# The Chemical Properties of Buckminsterfullerene (C$_{60}$) and the Birth and Infancy of Fulleroids

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While molecular materials based on the chemical reduction of buckminsterfullerene (C$_{60}$) have captured the limelight of the popular press and the scientific literature as well as the imagination of chemists and physicists,[1] the chemical derivatization of the fullerenes has been an equally intense area of active research.[2-8] Early clues to the reactivity of the fullerenes C$_{60}$ and C$_{70}$ came from results of cyclic voltammetry studies[9-11] which showed that the two fullerenes were actually *mild oxidizing* agents. This observation was in accord with the theoretically determined low-lying LUMO orbitals[12] of C$_{60}$ but did not provide a microscopic, structure–property relationship picture of the origin of the high electron affinity of the molecule.

"C$_{60}$"
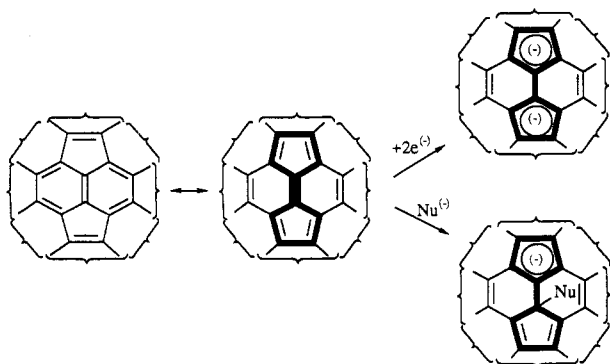
Close examination of a C$_{60}$ "ball and stick" model revealed that there were a number of pyracyclene units in the cluster, and on the basis of the premise that pyracyclene is a $4n\pi$ system,[13] it was hypothesized that each unit would provide a driving force for the capture of up to two electrons either by direct electron transfer to give a $4n + 2\ \pi$ electron dianion or in the form of a lone pair to give a "cyclopentadienide" monoadduct as shown above.

Fullerene C$_{60}$ was therefore assigned the symbolic representation shown below to emphasize the importance of the pyracyclene moieties vis-à-vis the chemical reactivity of the cluster.

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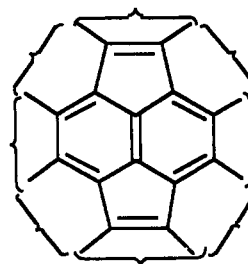
Independently, when Fagan attempted to prepare transition-metal derivatives of C$_{60}$, he arrived at a similar conclusion about fullerene reactivity.[14]

To test our fullerene reactivity hypothesis, we decided to allow C$_{60}$ to react with a number of nucleophiles (amines,[15] phosphines,[15] a Grignard reagent,[15] organolithium reagents,[15] thiolate,[15] methoxide,[16] and phen-

(1) Please refer to Accounts by Haddon, by Diederich and Whetten, and by Fischer, Heiney, and Smith in this issue.

(2) Please refer to Accounts by Fagan, Calabrese, and Malone and by Hawkins in this issue.

(3) Wudl, F.; Hirsch, A.; Khemani, K. C.; Suzuki, T.; Allemand, P.-M.; Koch, A.; Srdanov, G. Presented at the 200th National Meeting of the American Chemical Society, Atlanta, GA, April 1991. In *Fullerenes: Synthesis, Properties and Chemistry of Large Carbon Clusters*; Hammond, G. S., Kuck, V. J., Eds.; American Chemical Society: Washington, DC, 1992; p 161.

(4) Bausch, J. W.; Prakash, S. G. K.; Olah, G. A. *J. Am. Chem. Soc.* 1991, *113*, 3205.

(5) Cox, D. M.; Behal, S.; Disko, M.; Gorun, S. M.; Greaney, M.; Hsu, C. S.; Kollin, E. B.; Millar, J.; Robbins, J.; Robbins, W.; Sherwood, R. D.; Tindall, P. *J. Am. Chem. Soc.* 1991, *113*, 2940. Greaney, M. A.; Gorun, S. M. *J. Phys. Chem.* 1991, *95*, 7142.

