Systematic Inflation of Buckminsterfullerene C_{60}: Synthesis of Diphenyl Fulleroids C_{61} to C_{66}

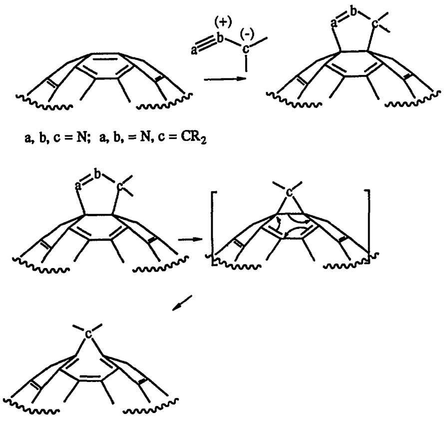
T. SUZUKI, Q. LI, K. C. KHEMANI, F. WUDL,* Ö. ALMARSSON

The synthesis of a new family of spheroidal carbon molecules derived from the fullerenes is described. The fulleroids are produced by incremental addition of a divalent carbon equivalent that has two phenyl (Ph) rings to fullerene C_{60}. The fulleroids Ph_2C_{61}, Ph_4C_{62}, Ph_6C_{63}, Ph_8C_{64}, $Ph_{10}C_{65}$, and $Ph_{12}C_{66}$ have been prepared and characterized.

THE FULLERENES, PARTICULARLY C_{60}, have been well characterized (*1–3*), but few reports about their chemical reactivity appeared (*4–6*). It has been proposed that the relatively high electronegativity of this carbon cluster was due to its pyracylene character (*2*). Further, the inter–five-membered ring bonds are fulvenoid and are potent electrophilic as well as dienophilic and dipolarophilic sites (*5, 7*).

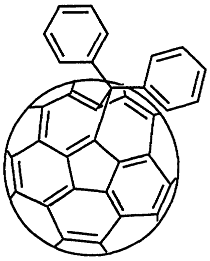
Although nucleophilic addition reactions to C_{60} produce a myriad of products (*7*), the electronic character of the products is altered drastically relative to C_{60} to the point that only minor "conjugation" (*8*) remains (color bleaching to yellow) (*7*). However, the basic fullerene skeleton could be modified, while retaining the same number of "π" (*8*) orbitals and attendant unusual electronic character, by a strategy that takes advantage of: (i) the norcaradiene-cycloheptatriene rearrangement; (ii) the aromatic character of the methano[10]annulenes (*9*); and (iii) the dipolarophilicity of C_{60} (Scheme 1):

A survey of C_{60} reactivity with the dipoles ethyl diazoacetate (*10*) and phenyl diazomethane (*10*) indicated that they add smoothly and, under some conditions, lose N_2. The incomplete pyrolytic nitrogen loss could be attributed to hydrogen migration with concomitant imine formation, as determined by infrared spectroscopy. Also, because the carbon atom bearing the diazo function is asymmetrically substituted, phenyldiazomethane addition gave a large number of isomers upon multiple reaction. In order to prevent hydrogen migration and to reduce the potential number of isomers, we decided to study the reaction of C_{60} with diphenyldiazomethane. We found that this strategy worked and report a method for fullerene inflation (spherical expansion) to produce "fulleroids" (*11*), expanded fullerenes whose basic electronic properties [ultraviolet-visible (UV-vis) spectroscopy and cyclic voltammetry] are retained.



Scheme 1

Reaction of C_{60} with more than one equivalent of diphenyldiazomethane in toluene at room temperature for ~1 hour produced a monoadduct diphenyl fulleroid C_{61} (*12*). Apparently because compound **1** is similar in molecular shape to $C_{60}Pt(PPh_3)_2$ (*4*), just as its organometallic analog, it is less soluble in benzene than C_{60} and thus could be obtained in ~40% yield. It was isolated and purified by chromatography on silica gel. Based on its spectroscopic and physico-chemical properties [see (*13*) and Table 1] we propose structure **1** depicted below and in Fig. 1.



