

Account / Revue

[60]Fullerene–acene chemistry: a review

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Abstract

Acenes represent interesting platforms on which to add [60]fullerenes via Diels–Alder cycloaddition reactions. For unsubstituted acenes, the most reactive positions are the center-most rings. Large acenes can accommodate more than one [60]fullerene cycloaddition and these reactions become facile once suitable directing substituents (e.g. phenyl groups) are added to the acene. In these cases, [60]fullerenes add in a *syn*-diastereoselective fashion due to favorable π – π stacking interactions between adjacent [60]fullerene moieties. The π – π stacking interactions provide further stabilization to these adducts. Several *cis*-bis[60]fullerene–acene adducts have been prepared in modest to excellent yield and one *cis,cis*-tris[60]fullerene–heptacene adduct has also been prepared. **To cite this article: J.B. Briggs and G.P. Miller, C. R. Chimie 9 (2006).**

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Keywords: [60]Fullerene; Acene; *Syn*-addition; π – π Stacking; π -Stacking; Pentacene; Heptacene

1. Introduction

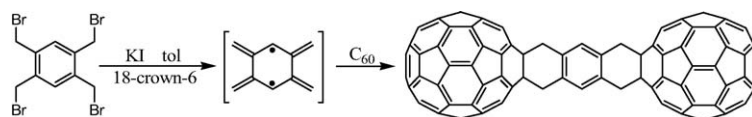
Cycloaddition reactions are amongst the most important reactions for preparing functionalized fullerenes. Fullerenes are known to participate in a variety of cycloaddition reactions [1] including [1 + 2], [2 + 2], [3 + 2], [4 + 2], [6 + 2] and [8 + 2], but the [4 + 2] or Diels–Alder cycloaddition is by far the most studied and most useful fullerene cycloaddition reaction. A host of Diels–Alder dienes including traditional open chain 1,3-dienes, cyclic dienes, and heterodienes are known to react with [60]fullerene [2]. Like other Diels–Alder reactions, those involving [60]fullerene are believed to be concerted, stereospecific processes. They occur with complete regioselectivity such that the dienes add exclusively across 6,6 junctions on the [60]fullerene cage.

Due to its versatility, the Diels–Alder cycloaddition can be used to construct bis[60]fullerene and tris[60]fullerene adducts in which two or three fullerene moieties are held on a single molecule [3]. These exotic structures are beautiful synthetic targets but they also have interesting chemical and electronic properties. Thus, Belik et al. [4] used the two directional diene *bis-o*-quinodimethane to make a bis[60]fullerene adduct in which a flexible durene-type spacer separates the [60]fullerene moieties. The *bis-o*-quinodimethane diene was generated from two iodine induced 1,4-eliminations on 1,2,4,5-*tetrakis*(bromomethyl)benzene (Scheme 1).

Paquette and Graham [5] prepared novel bis[60]fullerene ‘ladder’ compounds in which the fullerene moieties are separated by repeating 1,4-cyclohexadienyl units. These molecules were prepared by reacting appropriate bifunctional dienes (Fig. 1) with C₆₀ in boiling toluene (Scheme 2). A similar methodology was utilized to extend this chemistry in three directions. Pa-

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Scheme 1. Bis[60]fullerene adduct prepared by Belik et al. via reaction with *bis-o*-quinodimethane (see [4]).

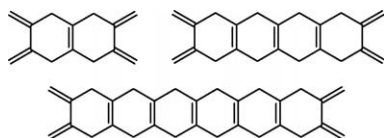
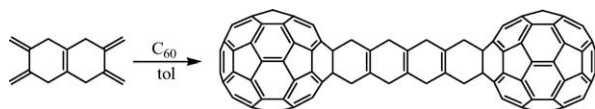


Fig. 1. 1,4-Cyclohexadienyl ladders: bifunctional dienes.



Scheme 2. Bis[60]fullerene 'ladder' compound prepared by Paquette and Graham (see [5]).

quette and Trego [6] used the bicyclic threefold diene hericene to generate a tris[60]fullerene–hericene adduct (Fig. 2) in 9% yield.

An interesting bis[60]fullerene adduct that places the two fullerene moieties in very close proximity to one another was reported by Murata et al. [7]. Using a solid-state high speed vibrational milling (HSVM) technique, the mechanochemical reaction between C_{60} and phthalazine was shown to produce an interesting bis[60]fullerene adduct in 14% yield (Scheme 3). The reaction

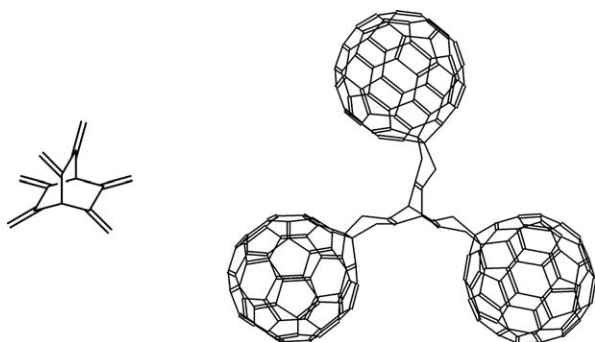
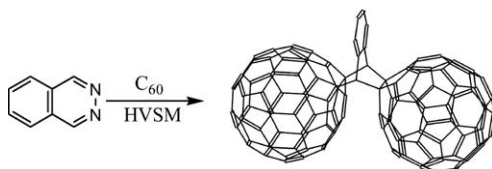


Fig. 2. Left: Hericene. Right: Hericene-tris[60]fullerene adduct prepared by Paquette and Trego (see [6]).



