ORGANIC
LETTERS

2003
Vol. 5, No. 22
4199−4202

Fullerene–Acene Chemistry: Single-Crystal X-ray Structures for a [60]Fullerene–Pentacene Monoadduct and a *cis*-Bis[60]fullerene Adduct of 6,13-Diphenylpentacene

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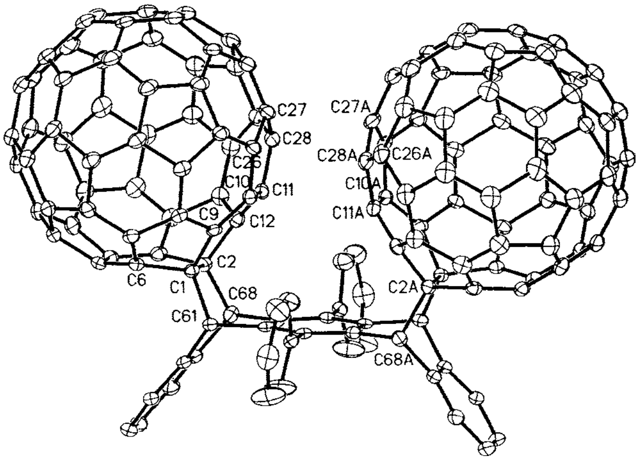
Received August 28, 2003

ABSTRACT



Crystal structures of the *cis*-bis[60]fullerene adduct of 6,13-diphenylpentacene (with the closest carbon atoms on adjacent fullerenes only 3.065(8) Å apart) and the [60]fullerene–pentacene monoadduct are in remarkably close agreement with the MM2 calculated structures.

Molecules containing multiple [60]fullerene moieties are interesting synthetic targets as they possess unusual electronic[1] and electrochemical[2] properties. Recently, we reported that a double-Diels−Alder cycloaddition of two [60]fullerenes across 6,13-diphenylpentacene produced a new bis-[60]fullerene adduct, **1**, in which the two [60]fullerene moieties are held along the same face of a five-ring acene

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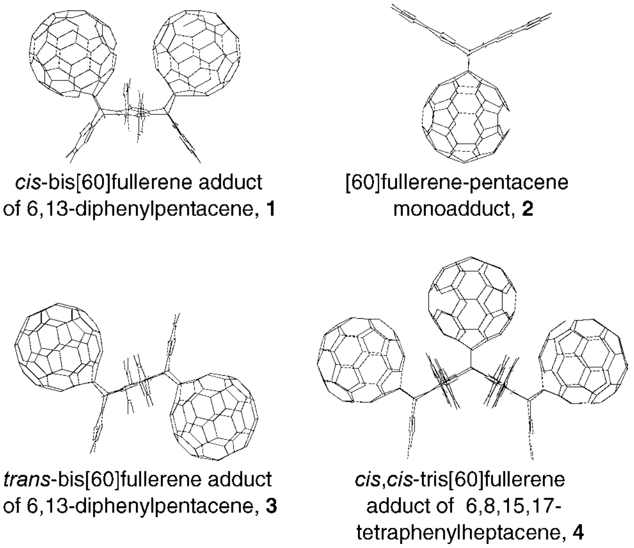
10.1021/ol035646l CCC: $25.00

Scheme 1. Fullerene−Acene Adducts



cis-bis[60]fullerene adduct of 6,13-diphenylpentacene, **1**

[60]fullerene-pentacene monoadduct, **2**

trans-bis[60]fullerene adduct of 6,13-diphenylpentacene, **3**

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

(Scheme 1).[3] The cycloadditions occur with complete regioselectivity; the fullerenes add exclusively across the 5,14 and 7,12 carbons of the 6,13-diphenylpentacene backbone. In contrast, the solution-phase reaction between [60]fullerene and unsubstituted pentacene produces Diels−Alder monoadduct **2** in regioselective fashion.[4]

Most interestingly, the regioselective formation of **1** is highly cis diastereoselective. Only traces (at most) of the corresponding trans diastereomer, **3**, are observed to form. Experimental and computational results[3b,5] suggest that favorable fullerene−fullerene π-stacking interactions in **1** as well as the transition state leading to **1** are responsible for the observed diastereoselectivity. We now report a single-crystal X-ray diffraction structure for *cis*-bisadduct **1** that measures the spacing between the [60]fullerene moieties. Additionally, a single-crystal X-ray diffraction structure for the [60]fullerene−pentacene Diels−Alder monoadduct, **2**, is also reported.

