

Synthesis of a Rigid "Ball-and-Chain" Donor–Acceptor System through Diels–Alder Functionalization of Buckminsterfullerene (C₆₀)

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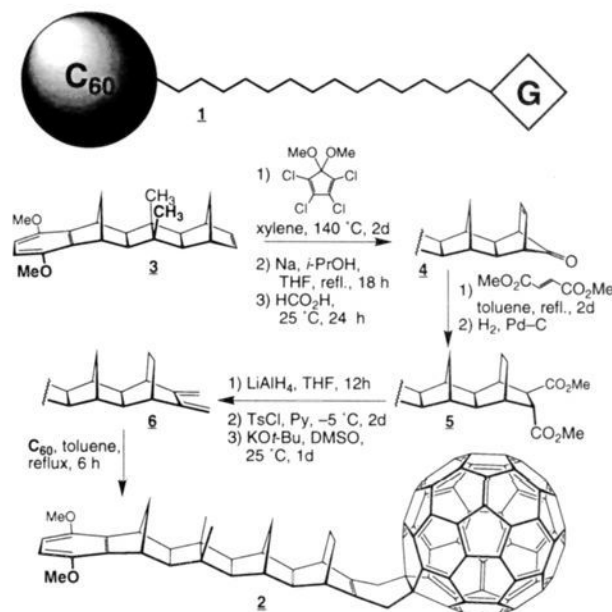
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The chemistry of buckminsterfullerene (C₆₀)^{1,2} has become a rapidly developing area of research, particularly in light of its unusual redox properties^{3a,b} and the ability of its alkali metal salts to display conductivity and superconductivity.^{3c–e} Although much work has been done on solid-state materials based on C₆₀,^{3c–f} increasing attention is being devoted to exploring the derivatization of C₆₀ through the addition of a variety of reagents including transition metals,^{4a–c} nucleophiles,^{4d,e} carbenes and analogs,^{4d,f–k} benzyne,^{4l} and dienes.^{4d,m,n,5a}

Encouraged by our recent results in the functionalization of C₆₀ through Diels–Alder reactions,⁵ we sought to develop a novel type of derivative of C₆₀ by creating "ball-and-chain" systems (**1**, Scheme I), in which the C₆₀ unit and another functional group, **G**, are attached to a rigid polycyclic chain or bridge.⁶ These systems should provide unprecedented insight into a variety of long-range intramolecular processes between C₆₀ and **G**, including

Scheme I



energy and electron transfer, and would complement the corresponding intermolecular processes studied so far.^{3f,7}

We are pleased to report the synthesis of our first "ball-and-chain" molecule (**2**) in which the chain comprises a rigid polynorbornyl–bicyclo[2.2.0]hexyl bridge which has been used extensively by the UNSW group in the construction of several donor–bridge–acceptor systems.^{8,9} The key feature of the present work is the Diels–Alder reaction between C₆₀ and the novel bridge diene **6** affording the "ball-and-chain" adduct **2**.

The norbornene **3** was obtained in several steps from the Diels–Alder adduct of *p*-benzoquinone and cyclopentadiene using procedures previously employed in the synthesis of the corresponding dimethoxynaphthalene system.^{9a} Diels–Alder reaction of **3** with dimethoxytetrachlorocyclopentadiene, followed by reductive dechlorination and subsequent deketalization with formic acid, gave **4** (61%). Ketone **4** is thermally labile to cheletropic CO loss, and the resulting 1,3-diene was trapped *in situ* by dimethyl fumarate to give a Diels–Alder adduct which afforded **5** after hydrogenation (94%). Formation of diene **6** from **5** using standard procedures occurred in 36% yield.¹⁰

Addition of 1 equiv of **6** via syringe pump to a solution of C₆₀ heated at reflux in toluene afforded the stable adduct **2** in 63% yield (99% based on recovered C₆₀). The ¹H and ¹³C NMR spectra of **2** confirm the expected structure.¹¹ A total of 14 lines

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are observed in the aliphatic region of the ^{13}C NMR spectrum, including the sp^3 -hybridized carbons of C_{60} appearing at 66.2 ppm. A total of 34 out of the 35 expected lines for the fullerene and aromatic/alkenyl carbons are observed between 105 and 160 ppm. Thirty of these peaks appear as pairs (i.e. 15×2 peaks), as expected from the C_s symmetry of the fullerene framework. The remaining four peaks in the spectrum (108.46, 136.27, 147.37, and 147.47 ppm) result from the four types of aromatic/alkenyl carbons and one type of fullerene carbon, the absorption at 147.46 ppm arising from two coincidental chemical shifts.

The crystal structure of adduct **2** is shown in Figure 1a.¹² The addition of diene **6** to C_{60} has occurred at the reactive 6,6-ring junction of C_{60} .^{5a} The bond between the sp^3 -hybridized carbons C(1)–C(2) of C_{60} is elongated to 1.62(2) Å as observed for our previous Diels–Alder adduct.^{5a} The distance between the center of the 1,4-dimethoxybenzene (DMB) unit and the median of the C(1)–C(2) bond is 12.34 Å.