Scheme 3. Bis[60]fullerene adduct prepared by Murata et al. under HSVM conditions (see [7]).

proceeds through an initial [4 + 2] cycloaddition followed by loss of N_2 in a retro-Diels–Alder reaction, followed by a second [4 + 2] cycloaddition of C_{60} . Interestingly, this bis[60]fullerene adduct is not observed when the reaction is conducted in solution. Instead, an open cage fullerene hydrocarbon is formed.

We recognized the potential utility of using large acenes as platforms on which to cycloadd [60]fullerene and began pursuing the formation of bis[60]fullerene–acene and tris[60]fullerene–acene adducts in 1995. These studies have led us to a greater understanding of the factors that influence Diels–Alder cycloadditions of [60]fullerene, especially inter- and intramolecular π – π stacking interactions between [60]fullerenes. In the process, we discovered several [60]fullerene Diels–Alder reactions that proceed with remarkable diastereoselectivity. The remainder of this review will focus on acenes and their Diels–Alder reactivity with [60]fullerene.

2. Acenes and Erich Clar

Acenes belong to the family of organic molecules known as polycyclic aromatic hydrocarbons (PAHs). Specifically, they are a subcategory of the PAH family in that they are alternant *cata*-annulated benzenoid ring systems [8]. In other words, acenes are a linear array of fused benzene rings, the smallest of which is the 2-ring system naphthalene. The name 'acene' was coined by the father of modern PAH chemistry, Clar [9]. The name is derived from one of the most common acenes, anthracene. Thus, the oft-used moniker 'linear acene' is redundant since the term 'linear' is already implied in Clar's definition.

Clar was born in Czech-Sudetenland and subsequently relocated to Glasgow in 1946. He was a Professor of Chemistry at Glasgow University from 1953 until 1972. Clar published over 170 research papers and monographs beginning in the late 1920s and continuing until the early 1980s. These contributions include the classic monograph *Polycyclic Hydrocarbons* which is still recognized today as an indispensable reference. Clar was posthumously awarded the first 'Polycyclic Aromatic Hydrocarbon Research Award' at the 11th International Symposium on Polynuclear Aromatic Hydrocarbons, September 24, 1987. He died just a few

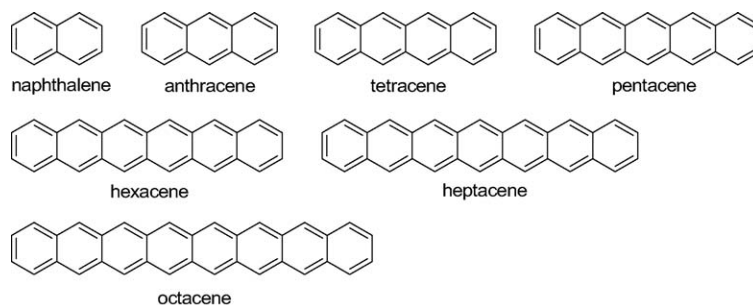


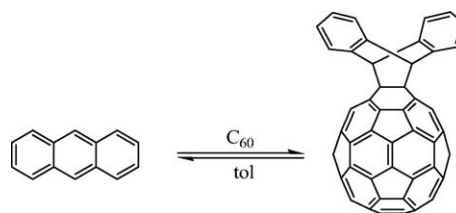
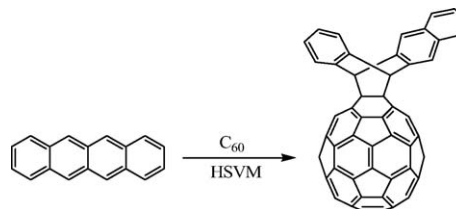
Fig. 3. Structures and names of the known acenes.

days before news of the award reached his home in 1987. Without question, Clar's contributions toward acene syntheses paved the way for today's numerous applications. Indeed, acenes possess a set of physical and chemical properties that make them interesting components of oriented thin films [10], organic light emitting diodes (LEDs) [11], organic field-effect transistors (FETs) [12], liquid crystals with enhanced electron transport [13], and single crystal semi-conductors [14]. They also exhibit interesting chemistries including their propensity to cycloadd [60]fullerene in *syn*-diastereoselective fashion (vide infra). The known acenes are shown in Fig. 3 with all but octacene having been prepared by Clar. While larger acenes are easily envisioned, these compounds have never been successfully prepared and characterized due mostly to their photo-instability, high reactivity, and poor solubility.

3. [60]Fullerene–acene chemistry

The first [60]fullerene–acene reaction studied was that between [60]fullerene and anthracene. Schlueter et al. [15] reported that upon boiling a toluene solution of anthracene and [60]fullerene for 3 days, the corresponding [60]fullerene–anthracene monoadduct is formed and isolated in 13% yield. The [60]fullerene–anthracene monoadduct is not a thermally stable molecule, a characteristic highlighted by Tsuda et al. [16] who observed a temperature dependence on the yield of monoadduct formed. Thus, for reactions run in toluene solution at 50, 80 and 100 °C, [60]fullerene–anthracene monoadduct yields of 24%, 17% and 8.5%, respectively, were observed. The reaction is reversible (Scheme 4) with reactants favored at higher temperatures. In practice, one observes that isolated [60]fullerene–anthracene monoadduct begins to thermally degrade at approximately 60 °C.

