Completely Regioselective, Highly Stereoselective Syntheses of *cis*-Bisfullerene[60] Adducts of 6,13-Disubstituted Pentacenes

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ABSTRACT



cis-Bisfullerene[60] adducts of 6,13-disubstituted pentacenes (R = Ph, 4'-hydroxymethylphenyl) are synthesized in 75% to 85% isolated yields under kinetically controlled Diels–Alder conditions. The cycloadditions are completely regioselective and highly stereoselective, with only traces of the diastereomeric *trans*-bisfullerene[60] adducts forming.

We have been interested in the Diels-Alder chemistry between C_{60} and large linear acenes such as pentacene for several years. Our initial studies¹ indicated that 1 equiv of C_{60} cycloadds across the central 6,13-carbons of pentacene heated at reflux in toluene to yield the C_{2v} symmetric monoadduct **1** in 59% uncorrected yield. Utilizing a 10-fold



excess of C_{60} pushes the yield of monoadduct **1** to 86% on the basis of pentacene consumed.

Of greater interest to us is the exploitation of multiple reaction sites on large linear acenes in order to prepare bisfullerene[60] adducts. The *trans*- and *cis*-bisfullerene[60] pentacene adducts **3** and **4** are representative examples. **4** is



a particularly desirable product due to the close proximity between the two fullerene[60] moieties and the expectation that this and related structures may possess intriguing electronic behaviors. Upon reacting C_{60} and pentacene directly, we found no evidence for the formation of either **3** or **4**. C_s symmetric monoadduct **2** is a necessary precursor

⁽¹⁾ Mack, J.; Miller, G. P. Fullerene Sci., Technol. 1997, 5, 607.

to **3** and **4**, and it too was absent from C_{60} -pentacene product slates, suggesting that we needed a different route to prepare **3** and **4**. Utilizing the plan outlined in Scheme 1, 5,14-



azabridged pentacene **5** was successfully synthesized. *N*-Methylisoindole and 4,5-dibromobenzyne are key intermediates in the synthesis which utilizes Gribble's convenient N-oxidation of azabridged aromatics² with concomitant rearomatization. Upon reacting C_{60} with **5**, however, we did not isolate a standard Diels–Alder adduct but rather an adduct consistent with fullerene[60] insertion into the bridgehead C–N bond of **5**. We continue to study this unexpected reaction and will report the details separately.

Two years after our initial C_{60} —pentacene publication¹ and after our synthesis of **5**, Komatsu and co-workers reported³ a solid state, high-speed vibration milling synthesis of *trans*-bisfullerene[60] pentacene adduct **3** in 11% yield. Because of the low yield of **3** and the apparent absence of *cis*-bisfullerene[60] pentacene adduct **4** in the solid-state synthesis, we continued to seek high-yielding syntheses of both *cis*- and *trans*-bisfullerene[60] adducts of linear acenes.

We now report facile syntheses of *cis*-bisfullerene[60] adducts of 6,13-disubstituted pentacenes under kinetically controlled Diels-Alder conditions. The reactions occur with complete regioselectivity, with cycloadditions occurring exclusively at the 5,14- and 7,12-carbons of the pentacene backbone. Moreover, the reactions are highly stereoselective. *cis*-Bisfullerene[60] adducts **6** and **7** are produced in 85% and 75% isolated yields, respectively, with only traces of the diastereomeric *trans*-bisfullerene[60] adducts **8** and **9** formed.



