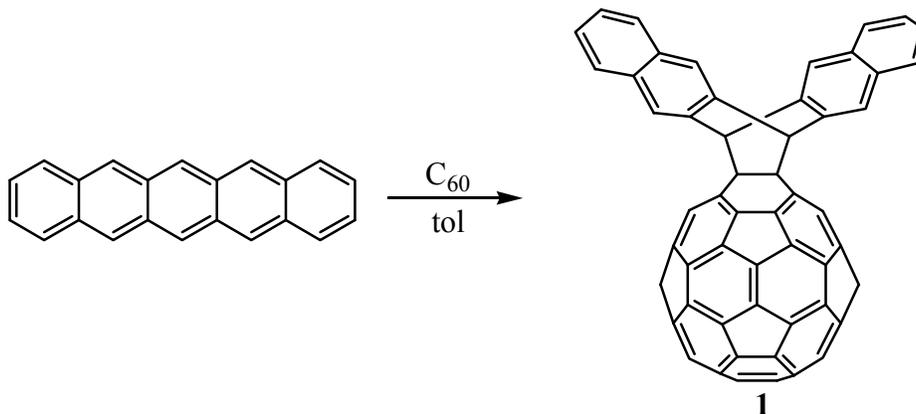


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Interested in the possibility that two [60]fullerenes could cycloadd across a single pentacene backbone, we studied the reaction between pentacene and [60]fullerene in boiling toluene. Under these conditions, a C_{2v} symmetric [60]fullerene-pentacene monoadduct, **1**, forms in 54% yield (Scheme 1), a result of [60]fullerene cycloaddition across the central 6,13 carbons of the pentacene backbone (Mack, J.; Miller, G. P., *Full. Sci. Tech.* **1997**, *5*, 607-614).



Scheme 1. Solution phase Diels-Alder cycloaddition between [60]fullerene and pentacene proceeds regioselectively across the central ring of pentacene.

Using a five-fold excess of [60]fullerene, the yield of C_{2v} **1** can be increased to 90%. The reaction is highly regioselective and shows no evidence for formation of either a C_s symmetric monoadduct (i.e., resulting from addition across the 5,14 carbons of the pentacene backbone), or the *cis* or *trans*-bis[60]fullerene-pentacene adducts, **2** and **3** respectively (Figure 1).

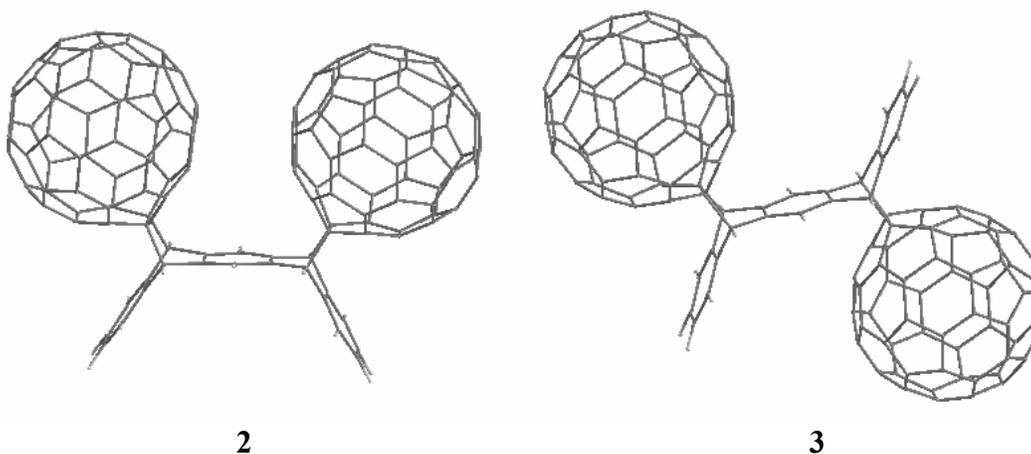


Figure 1. *Cis* and *trans*-bis[60]fullerene-pentacene adducts, **2** and **3** respectively.

An X-ray crystal structure (Figure 2) of **1** reveals a similar nested crystal packing as reported by Kräutler and coworkers for the [60]fullerene-anthracene monoadduct crystal (Miller, G. P.; Briggs, J.; Mack, J.; Lord, P. A.; Olmstead, M. M.; Balch, A. L., *Org. Lett.* **2003**, *5*, 4199-4202). Thus, each [60]fullerene moiety nests inside the pentacene arms of an adjacent [60]fullerene-pentacene monoadduct molecule.