Komatsu and co-workers studied the reaction between anthracene and [60]fullerene under HSVM conditions producing the [60]fullerene–anthracene mono-

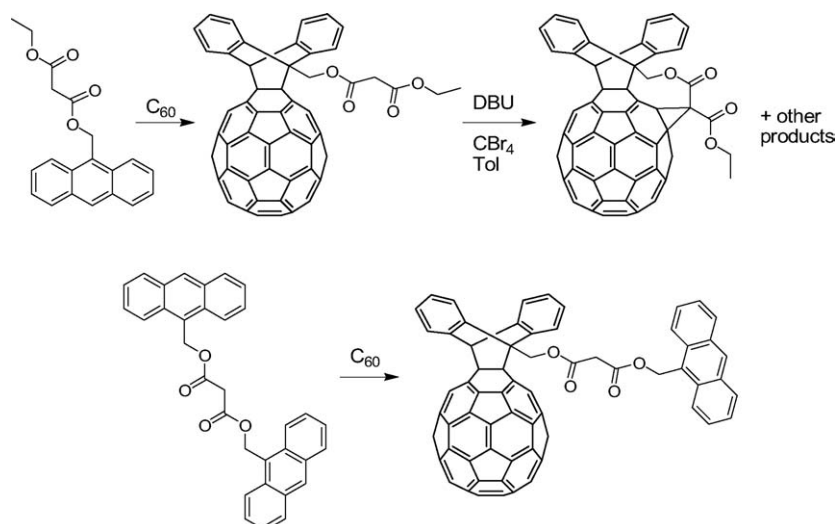
Scheme 4. Reversible Diels–Alder reaction between C₆₀ and anthracene (see [16–18]).

Scheme 5. Mechanochemical synthesis of a [60]fullerene–tetracene monoadduct by Komatsu and co-workers (see [18]).

adduct in 55% yield. When tetracene and [60]fullerene are reacted under HSVM conditions, the corresponding [60]fullerene–tetracene monoadduct (Scheme 5) is produced in 61% yield [17].

Sarova and Berberan-Santos [18] studied the kinetics of [60]fullerene cycloaddition across anthracene and tetracene, as well as the kinetics of the corresponding retro-Diels–Alder reactions. Tetracene cycloadds faster than anthracene and the corresponding [60]fullerene–tetracene monoadduct is slower to undergo a retro-Diels–Alder reaction. Larger acenes are long known to react faster than smaller acenes in Diels–Alder reactions [19]. Likewise, pentacene reacts noticeably faster with [60]fullerene than does tetracene and the corresponding [60]fullerene–pentacene monoadduct (vide infra) is less inclined to decompose via a retro-Diels–Alder reaction.

Herranz and Echegoyen [20] studied the thermal and electrochemical stability of the Diels–Alder adducts prepared upon reacting [60]fullerene with 9-anthracene-

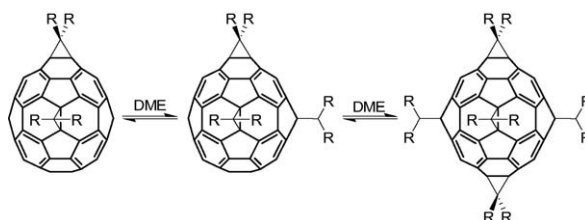


Scheme 6. Diels–Alder adducts prepared by Herranz and Echegoyen upon reacting [60]fullerene with 9-anthracenylmethyl ethyl malonate (top) and di-9-anthracenylmethyl malonate (bottom). See [20].

nylmethyl ethyl malonate and di-9-anthracenylmethyl malonate (Scheme 6). While both adducts showed signs of thermal degradation at temperatures as low as 50 °C, the adduct of 9-anthracenylmethyl ethyl malonate was shown to be stable to electroreductive (controlled potential electrolysis) conditions. Base promoted Bingel reactions involving the adduct of 9-anthracenylmethyl ethyl malonate lead to multiple products including both intramolecular cyclopropanation product (Scheme 6) and some dimeric species (i.e. products of intermolecular reactions).

While a lack of thermal stability in [60]fullerene-anthracene adducts can be problematic in some applications, it can be advantageous in others. Wang suggested the use of silica or resin-supported 9-substituted anthracenes for the separation of fullerenes from complex mixtures. The concept has yet to be demonstrated, but Wang did study the retro-Diels–Alder rates for three [60]fullerene-anthracene monoadducts using 9-substituted anthracenes as diene [21]. Not surprisingly, these adducts decompose at relatively low temperatures (i.e. < 60 °C). A suitably bulky 9-substituted or 9,10-disubstituted anthracene may undergo facile retro-Diels–Alder reactions at or near room temperature, enabling a resolution of fullerenes on modified silica or resin.

Indeed, Hirsch and co-workers successfully exploited the thermal reversibility of the Diels–Alder reaction between [60]fullerene and 9,10-dimethylantracene (DMA) for synthetic gain. Noting regioselective formation of *equatorial* (*e*) bisadducts and *e,e*-triadducts in Bingel addition chemistries (i.e. base promoted cyclopropanations via bromomalonates),



Scheme 7. Formation of a Bingel-type T_h symmetric hexakisadduct (right, $R = \text{CO}_2R'$) by Lamparth et al. using excess DMA as reversible templating agents. See [22]. The sixth cyclopropanation is not seen in this view of the hexakisadduct.