(6) Olah, G. A.; Bucsi, I.; Lambert, C.; Aniszfeld, R.; Trivedi, N. J.; Sensharama, D.; Prakash, G. K. S. *J. Am. Chem. Soc.* 1991, *113*, 9385. Olah, G. A.; Bucsi, I.; Lambert, C.; Aniszfeld, R.; Trivedi, N. J.; Sensharama, D.; Prakash, G. K. S. *J. Am. Chem. Soc.* 1991, *113*, 9387.

(7) Selig, H.; Lifshitz, C.; Peres, T.; Fischer, J. E.; McGhie, A. R.; Romanow, W. J.; McCauley, J. P., Jr.; Smith, A. B., III. *J. Am. Chem. Soc.* 1991, *113*, 5475.

(8) Wood, J. M.; Kahr, B.; Hoke, S. H., II; Dejarme, L.; Cooks, R. G.; Ben-Amotz, D. *J. Am. Chem. Soc.* 1991, *113*, 5907.

(9) Haufler, R. E.; Conceicao, J.; Chibante, L. P. F.; Chai, Y.; Byrne, N. E.; Flanagan, S.; Haley, M. M.; O'Brien, S. C.; Pan, C.; Xiao, Z.; Billups, W. E.; Ciufolini, M. A.; Hauge, R. H.; Margrave, J. L.; Wilson, L. J.; Curl, R. F.; Smalley, R. E. *J. Phys. Chem.* 1990, *94*, 8634.

(10) Allemand, P.-M.; Koch, A.; Wudl, F.; Rubin, Y.; Diederich, F.; Alvarez, M. M.; Anz, S. J.; Whetten, R. L. *J. Am. Chem. Soc.* 1991, *113*, 1050.

(11) Dubois, D.; Kadish, K. M.; Flanagan, S.; Wilson, L. J. *J. Am. Chem. Soc.* 1991, *113*, 7773.

(12) Please see the Account by Haddon in this issue.

(13) Only the circulating electrons (electrons around the periphery of the pyracyclene) are counted. Trost, B. M.; Bright, G. M.; Frihart, C.; Brittelli, D. *J. Am. Chem. Soc.* 1971, *93*, 737.

(14) Please refer to the Account by Fagan in this issue.

(15) Hirsch, A.; Koch, A.; Shi, S. Unpublished (1991). These nucleophiles gave mixtures which were difficult to characterize. The product of lithium methoxide addition was a mixture of lithium fulleroxides. Apparently the methoxy fulleride products of initial addition were demethylated by excess reagent.

oxide[16]). To further support our hypothesis, we had to determine if the pyracyclene inter-five-membered-ring bonds were dienophilic and dipolarophilic. Indeed, C_{60} gave adducts with anthracene, cyclopentadiene, and furan[16] as well as isobenzofuran.[16] The dipoles *p*-nitrophenyl azide, ethyl diazoacetate, and phenyldiazomethane were also found to add to C_{60}.[15]

At the beginning of the investigation of the chemical reactivity of C_{60}, we were limited by the small quantities available, and a large excess of reagent was always used in order to convert all the available active sites on the fullerene. Later, when more material was procurable through the use of our fullerene benchtop reactor[17] and from commercial sources, we were able to explore some of the reactions in greater detail.

In this Account the emphasis is on the high electron affinity of buckminsterfullerene, where reductions, nucleophilic additions, and oxidative additions of low-valent transition metals[2] are considered as the sole avenues to fullerene C_{60} functionalization and modification. However, it should be mentioned that *electrophilic* additions (Lewis acid-mediated fullerene phenylation as well as bromination and chlorination,[6] and cation-mediated hydroxylation/alkoxylation[18,19]) have also been reported.

Functionalization of Fullerene C_{60} and the Preparation of Fulleroids

The discovery of fullerene C_{60}'s electrophilicity, dienophilicity, and dipolarophilicity, while important, was not sufficient to provide a recipe for systematic, selective functionalization. Most early attempts to do so led to intractable mixtures. Two exceptions were $Et_3BH^-Li^+$ (single hydride addition)[3,15] and morpholine (hexaadduct formation).[20] A major disadvantage of nucleophilic and electrophilic addition reactions to the double bonds is that "conjugation" sites are removed. An extreme case is the production of "hairy balls" by addition of excess ethylenediamine to C_{60} to produce a water-soluble polyamine which is only slightly yellow in color.[3]

