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Synthesis of *m*-Phenylene- and *p*-Phenylenebis(phenylfulleroids): Two-Pearl Sections of Pearl Necklace Polymers[†]

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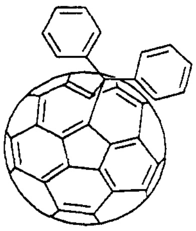
Buckminsterfullerene, C_{60},[1] exhibits unusual electrophilicity of six special (pyracyclenoid) double bonds[2] which render it reactive toward reducing agents,[3] nucleophiles,[4] dienes,[4] dipoles,[4] and a number of zero-valent transition metals.[5] While such electrophilicity gives the synthetic chemist a "handle" on possible approaches to fullerene functionalization, the nucleophilicity of C_{60} is also being pursued by several groups.[6] To date, the most effective systematic functionalization of C_{60} is the production of fulleroids: expanded fullerenes which retain the fullerene electronic structure.[7] Thus fulleroids Ph_2C_{61}–$Ph_{12}C_{66}$ (see representation of Ph_2C_{61}) have been prepared and characterized.[7] Fulleroid formation opens the possibility for the synthesis of, inter alia, two types of polymers:[8] "pearl necklace" and "charm bracelet".[9] The former is a hypothetical polymer in which the C_{60} is part of the backbone, and the latter is a polymer in which C_{60} is attached to a side chain of a traditional polymer.



Fulleroid Ph_2C_{61}

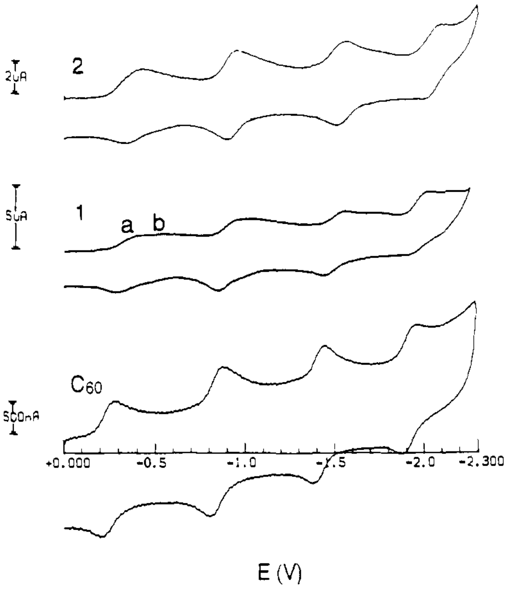
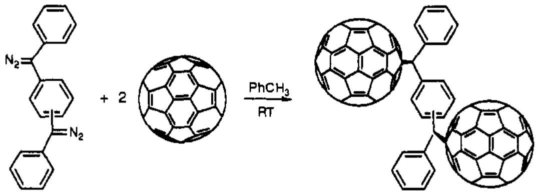


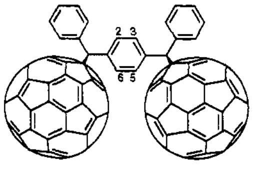
Figure 1. Comparative cyclic voltammetry of C_{60}, bis(fulleroid) **1**, and bis(fulleroid) **2** in THF with 0.1 M $TBABF_4$ as supporting electrolyte; Pt working and counter electrodes; Ag/AgCl reference electrode; scan rate, 1000 mV/s.

Scheme I



3, *para*; 4, *meta*

In this communication we demonstrate that the synthetic method for the generation of the diphenylfulleroids can be extended to produce the para (**1**) and meta (**2**) phenylenebis(phenylfulleroido) isomers. In the representations of **1** and **2**, the "wedge" bond between the sphere and the atom attached to the phenylene moiety implies a "methano bridge" as in 1,6-methano[10]annulene. The compounds were prepared according to Scheme I.



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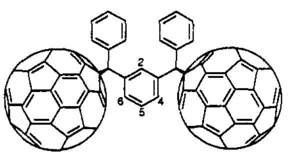

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When compound **3** or **4**[10,11] was allowed to react with C_{60}, product **1** or **2** was isolated in 39% or 51% yield, respectively.[12]

[†] Presented in part at the Materials and Research Society Meeting, Boston, MA, December 1991.