Hirsch demonstrated that adding an excess of DMA to [60]fullerene creates an equilibrium mixture containing $e\text{-C}_{60}(\text{DMA})_2$ and $e,e\text{-C}_{60}(\text{DMA})_3$ templates that direct subsequent cycloadditions to the remaining *equatorial* sites [22]. The method allows the synthesis of a number of Bingel-type T_h symmetric hexakisadducts, $\text{C}_{60}(\text{COOR})_{12}$ (Scheme 7), in yields up to 50%. Thus, the reversible addition of DMA promotes regioselective (irreversible) cyclopropanation in the presence of bromomalonate and DBU leading ultimately to T_h symmetric hexakisadducts in which all *equatorial* sites are cyclopropanated.

Kräutler et al. [23] discovered that heating an X-ray quality crystal of the [60]fullerene-anthracene monoadduct to 180 °C for 10 min produced a 1:1 mixture of the antipodal (*trans*-1) [60]fullerene-bisanthracene adduct (Fig. 4) and C_{60} in 48% yield. They attribute this unique solid-state reaction to crystal stacking of the [60]fullerene-anthracene monoadduct molecules which places the anthracene moiety of one molecule in close

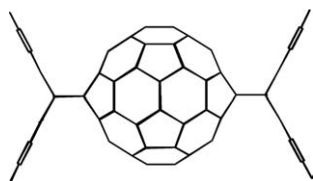
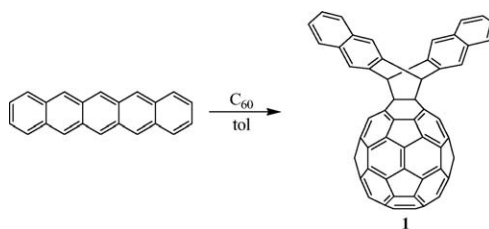


Fig. 4. Krätzler's antipodal (*trans*-1) [60]fullerene-bisanthracene adduct (see [23]).

proximity to the antipodal (*trans*-1) position of an adjacent [60]fullerene-anthracene monoadduct. Heating the crystal induces retro-Diels–Alder reactions producing ‘free’ anthracene molecules in the crystal lattice. The freed anthracene molecules can cycloadd to the same [60]fullerene from which they came or alternatively to an adjacent [60]fullerene-anthracene monoadduct. In this latter instance, a *trans*-1 [60]fullerene-bisanthracene adduct molecule is produced. Although the reaction is limited in scope, Krätzler's method represents one of the very few options available to fullerene chemists to prepare a *trans*-1 bisadduct in reasonable yield. Krätzler et al. [24] was successful in extending this methodology to a number of different substituted anthracenes.

Interested in the possibility that two [60]fullerenes could cycloadd across a single pentacene backbone, Mack and Miller [25] 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 8), a result of [60]fullerene cycloaddition across the central 6,13 carbons of the pentacene backbone. Using a fivefold 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,



Scheme 8. Solution phase Diels–Alder cycloaddition between [60] fullerene and pentacene proceeds regioselectively across the central ring of pentacene (see [25]).

2 and **3**, respectively (Fig. 5), as sought by Krätzler et al. [24]. An X-ray crystal structure (Fig. 6) of **1** reveals [26] a similar nested crystal packing as reported by Krätzler and co-workers for the [60]fullerene-anthracene monoadduct crystal [23]. Thus, each [60]fullerene moiety nests inside the pentacene arms of an adjacent [60]fullerene-pentacene monoadduct molecule.

Murata et al. [17] subsequently demonstrated that a bis[60]fullerene adduct of pentacene could be prepared in low yield using the HSVM technique. Under mechanochemical conditions, C_{2v} **1** was isolated in 19% yield along with a bis[60]fullerene-pentacene adduct in 11% yield. Murata et al. assigned an *anti*-stereochemistry (i.e. **3**) to the bis[60]fullerene-pentacene adduct prepared under HSVM conditions, but this assignment is likely in error (vide infra).

4. Diastereoselective [60]fullerene cycloadditions across 6,13-disubstituted pentacenes

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 [27]. Likewise, the probability of forming **2** and **3** in good to

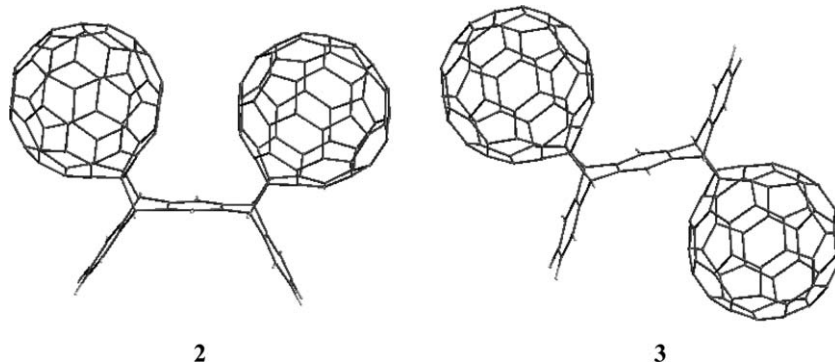


Fig. 5. *Cis*- and *trans*-bis[60]fullerene-pentacene adducts, **2** and **3**, respectively, sought by Mack and Miller (see [25]).