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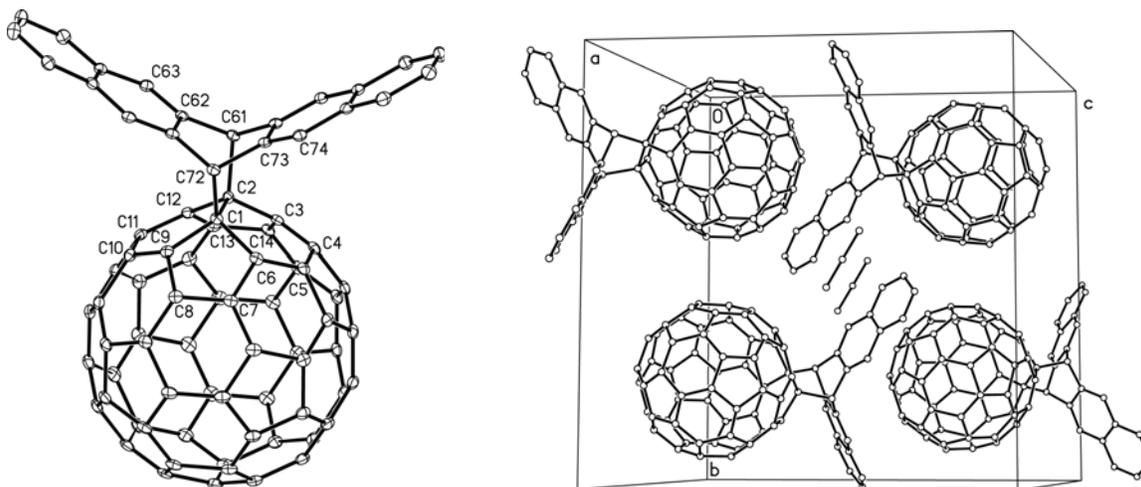


Figure 2. X-ray crystal structure of C_{2v} [60]fullerene-pentacene monoadduct **1**.

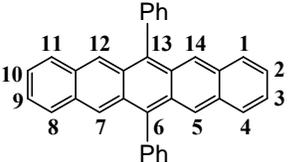
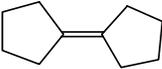
Komatsu and co-workers demonstrated that a bis[60]fullerene adduct of pentacene could be prepared in low yield using the HSVM technique (Murata, Y.; Kato, N.; Fujiwara, K.; Komatsu, K., *J. Org. Chem.* **1999**, *64*, 3483-3488). Under mechanochemical conditions, C_{2v} **1** was isolated in 19% yield along with a bis[60]fullerene-pentacene adduct in 11% yield. Komatsu assigned an *anti* stereochemistry (i.e., **3**) to the bis[60]fullerene-pentacene adduct prepared under HSVM conditions, but this assignment is almost certainly in error (*vide infra*).

FORMATION OF BIS AND TRIS [60]FULLERENE-ACENE ADDUCTS

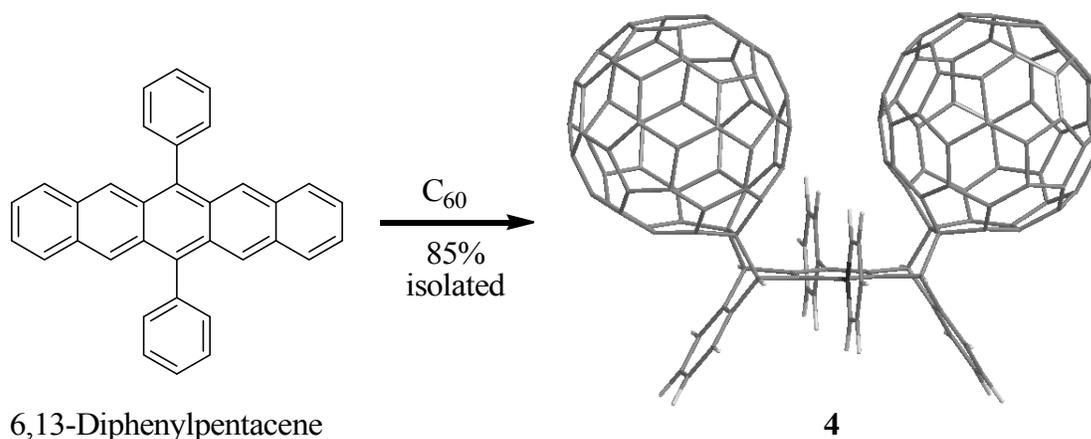
Formation of either **2** or **3** requires initial cycloaddition of [60]fullerene across the 5,14 carbons of pentacene to yield a C_s symmetric monoadduct. However, semi-empirical calculations reveal that 6,13 cycloaddition across pentacene is both kinetically and thermodynamically preferred to 5,14 cycloaddition (Miller, G. P.; Mack, J., *Org. Lett.* **2000**, *2*, 3979-3982). Likewise, the probability of forming **2** and **3** in good to excellent yield from [60]fullerene and pentacene is remote. Consequently, we sought new reactions where the preference for 6,13 cycloaddition across a pentacene backbone would be reduced. PM3 calculations indicate that phenyl substituents at the 6,13 positions of pentacene are sufficiently large as to bias the energetics such that 5,14 cycloaddition is both kinetically and thermodynamically preferred (Table 1). Surprisingly, a relatively large kinetic bias already exists for the cycloaddition of the small dienophile ethylene. With a larger dienophile like bicyclopentylidene, the kinetic and thermodynamic bias towards 5,14 cycloaddition is truly impressive.

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Table 1. PM3 semi-empirical calculations reveal a kinetic and thermodynamic bias for 5,14 cycloaddition across 6,13-diphenylpentacene.

Diene		PM3 Ground State and Transition State Energies (kcal/mol)	
		6,13 Cycloaddition	5,14 Cycloaddition
Dienophiles	$\text{H}_2\text{C}=\text{CH}_2$	$E_{\text{TS}} = 211.4$	$E_{\text{TS}} = 207.4$ $\Delta E_{\text{TS}} = 4$
		$E_{\text{TS}} = 201.1$	$E_{\text{TS}} = 181.3$ $\Delta E_{\text{TS}} = 19.8$
		$\Delta H_f^\circ = 151.5$	$\Delta H_f^\circ = 122.6$ $\Delta\Delta H_f^\circ = 28.9$

Guided by these calculations, we prepared 6,13-diphenylpentacene and reacted it with excess [60]fullerene (Scheme 2).