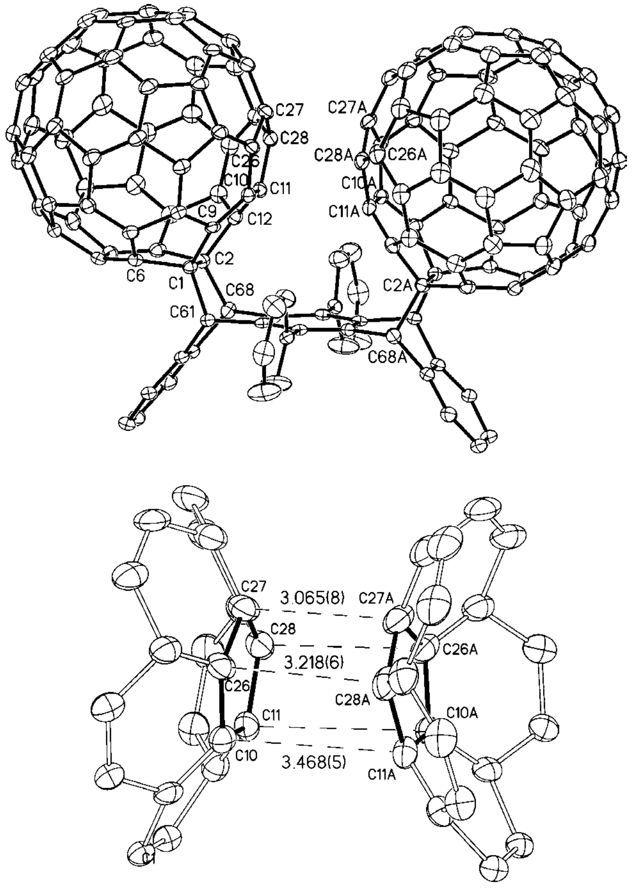


Figure 1. Top: perspective view of **1** in **1**·4.5 $\mathrm{CS_2}$ showing 50% thermal contours for all non-hydrogen atoms. Selected bond distances: C1−C2, 1.605(5) Å; C1−C6, 1.534(5) Å; C1−C61, 1.593(5) Å; C2−C3, 1.530(5) Å; C2−C12, 1.524(5) Å; C2−C68, 1.586(5) Å. Bottom: expanded view of the region of contact between the two fullerenes with the nonbonded C···C distances.

Crystals of **1**·4.5$\mathrm{CS_2}$ were grown by vapor diffusion of 2:8 $\mathrm{CS_2}$/*n*-hexane into a solution of **1** in 8:2 $\mathrm{CS_2}$/*n*-hexane.[6] Figure 1 shows a drawing of the molecule and an enlargement of the region where the two fullerenes make closest contact. The molecule is situated on a crystallographic 2-fold axis that runs perpendicular to the central benzene ring of the pentacene backbone. The structure confirms the location of the two fullerene cages on the same side (syn) of the pentacene backbone. The pentacene moiety is folded in two places where the fullerene additions have occurred. The fold angle, the angle between the planes of the terminal and central benzene rings of the pentacene backbone, is 123.2°. The presence of the two fullerene neighbors does not produce any unusual distortions of the central platform of the pentacene backbone that extends from C68 to C68A. This portion is nearly planar, with C68 showing the largest out-of-plane distance, 0.072 Å.

Two five-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 five-membered rings, furthest removed from the pentacene backbone. The distance between the centers of the abutting

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(6) Crystal data for **1**·4.5$\mathrm{CS_2}$. $\mathrm{C_{158.5}H_{22}S_9}$: black plate, monoclinic, space group *C*2/*c*1, a = 33.0398(13) Å, b = 14.6690(6) Å, c = 19.9868(8) Å, β = 103.814(1)°, V = 0406.6(7) Å^3, Z = 4, λ = 0.71073 Å, D_c = 1.564 Mg/m^3; μ = 0.282 mm^{-1}; T = 90(2) K; 65 386 reflections collected; 10 790 independent (R_{int} = 0.083) included in the refinement; min/max transmission = 0.846/0.952; Patterson and difference Fourier methods solution (SHELXS-97; Sheldrick, G. M.; University of Göttingen: Göttingen, Germany, 1990); full-matrix least squares based on F^2 (SHELXL-97; Sheldrick, G. M.; University of Göttingen: Göttingen, Germany, 1998); $R1$ = 0.144, w$R2$ = 0.256 for all data; conventional $R1$ = 0.079 computed for 5461 observed data ($>2\sigma(I)$) with 14 restraints and 763 parameters.