6: R = Ph; 7: R = 4'-hydroxymethylphenyl



8: R = Ph; 9: R = 4'-hydroxymethylphenyl

Synthetic Design and Execution. Semiempirical calculations were utilized to design practical, high-yielding syntheses of bisfullerene[60] adducts. While AM1 and PM3 semiempirical methods are considered unreliable for describing reaction thermochemistry and/or reaction kinetics with systems incorporating third row elements, they do a reasonable job of predicting trends in ground-state geometries, $\Delta H_{\rm f}^{\rm o}$ values, and transition state structures with purely hydrocarbon systems.⁴ We place confidence in the qualitative trends established by these calculations. Thus, PM3 thermochemical comparisons indicate that $\mathbf{1}$ is enthalpically preferred to 2 ($\Delta\Delta H_{\rm f}^{\rm o} = 4.0$ kcal/mol). Additionally, PM3 transition state modeling with bicyclopentylidene as dienophile suggests that cycloaddition across the central 6,13carbons of pentacene is kinetically preferred to cycloaddition across the 5,14-carbons ($\Delta \Delta H^{\neq} = 1.4$ kcal/mol). Consequently, C_{2v} monoadduct 1 is expected to be both the kinetically and thermodynamically preferred monoadduct product in the reaction between C_{60} and pentacene.

PM3-calculated energetics for the C_{60} /pentacene reaction change dramatically when a 6,13-disubstituted pentacene is utilized in place of parent pentacene. For example, 6,13diphenylpentacene shows both a kinetic and thermodynamic preference for cycloaddition across its 5,14- (or 7,12-) rather than its 6,13-carbons (Table 1). Moreover, the kinetic and

Table 1.	PM3-Calculated Diels-Alder Reactivity of
6,13-Diph	enylpentacene

	$\Delta H_{\rm f}^{\rm 0}/\Delta H_{\rm RXN}^{\rm 0}$ (kcal/mol)		∆ <i>H</i> ≠ (kcal/mol)	
dienophile	6,13-product	5,14-product	6,13-T.S.	5,14-TS
C_2H_4	147.8/-32.4	138.6/-41.5	211.4	207.4
$\bigcirc \neg \bigcirc$	151.5/+12.3	122.6/-16.5	201.1	181.3

thermodynamic bias toward 5,14-cycloaddition increases with increasing size of the dienophile. With bicyclopentylidene, cycloaddition across the 6,13-carbons of 6,13-diphenylpentacene is already endothermic. A careful review of the

⁽²⁾ Gribble, G.; Allen, R. W. Tetrahedron Lett. 1976, 3673.

⁽³⁾ Murata, Y.; Kato, N.; Fujiwara, K.; Komatsu, K. J. Org. Chem. **1999**, 64, 3483.

literature lends credibility to the calculations. Allen and Bell reported^{5a} dual reactivity between 6,13-diphenylpentacene and maleic anhydride as part of a rich study of pentacenequinone formation and reactivity. They observed formation of both a monoanhydride, with cycloaddition reported across the central 6,13- carbons,^{5b} and a dianhydride, with two cycloadditions across the 5,14- and 7,12-carbons, respectively, in xylene heated at reflux.

Upon preparing 6,13-diphenylpentacene and 6,13-di(4'hydroxymethylphenyl)pentacene⁶ and separately reacting each with a 5-fold excess of C₆₀ in CS₂ heated at reflux for 24 h, *cis*-bisfullerene[60] adducts **6** and **7** are formed in 85% and 75% isolated yields, respectively. When **6** and **7** are heated at reflux in CHCl₃ (bp 62 °C) for an extended time period, no detectable retro-Diels–Alder reaction results, thereby confirming the kinetically controlled nature of the forward reactions run in CS₂ heated at reflux (bp 46.2 °C).

Structural Characterization of 6 and 7. A careful examination of analytical data firmly establishes 6 and 7 as cis-bisfullerene[60] adducts. ¹H NMR spectra for 6 and 7 each show a single methine singlet at 5.7 ppm which integrates for 4 protons. This shift compares favorably to the 6.1 ppm value for the methine protons in $1.^{1}$ Like 1, 6 and 7 each show 1 set of AA'MM' multiplets that are centered at 7.45 and 7.60 ppm for 6 and 7.43 and 7.56 ppm for 7. Unlike 1, 6 and 7 show no XX' singlets in their ¹H NMR spectra. The absence of XX' singlets implicates 6 and 7 as bisfullerene[60] regioisomers in which fullerene[60] cycloadditions have occurred across the 5,14- and 7,12-carbons of their respective pentacene backbones. Positive ion electrospray mass spectra of diol 7 show a strong [M·Na⁺] signal at m/z = 1954,⁷ confirming formation of a bisfullerene[60] adduct and validating the ¹H NMR interpretation.