Scheme 2. Diastereoselective synthesis of *cis*-bis[60]fullerene-diphenylpentacene adduct, **4**.

Remarkably, the reaction proceeds with complete *syn* diastereoselectivity leading to the C_{2v} symmetric *cis*-bis[60]fullerene-diphenylpentacene adduct, **4**, in 85% isolated yield (Miller, G. P.; Mack, J., *Org. Lett.* **2000**, *2*, 3979-3982). The *syn* diastereoselectivity was originally deduced by a careful examination of ^1H and ^{13}C NMR spectra. For example, the ^1H NMR spectrum for C_{2v} **4** reveals a set of 5 phenyl ^1H NMR signals (2 quasi-doublets and 3 quasi-triplets) for the phenyl substituents that rotate slowly on the NMR timescale (Figure 3). These signals cluster around the expected AA'MM' pattern for the remaining aromatic protons on the pentacene backbone. Had

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the C_{2h} *trans*-bis[60]fullerene-diphenylpentacene adduct formed, only 3 ^1H NMR signals (1 quasi-doublet and 2 quasi-triplets) would have been observed for the phenyl substituents, regardless of their rate of rotation.

An X-ray crystal structure (Figure 4) was subsequently obtained (Miller, G. P.; Briggs, J.; Mack, J.; Lord, P. A.; Olmstead, M. M.; Balch, A. L., *Org. Lett.* **2003**, *5*, 4199-4202) for **4** confirming the NMR structural characterization. The crystal structure reveals that two 5-membered rings on adjacent fullerene moieties directly face each other but are not quite parallel to one another. Due to the constraints provided by the pentacene backbone, these abutting rings have an eclipsed orientation. The carbon atoms that make the closest contact are 3.065(8) Å apart and lie at the top of the nearest neighbor 5-membered rings, furthest removed from the pentacene backbone. The distance between the centers of the abutting pentagons is 3.284 Å. The centroid-to-centroid distance between adjacent fullerenes is 9.805 Å. For comparison, the analogous centroid-to-centroid distance in pristine [60]fullerene, which is orientationally disordered, is 9.94 Å at 110 K while the corresponding distances in $C_{60}\cdot 4C_6H_6$ (Olmstead, M. M.; Lee, H. M.; Balch, A. L., *Unpublished Results*) and in $2C_{60}\cdot 3CS_2$ (Olmstead, M. M.; Jiang, F.; Balch, A. L., *Chem. Commun.* **2000**, 483-484), in their low temperature ordered phases are 9.8722 Å (90 K) and 9.9217 Å (93 K) respectively. In none of these structures do pentagons directly face each other in an eclipsed fashion.

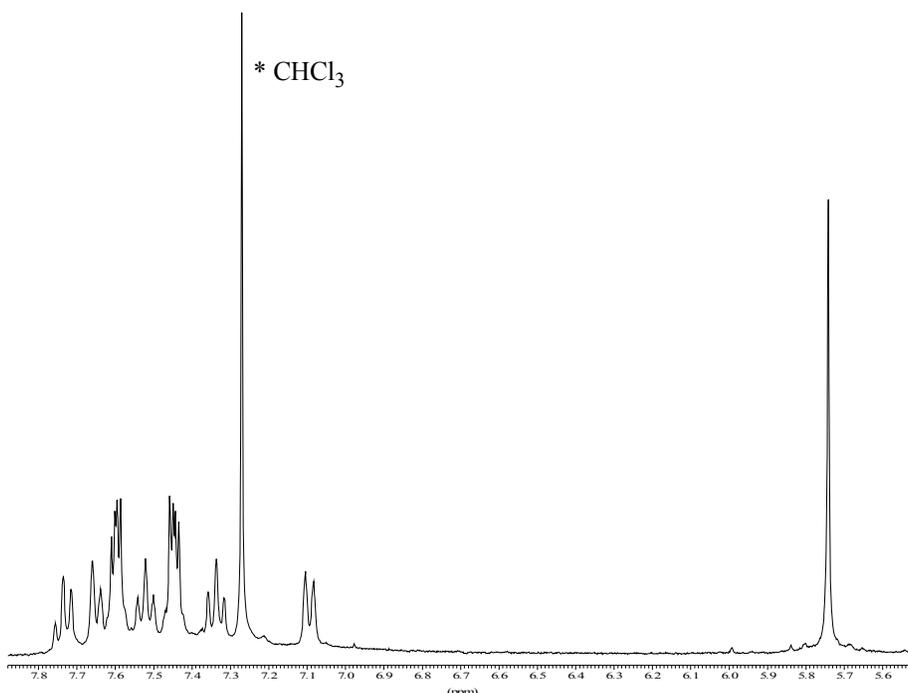


Figure 3. ^1H NMR spectrum of *cis*-bis[60]fullerene-diphenylpentacene adduct, **4**.

