Poly(p-xylylene) exhibits three resonances at 37.85, 128.92, and 137.9 ppm. In place of the single sharp peak observed for C_{60}, an overlapping collection of resonances ranging from 129 to 150 ppm was observed for the C_{60}–p-xylylene copolymer (Figure 1c). Resonances due to the xylylene monomer unit in the copolymer lay at 38.0, 129.1, and 139.0 ppm. The remaining resonances are attributed to the functionalized C_{60} monomer unit. Identification of the peak at 57.8 ppm as arising from the benzylated C_{60} carbons was accomplished using interrupted decoupling experiments[7] and ^{13}C-labeling NMR experiments in which a copolymer prepared by reacting C_{60} with α,α'-^{13}C-labeled xylylene[8] displayed only benzylic methylene and methyl resonances at 37 and 23 ppm, respectively.

Thermal gravimetric analysis of the C_{60}–xylylene copolymer under nitrogen suggests that the material is cross-linked.[9] Whereas pure C_{60} decomposes between 650 and 700 °C[10] and poly(p-xylylene) depolymerizes at 475 °C,[11] the C_{60}–xylylene copolymer begins to slowly lose mass at 380 °C and continues to lose mass until 1000 °C where 66% of the original mass remains as a black powder.[12] At 475 °C, there is a minor mass loss (3%) attributed to depolymerization of poly(p-xylylene) existing either as a contaminant or as blocks of oligomeric poly(p-xylylene) incorporated into the copolymer. Elemental analysis[13] was used to calculate the composition of the copolymer. On the basis of the carbon:hydrogen ratio, the ratio of xylylene to C_{60} in the copolymer was determined to be 3.4:1.0.[14]

The infrared spectrum of the C_{60}–xylylene copolymer[15a] resembled that of neither the poly(p-xylylene)[15b] nor pure C_{60}.[16] Both aromatic and aliphatic C–H stretching bands and aromatic C–C stretching bands confirm the NMR data that xylylene monomer units are incorporated within the material. A slight band at 1780 cm^{-1} indicates that some oxidation to ketone has occurred in the copolymer. After exposure of the material to air for 4 weeks, the infrared spectrum revealed a much stronger and broader carbonyl absorption and a strong new C–O stretching band at 1098 cm^{-1}, indicating that the material is not air stable.[17]

In conclusion, we have discovered that free radical polymerization of C_{60} and p-xylylene leads to polymeric materials. The C_{60}–p-xylylene copolymer is insoluble, due to cross-linking through multiple benzylations on the C_{60} molecules. Solid-state ^{13}C CP MAS NMR revealed both xylylene and C_{60} components. Simple free radical chemistry can, therefore, be used to generate polymeric materials from fullerene compounds. The real challenge in such chemistry will be to limit the extent to which the radical additions take place so as to allow soluble polymeric derivatives of C_{60} to be prepared. A complete description of the chemical and physical properties of the copolymers will be forthcoming.

Acknowledgment. This work was supported by the United States Department of Energy under Contract No. DE-AC04-76DP00789.

Supplementary Material Available: Thermal gravimetric analyses, infrared spectra, interrupted decoupling experimental data, and ^{13}C-labeling experimental data (4 pages). Ordering information is given on any current masthead page.

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(7) In interrupted decoupling experiments, delays of 60–90 μs were inserted between cross polarization and acquisition. Because dipolar coupling depends on the inverse cube of the C–H distance, carbons with hydrogen substituents are typically more attenuated.

(8) α,α'-^{13}C-labeled xylylene was prepared by the flash thermolysis of α,α'-^{13}C-labeled p-xylene, 99 atom %, at 1000 °C.

(9) It is also possible, as pointed out by one of the referees, that branching in conjugation with the buckyball's intermolecular attractive forces could yield the same thermal stability.

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(12) Infrared analysis of the residue reveals loss of the majority of the absorption bands from the copolymer.

(13) Elemental analyses for carbon and hydrogen were carried out in duplicate on a Perkin-Elmer CHN elemental analyzer. The copolymer is relatively resistant to combustion, and care must be taken to insure that the sample is completely combusted.

(14) The xylylene:C_{60} ratio was calculated from the ratio of carbon to hydrogen (C, 96.6%; H, 3.4%) with the assumptions that all of the hydrogen in the material originated from xylylene monomers and that the comtribution from terminal xylylene monomers was negligible.

