

Table I. Propylaniline Spectral Data

transition ^a	freq. ^b cm ⁻¹	e ⁻ KE, eV	IP, eV	ΔIP, meV
0 ₀ ⁰ (g)	33210.2	0.816	7.419	9
0 ₀ ⁰ (a)	33265.1	0.840	7.410	
1 ₀ ⁰ (g)	34024.7	1.018	7.419	10
1 ₀ ⁰ (a)	34081.3	1.042	7.409	
1 ₀ ⁰ (g)	33948.3	0.999	7.419	9
1 ₀ ⁰ (a)	33997.9	1.020	7.410	

^a X₀⁰ corresponds to a transition between the vibrationless ground electronic state the $\nu = n$ level of mode X in the excited electronic state. ^b Experimental values of D. E. Powers et al. (ref 3).

X in the excited electronic state. 0₀⁰ corresponds to a purely electronic transition involving no vibrationally excited levels. Modes X are labeled with numbers or letters historically associated with aniline.¹⁰ With the frequency-doubled output from a picosecond dye laser tuned to the 1₀⁰ transition of *anti-p-n*-propylaniline, the time-of-flight photoelectron spectrum displayed in Figure 2 was recorded. Note that this spectrum is associated with the anti conformation only. Although the largest peak in this spectrum corresponds to production of ions in their 1¹ vibrational level, some ions are formed vibrationally unexcited (peak 1⁰). Assignments for most of the peaks in this spectrum have been derived as in our earlier aniline photoelectron study,¹¹ but only the 1⁰ peak is relevant to the present discussion. It is so clearly resolved that a very precise measurement of the adiabatic ionization potential of the molecule in this conformation can be obtained with the relation

$$IP = 2h\nu - KE_{\text{electron}}$$

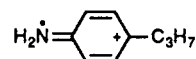
Photoelectron spectra similar to that displayed in Figure 2 were also recorded by exciting two other transitions of anti propylaniline along with corresponding gauche transitions. The first peak in each of these spectra corresponds to production of vibrationally unexcited ions and allows us to directly measure the adiabatic ionization potential for each conformation. As summarized in Table I, the difference between these ionization potentials is 9–10 meV, which is approximately 0.2 kcal/mol. Because we did not calibrate our spectrometer with a standard, the absolute accuracy of our ionization potential measurement is only ± 40 meV. However, the differences between ionization potentials should be accurate to ± 1 meV.

Theoretical ground-state conformations of propylaniline were estimated by AM1 calculations.¹² For the anti compound the three propyl carbons lie in a plane perpendicular to the aromatic ring. For the gauche compound the end carbon lies 73° on either side of that plane. Other orientations of the alkyl chain relative to the ring should be much higher in energy because of steric effects. At each conformation, STO-3G RHFSCF computations were performed to give relative energies. The ground state of the anti compound was calculated to be 45 meV (360 cm⁻¹, 1.0 kcal/mol) lower in energy than that of the gauche. Vertical ionization potentials were estimated by single-excitation configuration interactions for the ion. Although the absolute values obtained for the anti and gauche conformations, 4.637 and 4.658 eV, respectively, varied substantially from the experimental results indicated in Table I, their relative spacing of 21 meV was remarkably close to the experimentally measured 9–10 meV. Relative energies and IP's for rotational conformers should be fairly insensitive to electron correlation. There will be corrections for geometry relaxation in the ion, zero point energy changes, and basis set improvements. Although better calculations will be done, carbocation studies at this level of theory have produced the correct trends in stabilization energies.¹³

If we assume that interconversion of different molecular conformations is slow compared with the supersonic jet expansion process then the ratios of gauche and anti peaks in excitation spectra provide a measure of the relative abundance of the two conformations at the temperature of the stagnation zone of the nozzle. This in turn leads to an estimate of the relative energies of the two conformations. Because there are two equivalent gauche conformations for each anti conformation, the ratio of their absorptions should be given by

$$I_g/I_a = 2 \exp[-\Delta E/kT]$$

Powers et al. found that anti propylaniline transitions are roughly 1.5 times more intense than their gauche counterparts. Our data displayed in Figure 1 are in basic agreement with this. For a gas sample temperature of 343 K, this implies that the anti conformation is approximately 260 cm⁻¹ (0.74 kcal/mol) lower in energy than the gauche. This is in reasonable agreement with the 360-cm⁻¹ result obtained by calculation. It seems clear that the lower steric repulsion of the anti compound stabilizes it relative to the gauche conformer. This repulsive interaction between the alkyl chain and the ring is apparently magnified in the ion. Hyperconjugation stabilizes the important carbocation resonance structure



more when the propyl group is in an anti rather than gauche orientation.