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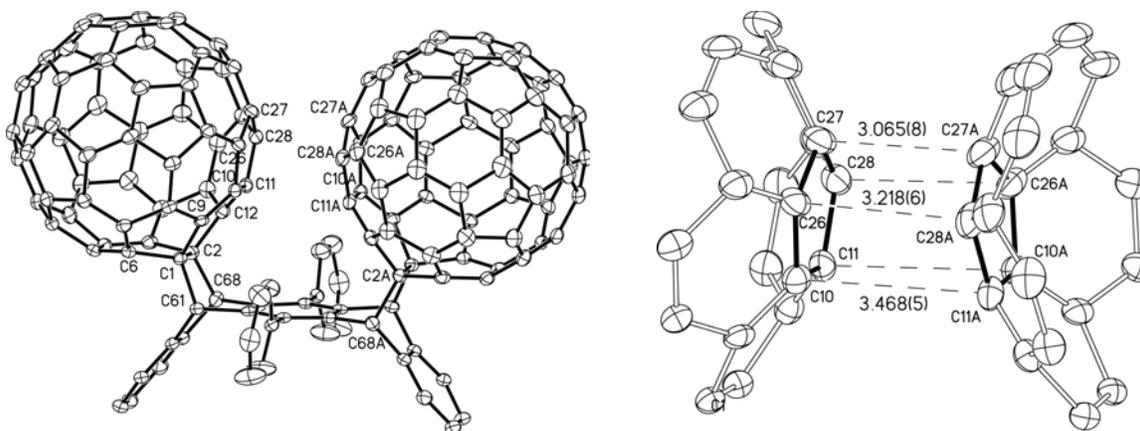
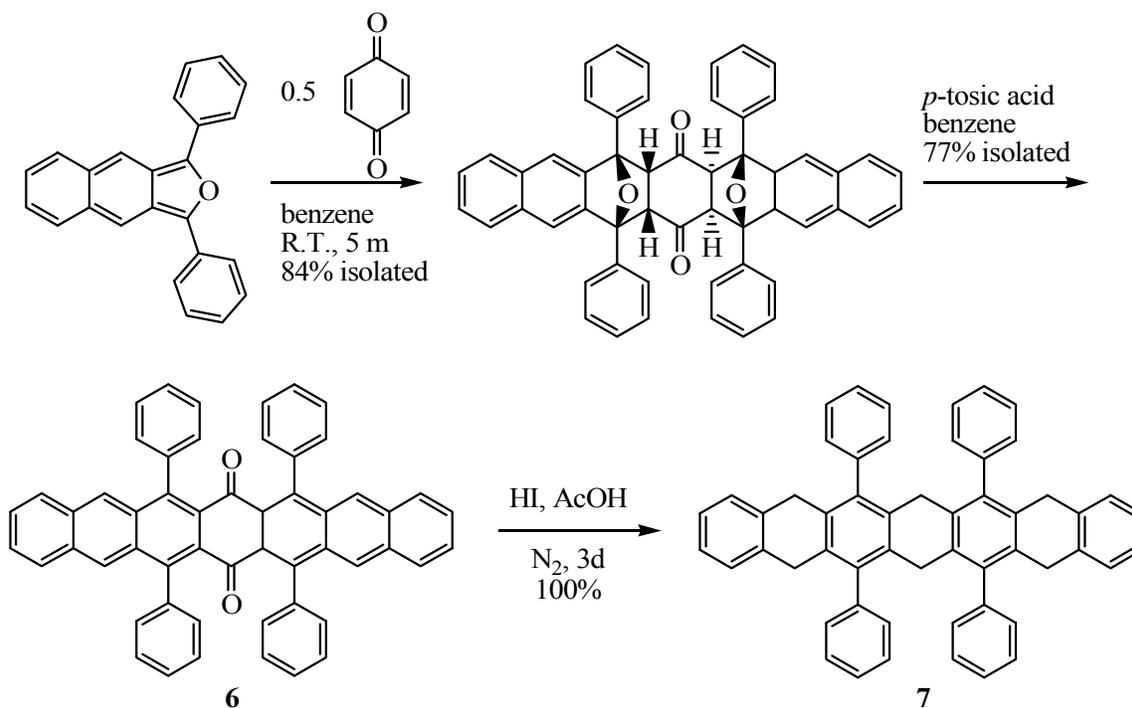


Figure 4. X-ray crystal structure for *cis*-bis[60]fullerene-diphenylpentacene adduct, **4**.

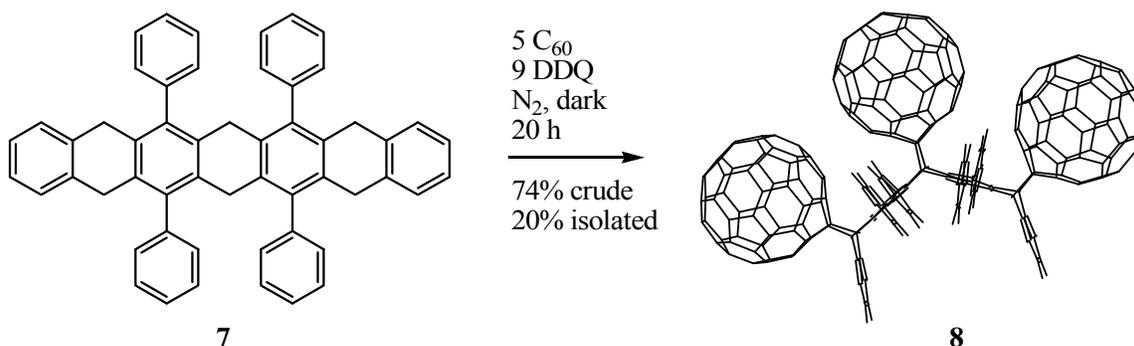
Although readily synthesized and isolated, 6,13-diphenylpentacene is unstable in solution. It sensitizes the formation of singlet oxygen in solution in ambient light, and the singlet oxygen readily cycloadds across the acene. For long-term storage, it is best to store 6,13-diphenylpentacene dry and in the dark. When stored in this manner, it is stable for months without noticeable decomposition.