pentagons is 3.284 Å. This distance is only slightly shorter than the 3.35 Å van der Waals spacing between adjacent sheets of graphite.[7] 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),[8] while the corresponding distances in $C_{60}{\cdot}4C_6H_6$[9] and in $2C_{60}{\cdot}3CS_2$,[10] 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. In the disordered structure of pristine [60]fullerene, the fullerene−fullerene contacts involve fullerene C═C bonds that lie over the centers of pentagons or hexagons of neighboring molecules. In $C_{60}{\cdot}4C_6H_6$[9] and in $2C_{60}{\cdot}3CS_2$,[10] the fullerenes are packed so that pentagons on adjacent molecules lie parallel to one another but are laterally shifted so that one carbon atom of the first pentagon lies almost directly above the center of the second, neighboring pentagon. Thus, this mode of packing avoids the eclipsed interactions found in **1**. In $2C_{60}{\cdot}3CS_2$, the separation between the planes of abutting pentagons is 3.138 Å and the lateral shift of the center of one pentagon versus the other is 1.629 Å, while in $C_{60}{\cdot}4C_6H_6$, the separation between neighboring pentagonal planes is 3.224 Å and the lateral shift is 1.156 Å.[10]

Crystals of **2**·2 CS_2 were obtained from vapor diffusion of 1:10 CS_2/*n*-pentane into a solution of the compound in 10:1 CS_2/*n*-pentane.[11] Figure 2 shows a drawing of the molecule. The asymmetric unit consists of one molecule of **2** and two molecules of CS_2. The fold angle of the pentacene, the angle between the least squares planes of the two naphthalene rings in the adduct, is 126.7°. This angle is similar to the fold angle (123.2°) in **1** and also similar to that found in *s*-dipentacene (127.4 Å), the photo dimer of pentacene that has a similar linkage.[12]

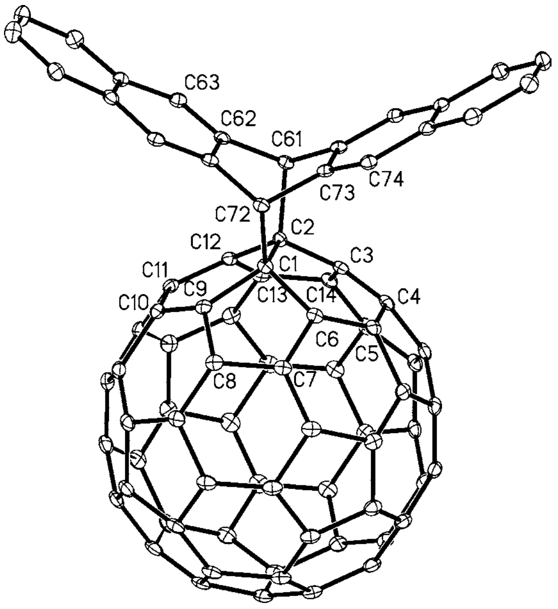

Figure 2. Perspective view of **2** in **2**·2CS_2 showing 50% thermal contours for all non-hydrogen atoms. Selected bond distances: C1−C2, 1.602(4) Å; C1−C6, 1.529(4) Å; C1−C72, 1.597(4) Å; C2−C3, 1.529(4) Å; C2−C12, 1.531(4) Å; C2−C61, 1.584(4) Å.

Figure 3 shows the packing of **2** in the solid state. The bent pentacene wings of the adduct embrace the fullerene portion of a neighboring adduct. Within the region of contact, the shortest nonbonded C···C distances are 3.17 and 3.20 Å. The mode of packing seen here is analogous to that proposed for the fullerene adduct with anthracene.[13] That adduct undergoes a remarkably specific anthracene-transfer reaction in the solid state to produce antipodal (*trans*-**1**) bisadduct, and solid-state packing has been established as crucial for this transformation.[13]

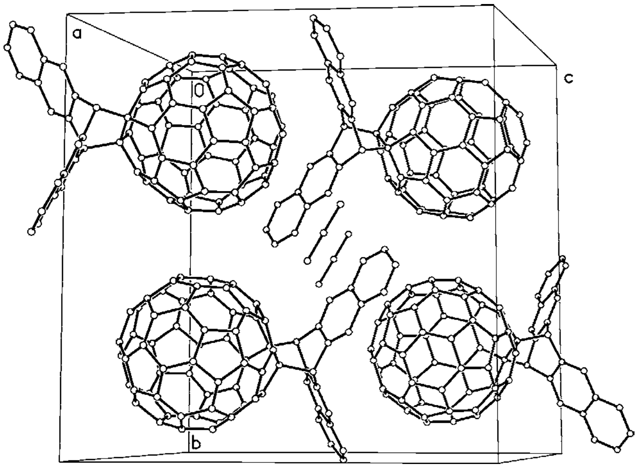

Figure 3. Drawing of the unit cell of **2**·2CS_2 showing the packing of the molecules.

