% isolated yield. Compound **7** is dehydrated with *p*-tosic acid in benzene to afford quinone **5** in 77% isolated yield.

A CS_2 solution containing **5** and a fivefold excess of [60]fullerene is refluxed in the dark under nitrogen for 70 h. NMR spectra of the crude [60]fullerene–acene quinone mixture reveal a 1.1:1 ratio of C_{2h} symmetric *trans*-bis[60]fullerene adduct **8** and C_{2v} symmetric *cis*-bis[60]fullerene adduct **9**. Excess [60]fullerene is removed by flash silica column chromatography with CS_2 as eluent. The remaining mixture is then subject to a second flash silica chromatographic separation using 1:1 (v/v) CS_2/CH_2Cl_2 as eluent. The first bis[60]fullerene adduct band to elute is assigned to the less polar *trans* adduct **8** ($R_f = 0.9$, 19% isolated yield). The second bis[60]fullerene adduct band to elute is assigned to the more polar *cis* adduct **9** ($R_f = 0.69$, 16% isolated yield). Because NMR spectroscopy cannot distinguish between the two diastereomers, the relative stereochemical assignments of **8** and **9** are based entirely on their order of elution off of the polar silica column. While far from ideal, we place some confidence in the assignment based upon known orders of elution for similar compounds. A small amount of a third band is also collected after **9** has completely eluted. A ^1H NMR spectrum suggests that this band includes the C_s symmetric monoadduct of **5** and [60]fullerene, **10**. Due to the low isolated yield of **10**, it was not thoroughly characterized. Both **8** and **9** are thermally unstable and are observed to readily degrade via retro-Diels–Alder reactions upon even mild heating. It is likely that some of compound **10** forms during work-up and separation of the reaction mixture via retro-Diels–Alder reactions of **8** and/or **9**.

The ^1H and ^{13}C NMR spectra for **8** and **9** are remarkably similar. When compared to the spectra for **5**, they provide compelling evidence for the formation of the structures shown. Thus, the ^1H NMR spectrum of **5** includes a set of AA′MM′ multiplets centered at approximately 7.35 and 7.80 ppm. These signals correspond to the equivalent sets of protons on the terminal benzene rings (i.e., the protons on C1–C4 and C10–C13) of the heptacene quinone backbone. A singlet is also observed at 8.16 ppm corresponding to the X protons at C5, C9, C14, and C18 of the heptacene quinone backbone. By contrast, separate ^1H NMR spectra for pure **8** and pure **9** reveal a new set of AA′MM′ multiplets and no X singlet whatsoever. In place of the X singlet is a new singlet at approximately 5.8 ppm that integrates for four protons. The new singlet corresponds to the four equivalent methine protons at the four new sp^3 cycloaddition sites (i.e., at C5, C18, and C9, C14). The results are uniquely consistent with double Diels–Alder cycloadditions across C5, C18 and C9, C14 of the heptacene quinone backbone. Analogous to compounds **2**[1] and **4**,[3] ^1H NMR spectra for **8** and **9** reveal 5 separate phenyl proton signals indicating slow rotation of the phenyl substituents on the NMR time scale.

^{13}C NMR spectra for either **8** or **9** are expected to show a total of 46 signals including 32 due to the fullerene moieties, 8 due to the heptacene quinone backbone and 6 due to the slowly rotating phenyl substituents. In total, 46 ^{13}C signals are observed for **8** and 43 ^{13}C signals are observed for **9**. In both cases, separate resonances are observed at approximately 55 and 71 ppm corresponding to the new sp^3 carbons on the heptacene quinone backbone (i.e., the methine carbons at C5, C18 and C9, C14) and the new sp^3 carbons on the [60]fullerene skeletons, respectively. The spectrum for **8** shows 43 unique sp^2 resonances between 125 and 155 ppm plus a single signal at 186.1 ppm that corresponds to the four equivalent quinone carbons. The spectrum for **9** shows 40 sp^2 resonances between 125 and 155 ppm plus a single signal at 186.2 ppm. The apparent absence of 3 sp^2 resonances between 125 and 155 ppm in the spectrum for **9**



Scheme 1. Synthesis of 6,8,15,17-tetraphenylheptacene-7,16-quinone, **5**.

is attributed to coincidental overlap in this congested region of the ^{13}C spectrum.