Scheme 3. Synthesis of 5,7,9,14,16,18-hexahydro-6,8,15,17-tetraphenylheptacene, **7**.

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We endeavored to extend our [60]fullerene-acene methodology to larger acene systems such as 6,8,15,17-tetraphenylheptacene, **5**. Acene **5** is predicted to be highly reactive and unstable. It was prepared from quinone **6** via compound **7** (Scheme 3). The stable, H-protected 5,7,9,14,16,18-hexahydro-6,8,15,17-tetraphenylheptacene, **7**, was reacted with DDQ in the presence of excess [60]fullerene to afford the *cis,cis*-tris[60]fullerene-tetraphenylheptacene adduct **8** (Scheme 4) in 74% crude and 20% isolated yield (Miller, G. P.; Briggs, J. *Org. Letters* **2003**, *5*, 4203). The *cis,cis*-tris[60]fullerene adduct **8** is the only product isolated in the reaction. The positive assignment of a *cis,cis* stereochemistry for **8** was enabled by MM2 calculations and a careful analysis of NMR data. Similar to the case with *cis*-bis[60]fullerene adduct **4**, the assignment was assisted by the slow rotation of phenyl substituents on **8**.



Scheme 4. Synthesis of *cis,cis*-tris[60]fullerene-tetraphenylheptacene adduct, **8**.

Utilizing H-protected acenes like compound **7** for fullerene-acene cycloaddition reactions has significant advantages. We recently published the first systematic study concerning the hydrogenation of acenes and acene quinones (Athans, A. J.; Briggs, J. B.; Jia, W.; Miller, G. P., *J. Mat. Chem.* **2007**, *17*, 2636–2641). Phenyl substituted acenes and acene quinones are hydrogenated in excellent yield and with complete regioselectivity using HI-AcOH. The resulting H-protected acenes bear alternating aromatic and non-aromatic rings and are stable, soluble molecules that may be stored indefinitely and then deprotected to afford the parent acenes.

THE ORIGIN OF SYN SELECTIVE ADDITIONS OF [60]FULLERENES ACROSS ACENES: [60]FULLERENE-[60]FULLERENE π - π STACKING INTERACTIONS

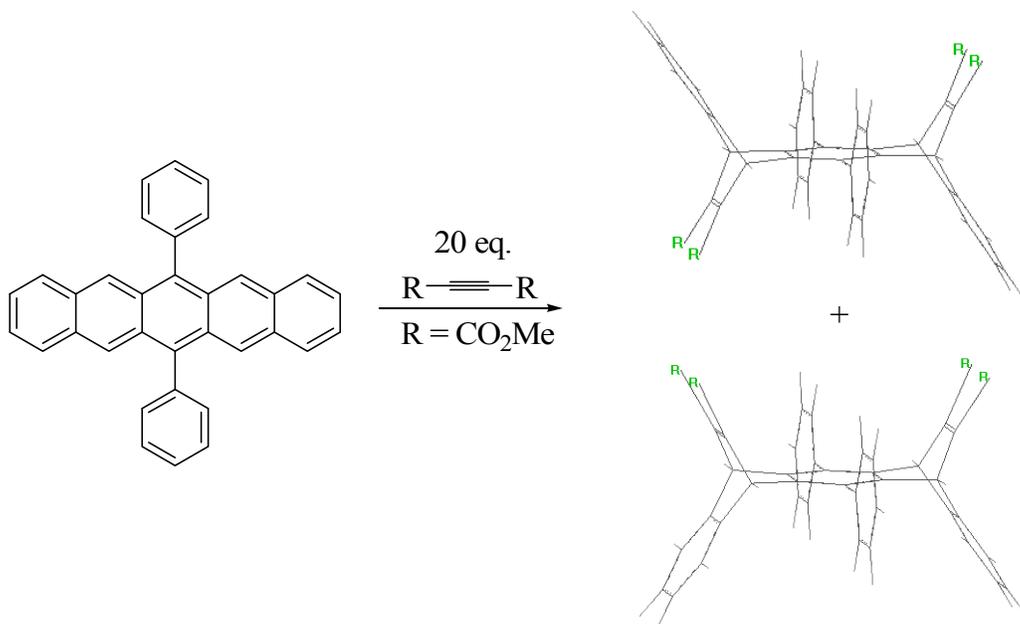
When [60]fullerenes add across large acenes, the reactions must proceed through initial formation of a [60]fullerene-acene monoadduct. Once formed, the first [60]fullerene addend effectively directs subsequent [60]fullerene additions across the same (*syn*) face of the acene via [60]fullerene-[60]fullerene π - π stacking interactions. The unique directing effect of [60]fullerene addends is exemplified by a study (Miller, G. P.; Mack, J.; Briggs, J., *Org. Letters*, **2000**, *2*, 3983) of the reaction between 6,13-diphenylpentacene and the small dienophile dimethyl acetylenedicarboxylate (DMAD). Using a 20-fold excess of DMAD in boiling toluene, a 1:1.3 mixture of *cis* and *trans*-bisDMAD-diphenylpentacene adducts form in quantitative yield (Scheme 5). The slight preference for the *trans*-bis-DMAD-diphenylpentacene adduct is likely

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due to a modest steric effect. Most importantly, the absence of *syn* diastereoselectivity in the DMAD reaction suggests that a special interaction must exist between adjacent [60]fullerene moieties in the reaction leading to **4**.