When Toshiyasu Suzuki surveyed the reaction of C_{60} with diazoalkanes, he obtained evidence, in the case of ethyl diazoacetate, that partitioning of the intermediate 1-pyrazoline to the 2-isomer and to a bridged molecule had occurred, as shown schematically below:
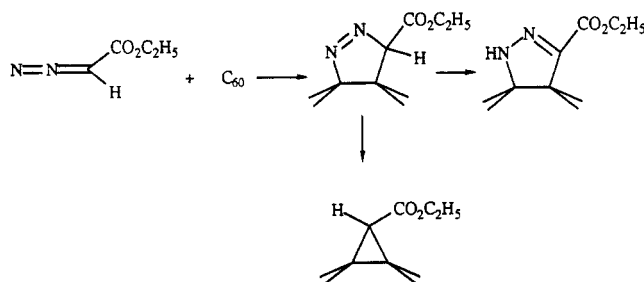
About this time, Professor F. Diederich informed us that, in a sample of higher fullerenes which we had sent

him, one of the components was actually $C_{70}O$, and because its UV–vis spectrum was essentially identical to that of C_{70}, in accord with precedent in bridged annulenes,[21] he assigned it[22] the ring-opened structure 1, assuming that the oxide existed as an oxofulleroid,[23] rather than an epoxyfullerene.[24] This observation led
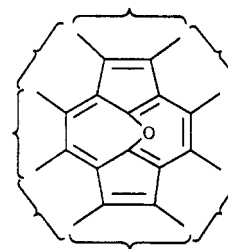
"$C_{70}O$"

1

us to reflect on the possibility of preparing specifically functionalized C_{60} compounds in which the electronic property of the fullerene remained essentially unperturbed, provided the dipolar addition product would be in a ring-opened form, and not as the "norcaradiene" shown above. The concept, as it appeared in print,[25] is depicted below, for a = b = N and c = CR_2:

a, b, c = N; a, b, = N, c = CR_2
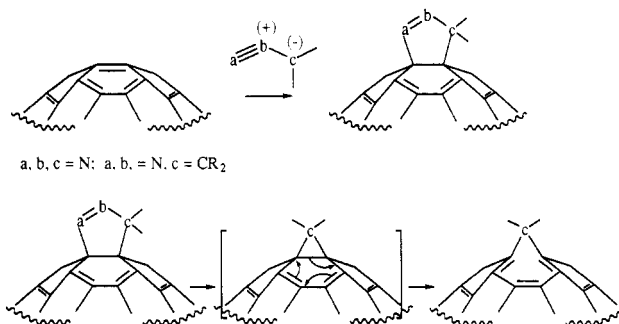
To make absolutely certain that there would be no prototropy, we decided to test the above concept with diphenyldiazomethane. Soon Toshiyasu was the beneficiary of Mother Nature's extreme kindness: (1) the pyrazoline intermediate lost nitrogen spontaneously at room temperature, (2) the product of *single* addition (isolated in >40% yield) was the least soluble component in the reaction mixture, and (3) each incremental diphenyldiazomethane addition product caused a decrease in reaction rate (10 days for hexaadduct formation).

The monoadduct's UV–vis spectrum was identical to that of C_{60} in the UV region but was different in the weakly absorbing visible region, and its cyclic voltammetry showed four reversible waves with a 0.08-V

(16) Suzuki, T.; White, T.; Rickborn, B. R. Unpublished (1991).
(17) Koch, A.; Khemani, K. C.; Wudl, F. *J. Org. Chem.* 1991, *56*, 4543.
(18) Chiang, L. Y.; Upasani, R.; Swirczewski, J. W. Presented at the Materials Research Society Meeting, Boston, MA, Dec 1991.
(19) Miller, G. P.; Hsu, C. S.; Chiang, L. Y.; Thomann, H.; Bernardo, M. Presented at the Materials Research Society Meeting, Boston, MA, Dec 1991.
(20) Hirsch, A.; Li, Q.; Wudl, F. *Angew. Chem.* 1991, *103*, 1339.

