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COMMUNICATION

High-yield, regiospecific *bis*-functionalization of C₇₀ using a Diels-Alder reaction in molten anthraceneVenkata S. Pavan K. Neti,^a Maira R. Cerón,^a A. Duarte-Ruiz,^{b*} Marilyn M. Olmstead,^{c*} Alan L. Balch^{c*} and Luis Echegoyen^{*a}⁵ Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX

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A regiospecific *bis*-adduct of C₇₀ with anthracene was prepared with unusually high yield (68%) by the Diels-Alder reaction in the absence of solvent (melt). The structure of the *bis*-adduct was an unexpected 12 o'clock isomer, as determined by single crystal X-ray diffraction, thermal gravimetric analysis (TGA) and spectroscopy.

Regiochemical control of *bis*-addition reactions on fullerenes has been, and continues to be, an important synthetic challenge. Common fullerene functionalization methods such as addition-elimination of halogenated malonates and 1,3-dipolar cycloadditions of ylides lead to multiple isomeric *bis*- and *tris*-adducts which are relatively difficult to separate using conventional column chromatography.¹⁻³ The presence of 30 equivalent double bonds on the surface of C₆₀ leads to low *bis*-adduct regioselectivity,⁴ and in the case of C₇₀ the number of possible isomers increases because there are eight different types of C-C double bonds and five different types of carbon atoms, due to the lower symmetry of this cage.^{5,6} Diederich *et al.* and Hirsch *et al.* developed elegant synthetic strategies, such as the 'tether directed remote functionalization' and the 'reversible template directed activation' methods, for regioselective *bis*-, *tris*-, and *tetakis*-additions to C₆₀ and C₇₀.⁵ In 1996, Kräutler *et al.* reported a topochemically-controlled conversion of the crystalline C₆₀-anthracene monoadduct into the *trans*-1 *bis*-adduct in 96% yield.^{6a} Subsequently, that group showed that heating an anthracene/C₆₀ mixture at 240° C produced the same *trans*-1 *bis*-adduct in 43.7 % yield along with 4.5 % of the monoadduct and 46.7 % of unreacted C₆₀ as the only products.^{6b} Such anthracene adducts are useful as protecting groups in guiding multiple additions to fullerenes.^{5c} Surprisingly, similar solvent-free Diels-Alder reactions with C₇₀ or other fullerenes have not been reported. Here, we report that the solvent-free addition of anthracene to C₇₀ yields only one regioisomer of the *bis*-adduct in remarkably high yield (68%).

Diederich *et al.* introduced a simple nomenclature to describe *bis*-adducts of C₇₀ where the addends are attached to α bonds on opposite ends of the C₇₀ molecule, which is usually the observed case.^{5b} These ten α double bonds radiate from the two pentagons at the poles of the molecule and are typically the most reactive. Assuming from previous observations that anthracenes will add to the more reactive [6,6] α bonds, three possible regioisomers can be formed, two of which exist as enantiomeric pairs, see Figure 1. The three possible *bis*-isomers are described as 12 o'clock, 2 o'clock and 5 o'clock, depending on the relative

orientation of the two adducts around the C₅ symmetry axis (see Figure 1). The 7 o'clock and 11 o'clock *bis*-adducts can also form (not shown in Figure 1), but since the adducts are identical, these correspond to enantiomers of the 5 o'clock and 2 o'clock isomers, respectively. Generally, formation of the 2 o'clock isomer is favored, as reported for the addition of Ir(CO)Cl(PPhMe₂)₂ to C₇₀⁷ and for formation of Bingel adducts of C₇₀.^{5b}

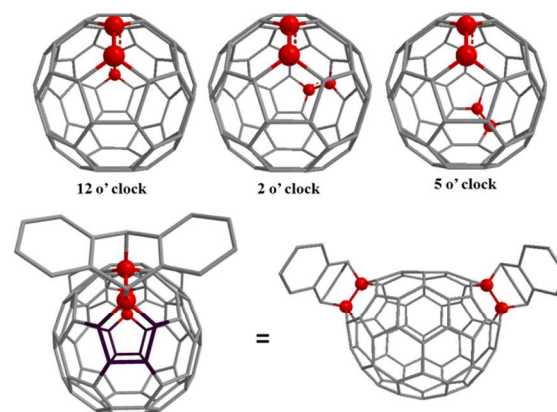


Figure 1. Representation of the possible *bis*-isomers of C₇₀ (above) and the structure of the 12 o'clock regioisomer (below).