Scheme 5. Reaction between 6,13-diphenylpentacene and DMAD produces a 1:1.3 mixture of *cis* and *trans*-bisDMAD-diphenylpentacene adducts.

Because even slight deformations from ideal π - π stacking geometries can impact binding energies (stabilities), we reasoned that sterically demanding 6,13-substituents on pentacene should diminish the *syn* diastereoselectivity of [60]fullerene addition. We successfully achieved steric disruption of [60]fullerene-[60]fullerene π - π stacking interactions in a *syn* transition state leading to a *cis*-bis[60]fullerene-acene adduct by utilizing the bulky acene di(trimethylsilylethynyl)pentacene (Miller, G. P.; Mack, J.; Briggs, J., *Org. Letters*, **2000**, 2, 3983). Computationally, di(trimethylsilylethynyl)pentacene, **9**, represents a reasonable compromise between 6,13-diphenylpentacene, which exhibits excellent reactivity, and a highly hindered acene like bis(trimethylsilyl)pentacene that would seemingly retard Diels-Alder reactivity. A PM3-MM2 hybrid *syn* transition state structure for the *cis*-bis[60]fullerene-di(trimethylsilylethynyl)pentacene adduct suggested mild steric disruption without a complete loss in reactivity. Compound **9** (Figure 5) was prepared and reacted with a 5-fold excess of [60]fullerene to produce a 2.5:1 ratio of bis[60]fullerene-di(trimethylsilylethynyl)pentacene adducts in an overall sluggish reaction (Miller, G. P.; Mack, J.; Briggs, J., *Org. Letters*, **2000**, 2, 3983). The starting acene lacks suitable stereochemical handles such that we cannot distinguish *cis* and *trans* product isomers, but the formation of a mixture of diastereomers rather than a single product confirms that the trimethylsilylethynyl substituents do indeed disrupt [60]fullerene-[60]fullerene π - π stacking interactions.

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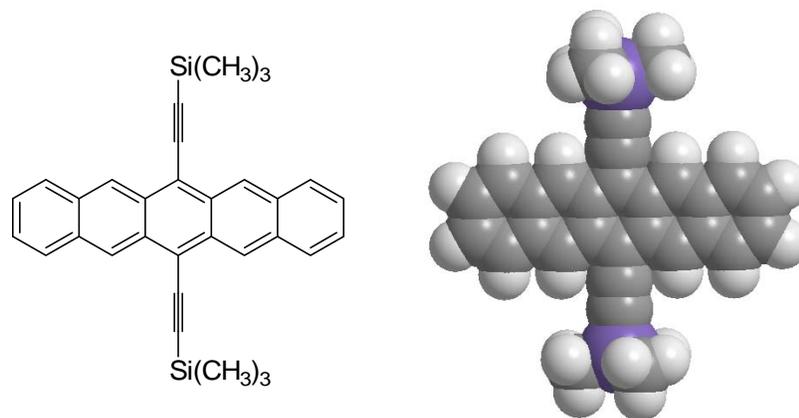


Figure 5. The sterically hindered di(trimethylsilylethynyl)pentacene, **9**.

We further probed the spatial requirements for [60]fullerene-[60]fullerene π - π stacking interactions by studying the reaction between [60]fullerene and 6,8,15,17-tetraphenylheptacene-7,16-quinone, **6**. Quinone **6** (Scheme 3) is unique in that it possesses two reactive anthracene moieties separated by a quinone ring. It is the central ring of each anthracene moiety that is reactive with [60]fullerene. These central rings are sufficiently far removed from one another that [60]fullerene-[60]fullerene π - π stacking interactions are negligible in the *syn* transition state. Calculations reveal the spatial separation of nearest neighbor carbon atoms in the *syn* transition state to be nearly 7 Å, well beyond the ideal 3.2-3.4 Å value for [60]fullerene-[60]fullerene π - π stacking. Upon reacting **6** with excess [60]fullerene, a 1:1.1 mixture of bis[60]fullerene adducts **10** and **11** form (Figure 6), the *trans* structure slightly preferred (Miller, G. P.; Briggs, J., *Tet. Lett.* **2004**, 477-481). The lack of *syn* diastereoselectivity in this reaction contrasts sharply with

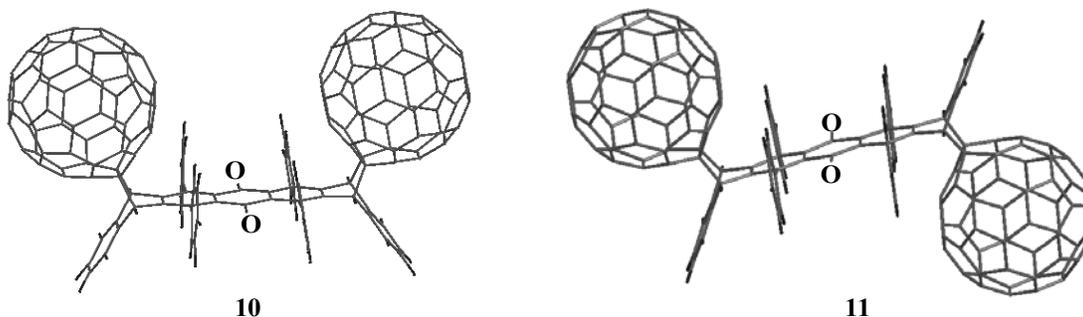


Figure 6. Reaction between 6,8,15,17-tetraphenylheptacene-7,16-quinone, **6**, and [60]fullerene produces a 1:1.1 mixture of *cis* and *trans*-bis[60]fullerene-tetraphenylheptacenequinone adducts, **10** and **11**.