In conclusion, we have demonstrated that ionization potentials of two differing molecular conformations of *n*-propylaniline can be precisely measured and thereby easily distinguished with laser photoelectron spectroscopy. Hartree–Fock calculations lead to remarkably accurate relative energies for the ground and ionic states of these conformations in contrast with their estimates for the absolute energies of these states. Future experiments and calculations will focus on aromatic compounds having somewhat longer side chains and a correspondingly larger number of stable conformations.

Acknowledgment. This work was supported by the National Science Foundation.

Halocarbonyl Cations^{†,1}

G. K. Surya Prakash,* Joseph W. Bausch, and George A. Olah*

Donald P. and Katherine B. Loker Hydrocarbon Research Institute and Department of Chemistry
University of Southern California
Los Angeles, California 90089-1661

Received January 10, 1991

Even though alkyl acylium ions (acyl cations) have been prepared and characterized under long-lived stable ion conditions in solution as well as in the solid state,² the corresponding halocarbonyl cations, XCO⁺ (2 X = F, Cl, Br, I) have not been observed. The acylium cation structures 1 are rationalized by the contributions from resonance hybrids of the oxocarbenium ion 1a and oxonium ion 1b forms, with the latter being the dominant contributor. In halocarbonyl cation 2 an additional resonance interaction involving a halogen nonbonded electron pair (structure 2c) is possible (back-donation, p–p interaction).

(10) Brand, J. C. D.; Williams, D. R.; Cook, T. J. *J. Mol. Spectrosc.* **1966**, 20, 359. Varsanyi, G. *Assignments for Vibrational Spectra of Seven Hundred Benzene Derivatives*; Wiley: New York, 1974.

(11) Meek, J. T.; Sekreta, E.; Wilson, W.; Viswanathan, K. S.; Reilly, J. P. *J. Chem. Phys.* **1985**, 82, 1741.

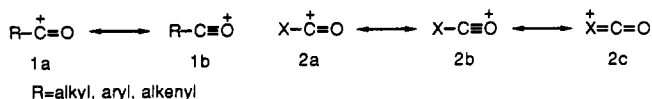
(12) AM1 developed by M. J. S. Dewar, implemented in MOPAC. MOPAC by J. Stewart, program No. 560 from QCPE.

(13) Davidson, E. R.; Shiner, V. J., Jr. *J. Am. Chem. Soc.* **1986**, 108, 3135.

[†] Dedicated to Professor Horst Prinzbach on the occasion of his 60th birthday.

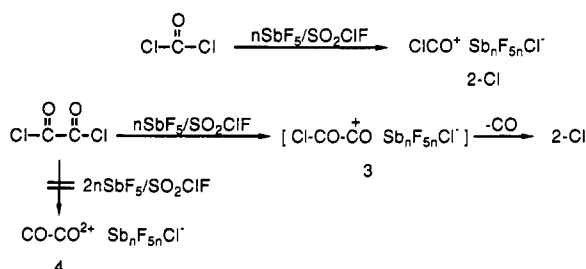
(1) Stable Carbocations. 280. Part 279: Olah, G. A.; Krishnamurthy, R.; Prakash, G. K. S. *J. Org. Chem.* **1990**, 55, 6061.

(2) Olah, G. A.; Germain, A.; White, A. M. In *Carbonium Ions*; Olah, G. A., Schleyer, P. v. R., Eds.; Wiley-Interscience: New York, 1976; Vol. 5, Chapter 35.

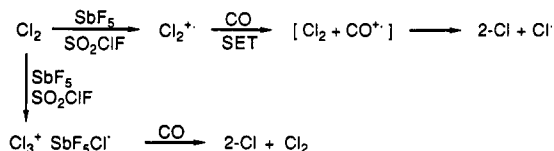


On the basis of electronegativity order⁴ $\text{F} > \text{Cl} > \text{Br} > \text{I}$, fluorine should inductively destabilize an adjacent carbocationic center the most. On the other hand, since fluorine is a relatively small atom possessing 2p nonbonded electron pairs, the back-donation to an adjacent empty p orbital (2p-2p overlap) is maximum. From a number of previous investigations,⁵ the order of positive charge stabilization of halogens has been found to be $\text{F} > \text{Cl} > \text{Br} > \text{I}$. Thus it was of interest to probe the stabilizing effect of halogens adjacent to an oxocarbenium center, since halocarbonyl cations are important intermediates in the Friedel-Crafts reactions of carbonyl halides.⁶