The synthetic procedure followed was essentially the same as that previously reported by Kräutler *et al.* with C₆₀.^{6b} C₇₀ was reacted with two equivalents of anthracene in the melted state under vacuum at 240° C for 2 hours. Purification of the crude mixture on a silica gel column using CS₂:hexane (7:3) as eluent yielded, in order of elution, unreacted C₇₀ and two compounds denoted as **1** and **2**. The major fraction of the reaction was compound **2**, which was isolated in 68% yield, followed by C₇₀ and compound **1** in 22% and 10% yield, respectively.

Characterization of the C₇₀-anthracene adducts was performed using field desorption mass spectrometry (FD-MS), MALDI-TOF, electrospray ionization mass spectrometry (ESI), ¹H and ¹³C-NMR, TGA, UV/Vis, IR, cyclic voltammetry, and single crystal X-ray diffraction.

The ¹H-NMR spectrum of compound **1** showed six resonances, and was identical to the spectrum reported for an anthracene C₇₀-*mono*-adduct (on an α position) obtained using a flame synthesis procedure (Fig. S1).⁸ This observation conclusively showed that **1**

is the *mono*-adduct. The $^1\text{H-NMR}$ spectrum of compound **2** exhibited a similar set of signals as observed for compound **1** but with significant chemical shift differences (Fig. S2). Attempts to obtain the parent peaks in the mass spectra for compounds **1** and **2** using a variety of ionization techniques (MALDI-TOF, ESI, and FD) were unsuccessful, indicating that both compounds are very unstable after ionization in the gas phase, readily undergoing retro Diels-Alder reactions. The MALDI-TOF, ESI, and FD mass spectra of the crude mixture and of the isolated compounds exhibited only one strong peak at m/z 840 due to C_{70} .

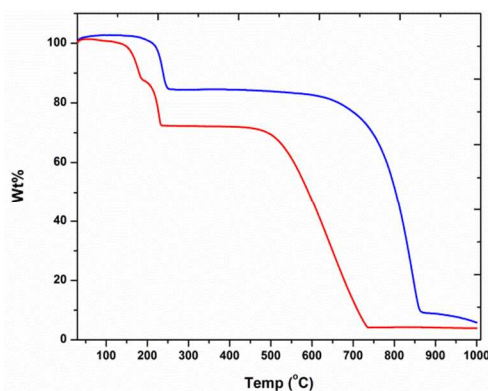


Figure 2. TGA of **1** (blue) and **2** (red) obtained up to 1000° C using a linear 3° C/min ramp method.

Thermogravimetric analyses (TGA) of **1** and **2** were performed by increasing the temperature at a rate of 3° C/min under a flow of N_2 (Fig. 2). A 17% weight loss (calculated value for the loss of one anthracene from **1**: 17.4%) was observed for **1** (transition onset at 180° C and midpoint at 220° C). A 31% weight loss was observed to occur in two discrete steps for **2** (calculated value for the loss of two successive anthracene molecules for a bis-adduct is 29.7%, first transition at 160° C and a second transition onset at 180° C and midpoint at 220° C). These results confirm the loss of a single anthracene unit from **1** and of two anthracene units from **2**. C_{70} was recovered after thermal treatment of **1** and **2** at 250° C under a N_2 atmosphere. We selectively removed only one anthracene from **2** at 190° C, but the mass balance was not quantitative. The UV-vis spectra of compound **2** is similar to those previously reported for 12 o'clock C_{70} bis-adducts,^{5c,9} exhibiting weak absorption maxima around 640nm and a strong absorption maximum at 442 nm (Fig. S4). The FT-IR spectra of **1**, **2** and C_{70} showed significant differences in the intensity of the bridgehead C-H stretching vibration bands (Fig. S5).

