ORGANIC
LETTERS

2000
Vol. 2, No. 25
3983−3986

π-Stacking Interactions in *cis*-Bisfullerene[60] Adducts of 6,13-Disubstituted Pentacenes

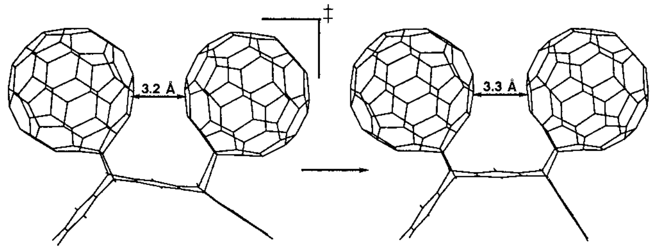
Glen P. Miller,* James Mack, and Jonathan Briggs

Department of Chemistry, University of New Hampshire,
Durham, New Hampshire 03824-3598

gpm@cisunix.unh.edu

Received August 16, 2000

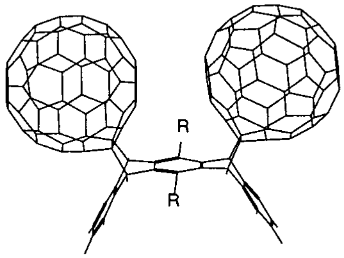
ABSTRACT



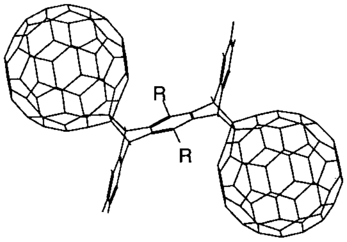
Experimental, molecular modeling, and model compound studies suggest that favorable fullerene[60] π-stacking interactions in the ground state and in *syn*-transition states account for the high *cis* stereoselectivities observed in the reactions between C_{60} and 6,13-disubstituted pentacenes.

Guided by semiempirical calculations, we recently found that a 6,13-disubstitution pattern on pentacene alters the energetics of fullerene[60] cycloaddition and enables completely regioselective syntheses of bisfullerene[60] adducts under kinetically controlled conditions.[1] *cis*-Bisfullerene[60] adducts **1** and **2** are synthesized in 85% and 75% isolated yields upon reacting a 5-fold excess of C_{60} with 6,13-diphenylpentacene and 6,13-di(4′-hydroxymethylphenyl)pentacene, respectively, in CS_2 heated at reflux for 24 h. Surprisingly, the reactions are highly *cis* stereoselective. Only traces of *trans*-bisfullerene[60] adducts **3** and **4** are detected in each reaction.

We now report that **1** and **2** are also stereoselectively synthesized under thermodynamically controlled conditions. We propose that favorable fullerene[60] π-stacking interactions in **1** and **2** and the *syn*-transition states preceding their formation are responsible for the unexpectedly high *cis* stereoselectivities observed in reactions between C_{60} and 6,-13-disubstituted pentacenes.



1: R = Ph; **2**: R = 4’-hydroxymethylphenyl



3: R = Ph; **4**: R = 4’-hydroxymethylphenyl

Model compound studies concur. The kinetically controlled reaction between 6,13-diphenylpentacene and the small dienophile dimethyl acetylenedicarboxylate is not accompanied by a high *cis* stereoselectivity, suggesting that the fullerene[60] moieties themselves must be altering the relative energetics of the *syn* and *anti* transition states leading to **1** and **2**. Molecular mechanics (MM2) and hybrid PM3-

---

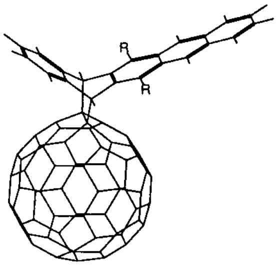
(1) Previous paper in this issue: Miller, G. P.; Mack, J. *Org. Lett.* **2000**, *2*, 3979.

