

Compounds **1** and **2** are dark brown-black solids which give a reddish-brown solution in carbon disulfide. Chromatographic separation afforded amorphous powders¹² 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 (H₂), 8.08 ppm (H_{4,6}), and 7.58 ppm (H₅)] 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 (Ph₂C₆₁). 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 voltammetry¹⁵ 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

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Supplementary Material Available: Experimental details for the syntheses of **1** and **2**, UV-vis absorption spectra and CV of C₆₀, **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.

(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*-CH₃C₆H₄)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 Bu₄NBF₄ 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 Bu₄NBF₄ are as follows: **1**, -218 mV; **2**, -200 mV; C₆₀ (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.; Khemani, K. C.; Li, Q.; Wudl, F. *J. Am. Chem. Soc.*, submitted).

(17) Flanagan, J. B.; Margel, S.; Bard, A. J.; Anson, F. C. *J. Am. Chem. Soc.* 1978, 100, 4248. Itaya, K.; Bard, A. J.; Szwarc, M. *Z. Phys. Chem. Neue Folge* 1978, 112, 1.

Dihydrofulleroid H₂C₆₁: Synthesis and Properties of the Parent Fulleroid

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Buckminsterfullerene (C₆₀)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 C₆₀.^{4,5} In this communication we report the preparation of the simplest, "parent" fulleroid (**2**) formed by the reaction of fullerene C₆₀ with diazomethane.⁶

Diazomethane reacts with C₆₀ to give a thermally unstable compound, (CH₂N₂)C₆₀ (**1**), in 44% yield. This compound has a singlet ¹H NMR peak at 6.51 ppm and 30 fulleroid ¹³C resonances,⁷ supporting the depicted C₂ 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 (H₂C₆₁) and 722-720 (C₆₀). The thermal decomposition was confirmed by TGA; weight loss, which corresponds to the conversion from (CH₂N₂)C₆₀ to H₂C₆₁ [Scheme I, calcd for H₂C₆₁/(CH₂N₂)C₆₀ 96.33, found 97.31], starts at 90 °C and is complete at 150 °C. Further heating up to 760 °C afforded C₆₀ as well as an insoluble residue [calcd for C₆₀/(CH₂N₂)C₆₀ 94.49, found 93.17].

When a toluene solution of (CH₂N₂)C₆₀ was heated to reflux, the color of the solution changed from brown to purple. Removal of the solvent afforded H₂C₆₁ quantitatively as a dark powder exhibiting solubility similar to that of C₆₀ but a different TLC R_f.

The UV-vis absorption of H₂C₆₁ is virtually identical to that of C₆₀.⁷ The cyclic voltammogram of H₂C₆₁ (El, -346; E2, -925; E3, -1497; E4, -1980 mV vs Ag/AgCl, THF) is the same as observed with Ph₂C₆₁.⁴ The IR spectrum of H₂C₆₁ 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 C₆₀ spectrum (1429, 1183, 577, 528 cm⁻¹).

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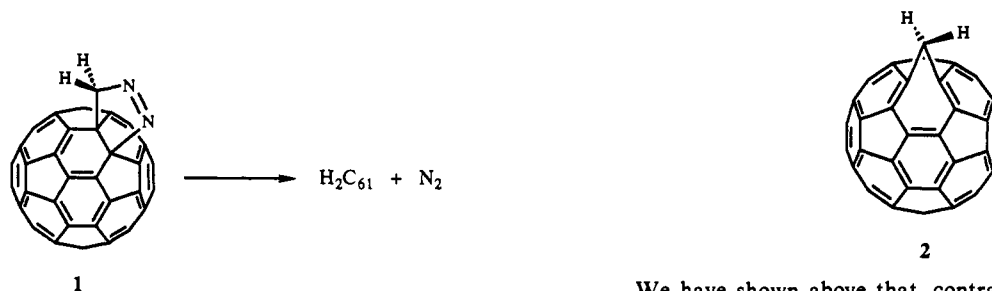
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(6) The title compound could be considered a methylene analog of C₆₀O, recently published by Creegan et al.: Creegan, K. M.; Robbins, J. L.; Robbins, W. K.; Millar, J. M.; Sherwood, R. D.; Tindall, P. J.; Cox, D. M.; Smith, A. B., III; McCauley, J. P., Jr.; Jones, D. R.; Gallagher, R. T. *J. Am. Chem. Soc.* 1992, 114, 1103.

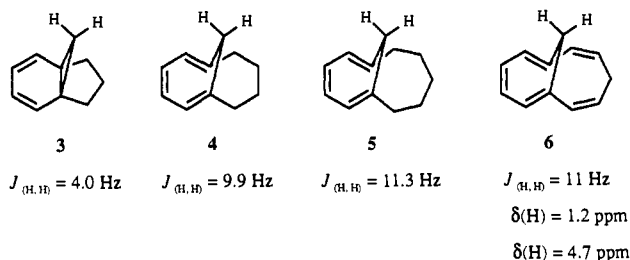
(7) See supplementary material. The two bridge carbons are at 94.19 and 120.62 ppm, and the bridge appears at 64.10 ppm.