Table 1. Redox Potentials (V)^[a] of **1**, **2** and C_{70}

Compound	C_{70}	1	2
$\text{E}^{0/+1}$	-	0.97	0.91
$\text{E}^{0/-1}$	-1.05	-1.18	-1.21
$\text{E}^{-1/-2}$	-1.41	-1.54	-1.53
$\text{E}^{-2/-3}$	-1.83	-1.92	-1.99

^[a] Values obtained by SWV in V vs Fc/Fc^+

The redox properties of **1**, **2** and C_{70} were determined using cyclic voltammetry (CV) at a scan rate of 100mV/s and by square wave voltammetry (SWV) in *o*-dichlorobenzene solutions using

0.05M of $n\text{-Bu}_4\text{NPF}_6$ as supporting electrolyte, see Figure 3. The CV results are summarized in Table 1. The electrochemical behavior of **1** showed three reversible reduction waves, which are cathodically shifted compared to those of C_{70} under the same experimental conditions. Compound **2** also showed three reversible reduction waves, which were further cathodically shifted compared to those of compound **1**. These results agree with previous reports of successive cathodic shifts upon double bond saturation by chemical functionalization.¹⁰ Compounds **1** and **2** showed one reversible oxidation wave.

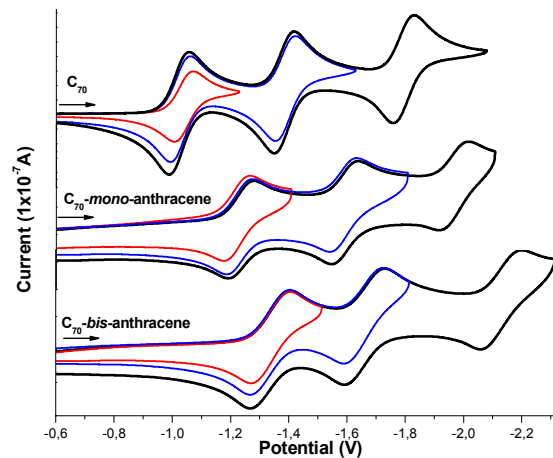


Figure 3. Cyclic voltammetry of 0.05mM of C_{70} , C_{70} -*mono*-anthracene (**1**) and C_{70} -*bis*-anthracene (**2**) (*o*-DCB containing 0.05M $n\text{-Bu}_4\text{NPF}_6$ at 100mV/s; using the redox couple Fc/Fc^+ as internal reference).

The regiochemistry of *bis*-adduct **2** was unambiguously established using X-ray crystallography. Black crystals grew as thin rectangular plates from a diffusion of hexane into a carbon disulfide solution of **2**. Crystallographic data were collected at the Advanced Light Source, Lawrence Berkeley Laboratory. The structure was solved in the tetragonal crystal system, space group $P4_2/\text{ncm}$ (no. 138) and revealed one-quarter of the molecule of **2** in the asymmetric unit. The crystallographic site symmetry of 2-mm confirmed that the molecule is the unexpected 12 o'clock *bis*-isomer with C_{2v} point symmetry, as shown in Figure 4(a). The 2-fold axis is vertical. The two perpendicular mirror planes pass through this axis. The structure contains a disordered interstitial hexane molecule with the same site symmetry. The utility SQUEEZE¹¹ was applied to remove its contribution from the structure. The fullerene [6:6] bond (C1-C2) at the site of the cycloaddition is elongated to 1.601(3) Å. The bonds C1-C29 and C2-C22 are also stretched, at 1.590(3) and 1.586(3) Å, respectively. As shown in Figure 4(b), viewed down the *c* axis, adjacent molecules efficiently pack in a wavy manner with the concave surface of anthracene well matched to the flattened convex part of C_{70} . This interaction can be viewed in the Electronic Supplementary Information as a movie in mpg format. These remarkable shape-complementary interactions are less perfect in the reported *bis*- and *tris*-adducts of C_{60} and anthracene.¹² The intermolecular distances are typical for $\pi\cdots\pi$ stacking with values in the range 3.18 – 3.45 Å. The layers above and below this layer follow the crystallographic 4_2 operation and yield the shortest fullerene \cdots fullerene contact of 3.118(3) Å. It is important to note that *bis*-Diels-Alder additions to C_{60} and C_{70} always result in multiple regioisomers (5 or 6 for C_{60} , see references 6c-d, and 8 in the case of C_{70} , see reference 9c), thus it is remarkable that only one *bis*-adduct isomer is observed in the present case.