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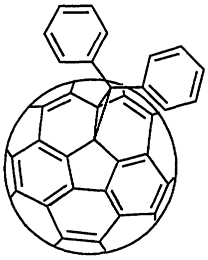
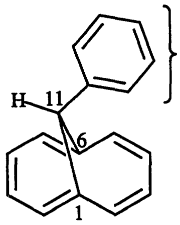


1a

The salient features that support the proposed structure, and not **1a**, are the similarities of the electronic spectrum (particularly wavelengths of absorption maxima at 212, 258, and 326 nm; see Fig. 1) and cyclic voltammetry of **1** and C_{60} (see Fig. 2 and Table 1). The $(Ph_3P)_2Pt$ analog has structure **1a** as determined by x-ray crystallography. The ring-closed nature of the derivative is reflected in a major change of its UV-vis spectrum relative to C_{60} as well as a shift of the first reduction wave by 340 mV negative relative to C_{60} (*14*). Although it is difficult to obtain a ^{13}C nuclear magnet resonance (NMR) spectrum of Ph_2C_{61}, due to insolubility, the ^{13}C NMR results on $Ph_{12}C_{66}$ show only three (broad) resonances in the fullerene region, which is in agreement with octahedral regiochemistry previously observed in the $[(Et_3P)_2Pt]_6C_{60}$ analog whose octahedral structure was determined by x-ray crystallography (*5*). The 11,11-diphenyl methano[10]annulene could be a reasonable model for ^{13}C chemical shift assignments; however, the compound does not exist. The closest analog is the 11-phenyl methano[10]annulene, whose relevant chemical shifts are shown below (*15*):



$C_{ortho} = 127.15$ $H_{ortho} = 6.80$
$C_{meta} = 126.38$ $H_{meta} = 6.97$
$C_{para} = 125.62$ $H_{para} = 6.97$

$C_{1,6} = 117.40$

$C_{11} = 46.32$

Since the unsubstituted C_{11} has a chemical shift of 35 ppm and the monophenyl derivative's chemical shift is ~46 ppm, one additional phenyl on the 11-carbon would be

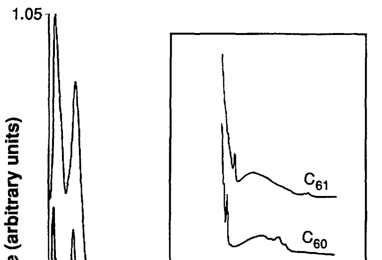


Fig. 1. Comparative ultraviolet-visible spectra of C_{60} and Ph_2C_{61} (labeled "C_{61}"). The inset is the 700- to 350-nm region at 20 times the gain. The absorbance of two spectra has not been normalized.

T. Suzuki, Q. Li, K. C. Khemani, F. Wudl, Institute for Polymers and Organic Solids and Departments of Physics and Chemistry, University of California, Santa Barbara, CA 93106.
Ö. Almarsson, Department of Chemistry, University of California, Santa Barbara, CA 93106.

*To whom correspondence should be addressed.

Table 1. Cyclic voltammetry of the diphenyl fulleroids Ph_2C_{61} to $Ph_{12}C_{66}$. Experimental conditions: Pt working and counterelectrodes; Ag/AgCl/3M NaCl, reference electrode; Ferrocene internal reference (+620 mV); 0.1 M $TBABF_4$ (tetrabutylammonium fluoroborate) in THF (tetrahydrofuran) in a dry box.

