A Diels–Alder Adduct of C_{60} containing Hydroxyquinone Functionalities

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Two new Diels–Alder adducts of C_{60} have been prepared from 1,3-diphenylisobenzofuran and the *ortho*-quinodimethane generated from 1,4-dihydroxy-2,3-bis(bromomethyl)anthraquinone: the dihydroxy anthraquinone–C_{60} adduct readily undergoes deprotonation to give the corresponding dianion.

The electron withdrawing nature of the closed cage alkene C_{60} makes it an excellent dienophile for Diels–Alder [4 + 2] cycloaddition.[1] The [4 + 2] cycloaddition involves exclusive addition to the 6–6 bonds.[1–4] However, many Diels–Alder C_{60}-adducts are unstable and undergo retro reactions.[2–4] Thermally stable adducts are formed using *iso*-benzofurans[3] or *ortho*-quinodimethanes[4] as a consequence of the aromatization in the C_{60} cycloaddition product. We have used this strategy to prepare C_{60} compounds containing functional groups, as described below.

The compounds 1,3-diphenylisobenzofuran **1** and the *ortho*-quinodimethane **2** generated *in situ* from 1,4-dihydroxy-2,3-bis(bromomethyl)anthraquinone **3** have been reacted with C_{60}.

Thus the synthesis of the brown C_{60}-1,3-diphenylisobenzofuran adduct **4** was achieved by mixing together equimolar solutions of C_{60} and **1** in benzene at room temperature. The resulting red solution with a blue fluorescence was stirred overnight. The solution was concentrated and **4** precipitated on addition of pentane.† The ^1H NMR of **4** was similar to the starting diene **1** except that the peaks have shifted *ca.* 0.2 ppm downfield. The ^{13}C NMR spectrum is consistent with a C_s symmetry for the molecule. Hence, there are 31 bands in the fullerene region and seven signals between 132 and 121 ppm assignable to the benzoisofuran side chain. Two peaks at 96 and 82 ppm may be assigned to the sp^3 carbons of the furan and C_{60} moieties of the adduct, respectively. **4** was soluble in aromatic solvents but only sparingly soluble in polar solvents.

The iodide induced 1,4-elimination at 1,4-dihydroxy-2,3-bis(bromomethyl)anthraquinone **3** gives *in situ* formation of the *ortho*-quinodimethane **2**.[5,6] Compound **5** was prepared by adding dropwise a saturated red toluene solution of 1.1 equiv. of **3** to a refluxing purple toluene solution of C_{60}, 18-crown-6 (10 equiv.) and potassium iodide (2.2 equiv.). The resulting brown reaction mixture was refluxed for 8 h. The product was precipitated with an acetone–water mixture (20 : 1), washed three times with acetone, twice with pentane and dried in vacuum giving pure **5** in 83% yield.¶ Spectroscopic data showed no evidence for the formation of a diadduct. The solubility of **5** is comparable to C_{60}, and no decomposition in air was observed until 300 °C. The ^{13}C NMR spectra of **5** showed 25 lines consistent with the C_{2v} symmetry for the molecule, thus there are 17 lines for the C_{60} moiety and 8 lines for the functionalized anthraquinone ligand. At 25 °C the ^1H NMR spectrum of **5** showed a broad singlet at 4.68 ppm due to the methylene protons (H_a, H_e), multiplets at 8.16 and 7.46 ppm due to the aromatic protons and a singlet at 13.42 ppm due to the two hydroxy protons. The broad singlet for the methylene protons H_a, H_e suggested a low conformational inversion barrier on the NMR time scale. Variable temperature experiments showed two signals for H_a and H_e coalesce at *ca.* 6 °C and on cooling to −40 °C they resolved into two doublets at 4.98 and 4.02 ppm with a geminal coupling constant of 14.5 Hz.

Treatment of **5** with 2 equiv. of sodium *tert*-butoxide in the presence of 15-crown-5 gave the dark blue salt **6**.§ The compound **6** is slightly soluble in THF, very sparingly soluble in acetonitrile and insoluble in aromatic solvents. The low solubility of **6** in THF at room temperature prevented an acceptable ^1H NMR from being obtained. However, at 50 °C the methylene protons appeared at 5.20 and 4.88 ppm which indicates that the conformational inversion does not occur below this temperature.

The UV–VIS spectra of **4**, **5** and **6** all exhibit typical peaks assignable to the fullerene moiety at *ca.* 220, 255, and 330 nm. In addition there is a broad band at 450–600 nm exhibiting different fine structures for each of the adducts.

We are currently exploring the polymer and coordination chemistry of **4**, **5** and **6**.