Slow addition of a precooled solution of phosgene (COCl_2) in SO_2ClF to a stirred solution of a 5-fold excess of $\text{SbF}_5/\text{SO}_2\text{ClF}$ maintained at -78°C (dry ice acetone bath) initially gave a turbid solution, which upon rapid mixing on a Vortex stirrer became clear. The 75-MHz ^{13}C NMR spectrum of the solution obtained at -80°C showed a sharp resonance at $\delta(^{13}\text{C})$ 133.7, shielded compared to its progenitor phosgene⁸ by 8.1 ppm. We assign the signal to the chlorocarbonyl cation ClCO^+ (2-Cl). The same ion was also obtained by the ionization of oxalyl chloride with $\text{SbF}_5/\text{SO}_2\text{ClF}$ at -78°C . The initially formed chlorooxalyl cation 3 immediately decarbonylates to ClCO^+ under the conditions. There was also no evidence obtained for the formation of the oxalyl dication 4.



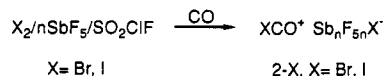
Finally, the chlorocarbonyl cation (2-Cl) was also obtained by slowly passing CO through a Cl_2/SbF_5 solution. The Cl_2/SbF_5 system is known to be a source of highly reactive Cl_2^{+} radical cation,⁹ which can accept an electron from CO via single electron transfer (SET) to form CO^{+} . Quenching of CO^{+} by Cl^+ would result in ClCO^+ . Alternatively, the existence¹⁰ of Cl_3^+ cation has also been demonstrated in the Cl_2/SbF_5 solution. This species can directly react with CO to form ClCO^+ (as well as molecular chlorine, which can again undergo oxidation).



In all reactions a minor species giving a doublet signal ($J_{\text{C-F}} \sim 375$ Hz) in the ^{13}C NMR spectrum was detected whose chemical shift varied from sample to sample ($\delta(^{13}\text{C})$ 150–175), indicative of the formation of carbonyl chloride fluoride O-complexed with the strong Lewis acidic SbF_5 . Upon warming of the solution, the complex tends to disappear with the evolution of highly stable carbonyl fluoride (fluorophosgene). However, no

evidence was obtained for the formation of persistent FCO^+ . Furthermore, oxalyl fluoride did not ionize under the reaction conditions to give the fluorocarbonyl cation or the oxalyl dication (OCCO^{2+}) although theory indicates that both are minima (vide infra).

We also prepared bromocarbonyl cation, BrCO^+ , by passing CO through a solution of $\text{Br}_2/\text{SbF}_5/\text{SO}_2\text{ClF}$. In this case it appears that Br_3^+ cation¹¹ directly reacts with CO. BrCO^+ was observed as a singlet at $\delta(^{13}\text{C})$ 127.0 (a deshielding of 23.6 ppm from COBr_2).⁸ The deshielding observed in this case can be rationalized by the loss of a highly polarizable bromine atom from the precursor. Furthermore, we were also successful in preparing iodocarbonyl cation, ICO^+ , by reacting CO with $\text{I}_2/\text{SbF}_5/\text{SO}_2\text{ClF}$ solution. However, the observed NMR peak was very broad at $\delta(^{13}\text{C})$ 100.4 due to contamination of the solution with paramagnetic I_2^+ cation persistent in the solution.¹²



Acetyl cation CH_3CO^+ shows the carbonyl absorption at $\delta(^{13}\text{C})$ 149.5.¹³ The shielding observed in going from acetyl to chloro-, bromo-, and iodocarbonyl cations (replacing CH_3 with Cl, Br, and I, respectively) can be explained by the stabilization of positive charge by nonbonded lone-pair back-donation involving structures 2c. The shielding order observed in going from chloro- to bromo- to iodocarbonyl cations can be easily rationalized by the heavy-atom effect even though the back-bonding order is $\text{Cl} > \text{Br} > \text{I}$. Such effects have been observed earlier in the case of trihalomethyl cations.¹⁴

To study these effects further we have carried out ab initio theoretical calculations¹⁵ on halocarbonyl cations at the STO-3G* level of theory.¹⁶ All three halocarbonyl ions (2-Cl, 2-Br, and 2-I) are minima on the potential surface and do not dissociate into X^+ and CO. The optimized bond lengths and Mulliken atomic charges are indicated below. Obviously, the calculated Mulliken atomic charges at this level of theory do not clearly reflect the observed experimental results.