Molecular mechanics (MM) calculations predict the structures of **1** and **2** with a high degree of accuracy (Table 1). Semiempirical calculations fare far worse, presumably because they do not account for van der Waals interactions. It is instructive to compare the details of the MM calculations

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[11] Crystal data for **2**·2CS_2. $C_{84}H_{14}S_4$: black wedge, monoclinic, space group $P2_1/n$, $a = 13.1275(14)$ Å, $b = 19.600(2)$ Å, $c = 18.828(2)$ Å, $\beta = 105.288(2)°$, $V = 4673.0(9)$ Å^3, $Z = 4$, $\lambda = 0.71073$ Å, $D_c = 1.636$ Mg/m^3; $\mu = 1.636$ mm^{-1}; $T = 90(2)$ K; 63 005 reflections collected; 13 580 independent ($R_{int} = 0.091$) included in the refinement; min/max transmission = 0.846/0.952; Patterson and difference Fourier methods solution (SHELXS-97, Sheldrick, G. M.; University of Göttingen: Göttingen, Germany, 1990); full-matrix least squares based on F^2 (SHELXL-97; Sheldrick, G. M.; University of Göttingen: Göttingen, Germany, 1998); $R1 = 0.137$, w$R2 = 0.164$ for all data; conventional $R1 = 0.059$ computed for 7210 observed data ($>2\sigma(I)$) with 0 restraints and 847 parameters.

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Table 1. X-ray Crystal and MM2 Calculated Structural Parameters

	parameter	X-ray	MM2	AM1	PM3
1	C⋯C (Å, closest contact, adjacent fullerenes)	3.065(8)	3.08	4.23	4.25
	centroid-to-centroid (Å, adjacent fullerenes)	9.805	9.84	10.91	10.90
	centroid-to-centroid (Å, adjacent five-membered rings)	3.284	3.32	4.28	4.29
	pentacene fold angle (deg)	123.2	127.6	123.4	123.5
	C−C (Å, C(full)−C(pent))	1.593(5) 1.586(5)	1.55	1.56	1.56
	C−C (Å, C1−C2)	1.605(5)	1.56	1.58	1.59
2	pentacene fold angle (deg)	126.7	129.1	121.6	122.0
	C−C (Å, C(full)−C(pt))	1.597(4) 1.584(4)	1.55	1.56	1.56
	C−C (Å, C1−C2)	1.602(4)	1.56	1.58	1.59

for **1** and **3**. The calculated strain energies are nearly identical in every category except van der Waals interactions. Here, compound **1** holds a 4 kcal/mol advantage over **3** and this figure presumably approximates the additional van der Waals stabilization of **1**. Considering the reasonable match between the MM calculated structure and the crystal structure for **1**, we place some faith in this number. Nonetheless, an experimental measure of the energetics associated with fullerene−fullerene π-stacking would be preferred. Efforts toward this end are currently underway.

While higher-level calculations (e.g., DFT) would likely outperform AM1 and PM3 methods, the success of MM programs in predicting the structures of **1** and **2** is significant from a practical point of view. It suggests that computationally undemanding MM calculations may be used to guide further experimentation between [60]fullerene and acenes, including the synthesis of larger adducts. Thus, MM2 calculations predict that the *cis,cis*-tris[60]fullerene adduct of 6,18,15,17-tetraphenylheptacene, **4**, is 3 and 4 kcal/mol more stable than the corresponding trans,trans and cis,trans diastereomers, respectively. Consequently, the synthesis and Diels−Alder reactivity of 6,18,15,17-tetraphenylheptacene becomes an attractive goal.

In summary, X-ray crystal structures for *cis*-bis[60]fullerene adduct **1** and [60]fullerene−pentacene monoadduct **2** are reported. The 3.065(8) Å (atoms of closest contact) and 9.805 Å (fullerene centroid-to-centroid) distances between adjacent [60]fullerenes in **1** show the importance of van der Waals interactions in stabilizing this adduct. MM2 calculated structures for compounds **1** and **2** are remarkably close to the corresponding crystal structures. This agreement suggests that readily implemented MM calculations may be used to guide further experiments between fullerenes and acenes.

Acknowledgment. The authors thank the National Science Foundation (Grant CHE 0070291 to A.L.B.) and the University of New Hampshire for financial assistance and the New England Board of Higher Education (NEBHE) for a Doctoral Scholars Fellowship for J.M.

Supporting Information Available: X-ray crystallographic data for **1**·4.5CS_2 and **2**·2CS_2 in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

OL035646L