Matrix assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectrometry experiments performed on pure samples of both **8** and **9** reveal well-resolved isotopic multiplets corresponding to [60]fullerene cation ($m/z = 720$, 721, 722) and the cation of 6,8,15,17-tetraphenylheptacene-7,16-quinone, $\mathbf{5}^+$ ($m/z =$ 712, 713, 714, 715). The spectra also reveal a weak multiplet at $m/z = 1432$, 1433 corresponding to $\mathbf{10}^+$. No signal corresponding to the molecular ions $\mathbf{8}^+$ or $\mathbf{9}^+$ ($m/z = 2152$) could be seen. The detection of weak signals for $\mathbf{10}^+$ and no signals for $\mathbf{8}^+$ or $\mathbf{9}^+$ indicates facile retro-Diels–Alder degradation of **8** and **9**, probably during laser desorption. Electrospray-ionization time-of-flight (EI-TOF) experiments gave similar results.

3. Discussion

Noncovalent interactions between electron rich arenes and electron poor [60]fullerene have been successfully utilized in the synthesis of several supramolecular structures. The electron rich arenes include hydroquinone,[7] cyclotriveratrylene[8] and various calixarenes.[9] In these assemblies, weak π–π donor–acceptor interactions contribute to the supramolecular assembly while fullerene–arene van der Waals interactions help to stabilize the resulting complex. Because [60]fullerene is an exceptionally weak electron donor, π–π donor–acceptor interactions cannot be invoked to describe assemblies of multiple [60]fullerenes. [60]Fullerene–[60]fullerene interactions must be purely van der Waals (i.e., π-stacking) in nature.[10] Like any van der Waals interaction, [60]fullerene–[60]fullerene π-stacking should be a combination of long-range attractive and short-range repulsive forces. Bringing the [60]fullerene moieties too close to one another would result in severe electrostatic repulsions. Moving the [60]fullerene moieties too far from one another would result in no attractive interaction and no stabilization of the resulting structure. Thus, effective π-stacking requires optimal spacing of adjacent [60]fullerenes.

Because the ^{1}H and ^{13}C NMR spectra for **8** and **9** are so similar, the [60]fullerene moieties on **8** and **9** must experience nearly identical electronic environments. Consequently, the [60]fullerene moieties on *cis*-bis[60]fullerene adduct **9** must not interact (i.e., π-stack) with one another in the ground state. This conclusion is hardly surprising given that the MM2 structure for **9** shows the carbon atoms of closest contact on adjacent [60]fullerenes to be approximately 7 Å apart. This distance is well beyond the [60]fullerene–[60]fullerene van der Waals separation of 3.194(2) Å that is observed in ordered crystals of [60]fullerene·4benzene at 93 K.[11] Most important, there is no preference for the *syn* addition of [60]fullerene across quinone **5**. Instead, there is actually a slight (1.1:1) preference for *anti* addition. This contrasts sharply with the highly diastereoselective *syn* addition of [60]fullerenes across 6,13-diphenylpentacene, **1**, and 6,8,15,17-tetraphenylheptacene, **3**. In each of these latter cases, the Diels–Alder reactive sites on the corresponding acenes are properly positioned to accommodate [60]fullerene–[60]fullerene π-stacking. Thus, both MM2 and X-ray crystal structures[4] place the atoms of closest contact between adjacent [60]fullerene moieties on **2** at 3.1 Å apart. Similarly, MM2 calculations place the atoms of closest contact between adjacent [60]fullerene moieties on **3** at 3.1 Å apart. The link between spatially dependent [60]fullerene–[60]fullerene π-stacking interactions and the diastereoselective *syn* addition of [60]fullerenes across acenes appears incontrovertible.