(21) Vogel, E. *Pure Appl. Chem.* 1982, *54*, 1015.
(22) Diederich, F.; Ettl, R.; Rubin, Y.; Whetten, R. L.; Beck, R. D.; Alvarez, M. M.; Anz, S. J.; Sensharma, D.; Wudl, F.; Khemani, K. C.; Koch, A. *Science* 1991, *252*, 548.
(23) Fulleroid is a term introduced to describe an expanded fullerene where the electronic properties and number of π electrons remain unchanged with respect to the unexpanded fullerene.
(24) A C_{60} oxide, where the structure assignment was of a closed epoxide rather than a fulleroid, has recently been prepared: Creegan, K. M.; Robbins, J. L.; Robbins, W. K.; Millar, J. M.; Sherwood, R. D.; Tindall, P. J.; Cox, D. M.; McCauley, J. P., Jr.; Jones, D. R.; Gallagher, R. T.; Smith, A. B., III. *J. Am. Chem. Soc.*, in press. Elemes, Y.; Silverman, S.; Sheu, C.; Kao, M.; Foote, C. S.; Alvarez, M. M.; Whetten, R. L. *Angew. Chem.*, in press.
(25) Suzuki, T.; Li, Q.; Khemani, K. C.; Wudl, F.; Almarsson, Ö. *Science* 1991, *254*, 1186.

cathodic shift of the first reduction peak (-335, -920, -1470, and -1929 mV)[26] relative to C_{60} (-228, -826, -1418, and -1916 mV, under the same conditions).[26] We also asked Örn Almarsson, a student in Professor T. C. Bruice's group, to produce a computer model of a diphenyl fulleroid, Ph_2C_{61}. The model calculations revealed that the ring-opened form was thermodynamically more stable. Mainly on the basis of these data, we concluded that the monoadduct existed as depicted in structures 2–12, but in the publication[25] we inserted the caveat, "Although the above offer strong support for the proposed structure, the definitive structure proof requires x-ray crystallographic evidence".[25] Since the adduct resembled C_{60} in its electronic properties, we called it a fulleroid.[23,25]

Soon Toshiyasu was able to grow crystals of Ph_2C_{61}, and while a complete data set was collected in Chuck Strouse's group at UCLA, neither Saeed Khan (UCLA) nor Gordana Srdanov (UCSB) could solve the structure. There appeared to be too much disorder. It was decided to prepare the $(p\text{-}BrC_6H_4)_2C_{61}$, with the hope that the heavy atom would help.

In the meantime, in collaboration with Tom White from Professor B. R. Rickborn's group, Toshiyasu prepared an isobenzofuran monoadduct, and much to our surprise, the UV–vis and cyclic voltammetry were *identical* to those of Ph_2C_{61}! So our conclusion for the structure of the fulleroids was apparently on very shaky ground because apparently saturation of a sole double bond of C_{60} is not sufficient to significantly alter its electronic spectrum or its electrochemistry. Fortunately, Toshiyasu had also prepared a sample of $PhHC_{61}$, where the methine carbon was 99% ^{13}C enriched. Kishan Khemani soon found very gratifying NMR results. The chemical shift of the methine carbon was 53.6 ppm, much too low field for a cyclopropane, and the $^{13}C\text{-}^1H$ coupling constant was 140 ppm, in excellent agreement with the value $J_{C\text{-}H}$ of 11-phenyl-1,6-methano[10]annulene (139 ppm).[27] We were now confident that, at least for the monophenyl-substituted fulleroid, the transannular bond was open.

Soon thereafter, Songqing Shi prepared beautiful, tiny hexagonal prism crystals of $(p\text{-}BrC_6H_4)_2C_{61}$. The data was again collected to UCLA and the structure solved by Saeed Khan. The critical transannular bond length was found to be 1.84 Å, *somewhat shorter*[28] than that observed in most methanol[10]annulenes (2.1 Å) but still considerably longer than a fullerene bond (1.37–1.47 Å),[29] proving, together with the above ^{13}C NMR data, that the transannular bond was broken in accord with the fulleroid formation concept described earlier in this section.