The crystal packing structure of **2** (Figure 1b) is very interesting and aesthetically pleasing in that the adducts are paired up, with the C_{60} unit of one partner nestling up to the DMB-terminated chain of the other, and *vice versa*.¹³ The cyclohexene ring in **2** defined by C(1)–C(2)–C(64)–C(63)–C(62)–C(61) can adopt two nondegenerate boat conformations, namely, an extended one, which is observed in the crystal,¹⁴ and a folded one. MM3 calculations¹⁵ predict the folded conformation to be more stable than the extended one by 0.34 kcal/mol. If this effect is real,¹⁶ then crystal-packing forces and/or intermolecular electrostatic and π -stacking interactions between the C_{60} and DMB groups are responsible for the observed extended conformation in the solid state. The extended structure appears to optimize these interactions in the crystal; the two polynorbornyl–bicyclo[2.2.0]hexyl bridges and the C_{60} surfaces in the pairs lie within van der Waals distances. The average of the C–H contact distances is 3.09 Å between the polynorbornyl–bicyclo[2.2.0]hexyl hydrogens pointing inward and carbons C(19), C(20), C(33), C(34), C(35), and C(39) of C_{60} , and 3.52 Å for C–C contact

(10) Representative physical data for diene **6**: mp 212–213 °C; ^1H NMR (300 MHz, CDCl_3) δ (ppm) 0.89 (s, 6H, CH_3), 1.43 (d, $J = 9.0$ Hz, 2H), 1.45 (br s, 2H), 1.52 (dt, $J = 1.5, 9.2$ Hz, 2H), 1.72 (br d, $J = 9.2$ Hz, 1H), 1.86 (br d, $J = 9.3$ Hz, 2H), 1.88 (s, 2H), 1.94 (s, 2H), 1.98 (d, $J = 9.2$ Hz, 1H), 2.07 (br s, 2H), 2.31 (br s, 2H), 3.47 (s, 2H), 3.79 (s, 6H, OCH_3), 4.69 (s, 2H), 5.23 (d, $J = 1.1$ Hz, 2H), 6.60 (s, 2H); ^{13}C NMR (75 MHz, CDCl_3) δ (ppm) 9.60 (CH_3), 22.31 (CH_2), 31.12 (CH_2), 39.31 (CH), 40.24 (CH), 40.70 (CH), 43.60 (CH_2), 43.69 (C), 45.04 (CH), 49.74 (CH), 53.82 (CH), 56.10 (OCH_3), 102.55 ($=\text{CH}_2$), 109.00 (CH arom), 136.79 (C arom), 147.80 (C arom), 150.93 ($=\text{C}$). Anal. Calcd for $\text{C}_{37}\text{H}_{38}\text{O}_2$ (454.66): C, 84.54; H, 8.42. Found: C, 83.80; H, 8.48.

(11) Representative physical data for adduct **2**: ^1H NMR (500 MHz, $\text{CS}_2/\text{CDCl}_3$, 5:1) δ (ppm) 0.92 (s, 6H, CH_3), 1.45 (dt, $J = 1.6, 9.3$ Hz, 1H), 1.56 (br d, $J = 11.1$ Hz, 1H), 1.61 (br d, $J = 7.6$ Hz, 2H), 1.69 (br d, $J = 9.3$ Hz, 1H), 1.72 (br s, 2H), 1.89 (s, 2H), 1.92 (s, 2H), 1.96 (br d, $J = 7.5$ Hz, 2H), 2.07 (br d, $J = 11.5$ Hz, 1H), 2.11 (br s, 2H), 2.82 (br s, 2H), 3.41 (s, 2H), 3.72 (s, 6H, OCH_3), 4.0–4.15 (AB q, $J = 14.0$ Hz, 4H, allyl CH_2), 6.46 (s, 2H); ^{13}C NMR (125.8 MHz) δ (ppm) 9.63, 22.66, 30.64, 37.74, 38.97, 40.14, 43.36, 43.41, 43.95, 46.27, 49.81, 54.21, 55.33, 66.21, 108.46, 135.14, 135.16, 136.27, 139.88, 139.90, 141.31, 141.33, 141.80, 141.85, 142.12, 142.22, 142.34, 142.54, 142.83, 142.89, 144.47, 144.49, 145.16, 145.17, 145.19, 145.20, 145.25, 145.52, 145.71, 145.97, 145.98, 146.23, 146.27, 147.37, 147.47, 157.48, 158.00. Anal. Calcd for $\text{C}_{92}\text{H}_{38}\text{O}_2$ (1175.33): C, 94.02; H, 3.26. Found: C, 94.08; H, 2.94.