It is interesting to note that **8** and **9** differ from **2** in that they undergo facile retro-Diels–Alder reactions at temperatures marginally above 25 °C. Similarly, the [60]fullerene–anthracene monoadduct is reported[12] to undergo a facile retro-Diels–Alder reaction at relatively low temperatures. Compound **2** on the other hand is thermally stable to temperatures in excess of 100 °C. The increased thermal stability of **2** can be largely attributed to the stabilizing nature of [60]fullerene–[60]fullerene π-stacking interactions.

Recently, other groups have exploited [60]fullerene–[60]fullerene π-stacking interactions for synthetic gain. Thus, following supramolecular construction of a beautiful honeycomb template on a silver terminated silicon surface, heptameric clusters of [60]fullerene were self-assembled within the pores of the template.[13] Each cluster of seven [60]fullerenes self-orders into a compact, hexagonal array in which each [60]fullerene molecule simultaneously π-stacks with three or more adjacent [60]fullerenes. Other examples include the highly intriguing nanoscopic peapod structures[14] prepared by self-assembling [60]fullerenes inside carbon nanotubes. These assemblies contain chains of π-stacked [60]fullerene molecules, each sitting at van der Waals distance from the next. The successful syntheses of these spectacular supramolecular structures along with compounds **2** and **4** suggests that [60]fullerene–[60]fullerene π-stacking is a new and powerful noncovalent interaction that can drive the assembly of highly interesting structures.

4. Summary and conclusion

The reaction between 6,8,15,17-tetraphenylheptacene-7,16-quinone and excess [60]fullerene leads to two unique bis[60]fullerene adducts, C_{2h} symmetric **8** and C_{2v} symmetric **9**, as well as smaller amounts of C_s symmetric monoadduct **10**. Bisadduct **8** is formed in a slight excess (1.1:1) over **9**. The lack of *syn* diastereoselectivity in this reaction contrasts sharply with the highly diastereoselective *syn* addition of [60]fullerenes across 6,13-diphenylpentacene and 6,8,15,17-tetraphenylheptacene. The presence or absence of *syn* diastereoselectivity in these reactions is closely linked to spatially dependent

[60]fullerene–[60]fullerene π-stacking interactions. Diels–Alder reactive sites on 6,13-diphenylpentacene and 6,8,15,17-tetraphenylheptacene are ideally spaced to accommodate [60]fullerene–[60]fullerene π-stacking while those on quinone **5** are not.

5. Experimental

Modified Cava synthesis of 1,3-diphenylnaphtho[2,3-c]-furan, **6**: The Cava synthesis[5] of **6** begins with a sodium dichromate oxidation of 2,3-dimethylnaphthalene to form naphthalene-2,3-dicarboxylic acid. Due to the inaccessibility of 2,3-dimethylnaphthalene, we reacted α,α,α′,α′-tetrabromo-*o*-xylene (48 mmol) with maleic anhydride (92 mmol) and NaI (347 mmol) in DMF solvent (70°, 19 h).[15] The initially formed 2,3-naphthalic anhydride hydrolyses during aqueous work-up to give naphthalene-2,3-dicarboxylic acid in 73% isolated yield.

5.1. 6,8,15,17-Tetraphenyl-6,17:8,15-dioxido-6,6a,7,7a,8,15,15a,16,16a,17- decahydro-7,16-heptacene quinone, 7