10.1021/ol0064720 CCC: \$19.00

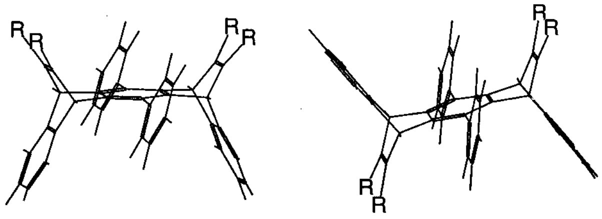
MM2 calculations are also consistent with fullerene[60] π-stacking interactions, as is the loss in *cis* stereoselectivity observed upon reacting C_{60} with a sterically demanding 6,13-disubstituted pentacene.

Thermodynamically Controlled Diels−Alder Cyclizations. In *o*-dichlorobenzene (ODCB, bp 180 °C) heated at reflux, retro-Diels−Alder cyclization of **1** and **2** is rapid. Upon reacting a 5-fold excess of C_{60} with 6,13-di(4′-hydroxymethylphenyl)pentacene in ODCB for 24 h, **2** is formed in approximately 55% yield. The remaining product slate analyzes for 2 oligomeric structures (~43% combined yield) apparently derived via the Diels−Alder condensation of C_s monoadduct **6** and *cis*-bisfullerene[60] adduct **2**. The oligomeric structures are readily distinguished from **2** and **4** on the basis of their ^{1}H NMR spectra. Notably, **4** is not formed in detectable quantities under these thermodynamically controlled reaction conditions. Consequently, we surmise that *cis*-bisfullerene[60] adducts are not only kinetically but also thermodynamically preferred to their *trans* diastereomers. We propose that favorable fullerene[60] π-stacking interactions in the ground state render *cis*-bisfullerene[60] adducts more stable than their *trans* diastereomers.

Kinetically Controlled Cycloaddition with a Small Dienophile. The reactions leading to **1** and **2** must proceed through C_s symmetric monoadducts **5** and **6**, neither of which has been isolated but both of which can be spectroscopically observed upon running reactions with a 1:1 C_{60}:6,13-disubstituted pentacene stoichiometry.[2] A second C_{60} reactant can approach **5** or **6** in either a *syn* or *anti* fashion, the *syn* approach leading to **1** or **2**, respectively. An *anti* approach would appear to be less congested than *syn*, but the exceedingly low yields of **3** and **4** suggest that factors other than sterics are operating at the respective transition states. A 6,13-disubstitution pattern on pentacene offers no obvious kinetic bias toward a *syn* or *anti* approach of the second dienophile, and this has been verified experimentally by studying the reaction between 6,13-diphenylpentacene and the small dienophile dimethyl acetylenedicarboxylate (DMAD). When 6,13-diphenylpentacene and a 5-fold excess of DMAD in toluene are heated at reflux for 2 h, a mixture of monoDMAD (40%) and bisDMAD adducts (60% overall) is observed, the *cis*- and *trans*-bisDMAD adducts **7** and **8** forming in a 1:1.3 ratio.[3] Reacting a 20-fold excess of DMAD with 6,13-diphenylpentacene in toluene heated at reflux for 48 h results in quantitative conversion of all 6,13-diphenylpentacene to a 1:1.3 mixture of **7** and **8**.



5: R = Ph; **6**: R = 4’-hydroxymethylphenyl



7 **8**

cis- and *trans*-bisDMAD adducts of 6,13-diphenyl pentacene, R = CO_2CH_3

Noteworthy, adding **7** to toluene heated at reflux for 1 week results in no detectable retro-Diels−Alder reaction, confirming the kinetically controlled nature of the forward reaction run in toluene. The lack of stereoselectivity observed in the DMAD reaction implies that the highly *cis* stereoselective syntheses of **1** and **2** under kinetically controlled conditions are special cases. That is, *the fullerene[60] moieties themselves must be altering the relative energetics of the syn and anti transition states*. Finding no reason to expect a heightened *anti* transition state energy with fullerene[60] as dienophile, we surmise that favorable interactions must be lowering the *syn* transition state energies. Specifically, we propose that the *syn* transition states leading to **1** and **2** experience favorable fullerene[60] π-stacking interactions.