Scan rate (mV/s)	Peak position (mV)						
	C_{60}	C_{61}	C_{62}	C_{63}	C_{64}	C_{65}	C_{66}
100	−228	−335	−439	−554	−643	−809	−900
	−826	−920	−974	−1072	−1150	−1278	−1385
	−1418	−1470	−1609	−1632	−1669	−1820	−1915
	−1916	−1929	−1995	−2025	−2120	−2135	
1000	−238	−346	−472	−562	−646	−785	−886
	−838	−924	−988	−1101	−1191	−1350	−1406
	−1418	−1476	−1549	−1654	−1730	−1930	−2001
	−1921	−1953	−1976	−2060	−2150		

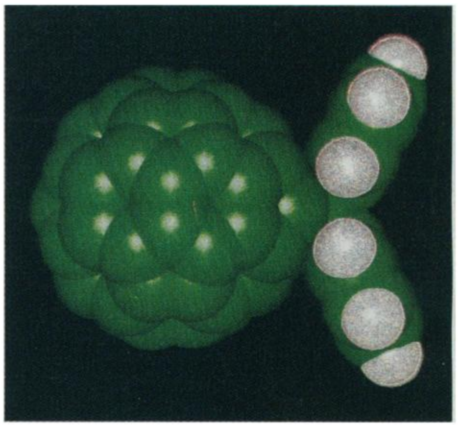


Fig. 3. Computer-generated model of Ph_2C_{61}. Note the minor perturbation on the structure of C_{60} caused by the methylene carbon of the diphenylmethylene group.

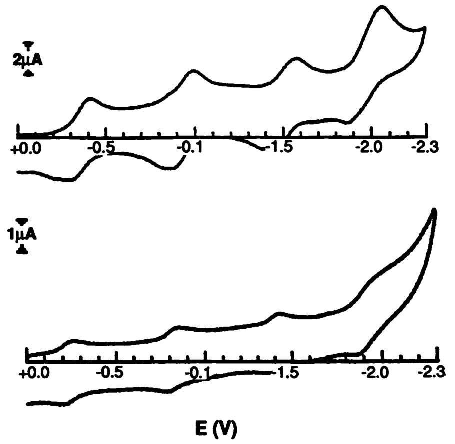
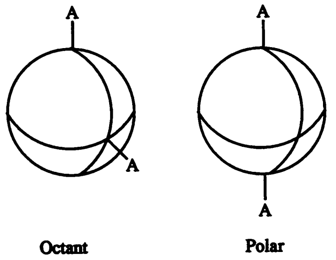


Fig. 2. Comparative cyclic voltammograms of C_{60} (bottom) and Ph_2C_{61} (top) versus Ag/Ag^+ as a reference in tetrahydrofuran with tetrabutylammonium fluoroborate as a supporting electrolyte; a Pt disk and a Pt wire were used as working and counterelectrodes, respectively.

expected to further deshield it to a chemical shift of ~60 ppm. We have not observed any resonances in this region of the ^{13}C NMR spectrum of $Ph_{12}C_{66}$; possibly because of: (i) the expected weakness of the quaternary carbon intensity; (ii) a combination of weak signal and signal broadening observed in most organic fullerene derivatives; or (iii) the strong deshielding effect of the fulleroid electronic structure shifts the resonance to coincide with the aromatic carbon region. An interesting result in the comparison of the fulleroid with methano[10]annulene is the chemical shift of the ortho phenyl hydrogens; in the former they appear at 8.4 ppm (deshielded relative to the meta and para hydrogens), whereas in the later they appear at 6.8 ppm (slightly shielded relative to the meta and para hydrogens).

Whereas the NMR spectra of Ph_4C_{62} are complicated due to restricted rotation around the C–Ph bonds (see Fig. 1), recent results on the similar adduct with 9-diazofluorene (9-Fl), $(9\text{-Fl})_2C_{62}$, in which C–Ph rotation cannot occur, show that only two isomers, "octant" and "polar," were produced (*16*).