(12) Compound **2** ($\text{C}_{92}\text{H}_{38}\text{O}_2 \cdot 1.5\text{C}_6\text{H}_5\text{Cl}$; $M_r = 1344.17$) crystallized in the monoclinic space group $P2_1/n$ with cell dimensions of $a = 25.180(5)$ Å, $b = 10.136(2)$ Å, and $c = 25.241(5)$ Å, $\beta = 112.35(1)^\circ$, $V = 5958(2)$ Å³, and an occupation of $Z = 4$ in the unit cell. Data were collected at 20 °C on a Rigaku AFC5R diffractometer using graphite-monochromated $\text{Cu K}\alpha$ radiation, to a maximum $2\theta = 115^\circ$, giving 8615 unique reflections; the structure was solved by direct methods (SHELX86), yielding $R = 0.116$, $R_w = 0.136$ for 2604 independent reflections with $F > 6\sigma(F)$.

(13) For a chelate-like interaction in an iridium–phosphine complex of C_{60} , see: Balch, A. L.; Catalano, V. J.; Lee, J. W.; Olmstead, M. M. *J. Am. Chem. Soc.* 1992, 114, 5455–5457.

(14) The angle between the two mean planes defined by C(61)–C(1)–C(2)–C(64) and C(61)–C(62)–C(63)–C(64) is 128° .

(15) MacroModel 3.5, C. Still, Columbia University, SGI version.

(16) Line shape analysis (^1H NMR) of the CH_2 -allylic absorptions of **2** shows that one of the conformers is approximately 0.65 kcal/mol (-110°C) higher in energy than the other: Freedberg, D. I.; Anet, F. A. L. Unpublished results.

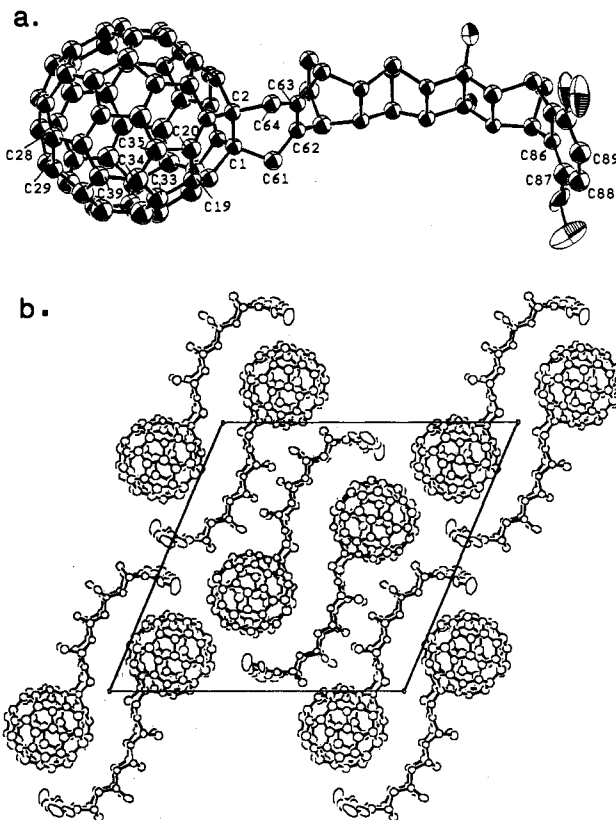


Figure 1. (a) X-ray crystal structure of the Diels–Alder adduct **2**. (b) View of the crystal packing structure of **2** down the b -axis, a -axis pointing to the right. Of the two types of disordered chlorobenzene molecules present in the crystal lattice (not shown for clarity), one is at the inversion center and the other at a general position.

distances between the aromatic carbons C(87), C(88), C(89), and C(90) of the DMB unit and carbons C(28) and C(29) of C_{60} . The shortest H–H distance between axial hydrogens on carbons C(61) and C(64) of paired units is 2.59 Å.

Our preliminary studies have led to a potentially versatile approach to rigid C_{60} “ball-and-chain” bichromophoric systems **1**, in which the chain length and configuration can be systematically altered and a variety of functional groups G appended.¹⁷ Such systems should have interesting electrical, photophysical, and chemical properties that might make them useful materials for the rational design of novel molecular electronics devices.¹⁸

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Supplementary Material Available: Experimental details of the crystal structure determination of **2**, fully labeled view of the structure, and tables of atomic coordinates, equivalent isotropic thermal parameters, bond angles, and bond lengths (17 pages); listing of observed and calculated structure factors for **2** (11 pages). Ordering information is given on any current masthead page.

(17) Diene precursors of **1** currently being synthesized at UNSW include $G = 1,2$ -dithiane, porphyrin,^{9d} 3,6-di(2'-pyridyl)pyridazine,^{9b} and dipyrrolo[3,2- a :2',3'- c']phenazine. The latter two groups will enable entry into transition metal complexes of “ball-and-chain” systems.

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