(15) (a) Infrared spectral data of the C_{60}–p-xylylene copolymer (KBr): 3018, 2921, 2854, 1780, 1607, 1512, 1438, 1418, 1186, 1021, 820.4, 765.1, 727.8, 674.8, 543.2, 525.4 cm^{-1}. (b) Joesten, B. L. *Polym. Prepr.* (*Am. Chem. Soc., Div. Polym. Chem.*) **1972**, *13*, 1948.

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Electrochemical Detection of C_{60}^{6-} and C_{70}^{6-}: Enhanced Stability of Fullerides in Solution

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Although theory predicts that the LUMO of C_{60} should be able to accept at least six electrons to form diamagnetic C_{60}^{6-},[1-3] the latter species has so far eluded direct characterization in solution.[4-9] The existence of the hexaanionic molecule in the solid state is inferred from the formation of species such as K_6C_{60}, which have been well characterized by a variety of techniques, including solid-state ^{13}C NMR spectroscopy.[10] Part of the impetus behind the present work stemmed from the desire to generate and detect C_{60}^{6-} in a relatively stable environment in order to confirm the theoretical predictions.[1-3] The development of a general method capable of generating stable C_{60}^{n-} species, where $n = 1$–6, was another important driving force behind the present work.

There have been several reports concerning the electrochemical properties of C_{60} (and C_{70}).[4-9] One recent report by Wudl et al. described the reversible, three-electron electrochemical reduction leading to C_{60}^{3-}.[4] After this communication, Dubois and Kadish reported the observation of an additional reduction wave for C_{60} and the electrochemical formation and detection of C_{70}^{4-}.[4,5] The most recent and, to our knowledge, the only report of five reversible reduction processes for C_{60}, leading to C_{60}^{5-}, was also reported recently by Kadish et al.[6] These authors also studied the electrochemical properties of C_{70}, but no voltammetric data were presented for this compound.[6] They pointed out that several new peaks appeared after the fourth reduction of C_{70}, but that none could be unambiguously assigned to C_{70}^{5-}.

A wider expansion of the available potential window down to −3.3 V vs Fc/Fc$^+$ is reported in this communication. This was accomplished by the use of a mixed solvent system and low temperature. On the basis of supporting electrolyte and fullerene solubility considerations, the optimal solvent composition was between 15 and 20% by volume of acetonitrile in toluene. These new conditions have allowed the first observation of the sixth

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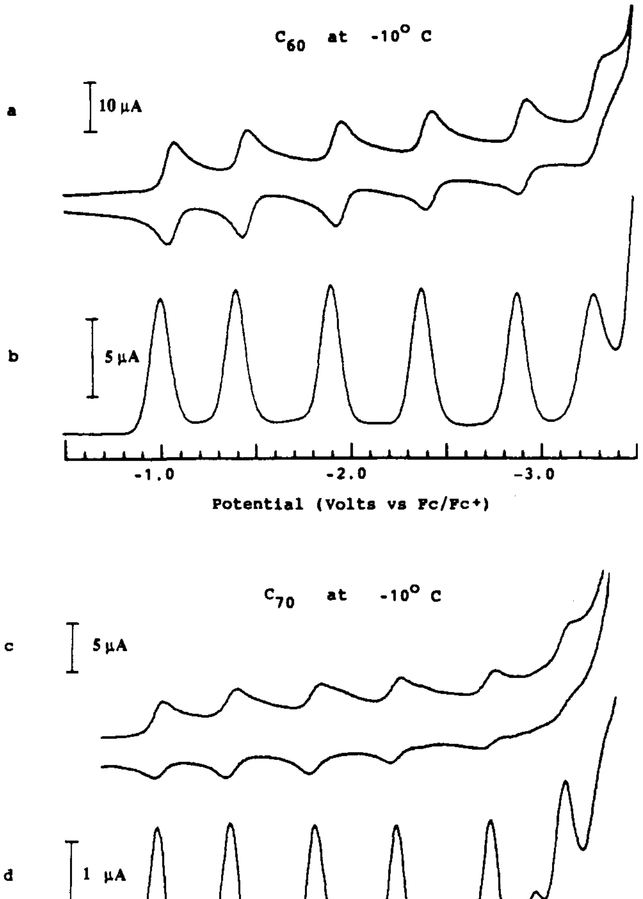