Additional corroborating support for the "open" structure type **1** was obtained from results of molecular modeling calculations. The release of strain on going from C_{60} to **1** and from **1a** to **1** was confirmed by a molecular modeling calculation with CHARMm (*17*). Although the total energy per molecule is not an accurate number, the relative energies may be more reliable; thus, C_{60} = 1198, H_2C_{61} = 1127, Ph_2C_{61} = 1165, Ph_4C_{62} = 1145, Ph_8C_{64} = 1104, and $Ph_{12}C_{66}$ = 1059 kcal/mol, respectively. The "norcaradienoid" form (**1a**), that is, with an unopened cyclopropane, has a minimized energy of 1196 kcal/mol, 31 kcal/mol greater in energy than the proposed structure **1**. The space-filling model structure in Fig. 3 was generated with the Quanta program, above. Although the above offer strong support for the proposed structure, the definitive structure proof requires x-ray crystallographic evidence.

More extended reaction times with different stoichiometries afforded the diphenyl fulleroids C_{62}, C_{63}, C_{64}, C_{65}, and C_{66}. The latter took 8 to 10 days to be formed from a large excess over six equivalents of diphenyl diazomethane. As can be seen in Table 1, with increasing inflation, the fulleroids become more electropositive, which may be a result of a combination of: (i) strain relief; (ii) more π-like overlap due to greater p character of the 60 p_z orbitals; or (iii) with increasing inflation, closure to the norcaradienoid form may occur. We also note that: (i) the only correct elemental analysis is that of $Ph_{12}C_{66}$ (*13*) and (ii) the NMR resonance lines are broad (for which we have no simple explanation). After investigating the chemistry of C_{60} for some time (*7*), we learned that most elemental analyses of C_{60} derivatives give consistently low carbon values. Perhaps as the hydrogen content of the molecule increases, combustion is more complete, which would be the case with $Ph_{12}C_{66}$.

Although one may read that C_{60} will have as profound an influence in organic chemistry as benzene had, for example, in the dye industry, this view is unlikely to be realized because benzene undergoes electrophilic substitution of its hydrogen atoms but C_{60} has no easily replaceable hydrogen atoms. However, with the discovery presented above, one could prepare essentially any functionalized fulleroid. The implication of this discovery is that specifically functionalized, spherically unsaturated molecules can be produced.