π-Stacking Interactions in Ground States and *syn* Transition States. Nonbonding interactions between aromatic systems play an important role in stabilizing conformations of numerous molecular systems including nucleic acids[4] and proteins.[5] In optimal arrangements, the aromatic rings are typically stacked face to face (π-stacking conformation), edge to face (T-shaped conformation), or face to face offset (parallel-displaced conformation). All 3 conformations are recognized minima on the potential energy surface of the gas-phase benzene dimer. Both MM and ab initio calculations[6] suggest optimal spacings of 3.7−4.1 Å between the centroids of face to face π-stacked benzene rings with binding energies on the order of 1−1.3 kcal/mol. With the toluene dimer, optimal spacings of 3.5−3.6 Å are predicted

---

(2) Reactions run with a 1:1 C_{60}:6,13-diarylpentacene stoichiometry are accompanied by the formation of bispentacene adducts of C_{60} which complicate separation and isolation of C_s monoadducts. 6,13-Dialkynylpentacenes, on the other hand, react sluggishly with C_{60}, enabling the formation and isolation of C_s monoadducts in good yield, irrespective of the starting stoichiometry. See text.

(3) EI-MS (*m/z*) **7**, 714 (M^+); **8**, 714 (M^+). The assignment of stereochemistries to **7** and **8** is based upon chromatographic order of elution (flash silica column), the more polar *cis*-**7** eluting last. Also, **7** and **8** have been characterized by NMR spectroscopy (^{1}H, ^{13}C, DEPT). See ref 1 for details.

(4) Saenger, W. *Principles of Nucleic Acid Structure*; Springer-Verlag: New York, 1984.

(5) (a) Burley, S. K.; Pesko, G. A. *Science* **1985**, *229*, 23. (b) Hunter, C. A.; Singh, J.; Thornton, J. M. *J. Mol. Biol.* **1991**, *218*, 837.

(6) (a) Chipot, C.; Jaffe, R.; Maigret, B.; Pearlman, D. A.; Kollman, P. A. *J. Am. Chem. Soc.* **1996**, *118*, 11217. (b) Hobza, P.; Selzle, H. L.; Schlag, E. W. *J. Phys. Chem.* **1996**, *100*, 18790.

with binding energies on the order of 2.5−2.6 kcal/mol.[6a] Interactions of this magnitude could certainly influence the relative ground state and transition state energetics of **1**, **2**, **3**, and **4** such that **1** and **2** dominate. However, there are numerous structural differences between **1** and **2** and benzene or toluene π-stacks, and any comparisons between the two systems must take these differences into account.

First, nearest neighbor carbon atoms on adjacent fullerene[60] cages in **1** and **2** reside on C_5, not C_6, rings (Figure 1).

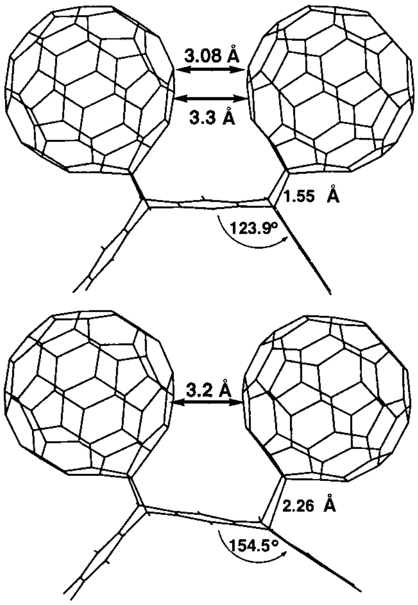


Figure 1. MM2 calculated ground state (top) and PM3-MM2 calculated *syn* transition state (bottom) for the *cis*-bisfullerene[60] adduct of pentacene.

When the separate planes defined by the atoms of each C_5 ring are dropped an equal distance to a horizontal plane, the corresponding base angles, θ, are 86°, indicating that the nearest neighbor C_5 rings are nearly parallel to one another (parallel at $\theta = 90°$). Because curvature inherent to the fullerene surface renders each C atom of the fullerene[60] moieties pyramidalized[7] (the pyramidalization angle for C_{60} is 11.6°), p-orbitals radiating from nearest neighbor C_5 rings do not point directly toward one another. This structural feature leads one to predict that optimal π-stacking geometries for **1** and **2** should place nearest neighbor C_5 rings somewhat closer together than the 3.5−4.1 Å separation predicted for benzene and toluene π-stacks. MM2 calculations place the centroids of the nearest neighbor C_5 rings 3.3 Å apart, with the carbons of closest contact 3.08 Å apart (Figure 1).