Importantly, the aromatic protons of the 6,13-diphenyl and 6,13-di(4'-hydroxymethylphenyl) substituents on **6** and **7** give rise to 5 and 4 unique ¹H NMR signals (2 doublets and 3 triplets for **6**; 4 doublets for **7** (Figure 1)), respectively, each signal integrating for 2 total protons. This result has both conformational and stereochemical implications. Thus, the 6,13-diphenyl and 6,13-di(4'-hydroxymethylphenyl) substituents on **6** and **7** must be rotating slowly on the NMR time scale. Moreover, bisfullerene[60] adducts **6** and **7** must possess a $C_{2\nu}$ cis rather than a C_{2h} trans structure. C_{2h} symmetric **8** and **9** would show 3 and 2 unique 6,13-diaryl ¹H NMR signals, irrespective of slow phenyl (or 4'-hydroxymethylphenyl) rotation. Thus, unlike the situation with $C_{2\nu}$ **6** and **7**, the NMR spectra for C_{2h} **8** and **9** are not qualitatively influenced by slow 6,13-diaryl rotation.

The ¹H NMR evidence for *cis* stereochemistries in **6** and **7** is fully corroborated by ¹³C NMR and DEPT spectra. $C_{2\nu}$ symmetric **6** and **7** possess 30 fullerenic carbon signals each in their ¹³C NMR spectra, including a few with coincidental overlap in the crowded sp² region between 135 and 157 ppm. The additional signals observed in the 42- and 43-line ¹³C NMR spectra for **6** and **7** include 6 from the pentacene backbone (equivalents sets of pentacene carbons: C1',4',8',-11'; C2',3',9',10'; C4a',7a',11a',14a'; C5',7',12',14'; C5a',-6a',12a',13a'; C6',13') and an additional set of either 6 (for



Figure 1. Aromatic region of ¹H NMR spectrum of **7** showing AA'MM' multiplets of the pentacene backbone (4H each, 7.43 and 7.56 ppm) along with 4 doublets (2H each) of the slowly rotating 6,13-di(4'-hydroxymethylphenyl) substituents. The large singlet at 7.27 ppm is residual CHCl₃ in CDCl₃.

6) or 7 (for 7) signals derived from the slowly rotating 6,-13-diphenyl or 6,13-di(4'-hydroxymethylphenyl) substituents, respectively. Noteworthy, the aromatic methine signals on 6 and 7 are all clustered between 125 and 130 ppm, well resolved from other ¹³C NMR signals. A DEPT spectrum of 7 confirms this assignment of aromatic methines. A careful examination of the region reveals 7 signals for 6 including 5 that are roughly one-half the intensity of the remaining 2 (Figure 2). The 5 weaker signals correspond to the 5 aromatic



Figure 2. Aromatic methine region of ¹³C NMR spectrum of 6.

methines (2 C each) on the slowly rotating 6,13-diphenyl substituents while the 2 stronger signals correspond to the aromatic methines on the pentacene backbone (4 C each, C1',4',8',11' and C2',3',9',10'). Similarly, the DEPT spectrum for **7** reveals 6 aromatic methines between 125 and 130 ppm, 4 of roughly one-half the intensity of the remaining 2. C_{2h}

symmetric *trans*-bisfullerene[60] adducts **8** and **9** would only show a total of 5 and 4 aromatic methine signals, irrespective of hindered phenyl (or 4'-hydroxymethylphenyl) rotation.