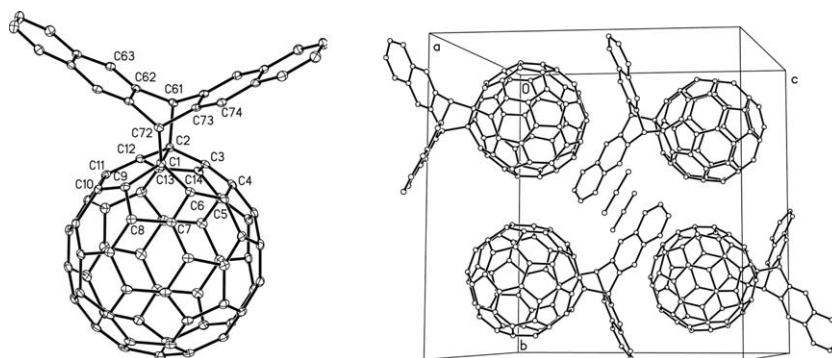


Fig. 6. X-ray crystal structure of C_{2v} [60]fullerene-pentacene monoadduct **1** (reprinted with permission from [26]).

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 (Fig. 7). 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. Guided by these calculations, we prepared 6,13-diphenylpentacene and reacted it with excess [60]fullerene (Scheme 9). 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 [27]. 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 signals (two quasi-doublets and three quasi-triplets) for the phenyl substituents that rotate slowly on the NMR timescale (Fig. 8). These signals cluster around the expected AA'MM' pattern for the remaining aromatic protons on the pentacene backbone. Had the C_{2h} *trans*-bis[60]fullerene-diphenylpentacene adduct formed, only three ^1H NMR signals (one quasi-doublet and two quasi-triplets) would have been observed for the phenyl substituents, regardless of their rate of rotation.

An X-ray crystal structure (Fig. 9) was subsequently obtained [26] 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 penta-


Diene	Dienophiles	PM3 Ground State and Transition State Energies (kcal/mol)	
		6,13 Cycloaddition	5,14 Cycloaddition
	<chem>H2C=CH2</chem>	$E_{\text{TS}} = 211.4$	$E_{\text{TS}} = 207.4$ $\Delta E_{\text{TS}} = 4$
		$E_{\text{TS}} = 201.1$	$E_{\text{TS}} = 181.3$ $\Delta E_{\text{TS}} = 19.8$
		$\Delta H_f^\circ = 151.5$	$\Delta H_f^\circ = 122.6$ $\Delta\Delta H_f^\circ = 28.9$

Fig. 7. PM3 semi-empirical calculations reveal a kinetic and thermodynamic bias for 5,14 cycloaddition across 6,13-diphenylpentacene (see [27]).



Scheme 9. Diastereoselective synthesis of *cis*-bis[60]fullerene-diphenylpentacene adduct, **4**, by Miller and Mack (see [27]).

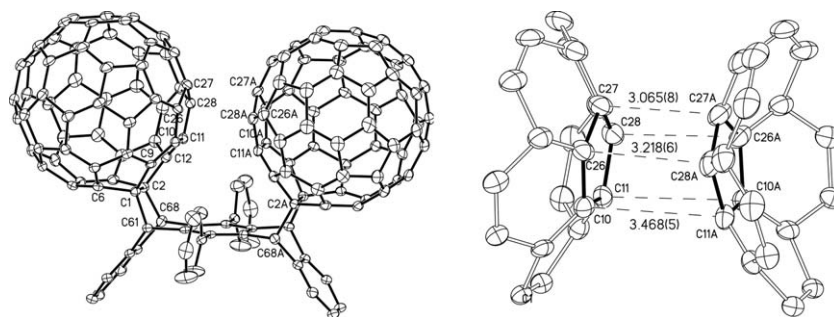


Fig. 9. X-ray crystal structure for *cis*-bis[60]fullerene-diphenylpentacene adduct, **4** (reprinted with permission from [26]).

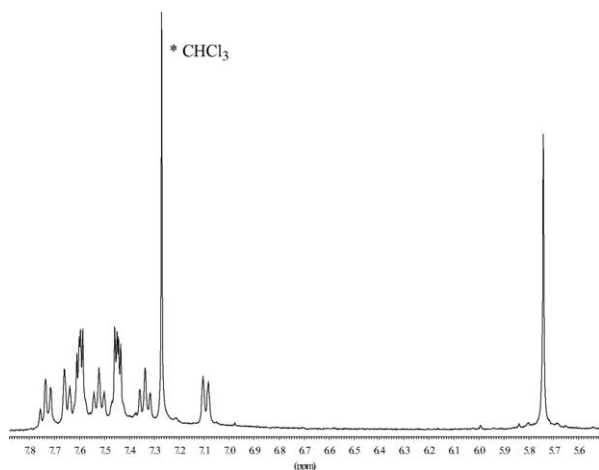


Fig. 8. ^1H NMR spectrum of *cis*-bis[60]fullerene-diphenylpentacene

cene 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 [28] while the corresponding distances in $\text{C}_{60}\cdot 4\text{C}_6\text{H}_6$ [29] and in $2\text{C}_{60}\cdot 3\text{CS}_2$ [30], 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. The *cis*-bis[60]fullerene adduct **4** shows excellent solubility in common organic solvents including chloroform. This solubility must be due in large part to the phenyl substituents on the pentacene backbone as the bis[60]fullerene-pentacene adduct pre-

pared under HSVM conditions exhibits poor solubility [17].