the highly diastereoselective *syn* addition of [60]fullerenes across 6,13-diphenylpentacene and 6,8,15,17-tetraphenylheptacene. Without question, the presence or absence of *syn* diastereoselectivity in these reactions is closely linked to spatially dependent [60]fullerene-[60]fullerene π - π stacking interactions. While the Diels-Alder reactive sites on 6,13-

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diphenylpentacene and 6,8,15,17-tetraphenylheptacene are ideally spaced to accommodate [60]fullerene-[60]fullerene π - π stacking, those on quinone **6** are not.

Finally, it is interesting to note that bis[60]fullerene adducts **10** and **11** undergo facile retro-Diels-Alder reactions at temperatures marginally above 25° C (Miller, G. P.; Briggs, J., *Tet. Lett.* **2004**, 477-481). These adducts are even less stable than [60]fullerene-anthracene monoadducts. Compounds **4** and **8** on the other hand are thermally stable to temperatures in excess of 100° C. The increased thermal stability of **4** and **8** can be largely attributed to the stabilizing nature of [60]fullerene-[60]fullerene π - π stacking interactions.

CYCLACENES AND SINGLE-WALLED NANOTUBULAR COMPOUNDS

Cycloaddition reactions between acenes and [60]fullerene produce beautiful molecules with highly interesting structures. Because large acenes can accommodate more than one [60]fullerene cycloaddition, bis and tris[60]fullerene adducts can be prepared. These reactions become facile once suitable directing substituents (e.g., phenyl groups) are added to the acene. In all cases, [60]fullerenes add in a *syn* diastereoselective fashion due to favorable π - π stacking interactions between adjacent [60]fullerene moieties.

We have suggested (Miller, G. P. et al., *J. Chem. Phys.* **2006**, *124*, 121102) that the highly diastereoselective *syn* additions of [60]fullerene across phenyl substituted acenes could be utilized in the rational synthesis of cyclacenes (Scheme 6). Intramolecular cyclization of acenes of different length could lead to cyclacenes of varying diameter. Supramolecular coupling of *cis,cis*-tris[60]fullerene adducts of substituted heptacenes represents a complementary approach towards cyclacenes, especially those with larger diameters. It has also been suggested that cyclacenes may be utilized in the synthesis of single-walled nanotubular compounds (SWNCs). Using a controlled, iterative synthesis, SWNCs of varying length could be prepared (Scheme 7).

Cyclacenes are cyclic acenes that map directly onto (n,0) zig-zag carbon nanotubes. Each [n]cyclacene represents a small cross-section or slice of an (n,0) zig-zag carbon nanotube with the slice taken perpendicular to the nanotube long-axis. Although long recognized as beautiful aromatic structures, the successful synthesis of a cyclacene remains an elusive goal. Cyclacenes have occasionally been identified as synthetic targets but efficient cyclization strategies are scarce as acenes are not prone to wrap up on themselves. Only Stoddart has elaborated a rational stereoselective synthetic methodology utilizing repetitive Diels-Alder reactions of bisdienes and bisdienophiles (See: (a) Girreser, U.; Giuffrida, D.; Kohnke, F. H.; Mathias, J. P.; Philp, D.; Stoddart, J. F., *Pure Appl. Chem.* **1993**, *65*, 119-125; (b) Ashton, P. R.; Isaacs, N. S.; Kohnke, F. H.; Slawin, A. M. Z.; Spencer, C. M.; Stoddart, J. F.; Williams, D. J., *Angew. Chem. Int. Ed. Engl.* **1988**, *27*, 966-969; (c) Kohnke, F. H.; Slawin, A. M. Z.; Stoddart, J. F.; Williams, D. J., *Angew. Chem. Int. Ed. Engl.* **1987**, *26*, 892-894). While the Stoddart strategy did not yield a cyclacene, it did produce beautiful cyclacene derivatives. A [60]fullerene-added acene strategy is unique because it utilizes favorable [60]fullerene-[60]fullerene π - π stacking interactions that can drive the formation of cyclacenes through reversible, *cis* diastereoselective [60]fullerene additions.