Hindered Rotation of 6,13-Diaryl Substituents. Hindered rotation of the 6,13-diphenyl and 6,13-di(4'-hydroxymethylphenyl) substituents on 6 and 7 is due to van der Waals repulsion between the *o*-hydrogens on the 6,13diphenyl rings and the immobilized methine hydrogens at the bridgehead positions (5,14- and 7,12-) of the respective pentacene backbones. The situation is akin to a 2,6disubstituted biphenyl in which both *o*-positions of one ring are substituted with 3° alkyl groups. The literature reveals several related cases of hindered phenyl rotation, a good comparison to 6 and 7 being the conformationally constrained *syn*-9-phenyl-2,11-dithia[3,3]metacyclophane **10**. Mitchell



syn-9-phenyl-2,11-dithia[3,3]metacyclophane 10

and co-workers published⁸ VT ¹H NMR spectra of **10** which show well-resolved *o*-protons on the 9-phenyl substituent at room temperature. Thus, the slowly rotating 9-phenyl substituent on **10** gives rise to 5 unique ¹H NMR resonances.



 C_{2v} cis- and C_{2h} trans-bisDMAD adducts of 6,13-diphenyl pentacene, $R = CO_2CH_3$

Better model compounds for comparison to **6** and **7** are available upon reacting 6,13-diphenylpentacene with dienophiles other than C_{60} . Excess dimethyl acetylenedicarboxylate (DMAD) reacts with 6,13-diphenylpentacene in toluene heated at reflux to give a 1:1.3 mixture of *cis*- and *trans*-bisDMAD adducts **11** and **12**, respectively. Following

isolation via flash silica chromatography (the more polar **11** eluting last), ¹H NMR spectra reveal 5 incompletely resolved 6,13-diphenyl ¹H resonances for $C_{2\nu}$ **11**. Conversely, C_{2h} **12** shows only 3 unique ¹H resonances for the 6,13-diphenyl rings. Most compelling, DEPT spectra for $C_{2\nu}$ **11** and C_{2h} **12** reveal 5 and 3 unique ¹³C methine resonances, respectively, for the 6,13-diaryl rings. The results are conclusive. Just as with $C_{2\nu}$ **6** and C_{2h} **7**, the 6,13-diphenyl rings on $C_{2\nu}$ **11** and C_{2h} **12** rotate slowly on the NMR time scale, enabling NMR methods to distinguish between the two diastereomers.

The separate reactions leading to 6 and 7 are each accompanied by the formation of trace quantities of another isomer, presumably 8 and 9, respectively. Noise-riddled ¹H NMR spectra are consistent with 8 and 9, but lack of sufficient sample size prevents complete characterizations.

In summary, a 6,13-disubstitution pattern on pentacene alters the energetics of fullerene[60] cycloaddition and enables the completely regioselective and highly stereoselective synthesis of *cis*-bisfullerene[60] adducts. Utilizing 6,-13-diphenylpentacene and 6,13-di(4'-hydroxymethylphenyl)pentacene, *cis*-bisfullerene[60] adducts **6** and **7** are synthesized in 85% and 75% isolated yields, respectively.

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Supporting Information Available: Spectroscopic data (including ¹H NMR, ¹³C NMR, DEPT, electrospray MS, and UV/vis spectra) for **6**, **7**, **11**, and **12**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(6) 6,13-Disubstituted pentacenes are prepared via organolithium addition to pentacenequinone followed by either SnCl₂- or KI-promoted aromatization of the corresponding diol. See ref 4. The stability of the 6,13-disubstituted pentacenes varies as a function of substitution. Oxidation and/or photo-dimerization are common degradation paths.

(7) MeOH solutions of 7 were employed for electrospray MS experiments. While excellent results could be obtained with polar diol 7, nonpolar hydrocarbon 6 showed poor solubility in MeOH and gave unsatisfactory results.

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