Although readily synthesized and isolated, 6,13-diphenylpentacene is photolytically unstable. It readily adds oxygen in solution in the presence of ambient light. 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 significant decomposition. In addition to 6,13-diphenylpentacene, a variety of other 6,13-disubstituted pentacenes were synthesized [31] as illustrated in Fig. 10.

Thus, a fivefold excess of [60]fullerene was reacted with 6,13-di(4'-hydroxymethylphenyl)pentacene, **5**, in CS_2 to produce the corresponding *cis*-bis[60]fullerene-di(hydroxymethylphenyl)pentacene adduct, **8**, in 75% isolated yield [27]. Hindered rotation of the hydroxymethylphenyl substituents once again allowed for complete stereochemical characterization, the product **8** forming in a highly *syn*-diastereoselective fashion (Fig. 11).

Similar conditions were utilized for the reaction between [60]fullerene and 6,13-diethynylphenylpentacene, **6**, to produce the corresponding C_s symmetric [60]fullerene-diethynylphenylpentacene monoadduct, **9**, in 83% isolated yield. In this reaction, the corresponding bis[60]fullerene-diethynylphenylpentacene adduct, **10**, is formed in only 14% isolated yield [32]. The sluggishness of the reaction with **6** is attributed to

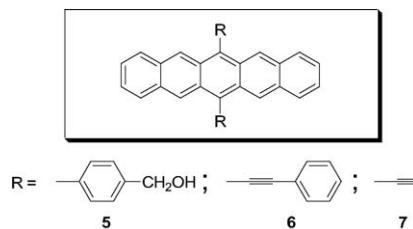


Fig. 10. Several 6,13-disubstituted pentacenes synthesized and reacted with [60]fullerene by Miller, Mack and Briggs (see [31]).

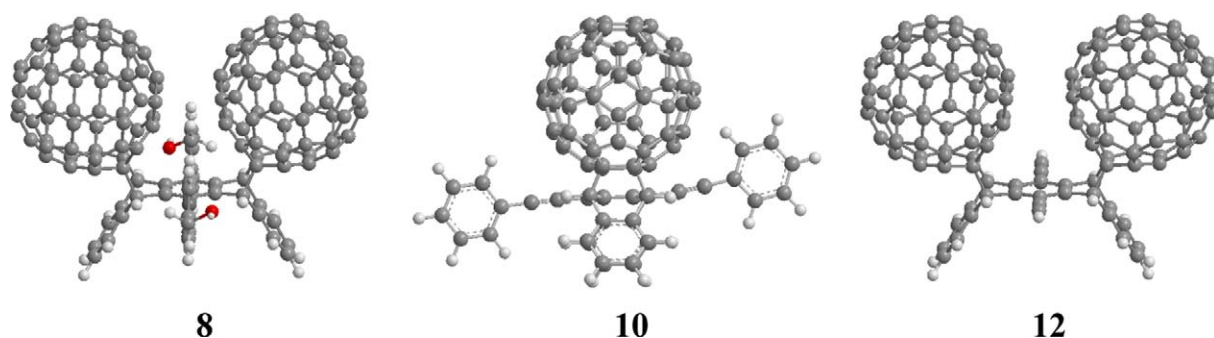


Fig. 11. Structures of bis[60]fullerene-acene adducts formed upon reacting [60]fullerene with 6,13-disubstituted pentacenes 5–7. Compound **10** is viewed along the long-axis of the pentacene backbone (see [27,31]).

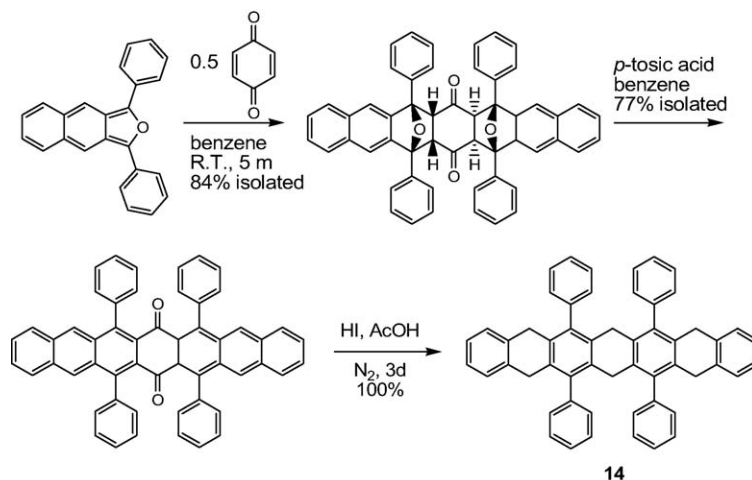
the alkynyl substituents. The electronegative sp hybridized carbons cause the pentacene backbone to be less electron rich and therefore less reactive in the Diels–Alder reaction. Due to the acetylene spacer, hindered rotation of the phenyl groups is not observed in this system. Consequently, the ^1H and ^{13}C NMR spectra do not distinguish between *cis*- and *trans*-bis[60]fullerene adducts. It is nonetheless certain that only one diastereomer forms in a highly selective reaction. Given the results discussed above, the product is likely to possess a *cis*-stereochemistry (Fig. 11).