Scheme 1



The ^1H NMR of the dihydrofulleroid shows *two* doublet peaks at 2.87 (H_A) and 6.35 (H_B) ppm in a 1:1 ratio. Spin decoupling revealed that the two sets of doublets ($J = 9.7$ Hz) are coupled. One hydrogen is remarkably deshielded relative to the other ($\Delta\delta = 3.48$ ppm). There are only a few cases reported where a $\Delta\delta > 3$ ppm was observed; of these, the most revealing is hydrocarbon **6**.⁸ In the latter, the relevant high-field and low-field protons appear at 1.2 and 4.7 ppm, respectively, i.e., 1.67 and 1.65 ppm upfield relative to the corresponding fulleroid hydrogens. In the case of fulleroids, it was shown that aromatic protons which are directly above the " π " system of the 6-rings are drastically deshielded,⁵ but a fulleroid with protons over a 5-ring has not yet been prepared; H_2C_{61} is the first case. Since aromatic ring currents cannot⁹ exist in **6** and $\Delta\delta$ is the same as in the fulleroid, we conclude that, as is the case for C_{60} ,¹⁰ there are no ring currents in the fulleroid spheroid.^{9,11}

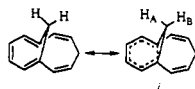
We propose structure **2** for H_2C_{61} on the basis of the above and the following: (i) The coupling constant of the methylene hydrogens is a good measure of the C-CH₂-C angle, as shown for the following sequence of bridged cycloheptatrienes.¹²



(ii) The ^{13}C NMR spectrum of $\text{H}_2(^{13}\text{C})\text{C}_{60}$ prepared from (99% ^{13}C) diazomethane shows a single peak at 38.85 ppm, which is in good agreement with that of methano[10]annulene (38.4 ppm), and 32 fulleroid resonances (135.15–149.25 ppm).^{7,13} (iii) The coupling constants between the methylene carbon and its hydrogens are $J(^{13}\text{C},\text{H}_A) = 145.0$ and $J(^{13}\text{C},\text{H}_B) = 147.8$ Hz, respectively, and are typical for methano[10]annulenes.¹⁴

(8) Vogel, E. *Aromaticity*; Ollis, O. D., Ed.; The Chemical Society: London, 1967, Vol. 21, p 142.

(9) If there were a ring current in the "cyclohexatriene" moiety of **6** (see i), then proton H_A would have a chemical shift of 0 to -1 ppm. However, Robert Haddon (private communication; also: Haddon, R. C. *Tetrahedron* 1972, 28, 3613, 3635) mentioned a possible danger of using model chemical shifts (MCS) in analyzing ring currents.



(10) Haddon, R. C.; Schneemeyer, L. F.; Waszczak, J. V.; Glarum, S. H.; Tycko, R.; Dabbad, G.; Kortan, A. R.; Muller, A. J.; Mujse, A. M.; Rosseinsky, M.; Zahurak, S. M.; Makhija, A. V.; Thiel, F. A.; Raghavachari, K.; Cockayne, E.; Elser, V. *Nature* 1991, 350, 46. Elser, V.; Haddon, R. C. *Nature* 1987, 325, 792.

(11) Another interpretation could be that two types of paramagnetic ring currents exist in fulleroids (and by extrapolation in fullerene C_{60} ; Pasquarello, A.; Schlüter, M.; Haddon, R. C. *Science*, submitted; private communication and preprint). If that were the case, as well as on the basis of previous results, we would conclude that the ring currents of the 6-rings are deshielding and those of the 5-rings are shielding.

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We have shown above that, contrary to all previous cases⁵ reported for fulleroid synthesis, (1) the intermediate pyrazoline can be isolated and characterized; (2) the first step of the fulleroid synthesis is a dipolar addition across the reactive 6-ring-6-ring (pyracyclene)^{15,16} junction; (3) thermal nitrogen loss occurs concomitantly with rearrangement (1,5-shift?); and (4) comparative ^1H NMR with a known bicyclic hydrocarbon incapable of sustaining an extended ring current indicates that there are no extended ring currents in the fulleroid " π " system.^{9,11}

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Supplementary Material Available: Complete spectroscopic characterization of pyrazoline **1** and fulleroid **2**, a cyclic voltammogram, a table of cyclic voltammetric data for C_{61} fulleroids, and a CHARMM computer modeling printout (14 pages). Ordering information is given on any current masthead page.

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The First X-ray Structure of a 1,1-Di-Grignard Compound: Bis(bromomagnesium)bis(trimethylsilyl)methane

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As a part of our research aimed at new 1,1-di-Grignard reagents,^{1,2} we have reported on the preparation of bis(bromomagnesium)bis(trimethylsilyl)methane (**1**),^{3a} it was obtained in a

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