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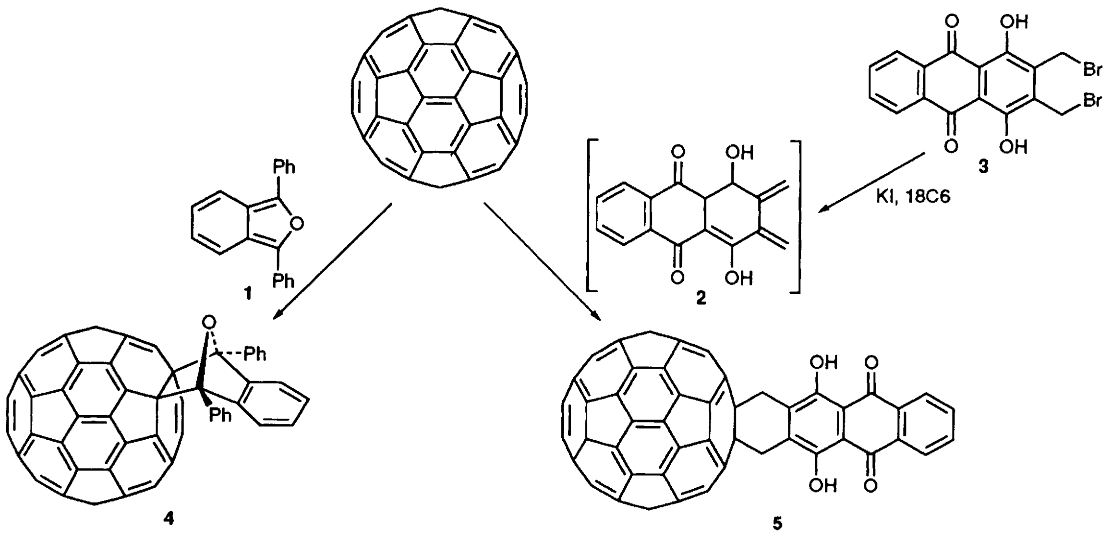
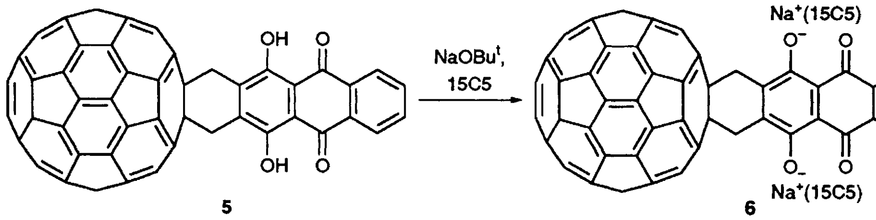


Scheme 1 Ph = C_6H_5, 18C6 = 18-crown-6



Scheme 2 15C5 = 15-crown-5

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Footnotes

† *Selected analytical and spectroscopic data* for **4**: Analysis calcd. for $C_{80}H_{14}O \cdot 3(C_6H_6)$: C, 96.0; H, 2.6. Found: C, 95.6; H, 2.3. IR/cm^{-1} (Nujol) 1093 (m); 1016 (m), 951 (w), 877 (m), 808 (m), 739 (s), 702 (s), 575 (w), 528 (s). ^{1}H NMR (300 MHz, CD_2Cl_2, 25 °C) δ 8.36, 7.91, 7.66, 7.55 (m, ArH). ^{13}C NMR [125 MHz, CS_2 + $(CD_3)_2CO$ (internal), 25 °C] δ 154–136 (s, 31 C_{60} signals), 132–121 (s, 7 benzoisofuran side chain signals); 96 (s, *COC*); 82 (s, sp^3 carbons C_{60}). UV-VIS (C_6H_6) 270, 334, 409, 435(sh), 538, 595, 698 nm.

¶ *Selected analytical and spectroscopic data* for **5**: Analysis calcd. for $C_{76}H_{10}O_4$: C, 92.5; H, 1.0. Found: C, 92.15; H, 1.0. IR/cm^{-1} (Nujol) 3450 (vw); 1622 (m); 1585 (m); 1417 (s); 1339 (s); 1311 (m); 1266 (vs); 1183 (w); 810 (w); 775 (m); 732 (m); 723 (m); 578 (vw); 528 (s). ^{1}H NMR (300 MHz, CS_2 + $C_6D_5CD_3$, 25 °C) δ 13.42 (s, 2H, O*H*); 8.16, 7.46 (m, 4H, ArH, AA'BB' system); 4.68 (s, br, 4H, C*H*$_2$). ^{13}C NMR [75.42 MHz, CS_2 + D_2O (external), 25 °C] δ 186 (s, *C*O); 155–110 (s, 16 C_{60} and 6 arene side chain signals); 65 (s, sp^3 carbons C_{60}); 37 (s, *C*H$_2$). UV-VIS (CH_2Cl_2): 229, 257, 328, 407, 437 (sh), 473, 489, 523 (sh) nm.

§ *Selected analytical and spectroscopic data* for **6**: Analysis calcd. for $C_{96}H_{48}O_{14}Na_2$: C, 78.4; H, 3.3; Na, 3.1. Found: C, 80.6; H, 2.6; Na, 2.3. IR/cm^{-1} (Nujol) 1628 (vw), 1602 (w), 1580 (s), 1351 (s), 1299 (m), 1247 (m), 1119 (s), 950 (m), 860 (vw), 769 (w), 738 (m), 676 (vw), 578 (vw), 528 (s). ^{1}H NMR (300 MHz, THF-D_8, 50 °C) δ 8.39, 7.62 (m, 4H, Ar*H*, AA'BB' system); 5.20 (s, br, 2H, C*H*$_2$); 4.88 (s, br, 2H, C*H*$_2$); 3.64 (s, 20H, OC*H*$_2$). UV-VIS (THF, nm): 257, 288 (sh), 327, 404, 435, 489, 525, 573, 616.

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