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11. We prefer fulleroid over "homo fullerene," as suggested to us by R. Haddon. The naming using the "homo" prefix gets unwieldy as in hexakis homo fullerene.
12. J. M. Wood *et al.* [*J. Am. Chem. Soc.* **113**, 5907 (1991)] have shown by mass spectrometry that species containing $C_{61}O$ to $C_{66}O$ occur in the crude extracts of fullerene preparation. These were not isolated nor characterized further.
13. Properties of the diphenyl fulleroids Ph_2C_{61} to $Ph_{12}C_{66}$. C_{60}: MW (molecular weight) 720; UV-vis [λ_{max} (absorption maximum), cyclohexane] 212, 257, 328, 404, 542, 598, and 620 nm. Ph_2C_{61}: MW 886.882; ^1H NMR (CS_2, $CDCl_3$) δ 8.02 (dd, $J = 7.5$, 1.2 Hz, 4H), 7.42 (t, $J = 7.5$ Hz, 4H), and 7.32 (t, $J = 7.5$ Hz, 2H); fast-atom-bombardment (FAB) MS weak 887, stronger 720 (C_{60}); infrared (IR) (KBr) 3020 (w), 1600 (w), 1510 (m), 1495 (m), 1450 (m), 1430 (m), 1385 (w), 1185 (m), 1160 (w), 1080 (w), 1030 (w), 1000 (w), 755 (sh), 740 (m), 700 (s), 575 (w), 550 (w), and 530 (s) cm^{-1}; and UV-vis (λ_{max}, cyclohexane) 212, 258, 326, 429, 495, and 695 nm. Analysis (Anal) for $C_{73}H_{10}$: calculated (calcd) C, 98.86, and H, 1.14; found C, 96.81, H, 1.27, and N, 0.00. Ph_4C_{62}: MW 1053.104; ^1H NMR (CD_2Cl_2) δ 8.4 to 6.8 (m, br, 20H); FAB MS 1055 to 1052 (M^+); IR (KBr) 3060 (w), 3025 (w), 1600 (m), 1585 (sh), 1495 (m), 1450 (m), 1380 (w), 1185 (w), 1160 (w), 1080 (w), 1030 (w), 1005 (sh), 840 (w), 800 (w), 740 (m), 700 (s), and 520 (br) cm^{-1}; and UV-vis (λ_{max}, cyclohexane) 214, 263, 327, and 510 nm; Anal for $C_{86}H_{20}$: calcd, C, 98.09 and H, 1.91; found C, 95.38, H, 2.48, N, 0.00, and 1.4% of residue. Ph_6C_{63}: MW 1219.326; ^1H NMR (CD_2Cl_2) δ 8.4 to 6.8 (m, br, 30H); FAB MS 1220 to 1218 (M^+); IR (KBr) 3060 (w), 3025 (w), 1600 (m), 1585 (sh), 1495 (m), 1450 (m), 1380 (w), 1330 (w), 1180 (w), 1155 (w), 1080 (w), 1030 (w), 1000 (w), 835 (w), 740 (m), 700 (s), and 530 (br) cm^{-1}; and UV-vis (λ_{max}, cyclohexane) 260 (sh) and 492 nm. Anal for $C_{99}H_{30}$: calcd C, 97.52 and H, 2.48; found C, 94.29, H, 2.59, N, 0.00, and 2.4% of residue. Ph_8C_{64}: MW 1385.548; ^1H NMR (CD_2Cl_2) δ; 8.4 to 6.8 (m, br, 40H); FAB MS 1386 to 1384 (M^+); IR (KBr) 3060 (w), 3025 (w), 1600 (m), 1580 (sh), 1495 (m), 1450 (m), 1380 (w), 1320 (w), 1185 (w), 1160 (w), 1080 (w), 1030 (w), 1000 (sh), 740 (m), 700 (s), and 530 (br) cm^{-1}; UV-vis (λ_{max}, cyclohexane) 270 (sh) and 485 nm (sh). Anal for $C_{112}H_{40}$: calcd C, 97.09 and H, 2.91; found C, 92.72, H, 3.26, and N, 0.00. $Ph_{10}C_{65}$: MW 1551.77; ^1H NMR (CD_2Cl_2) δ 8.4 to 6.8 (m, br, 50H); FAB MS 1553 to 1551 (M^+); IR (KBr) 3060 (w), 3025 (w), 1600 (m), 1585 (sh), 1495 (m), 1450 (m), 1380 (w), 1320 (w), 1185 (w), 1160 (w), 1080 (w), 1030 (w), 1005 (w), 840 (w), 740 (m), 700 (s), and 535 (br) cm^{-1}; UV-vis (λ_{max}, cyclohexane) 280 (sh) and 480 nm (sh). Anal for $C_{125}H_{50}$: calcd C, 96.75 and H, 3.25; found C, 94.97, H, 3.34, and N, 0.00. $Ph_{12}C_{66}$: MW 1717.992; ^1H NMR (CD_2Cl_2) δ 8.4 to 6.8 (m, br, 60H); ^{13}C NMR ($CDCl_3$) δ(all broad) 126.4, 127.4, 128.2, 129.1, 130.4, and 132.3 (all due to phenyl) and 140.0, 143.4, and 147.5 (fullerene); FAB MS 1718 to 1716 (M^+); IR (KBr) 3060 (w), 3025 (w), 1600 (m), 1585 (sh), 1495 (m), 1450 (m), 1185 (w), 1160 (w), 1080 (w), 1030 (w), 1000 (w), 840 (w), 740 (m), 700 (s), and 530 (br) cm^{-1}; UV-vis (λ_{max}, cyclohexane) 285 (sh) and 490 nm (sh); Anal for $C_{138}H_{60}$: calcd C, 96.48 and H, 3.52; found C, 96.08, H, 3.63, and N, 0.00.
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18. We thank the National Science Foundation for support through grants DMR-88-20933, DMR-91-11097, and CHE-89-08323, J. M. Hawkins for coordinates of the C_{60} osmylate, and E. Vogel for disclosing data in a personal communication.