(26) Pt working electrode and counterelectrode; Ag/AgCl/3 M NaCl, reference; ferrocene, internal reference (+620 mV); 0.1 M TBABF4 (tetrabutylammonium tetrafluoroborate)/THF in a drybox.
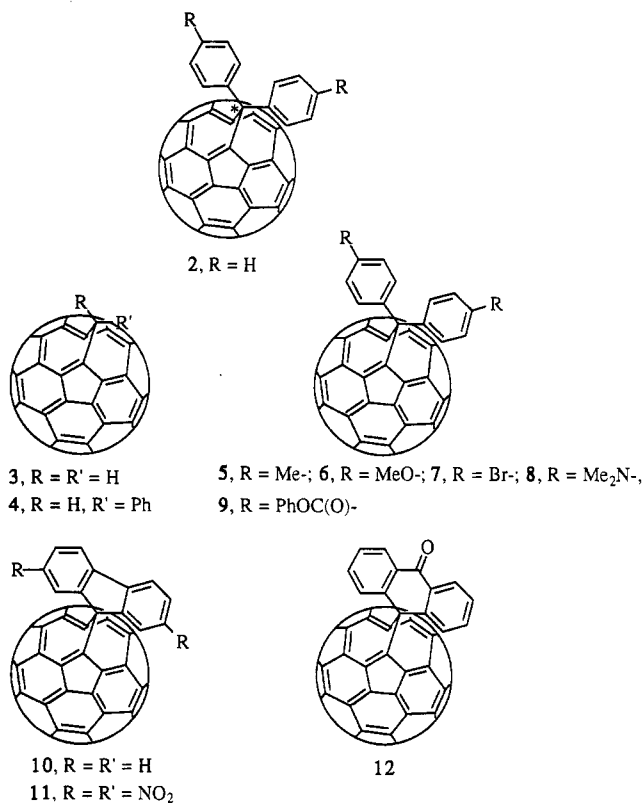
(27) Data provided kindly by Professor E. Vogel prior to publication.

(28) There are a number of methano[10]annulenes that have bond lengths of that order and that were considered to be in the annulene rather than the norcaradiene form. However, this interpretation of crystallographic results has come into question since the advent of solid-state CPMAS ^{13}C NMR. See: Haddon, R. C. *Tetrahedron* **1988**, *44*, 7611.

(29) At the time of this Account's writing, we are certain that the thermodynamically most stable isomer is the one depicted throughout the manuscript. One could speculate about the structure of one other isomer where the bridge spans a 6–5 ring juncture rather than the 6–6 juncture depicted in 1–12. We are uncertain about the structure of the third isomer, but it is apparent that structures 1–12 can be obtained by a series of allowed sigmatropic rearrangements of the bridge carbon.

Scope of the Fulleroid Synthesis

A. Monofulleroids. In quick succession, Toshiyasu Suzuki, together with Kishan Khemani, Gordana Srdanov, and Songqing Shi, prepared and characterized a number of fulleroids, 2–12. It is clear that fulleroid generation has ample scope. In this Account we describe the preparation of fulleroid C_{61} compounds only and not the "higher fulleroids" (C_{62}–C_{66}).

2, R = H

3, R = R' = H
4, R = H, R' = Ph

5, R = Me-; 6, R = MeO-; 7, R = Br-; 8, R = Me_2N-,
9, R = PhOC(O)-

10, R = R' = H
11, R = R' = NO_2

12

The *p,p'*-disubstituted-diphenyl fulleroids (2 and 5–9) are easily prepared because the raw materials are variously substituted benzophenones which are either commercially available or trivial to prepare and readily converted to stable diazomethanes via the hydrazones:

$$Ar_2CO + N_2H_4 \rightarrow Ar_2C{=}NNH_2 \xrightarrow{[O]} Ar_2C{=}N{=}N$$
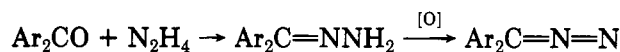
The first remarkable characteristic about the fulleroid formation reaction was that the product of single addition was a mixture of three isomers. This was found almost simultaneously by Toshiyasu Suzuki, who had prepared the ^{13}C bridge carbon labeled diphenyl fulleroid [asterisk in structure 2 (2*), below], and Kishan Khemani, who prepared the bis(*p*-methylphenyl) fulleroid (5). The former had three bridge carbon resonances in the ^{13}C NMR spectrum (37.5, 57.9, and 64.8 ppm), and the latter had three singlets in the methyl and a complex pattern in the aromatic resonance of its ^1H NMR spectrum. Later it was determined that 5–9 but not 4 nor 10–12 were also obtained as mixtures of at least two isomers.[29]