Figure 1. Reduction of C_{60} and C_{70} in CH_3CN/toluene at -10 °C using (a and c) cyclic voltammetry at a 100 mV/s scan rate and (b and d) differential pulse voltammetry (50-mV pulse, 50-ms pulse width, 300-ms period, 25 mV/s scan rate).

electron reduction for C_{60} and of the fifth and sixth electron reductions for C_{70}, leading to the formation of C_{60}^{6-} and C_{70}^{6-}. None of these had been previously observed. The highest temperature allowing resolution of the sixth reduction of C_{60} is approximately 5 °C. For C_{70} it is possible to observe the fifth and sixth reductions even at 25 °C. An added advantage of the present protocol is that these multiple reductions are all reversible and observed at very slow potential scan rates (100 mV/s) as opposed to those required in ref 6, ~20 V/s.[11]

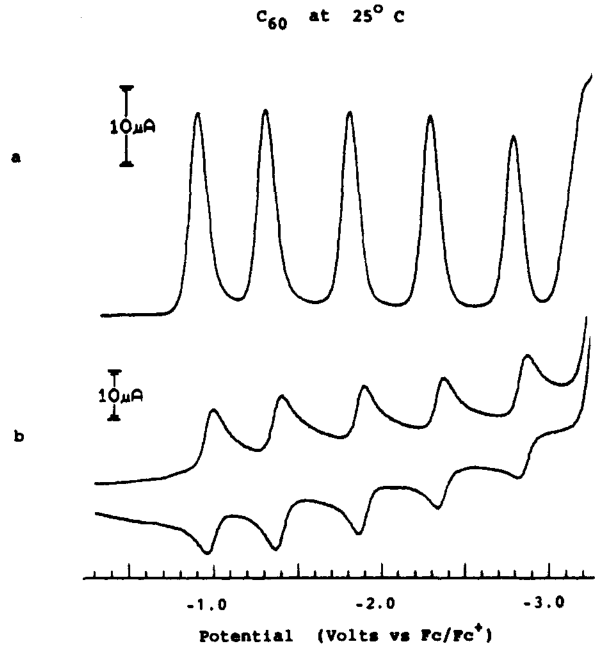

Figure 2. (a) Differential pulse voltammetry (80-mV pulse, 50-ms width, 200-ms pulse period, 10 mV/s scan rate) and (b) cyclic voltammetry at 100 mV/s of C_{60} in CH_3CN/toluene at 25 °C. Note that the sixth reduction is almost evident in the DPV.

Parts a and b of Figure 1 show the cyclic and differential pulse voltammograms of C_{60} at -10 °C, respectively. Chemical and electrochemical reversibilities are evident from this figure. The potentials measured, $E_{1/2}$, relative to Fc/Fc^+ were -0.98, -1.37, -1.87, -2.35, -2.85, and -3.26 V. In all cases successive potential values are closer than the corresponding ones measured by Kadish et al.[6] The significance of this observation must be related to the solvent composition.[4]

Parts c and d of Figure 1 show the -10 °C voltammograms, cyclic and differential pulse, for C_{70}. This C_{70} sample contained some C_{60} as an impurity, as judged by its mass spectrum. This is also evident from the voltammograms shown in Figure 1. The waves corresponding to C_{60} are observed as small shoulders to the right of the C_{70} waves. These diverge from the C_{70} ones as the potential becomes more negative. What is important to note from the voltammograms in Figure 1c,d is the fact that six reversible reduction waves are observed for C_{70} for the first time. The $E_{1/2}$ values for these six reduction processes, relative to Fc/Fc^+, are -0.97, -1.34, -1.78, -2.21, -2.70, and -3.07 V. There is only one wave which does not seem to correspond well to any of either C_{60} or C_{70}, at -2.94 V. It is 90 mV more negative than the closest C_{60} wave, which appears at -2.85 V. All other observed waves, including the -3.26-V wave, can be accounted for rather unequivocally by C_{60} and C_{70}.