Nearest neighbor C_5 rings should be slightly closer in the *syn* transition states preceding *cis*-bisfullerene[60] adducts where the flatter pentacene backbone pushes the fullerene[60] moieties closer together. Molecular orbital modeling of *syn* and *anti* transition states would be useful, but the large number of atoms involved in the calculation preclude us from doing so. Nonetheless, *syn* transition state structures can be crudely estimated from PM3 calculated transition states of smaller systems. Thus, upon locating the PM3 transition state structure preceding formation of the *cis*-bisethylene adduct of pentacene, the H atoms on each ethylene moiety are removed and replaced with 116 carbons in the form of 2 fullerene[60] cages. The lengths of the partially formed σ-bonds at the 5,14-positions of the pentacene backbone are artificially assigned values of 2.26 Å, reasonable for a concerted Diels−Alder transition state involving C_{60} and pentacene (Table 1). With these bond lengths and the entire pentacene backbone constrained, the rest of the structure is allowed to minimize via an iterative MM2 routine.[8] The resulting hybrid PM3-MM2 structure (Figure 1) suggests a centroid to centroid distance between nearest neighbor C_5 rings of 3.2 Å in the transition state preceding the *cis*-bisfullerene[60] adduct.

Table 1. PM3 Calculated Transition States

dienophile	diene	TS 5,14-bond lengths[a] (Å)
C_2H_4	pentacene	2.201
	6,13-diphenylpentacene	2.201
	6,13-bis(TMS-ethynyl)-pentacene	2.206
	pentacene	2.258
	6,13-diphenylpentacene	2.265
	6,13-bis(TMS-ethynyl)-pentacene	2.259

[a] Refers to the pair of identical, partially formed σ-bonds bearing an imaginary frequency at the 5,14-positions of the pentacene backbone.

Steric Disruption of π-Stacking Interactions in *syn* Transition States. To further investigate π-stacking interactions in *syn* transition states leading to *cis*-bisfullerene[60] adducts, we considered preparing a new pentacene structure with sterically demanding 6,13-substituents and then reacting it with C_{60} under kinetically controlled conditions. Sterically demanding 6,13-substituents introduce van der Waals repulsion to *cis*-bisfullerene[60] adducts by virtue of their close proximity to the fullerene[60] moieties. van der Waals repulsion is allayed by rocking the fullerene[60] moieties away from the 6,13-substituents and consequently away from each other. Because even slight deformations from ideal π-stacking geometries can impact binding energies[6] (stabilities), we reasoned that sterically demanding 6,13-substituents should diminish the *cis* stereoselectivity observed in bisfullerene[60] adduct formation. Several PM3-MM2 models of *syn* transition states preceding formation of *cis*-bis-

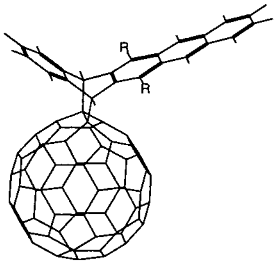
---

(7) (a) Haddon, R. C.; Raghavachari, K. *Tetrahedron* **1996**, *52*, 5207. (b) Haddon, R. C. *Science* **1993**, *261*, 1545.

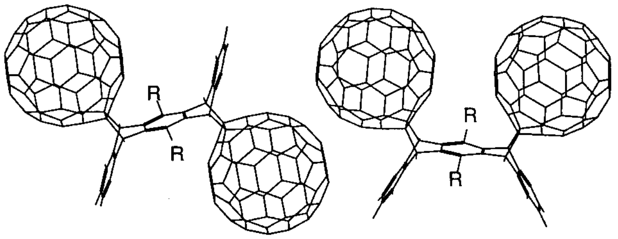
(8) This approach is similar to older force field methods of locating transition state structures where certain degrees of freedom (e.g., torsion angles) are restricted while allowing all other internal degrees of freedom to relax. See: Burkert, U.; Allinger, N. L. *Molecular Mechanics*; American Chemical Society: Washington, 1982; pp 72−76.