Toshiyasu Suzuki tested the hypothesis that one of the three (identical R_f by TLC) isomers of 2* was thermodynamically more stable by heating the "mixture" of isomers in toluene to reflux overnight. Much to our collective gratification, only the isomer with the 57.9 ppm resonance remained. Applying the same approach to 6, 8, and 9 simplified their NMR
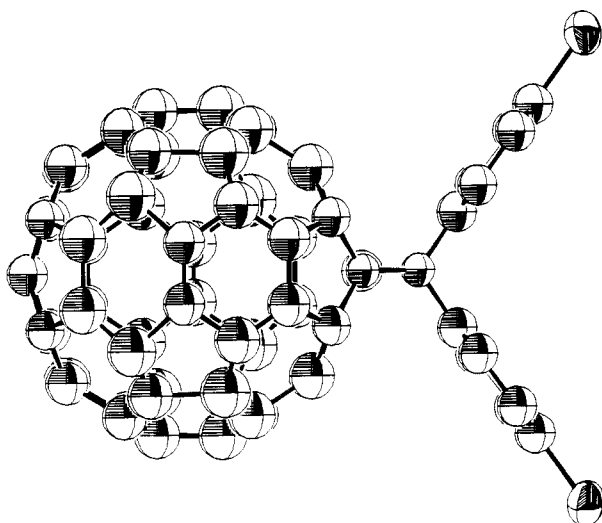
Figure 1. ORTEP representation of bis(bromophenyl) fulleroid. The crystal structure was determined on data collected at UCLA.[36]

spectra to coincide with the one expected for a single isomer. The same heat treatment was found to simplify and narrow the resonance lines in the NMR spectra of the higher fulleroids.

Crystals of **2**, **7**, and **8** were obtained without much difficulty. As mentioned above, the structure of **7** was solved, and currently an attempt to solve the structure of **8** is in progress.[30]

All fulleroids **2–11** have qualitatively very similar UV–vis spectra and cyclic voltammograms. The anthrone-derived fulleroid **12** has, in addition to the fulleroid CV waves, a wave due to the carbonyl redox system at –1300 mV,[26] almost overlapping the third wave of the fulleroid.

The electronic properties of the fulleroid moiety can be further probed by the chemical shift of the hydrogen atoms of the aromatic rings which are closest to the spheroid. As Figure 1 clearly shows, the ortho hydrogen atoms of diphenyl fulleroid **2** are the closest atoms to the surface of the sphere. These appear at 8.02 ppm, considerably deshielded relative to 2,2-diphenylpropane. The dominant motivation for the preparation of **10–12** was to answer the question, can we push the hydrogen atoms further into the fulleroid "π" system? As can be seen from Table I, the deshielding effect of the fulleroid is quite dramatic and in the opposite sense of the 1,6-methanol[10]annulenes. In the absence of more exploration, the simplest interpretation of these results is that if ring currents exist in the fulleroids (and by extension in the fullerenes), they are paramagnetic as expected from a nonaromatic or antiaromatic π system.

So far, we have demonstrated that fulleroid preparation is facile and versatile. We were then ready for the preparation of molecules which would have greater technological potential.

B. Bifulleroids, Pearl Necklaces, and Charm Bracelets. In principle one should be able to extend the fulleroid synthesis to the preparation of two types of polymers: one, where fulleroids are part of the backbone and the other, where fulleroids are pendant groups. The former have been dubbed "pearl necklace"

Table I
Selected ^{1}H NMR Chemical Shifts

compound	chemical shift of o-hydrogen atom (ppm rel to TMS)
2[a]	8.02
10[a]	8.76
11[a]	9.69
12[a]	8.40
2,2-diphenylpropane[b]	7.17
fluorene[c]	7.78
2-nitrofluorene[c]	8.30
anthrone[d]	7.50

[a] The chemical shift of the hydrogen atoms ortho to the bridge carbon atom is reported. [b] The chemical shift of the hydrogen atoms ortho to the dimethylbenzyl group is reported. [c] The chemical shift of the C(1)-H is reported. [d] The chemical shift of the H ortho to the methylene is reported.

polymers (PNP) and the latter "charm bracelet" polymers (CBP).[31]

For the preparation of CBPs, both **6** and **9** are masked monomers. Hydrolysis of the methyl ether of the former and the benzyl ester of the latter would afford a diphenol and dicarboxylic acid, respectively. So far we have been able to hydrolyze the ethers of **6** with BBr$_3$ in good yield[32] and are poised to prepare a number of poly(esters) and poly(urethanes) by polycondensation with a number of commercially available bis(acyl halides) and diisocyanates.