In conclusion, this work presents the first reversible generation of C_{60}^{6-}. More importantly, this was accomplished under the condition of very slow scan rates. It also presents the first observation of C_{70}^{5-} and C_{70}^{6-}. All of these fulleride species appear to be stable in solution, especially at -10 °C, under high vacuum, and in the time scale of the voltammetric experiments. Even at room temperature, C_{60}^{5-} appears to be stable, but spectroscopic confirmation is still necessary. Figure 2 shows the voltammograms of C_{60} under conditions identical with those used for Figure 1, except that the temperature was 25 °C. It seems evident from Figure 2 that it will be possible to generate C_{60}^{5-} at room temperature in order to study its properties in solution. The unusual stabilities and clean voltammetric data indicate that it will probably

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(11) Samples of C_{60} and C_{70} were obtained by following the general procedures reported by Ajie et al.[13] The C_{70} sample was further purified by double recrystallization from benzene. The electrochemical cell used was designed and constructed in-house and was very similar to that described in ref 12. Typically, a 7-8 × 10^{-4} M solution of C_{60}, or 4-5 × 10^{-4} M C_{70}, was placed in only the working compartment of the high-vacuum cell. $TBAPF_6$, 0.1 M, was used as supporting electrolyte. Highly purified acetonitrile and toluene from Aldrich were dried over P_2O_5, deaerated by repeated freeze-pump-thaw cycles, pumped to 10^{-5}-10^{-6} mmHg, and vapor transferred directly into the electrochemical cell.[12] The ratio of acetonitrile to toluene was 1:5.4 by volume. Voltammograms (cyclic and differential pulse) were recorded using a BAS-100 electrochemical analyzer interfaced with a Houston Instruments HIPLOT DMP-40 apparatus. Ohmic resistance was compensated 100% in all cases. A conventional three-electrode configuration was used, with a 3-mm-diameter glassy carbon electrode as the working electrode, a platinum counter electrode, and a silver wire as a pseudoreference. All measurements were recorded under high vacuum. Low-temperature experiments were performed by immersion of the cell in an external bath whose temperature was monitored.

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be possible to use these electrosynthetic methods to generate fullerides for ion-pairing studies by ESR spectroscopy. Such work is currently underway.

Acknowledgment. We thank the Chemistry Division of the National Science Foundation (Grant No. CHE-9011901) for support of this work. We also thank Professor Fulin Zuo and Dr. Tingsheng Li of the Physics Department of the University of Miami for the carbon soot sample from which the C_{60} and C_{70} were extracted.

X-ray Crystal Structure of the First Quaternary 1-Bicyclo[1.1.1]pentane Salt. The Shortest "Nonbonding" Carbon–Carbon Interaction Documented

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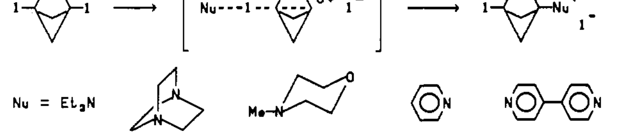
The simplest strained-cage molecule, bicyclo[1.1.1]pentane and its derivatives, e.g., [1.1.1]propellane, have received significant attention the last few years.[1] The shortest (1.83–1.91 Å) C_1–C_3 nonbonding distance ever reported, found in the bicyclo[1.1.1]pentanes,[2] leads to unusual chemical reactivity as well as unusual spectral properties for these compounds.

Recently it was proposed that the bicyclo[1.1.1]pentane framework may be used for the preparation of nanotechnology-important substrates[3] due to its unique through-cage electron-transfer ability.[4] For this purpose, however, the C_1–C_3 interatomic distance is critical, so that the task of finding 1,3-disubstituted bicyclo[1.1.1]pentanes with the shortest C_1–C_3 contacts is important.

With this goal in mind, we investigated pyridine salts containing the 3-iodobicyclo[1.1.1]pentane moiety which have recently been prepared by way of an unusually fast quaternization of tertiary amines and azoles with 1,3-diiodobicyclo[1.1.1]pentane:[5]



Considering the fact that in these salts the bicyclo[1.1.1]pentane moiety is substituted by a strong electron-withdrawing group (e.g., 1-pyridyl) with a full positive charge, these molecules could have very short C_1–C_3 distances. According to Wiberg,[6] the addition of strong electron-withdrawing groups attached to C_1 or C_3 would decrease the interatomic distance, whereas electron-donating substituents would increase this distance. Known X-ray data[2] are in good agreement with these predictions (see Scheme I).