p-Benzoquinone (0.240 g, 2.22 mmol) is added to a suspension of **6** (1.48 g, 4.63 mmol) in benzene (40 mL). The initial dark red suspension gives way to a light pink suspension upon stirring for approximately 5 min. The suspension is filtered and washed with hexane to afford **7** (1.39 g, 84%). ^{1}H NMR ($CDCl_3$) δ 3.40 (s, 2H); 4.43 (s, 2H); 6.72–6.77 (m, 4H); 7.14–7.19 (m, 4H); 7.28–7.38 (m, 6H); 7.44–7.49 (m, 2H); 7.57 (s, 2H); 7.65–7.74 (m, 8H); 7.76–7.80 (m, 2H); 7.89–7.94 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 58.16, 64.53, 89.43, 92.11, 118.03, 118.09, 121.62, 121.66, 125.85, 126.86, 126.94, 128.12, 128.33, 128.55, 128.79, 129.34, 132.65, 133.03, 134.25, 136.71, 143.83, 144.81, 204.57.

5.2. 6,8,15,17-Tetraphenylheptacene-7,16-quinone, 5

A mixture of compound **7** (1.39 g, 1.86 mmol), *p*-toluenesulfonic acid (1.34 g, 7.79 mmol) and benzene (50 mL) is heated to reflux for 15 h. The solution is initially light yellow, then pink, red, and eventually brown-black. The benzene solution is washed with saturated aqueous sodium bicarbonate solution, water, and brine and then concentrated under reduced pressure. The solid residue is washed with acetone (total volume approximately 100 mL) to afford the brownish-yellow **5** (1.02 g, 77.3%). ^{1}H NMR ($CDCl_3$) δ 7.33–7.37 (m, 8H); 7.41–7.46 (m, 16H); 7.78–7.81 (m, 4H); 8.16 (s, 4H); ^{13}C NMR ($CDCl_3$) δ 126.9, 127.3, 128.0, 128.5, 128.6, 130.2, 131.2, 132.2, 132.4, 137.6, 140.5, 189.0.

5.3. *trans*-Bis[60]fullerene adduct of 6,8,15,17-tetraphenylheptacene-7,16-quinone, 8

^{1}H NMR ($CDCl_3/CS_2$) δ 5.75 (s, 4H); 6.94–6.98 (m, 4H); 7.14–7.19 (m, 4H); 7.27–7.35 (m, 10.8H, coincident with residual chloroform and fortuitous benzene resonances); 7.42–7.47 (m, 8H); 7.52–7.56 (m, 4H); ^{13}C NMR ($CDCl_3/CS_2$) δ 54.71, 71.33, 125.82, 127.16, 127.76, 128.02, 128.07, 128.21, 128.60, 129.43, 134.03, 136.20, 136.84, 137.17, 137.69, 139.64, 139.90, 140.56, 141.51, 141.63, 141.81, 141.85, 141.87, 142.13, 142.42, 142.49, 142.72, 142.89, 142.97, 144.39, 144.49, 144.97, 145.05, 145.07, 145.18, 145.26, 145.31, 145.40, 146.06, 146.08, 146.28, 146.34, 147.39, 154.44, 154.91, 186.09.

5.4. *cis*-Bis[60]fullerene adduct of 6,8,15,17-tetraphenylheptacene-7,16-quinone, 9

^{1}H NMR ($CDCl_3/CS_2$) δ 5.77 (s, 4H); 6.89–6.91 (m, 4H); 7.12–7.17 (m, 4H); 7.27–7.31 (m, 6.4H, coincident with residual chloroform resonance); 7.39–7.42 (m, 4H); 7.45-7.51 (m, 8H); 7.57–7.61 (m, 4H); ^{13}C NMR ($CDCl_3/CS_2$) δ 54.75, 71.36, 125.77, 127.17, 127.82, 128.03, 128.18, 128.82, 129.24, 133.96, 136.17, 136.86, 137.33, 138.02, 139.62, 139.88, 140.48, 141.48, 141.62, 141.84, 141.88, 142.22, 142.43, 142.49, 142.74, 142.85, 142.99, 144.39, 144.49, 144.97, 145.09, 145.19, 145.27, 145.31, 145.32, 146.06, 146.08, 146.30, 146.36, 147.38, 154.43, 154.89, 186.20.

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