In one approach to the preparation of PNPs one can envision the use of bis(diazomethanes). To test if this idea was viable, Toshiyasu Suzuki allowed C$_{60}$ to react with the diazomethanes derived from m-phenylenebis(benzoyl) and p-phenylenebis(benzoyl). He was able to prepare compounds **13** and **14**, respectively.

13   14
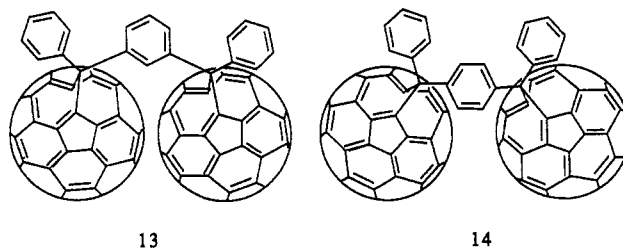
These are two-pearl sections of pearl necklace polymers. Interestingly, the "crude" compounds (single spot by TLC) had very broad NMR spectra, implying again the presence of several isomers. The heat treatment described above for the simple fulleroids worked, and clean, interpretable NMR spectra were recorded. Also, in line with previous observations on **10–12** (Table I), the hydrogen atom sandwiched between two spheres in **13** appeared at *8.8* ppm, compared to the *singlet* at 8.19 ppm of the four hydrogen atoms of the p-phenylene moiety of **14**. The CV of these bifulleroids revealed that the two fulleroids within a molecule are electronically *not independent*; each redox step consists of a double wave (two very close peaks).[33]

Even though these molecules were found to be quite insoluble[34] and thus very likely not good candidates for further reaction to produce macromolecules, attachment of solubilizing groups on the phenylene moiety will

(31) Amato, I. *Science* **1991**, *254*, 30 quoting F. Wudl.
(32) Shi, S.; Joshi, M. Unpublished.
(33) Suzuki, T.; Li, Q.; Khemani, K. C.; Wudl, F. *J. Am. Chem. Soc.*, submitted.
(34) (a) *Handbook of Conducting Polymers*; Skotheim, T. A., Ed.; Dekker: New York, 1986. (b) Patil, A. O.; Heeger, A. J.; Wudl, F. *Chem. Rev.* **1998**, *88*, 183 and references within.

undoubtedly render the polymers more tractable, as attested by the well-precedented case of solubilization of conjugated polymers.[34]

Future Directions and Conclusion

One can envision further applications of the fulleroid concept to the preparation of more exotic fulleroids which may have unusual materials properties. For example, alkylation of both nitrogens in 8 will lead to a fulleroid dication which upon two-electron reduction will lead to a "self-doped" fulleroid, akin to the self-doped conducting polymers.[34b] The self-doped fulleroid would be expected to be a metal. It may turn out to be a ferromagnet as well, if the LUMO of the fulleroids is of the same character as that of C_{60}. Further doping with 1 equiv of an alkali metal would produce a material which may undergo a transition to the superconducting state.

Although the higher fulleroids were not discussed in this Account, a C_{66} fulleroid (e.g., the C_{66} analogue of 9) would be a "natural" for "generation 1" in the preparation of very large dendrimers.[35]

With the Account about the discovery of the fulleroids presented above, members of the chemical community are furnished with a concept which will allow the preparation of essentially any functionalized fulleroid. Novel molecules with intricate, spherical architecture and as yet unknown properties await preparation.

(35) Caminati, G.; Gopidas, K.; Leheny, A. R.; Turro, N. J.; Tomalia, D. A. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* 1991, *32*, 602 and references within. Newcome, G. R.; Baker, G. R. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* 1991, *32*, 625 and references within. Hawker, C. J.; Wooley, K. L.; Fréchet, J. M. J. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* 1991, *32*, 623 and references within.

(36) Black parallelepiped, crystal dimensions, 0.1 × 0.12 × 0.05 mm. Monoclinic, $P2_1/m$; $a = 9.841$ (4) Å, $b = 17.36$ (1) Å, $c = 11.197$ (7) Å, $\beta = 102.58$ (5)°; $Z = 2$, $V = 1867.42$ Å^3, ρ(calcd) = 1.86 g/cm^3. Cu Kα (1.5418 Å).