fullerene[60] adducts were prepared and analyzed. The *syn* transition state structures derived from 6,13-bis(trimethylsilanyl)pentacene and 6,13-bis(*tert*-butyl)pentacene are highly hindered and suggest a potential loss in Diels−Alder reactivity. Conversely, the PM3-MM2 *syn* transition state structure derived from 6,13-bis(trimethylsilanylethynyl)pentacene suggests that the TMS groups should provide mild disruption to the *syn* transition state while not completely retarding reactivity.

6,13-Bis(trimethylsilanylethynyl)pentacene was prepared and reacted with a 5-fold excess of C_{60} in CS_2 heated at reflux. As with 6,13-diphenyl- and 6,13-di(4′-hydroxymethylphenyl)pentacene, fullerene[60] cycloadditions across 6,13-bis(trimethylsilanylethynyl)pentacene are completely regioselective. The reaction is, however, somewhat sluggish compared to the 6,13-diaryl systems. The lower rates of reaction can be partially attributed to a sterically hindered approach of the fullerene, but the greater electronegativity of the alkynyl substituents (sp hybridization) no doubt results in diminished diene nucleophilicity, and this electronic effect must also be operating. With the slower rates of cycloaddition, C_s monoadduct **9** can be isolated in 75% yield after 24 h of reaction time. Bisfullerene[60] adducts also form after 24 h, but longer reaction times (48−72 h) were employed to increase their yield. Although ^{1}H NMR spectra seem consistent with formation of only one bisfullerene[60] isomer, ^{13}C NMR spectra clearly demonstrate formation of both a *cis*- and *trans*-bisfullerene[60] adduct, **10** and **11**, respectively. One of the 2 diastereomers is formed in a roughly 2.5:1 excess, but NMR spectroscopy cannot distinguish between the *cis* and *trans* diastereomers in this case. The excess of 1 isomer combined with coincidental overlap account for the deceptively simple ^{1}H NMR spectrum. In the ^{13}C NMR spectrum, 4 sp^3 signals are observed at 56.3, 56.8, 71.9, and 72.5 ppm. The pair of high-field signals correspond to the bridgehead pentacene carbons (5′,14′- and 7′,12′-) while the pair at lower field correspond to the fullerenic sp^3 carbons (C1 and C2) on **10** and **11**. In the congested sp^2 region between 118 and 156 ppm, a total of 58 signals can be counted, including several especially large signals resulting from coincidental overlap. A total of 34 sp^2 carbons are expected for each isomer for a total of 68 sp^2 signals. Only 2 signals are observed in the sp region at 101.0 and 106.7, indicating coincidental overlap of *cis*- and *trans*-alkynyl carbons.



9: R = $C_2Si(CH_3)_3$



cis-**10** and *trans*-**11**: R = $C_2Si(CH_3)_3$

The loss of stereoselectivity accompanying reaction with bis(trimethylsilanylethynyl)pentacene is consistent with a disruption of fullerene[60] π-stacking in the *syn* transition state. The TMS groups in bis(trimethylsilanylethynyl)pentacene must also influence the energetics of the *anti* transition state leading to **11**, but to a different extent.

In summary, C_{60} reacts with 6,13-disubstituted pentacenes under both kinetically and thermodynamically controlled conditions to afford *cis*-bisfullerene[60] adducts with high stereoselectivity. Experimental, molecular modeling, and model compound studies combine to suggest that favorable fullerene[60] π-stacking interactions in ground states and in *syn* transitions states account for the high *cis* stereoselectivities observed. MM2 ground state calculations place nearest neighbor carbon atoms of the fullerene[60] moieties 3.08 Å apart with the centroids of nearest neighbor C_5 rings approximately 3.3 Å apart.

Acknowledgment. The authors thank the University System of New Hampshire for financial support. J.M. acknowledges the New England Board of Higher Education (NEBHE) for a NEBHE Doctoral Fellowship.

OL0064720