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(8) (a) Polymers containing a C_{60} unit in the backbone of a poly(*p*-xylylene) have recently been reported by Loy, D. A., and Assink, R. A., presented at the Materials Research Society Meeting, Boston, December 1991. (b) A charm bracelet, "fullerenated" poly(styrene), was prepared by Prakash and Olah: Prakash, S.; Olah, G. *J. Am. Chem. Soc.*, in press.

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Compounds **1** and **2** are dark brown-black solids which give a reddish-brown solution in carbon disulfide. Chromatographic separation afforded amorphous powders[12] which were only sparingly soluble in most nonpolar organic solvents and partially soluble in carbon disulfide. The ^1H NMR spectra of these dimers are very broad, indicating that they may consist of a number of isomers.[13] Upon heating in refluxing toluene, the single thermodynamic products of **1** and **2** (whose ^1H NMR spectra show sharp peaks) were obtained.[13] Interestingly, the hydrogens in the *p*-phenylene [8.19 ppm (s, 4 H, $H_{2,3,5,6}$)] and *m*-phenylene [8.80 ppm (H_2), 8.08 ppm ($H_{4,6}$), and 7.58 ppm (H_5)] are deshielded more than those in the phenyls [for **1**, 8.13 ($H_{2',6'}$), 7.49 ($H_{3',5'}$), and 7.39 ($H_{4'}$); for **2**, 8.07 ($H_{2',6'}$), 7.44 ($H_{3',5'}$), and 7.34 ($H_{4'}$)], apparently because they are influenced by the magnetic effects of *two* spherical molecules. Bis(fulleroids) **1** and **2** exhibit UV-vis spectra and cyclic voltammograms (CV) (Figure 1) which are indistinguishable from those of diphenylfulleroid (Ph_2C_{61}). Within experimental error, the peaks in the voltammograms of **1** and **2** are due to a two-electron process.[14] In the CV of **1**, there is another broad wave following each peak. Osteryoung square wave voltammetry[15] showed that each wave of **1** consists of two faradaic processes. The weaker wave associated with each "main" wave is due to an oligomer.[16] The more soluble dimer **2** could be purified more easily and hence shows essentially no "weak" waves. Addition of one electron to one ball has, as expected, no effect on the redox properties of its neighbor.[17]

In summary, we have shown that fullerene inflation reactions can yield molecules which are the basic unit of "pearl necklace" polymers,[9] in which the fulleroid becomes part of the polymer backbone. It is clear from the lack of solubility described above that, not unexpectedly, "naked" pearl necklace polymers will be insoluble and intractable and that one will need to approach their preparation by either a precursor polymer route or the incorporation of solubilizing groups. The syntheses of pearl necklace and charm bracelet polymers are being actively pursued and will be the subject of further publications.[16]

Acknowledgment. We thank the National Science Foundation for support through Grants DMR-88-20933, DMR-91-11097, and CHE-89-08323.

Supplementary Material Available: Experimental details for the syntheses of **1** and **2**, UV-vis absorption spectra and CV of C_{60}, **1**, and **2**, OSWV of reduction of **1** and **2**, and computer-generated models of **1** and **2** (5 pages). Ordering information is given on any current masthead page.

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(13) The "crude" products isolated by chromatography on silica gel of many fulleroids prepared in our group, which show broad NMR signals, are homogeneous by TLC. The conclusion that they must consist of a mixture of kinetic and thermodynamic products rests, inter alia, on the fact that the NMR spectrum of, for example, "crude" $(p\text{-}CH_3C_6H_4)_2Fd$ (Fd = fulleroid) showed *three* types of methyl groups, which collapsed to the expected single resonance upon heating in refluxing toluene overnight (K. C. Khemani, unpublished). Efforts to separate the isomers with novel chromatography columns (Vidac 201-TP-510: we thank Prof. Diederich for the information) are underway.

(14) The results of several runs of bulk electrolysis of **2** in HMPA with 0.2 M Bu_4NBF_4 are 1.9 ± 0.15 electrons for the first wave (Figure 1). Compound **1** was too insoluble to obtain meaningful results for the same experiment. Rest potentials in THF/0.1 M Bu_4NBF_4 are as follows: **1**, -218 mV; **2**, -200 mV; C_{60} (under the same conditions), -126 mV.