Diethynylpentacene, **7**, was also reacted with [60]fullerene. Since **7** is very unstable, it was generated and used as needed from 6,13-di(trimethylsilylethynyl)pentacene. Reaction of 6,13-di(trimethylsilylethynyl)pentacene with TBAF in chloroform followed by immediate purification on a short silica column affords a blue solution of **7** which was added directly to a solution of [60]fullerene in CS_2 . In this manner, the C_s symmetric [60]fullerene–6,13-diethynylpentacene monoadduct **11** was isolated in 2.2% yield while the bis[60]

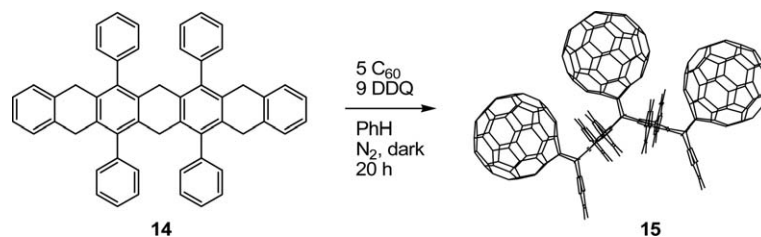
fullerene-6,13-diethynylpentacene adduct **12** was isolated in 8% yield [32]. These low isolated yields are attributed to both the reduced reactivity of **7** as well as difficulties in purifying sparingly soluble **11** and **12**.

5. A tris[60]fullerene adduct of 6,8,15,17-tetraphenylheptacene

We endeavored to extend our [60]fullerene-acene methodology to larger acene systems such as 6,8,15,17-tetraphenylheptacene, **13**. Acene **13** is predicted to be highly reactive and unstable. It was prepared and used in situ upon reacting the stable, H-protected 5,7,9,14,16,18-hexahydro-6,8,15,17-tetraphenylheptacene, **14** (Scheme 10), with DDQ in the presence of excess [60]fullerene to afford the *cis,cis*-tris[60]fullerene-tetraphenylheptacene adduct **15** (Scheme 11) in 74% crude and 20% isolated yield [33]. The *cis,cis*-tris[60]fullerene adduct **15** is the only product isolated in the reaction. The positive assignment of a *cis,cis*-stereochemistry for **15** was enabled by MM2 cal-



Scheme 10. Synthesis of 5,7,9,14,16,18-hexahydro-6,8,15,17-tetraphenylheptacene, **14**, by Miller and Briggs (see [33]).



Scheme 11. Synthesis of *cis,cis*-tris[60]fullerene-tetraphenylheptacene adduct, **15**, by Miller and Briggs (see [33]).

culations and a careful analysis of NMR data. Similar to the cases with *cis*-bis[60]fullerene adducts **4** and **8**, the stereochemical assignment for **15** was assisted by the slow rotation of phenyl substituents on **15**.

Given all of the data collected for reactions between [60]fullerene and 6,13-disubstituted pentacenes and 6,8,15,17-tetraphenylheptacene, there can be no doubt that [60]fullerenes prefer to cycloadd across large acenes in a *syn*-diastereoselective fashion. But what is the origin of this diastereoselectivity?

6. Why do [60]fullerenes add across large acenes in a *syn* diastereoselective fashion?

The origin of the *syn*-diastereoselective addition of [60]fullerenes across large acenes is favorable van der Waals or π - π stacking interactions between adjacent [60]fullerene moieties. There is ample experimental and computational evidence to support this conclusion.

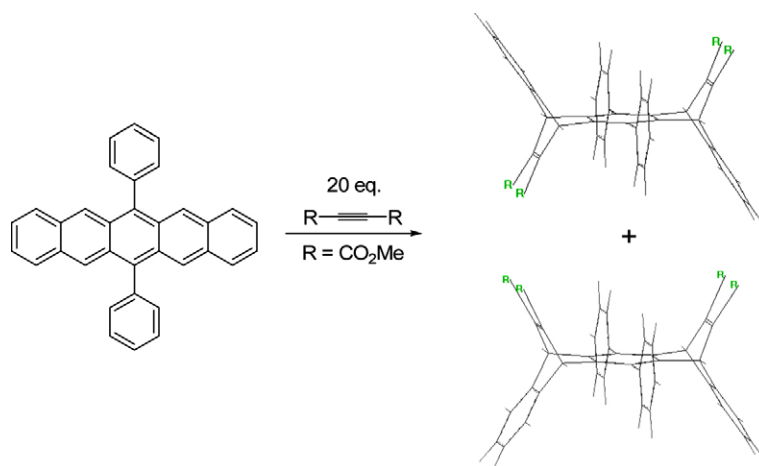
The X-ray crystal structure of *cis*-bis[60]fullerene-diphenylpentacene adduct, **4**, illustrates that the distance between the centers of the abutting pentagons on adjacent [60]fullerene moieties is 3.284 Å (Fig. 9). This distance is only slightly shorter than the 3.35 Å van der Waals spacing between adjacent sheets of planar graphite. Moreover, this is the approximate distance between the carbon layers of multi-walled carbon nanotubes (MWNTs), and between individual single-walled carbon nanotubes (SWNTs) that have bundled into rope-like structures. Could these similar clustering effects involving graphite, [60]fullerene, MWNTs and SWNTs – all different allotropes of sp^2 hybridized carbon – be a matter of coincidence? No. In all cases, the ‘clusters’ are stabilized by favorable π - π stacking interactions between the nanostructured carbon forms.