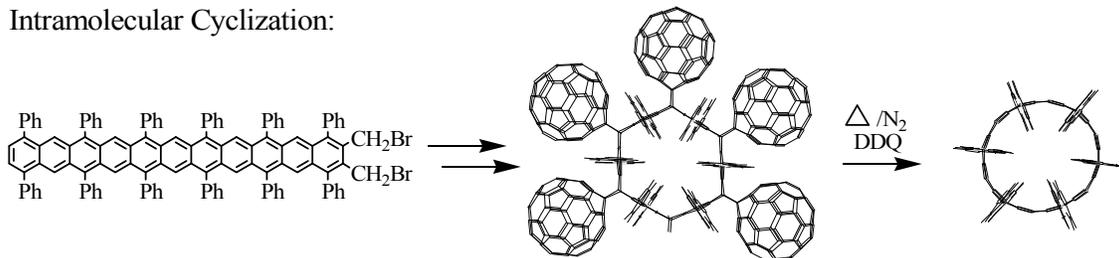
Ab initio density functional calculations have been utilized to determine the equilibrium atomic structure, stability, and electronic states of the proposed cyclacenes and SWNCs. The calculations indicate that SWNCs prepared from 12-membered cyclacenes with phenyl linkers are particularly stable. However, the large twist angle between the linker and the cyclacene surface significantly

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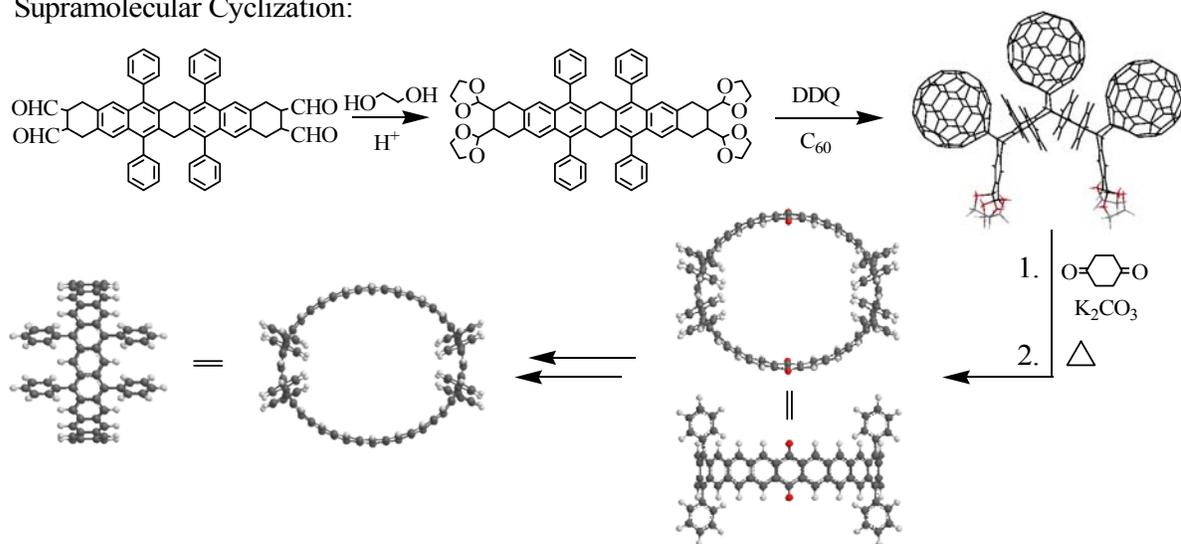
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reduces axial π conjugation, effectively decoupling the electronic systems of the cyclacenes. Consequently, the electronic structure of SWNCs with biphenyl linkers, including the fundamental band gap, is found to lie close to that of isolated cyclacene molecules. Density functional calculations further predict that tetrazine linkers are superior to biphenyls in terms of maximizing the axial π conjugation, reducing the fundamental band gap, and allowing the electrons in frontier orbitals to delocalize across the entire system. The judicious choice of cyclacene linkers enables a controlled modification of the characteristic twist angle θ between linker and cyclacene and is equivalent to band gap engineering (Miller, G. P.; Okano, S.; Tománek, D., *J. Chem. Phys.* **2006**, *124*, 121102).

Intramolecular Cyclization:

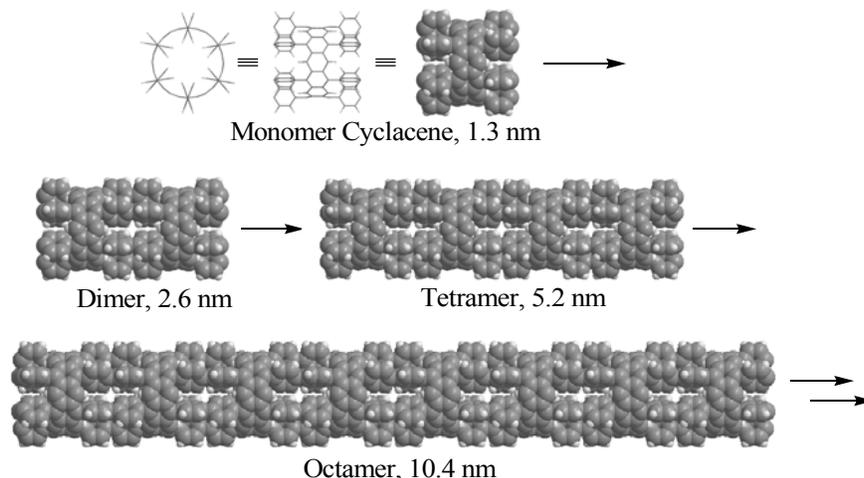


Supramolecular Cyclization:



Scheme 6. Proposed intramolecular and supramolecular paths to cyclacene compounds.

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Scheme 7. Iterative coupling of cyclacenes would produce single-walled nanotubular compounds (SWNCs) with uniform dimensions and properties.

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4203.

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Mack, J.; Miller, G. P., "**Synthesis and Characterization of a C₆₀-Pentacene Monoadduct,**" *Fullerene Sci. Technol.*, **1997**, *5*, 607.