(15) Osteryoung square wave voltammetry (OSWV) (Osteryoung, J. G.; O'Dea, J. J. In *Electroanalytical Chemistry*; Bard, A. J., Ed.; Dekker: New York, 1986; Vol. 14) is a pulse technique whose waveform consists of a pulse train of square waves superimposed on a staircase waveform, with one square wave cycle per staircase step. The forward pulse proceeds in the same direction as the staircase, but the reverse pulse can take place at any point on the step. Like differential pulse voltammetry (DPP), OSWV has the ability to discriminate against charging current and thus gives a peak-shaped curve for a faradaic process. However, OSWV implements an experiment at a much faster speed.

(16) Short charm bracelet poly(esters) show the same "weak" waves following the main wave (Shi, S.; Khemany, K. C.; Li, Q.; Wudl, F. *J. Am. Chem. Soc.*, submitted).

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Dihydrofulleroid H_2C_{61}: Synthesis and Properties of the Parent Fulleroid

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Buckminsterfullerene (C_{60})[1] is conveniently prepared and isolated.[2] Its chemical properties are being investigated with increasing interest.[3] The fulleroids are inflated fullerenes where up to six carbon atoms, each bearing two substituents, are added systematically to C_{60}.[4,5] In this communication we report the preparation of the simplest, "parent" fulleroid (**2**) formed by the reaction of fullerene C_{60} with diazomethane.[6]

Diazomethane reacts with C_{60} to give a thermally unstable compound, $(CH_2N_2)C_{60}$ (**1**), in 44% yield. This compound has a singlet ^1H NMR peak at 6.51 ppm and 30 fulleroid ^{13}C resonances,[7] supporting the depicted C_s symmetry. The IR (KBr mull) spectrum shows the expected N=N stretching vibration at 1560 cm^{-1}, which disappears when the KBr pellet is heated at 100 °C. The FAB mass spectrometry of the adduct shows peaks at 736-734 (H_2C_{61}) and 722-720 (C_{60}). The thermal decomposition was confirmed by TGA; weight loss, which corresponds to the conversion from $(CH_2N_2)C_{60}$ to H_2C_{61} [Scheme I, calcd for $H_2C_{61}/(CH_2N_2)C_{60}$ 96.33, found 97.31], starts at 90 °C and is complete at 150 °C. Further heating up to 760 °C afforded C_{60} as well as an insoluble residue [calcd for $C_{60}/(CH_2N_2)C_{60}$ 94.49, found 93.17].

When a toluene solution of $(CH_2N_2)C_{60}$ was heated to reflux, the color of the solution changed from brown to purple. Removal of the solvent afforded H_2C_{61} quantitatively as a dark powder exhibiting solubility similar to that of C_{60} but a different TLC R_f.

The UV-vis absorption of H_2C_{61} is virtually identical to that of C_{60}.[7] The cyclic voltammogram of H_2C_{61} (E1, -346; E2, -925; E3, -1497; E4, -1980 mV vs Ag/AgCl, THF) is the same as observed with Ph_2C_{61}.[4] The IR spectrum of H_2C_{61} shows peaks at 1427, 1229, 1172, 642, 623, 580, 570, 557, 539, 526, and 494 cm^{-1}, suggesting a dissymmetric, more complicated structure with some bands which correspond to those in the C_{60} spectrum (1429, 1183, 577, 528 cm^{-1}).

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(6) The title compound could be considered a methylene analog of $C_{60}O$, recently published by Creegan et al.: Creegan, K. M.; Robbins, J. L.; Robbins, W. K.; Millar, J. M.; Sherwood, R. D.; Tindall, P. J.; Cox, D. M.; Smith, A. B., III; McCauley, J. P., Jr.; Jones, D. R.; Gallagher, R. T. *J. Am. Chem. Soc.* **1992**, *114*, 1103.

(7) See supplementary material. The two bridge carbons are at 94.19 and 120.62 ppm, and the bridge appears at 64.10 ppm.

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