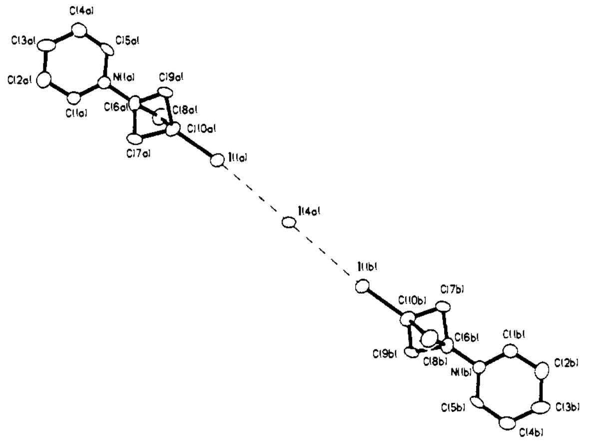
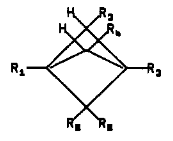


Figure 1. Molecular structure and labeling scheme for **1** (50% thermal ellipsoids): C(10)–C(6), 1.80 (2) Å; I(1)–I(4), 3.745 (1) Å; ∠I(1a)–I(4a)–I(1b), 180°; N(1)–C(6), 1.47 (2) Å; C(10)–C(7), 1.55 (2) Å; C(10)–C(8), 1.56 (2) Å; C(10)–C(9), 1.56 (1) Å; ∠C(10)–I(1)–I(4), 172.1°.

Scheme I



R_1	R_2	R_3	R_4	R_5	R_6	C_1 - C_3	Ref.
CCl_3	Cl	H	H	H	H	1.83(2) Å	2a
CCl_3	I	H	H	H	H	1.835(7)Å	2a
CH_3	COOH	H	H	H	H	1.873(2)Å	2b
COMe	COMe	H	H	H	H	1.874(6)Å	2c
H	H	H	H	Ph	OCONHPh(Br)	1.89 Å	2d
H	H	COOMe	COOMe	$-OCH_2CH_2O-$		1.903(3)Å*	2e
CH_3	COOMe	H	H	Cl	Cl	1.903(3)Å	2f

*For one of the stereoisomers -[1.898(3); 1.902(3); 1.903(3); 1.903(6); 1.907(3) Å] for other.

The crystallographic data[7] obtained by us for one compound of this type, 1-(1-pyridinio)-3-iodobicyclo[1.1.1]pentyl iodide/triiodide (**1**), did confirm our expectations, but it also gave important information about the structure of this new class of strained-cage salts (Figure 1).

The C_1–C_3 [C6–C10 on Figure 1] distance in **1** is extremely short (1.80 (2) Å). To our knowledge, this is not only the shortest nonbonding contact for bicyclo[1.1.1]pentanes but also for any known organic compound.

Another intriguing feature of this salt is the nonequivalence of two existing iodo anions in the crystal structure of **1**. The I_3^- anion has the usual structural parameters.[8] The I^- anion, on the other hand, occupies a very specific site in the crystal: it is located exactly between two cationic units (Figure 1), so that the angle I(1a)–I(4a)–I(1b) is 180° within experimental error. In addition, the interatomic distance between these iodine atoms is shorter than the sum of their van der Waals radii (3.745 vs 4.30 Å[9]), indicating

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(7) Crystals of **1** were obtained by slow evaporation of a diluted methanolic solution of 1-(1-pyridyl)-3-iodobicyclo[1.1.1]pentane iodide, which contained additional I_2: $(C_{10}H_{11}I_3N)_2$, triclinic, $P\bar{1}$; $a = 6.173$ (1) Å, $b = 9.607$ (2) Å, $c = 13.067$ (2) Å; $\alpha = 74.50$ (1)°, $\beta = 76.86$ (2)°, $\gamma = 72.03$ (2)°; $V = 701.3$ (2) Å^3, $Z = 1$, $d_{calcd} = 2.490$ g/cm^3, μ(Mo Kα) = 6.586 mm^{-1}. $R = 5.44\%$ ($R_w = 7.56\%$) for 1680 reflections at 173 K, $3.5 \leq 2\theta \leq 52°$, $F_o \geq 4.0\sigma(F_o)$, on a Siemens R3m/v diffractometer with Mo Kα ($\lambda = 0.71073$ Å) and a graphite monochromator.

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