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Evidence for Multiple Sources of Diamond from Primitive Chondrites

S. S. Russell, J. W. Arden, C. T. Pillinger

Fine-grained diamonds, the most abundant form of circumstellar dust isolated from primitive meteorites, have elemental and isotopic characteristics that are dependent on the host meteorite type. Carbon isotopic compositions vary from −32 to −38 per mil, and nitrogen associated with the diamond changes in overall abundance by over a factor of four from 0.2 to 0.9 weight percent, between ordinary and CM2-type chondrites. Although the ratio of carbon to nitrogen evolves in a distinctive way during combustion of diamond separates, metamorphic degassing of nitrogen is not the main cause of the differences in nitrogen content. The data suggest that intrinsic differences must have been inherited by the diamonds at the time of their formation and that the diamonds were distributed heterogeneously in the solar nebula during condensation. However, the hypothesis that a distinct nitrogen carrier remains hidden within the diamond cannot be ruled out.

NANOMETER-SIZED DIAMONDS WERE first identified in acid-resistant residues from carbonaceous and enstatite chondrites by Lewis *et al.* in 1987 (*1*), and have since been isolated from all groups of primitive chondrites in amounts up to 940 ppm (*2*, *3*). Although the diamond has a typical solar system–like carbon isotopic composition (*4*, *5*), it has been recognized as a circumstellar grain from the anomalous isotopic signatures of the associated elements N (*6*) and Xe (*7*). Nitrogen is a more satisfactory tracer than Xe because it is normally substituted in the tetrahedral lattice of diamond and therefore must be cogenetic, whereas Xe is simply trapped. The amounts of Xe encountered are so small that only one diamond crystal in 3×10^6 actually contains a ^{132}Xe atom, whereas N is sufficiently abundant for each diamond to contain several atoms. To investigate the information that N can provide about the source and history of these putative circumstellar grains, we conducted a systematic study of diamonds from five separate classes of chondritic meteorites.

Diamonds were concentrated from each meteorite by acid treatments that destroy virtually all other forms of C in the meteorites, as described in (*8*). To avoid contamination from N in reagents used for the colloidal separation of diamond from spinels and silicon carbide, the ammonia suspension technique (*1*, *3*) was not used. The extraction procedures that we adopted consisted of stepped combustion at very high resolution (temperature increments of 10°C); this procedure yielded release profiles showing that the N and C thought to be associated with diamond had been adequately resolved from other species (*9*). Most of the carbon isotopic values reported were obtained from diamond-rich samples in excess of 150 μg in mass and so could be measured with the use of a conventional dynamic mass spectrometer to a precision (±standard error) better than ±0.1 per mil (*10*). Nitrogen isotopic determinations on approximately 100-μg samples were made to a precision better than ±1 per mil with an instrument and method described in (*11*), so that nitrogen in the singly substituted state in diamond was converted to N_2 gas rather than condensable N-bearing species (*12*). Although the N abundance was measured absolutely, below we discuss primarily C/N ratios determined simultaneously on a single aliquot, because such an approach eliminates: (i) heterogenity problems involved in acquiring data for C from one aliquot and N from another; (ii) weighing errors on small specimens; and (iii) the difficulty of matching temperature scales.

The data (Fig. 1) show that the $\delta^{13}C$ values of diamond-rich fractions isolated

S. S. Russell and C. T. Pillinger, Planetary Sciences Unit, Department of Earth Sciences, Open University, Milton Keynes, United Kingdom MK7 6AA.
J. W. Arden, Department of Earth Sciences, Oxford University, Oxford, United Kingdom, OX1 3PR.