Conclusions

A remarkably high yield of only one regioisomeric *bis*-adduct of C₇₀ with anthracene was isolated for the first time from a reaction in the melt. The two anthracene molecules added to [6,6] double bonds in a 12 o'clock arrangement. Further synthetic evolution of this compound is under investigation in our laboratories, in efforts to prepare *tris* and higher adducts regioselectively.

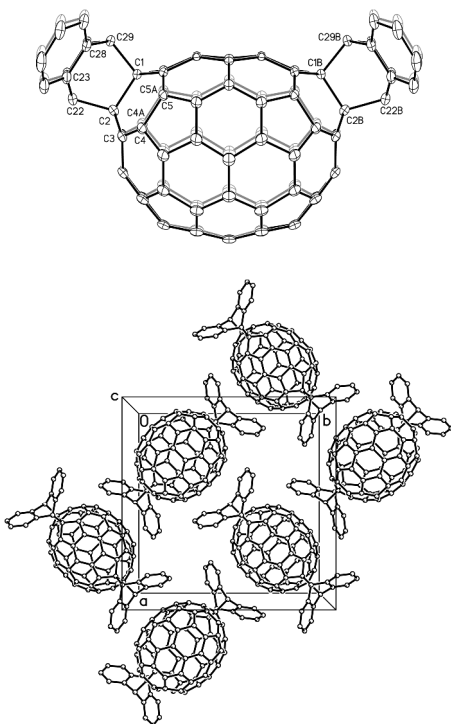


Figure 4. (a) The molecular structure of the C₇₀ *bis*-anthracene adduct, **2**. Hydrogen atoms are not shown for clarity. Thermal parameters are shown at the 30% probability level. (b) A layer perpendicular to the *c* axis showing intermolecular interactions between anthracene and C₇₀.

Acknowledgements

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Notes and references

Crystal data for C₇₀-bis-anthracene (C₉₈H₂₀, fw 1197.14): Black plate, 0.240 x 0.240 x 0.014 mm, tetragonal, space group, P4₂/ncm, *a* = 16.8655(8), *c* = 19.6001(10) Å, *V* = 5575.2(6) Å³, *Z* = 4, *D*_{calc} = 1.426 Mg m⁻³, *μ* = 0.097 mm⁻¹, *λ* = 0.7749 Å (synchrotron), *T* = 100(2) K; Bruker Apex II CCD detector; *ω* scans; 2*θ*_{max} = 63.27°; 65813 reflections collected; 3792 independent (*R*_{int} = 0.0496) included in the refinement; direct methods solution, full-matrix least-squares refinement based on *F*² (SHELXL-2013);¹³ conventional *R*1 = 0.0570 computed for 3386 observed data (*I* > 2σ(*I*)), *wR*2 = 0.1529 for all data; 235 parameters and 0 restraints.

^a Department of Chemistry, University of Texas at El Paso, El Paso, TX 79968, United States. Fax: +1 915-747-8807; Tel: +1 (915) 747-7573; E-mail: echehoven@utep.edu

^b Departamento de Química, Universidad Nacional de Colombia, Bogotá, Colombia.

^c Department of Chemistry, University of California, Davis, California, United States. E-mail: mmolmstead@ucdavis.edu; albalch@ucdavis.edu; Fax +1 (530) 752 2820; Tel +1 (530) 752 0941.

† Electronic Supplementary Information available: Experimental details, Fig. S1-S9. See DOI: 10.1039/b000000x/. CCDC 993667. A view of crystal packing in the *ab* plane as an mpg file.

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