	atomic charges	bond lengths, Å
ClCO^+	C +0.673	C-Cl 1.620
	O +0.079	C-O 1.148
	Cl +0.248	
BrCO^+	C +0.535	C-Br 1.730
	O +0.064	C-O 1.149
	Br +0.402	
ICO^+	C +0.404	C-I 1.965
	O +0.052	C-O 1.147
	I +0.544	

Furthermore, both the fluorocarbonyl cation (FCO^+) and the oxalyl dication (OCCO^{2+}) are minima.¹⁷ However, these two species were not observed when oxalyl fluoride was treated with $\text{SbF}_5/\text{SO}_2\text{ClF}$ since highly stable fluorophosgene is formed. It

(11) (a) Gillespie, R. J.; Morton, M. J. *J. Chem. Soc., Chem. Commun.* **1968**, 1565. (b) Gillespie, R. J.; Morton, M. J. *Inorg. Chem.* **1972**, *11*, 586.

(12) Gillespie, R. J.; Milne, J. B. *Inorg. Chem.* **1966**, *5*, 1577.

(13) Olah, G. A.; White, A. M. *J. Am. Chem. Soc.* **1967**, *89*, 7072.

(14) Olah, G. A.; Heiliger, L.; Prakash, G. K. S. *J. Am. Chem. Soc.* **1989**, *111*, 8020.

(15) Using an Alliant FX/40 computer and GAUSSIAN86 program: Frisch, M. J.; Binkley, J. S.; Schlegel, H. B.; Raghavachari, K.; Melius, C. F.; Martin, R. L.; Stewart, J. J. P.; Bobrowicz, F. W.; Rohlfing, C. M.; Kahn, L. R.; Defrees, D. J.; Seeger, R.; Whiteside, R. A.; Fox, D. J.; Fleuder, E. M.; Pople, J. A. *GAUSSIAN86*; Carnegie-Mellon Quantum Chemistry Publishing Unit: Pittsburgh, PA, 1986.

(16) The highest basis set available within GAUSSIAN86 for molecules containing bromine and iodine atoms is STO-3G*. The chlorocarbonyl cation, however, has been fully optimized at the MP2/6-311G** level and yields atomic charges of C (+0.604), O (-0.057), and Cl (+0.453) and bond lengths of C-O (1.137 Å) and C-Cl (1.565 Å).

(17) FCO^+ and OCCO^{2+} were both fully optimized at the MP2/6-31G* level and yielded the following atomic charges and bond lengths:

FCO^+ : F (-0.007), C (+1.126), O (-0.118), F-C (1.218 Å), C-O (1.140 Å)

OCCO^{2+} : C (+0.914), O (+0.086), C-C (1.442 Å), C-O (1.145 Å)

(3) Olah, G. A.; Iyer, P. S.; Prakash, G. K. S.; Krishnamurthy, V. V. *J. Org. Chem.* **1984**, *49*, 4317 and references cited therein.

(4) Olah, G. A. *Halonium Ions*; Wiley-Interscience: New York, 1973.

(5) Olah, G. A.; Mo, Y. K. In *Carbocation Ions*; Olah, G. A., Schleyer, P. v. R., Eds.; Wiley-Interscience: New York, 1976; Vol. 5, Chapter 36.

(6) Olah, G. A. *Friedel-Crafts Chemistry*; Wiley-Interscience: New York, 1973.

(7) Phosgene and other toxic substances used in this study were used with extreme care in a well-ventilated hood.

(8) Gombler, W. *Spectrochim. Acta* **1981**, *37A*, 57.

(9) Olah, G. A.; Heiliger, L. *J. Am. Chem. Soc.* **1990**, *112*, 3920.

(10) Gillespie, R. J.; Morton, M. J. *Inorg. Chem.* **1972**, *11*, 591.

is interesting to note that although the oxalyl dication is a minimum, the dimer of carbon monoxide, ethylenedione ($\text{O}=\text{C}=\text{C}=\text{O}$), is kinetically and thermodynamically unstable with respect to dissociation into 2 equiv of CO .¹⁸

It is also interesting to note that ClCO^+ is directly formed by the ionization of oxalyl chloride (vide supra). The intermediately formed chlorooxalyl cation 3 loses CO readily. At the 3-21G* level of theory ion, 3 (C_s symmetry employing standard bond lengths for the initial geometry) does not optimize to a minimum but rather dissociates into ClCO^+ and CO , verifying the experimental observation.

Acknowledgment. Support of our work by the National Institutes of Health is gratefully acknowledged.