A molecular mechanics (MM2) calculated ground state [34] for **2** is in excellent agreement with the X-ray crystal structure [26] for **4**. In the MM2 ground state structure, the distance between the centers of the abutting pentagons on adjacent [60]fullerene moieties is 3.3 Å. Nearest neighbor pentagons should be slightly

closer in the *syn* transition states preceding **2** and **4**, and indeed a PM3–MM2 hybrid transition state structure reveals a distance of 3.2 Å. It is interesting and informative to note that the semi-empirical methods (e.g. AM1, PM3, MNDO, etc.) fare poorly in predicting the structures of *cis*-bis and *cis,cis*-tris[60]fullerene-acene adducts because, unlike MM2, they are not parameterized to account for van der Waals interactions. That is, the MM2 calculated ground state for **4** matches the crystal structure so well because the MM2 force field specifically accounts for van der Waals interactions between adjacent [60]fullerene moieties.

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 [34] 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 12). The slight preference for the *trans*-bisDMAD–diphenylpentacene adduct is likely 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 [60]fullerene reaction.

Because even slight deformations from ideal π - π stacking geometries can impact binding energies [35] (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 6,13-di(trimethylsilyl)ethynylpentacene [34]. Computationally, 6,13-di(tri-



Scheme 12. Reaction between 6,13-diphenylpentacene and DMAD produces a 1:1.3 mixture of *cis* and *trans*-bisDMAD-diphenylpentacene adducts (see [34]).

methylsilylethynyl)pentacene, **16**, 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. Likewise, **16** (Fig. 12) was prepared and reacted with a fivefold excess of [60]fullerene to produce a 2.5:1 ratio of bis[60]fullerene-di(trimethylsilylethynyl)pentacene adducts in an overall sluggish reaction [34]. 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 suggests that the trimethylsilylethynyl substituents do indeed disrupt [60]fullerene–[60]fullerene π – π stacking interactions.

We further probed the spatial requirements for [60] fullerene–[60]fullerene π – π stacking interactions by

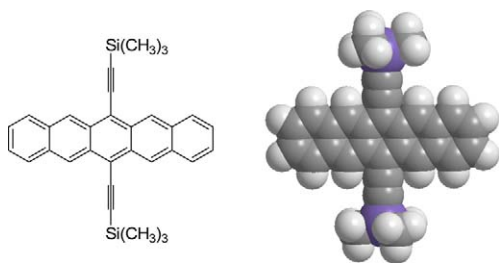


Fig. 12. The sterically hindered di(trimethylsilylethynyl)pentacene, **16** (see [34]).

studying the reaction between [60]fullerene and 6,8,15,17-tetraphenylheptacene–7,16-quinone, **17**. Quinone **17** (the penultimate structure of Scheme 10) 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 **17** with excess [60]fullerene, a 1:1.1 mixture of bis[60]fullerene adducts **18** and **19** form (Fig. 13) with the *trans* structure slightly preferred [36]. 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. 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-diphenylpentacene and 6,8,15,17-tetraphenylheptacene are ideally spaced to accommodate [60]fullerene–[60]fullerene π – π stacking, those on quinone **17** are not.

Finally, it is interesting to note that bis[60]fullerene adducts **18** and **19** undergo facile retro-Diels–Alder reactions at temperatures marginally above 25 °C [36]. These adducts are even less stable than [60]fullerene–anthracene monoadducts. Compounds **4** and **15** on the other hand are thermally stable to temperatures in ex-

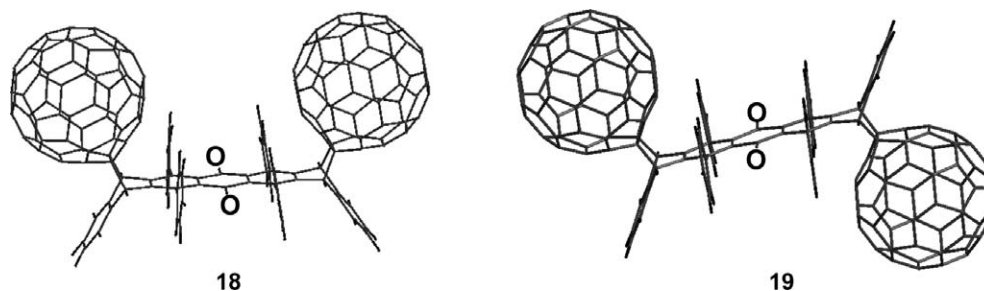


Fig. 13. Reaction between 6,8,15,17-tetraphenylheptacene-7,16-quinone, **17**, and [60]fullerene produces a 1:1 mixture of *cis* and *trans*-bis[60]fullerene-tetraphenylheptacenequinone adducts, **18** and **19**, respectively (see [36]).

cess of 100 °C. The increased thermal stability of **4** and **15** can be largely attributed to the stabilizing nature of [60]fullerene–[60]fullerene π – π stacking interactions.

7. Conclusions and future direction

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. In the future, the chemical, electrochemical and physical properties of [60]fullerene-acene adducts already prepared will be investigated. Moreover, the methodology will be extended to larger acenes such that tetrakis, pentakis, and even hexakis[60]fullerene-acene adducts can be prepared.

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