(18) Haddon, R. C.; Poppinger, D.; Radom, L. *J. Am. Chem. Soc.* **1975**, *97*, 1645.

Diamagnetic Polyanions of the C_{60} and C_{70} Fullerenes: Preparation, ^{13}C and ^7Li NMR Spectroscopic Observation, and Alkylation with Methyl Iodide to Polymethylated Fullerenes¹

Joseph W. Bausch, G. K. Surya Prakash, and George A. Olah*

Donald P. and Katherine B. Loker Hydrocarbon Research Institute and Department of Chemistry
University of Southern California
Los Angeles, California 90089-1661

Doris S. Tse, Donald C. Lorents, Young K. Bae, and Ripudaman Malhotra*

Chemistry and Molecular Physics Laboratories
SRI International, Menlo Park, California 94025-3493

Received January 14, 1991

In 1985 it was discovered that vaporization of graphite by laser irradiation produces a remarkably stable C_{60} cluster and to a lesser extent a stable C_{70} cluster as evidenced by mass spectrometry.² Kroto, Heath, O'Brien, Curl, and Smalley proposed the structure for the 60-carbon cluster to be a truncated icosahedron composed of 32 faces of which 12 are pentagonal and 20 are hexagonal, a structure analogous to a soccerball and reminiscent of the geodesic domes of Buckminster Fuller. Thus, C_{60} is commonly referred to as "buckminsterfullerene". The structural support for C_{60} as well as the related cluster C_{70} comes from a variety of experimental and theoretical studies.³⁻⁷

(1) Considered Novel Aromatic Systems. 11. Part 10: Bausch, J. W.; Gregory, P. S.; Olah, G. A.; Prakash, G. K. S.; Schleyer, P. v. R.; Segal, G. A. *J. Am. Chem. Soc.* **1989**, *111*, 3633.

(2) Kroto, H. W.; Heath, J. R.; O'Brien, S. C.; Curl, R. F.; Smalley, R. E. *Nature (London)* **1985**, *318*, 162. Also see: Rohlffing, E. A.; Cox, D. M.; Kaldor, A. *J. Chem. Phys.* **1984**, *81*, 3322.

(3) Heath, J. R.; O'Brien, S. C.; Zhang, Q.; Liu, Y.; Curl, R. F.; Kroto, H. W.; Tittel, F. K.; Smalley, R. E. *J. Am. Chem. Soc.* **1985**, *107*, 7779.

(4) (a) Haddon, R. C.; Brus, L. E.; Raghavachari, K. *Chem. Phys. Lett.* **1986**, *125*, 459. (b) Disch, R. L.; Schulman, J. M. *Chem. Phys. Lett.* **1986**, *125*, 465. (c) Haddon, R. C.; Brus, L. E.; Raghavachari, K. *Chem. Phys. Lett.* **1986**, *131*, 165. (d) Fowler, P. W.; Woolrich, J. *Chem. Phys. Lett.* **1986**, *127*, 78. (e) Stone, A. J.; Wales, D. J. *Chem. Phys. Lett.* **1986**, *128*, 501. (f) Newton, M. D.; Stanton, R. E. *J. Am. Chem. Soc.* **1986**, *108*, 2469. (g) Rudzinski, J. M.; Slanina, Z.; Togasi, M.; Osawa, E. *Thermochim. Acta* **1988**, *125*, 155. (h) Stanton, M. D.; Newton, R. E. *J. Phys. Chem.* **1988**, *92*, 2141. (i) Wu, Z. C.; Jelski, D. A.; George, T. F. *Chem. Phys. Lett.* **1988**, *137*, 291. (j) Weeks, D. E.; Harter, W. G. *Chem. Phys. Lett.* **1988**, *144*, 366. (k) Weeks, D. E.; Harter, W. G. *J. Chem. Phys.* **1989**, *90*, 4744. (l) Slanina, Z.; Rudzinski, J. M.; Togasi, M.; Osawa, E. *J. Mol. Struct.* **1989**, *202*, 169. (m) Fowler, P. W.; Lazzeretti, P.; Zanasi, R. *Chem. Phys. Lett.* **1990**, *165*, 79.

(5) (a) Kraetschmer, W.; Fostiropoulos, K.; Huffman, D. R. *Chem. Phys. Lett.* **1990**, *170*, 167. (b) Kraetschmer, W.; Lamb, L. W.; Fostiropoulos, K.; Huffman, D. R. *Nature* **1990**, *347*, 354.

(6) Taylor, R.; Hare, J. P.; Abdul-Sada, A. K.; Kroto, H. W. *J. Chem. Soc., Chem. Commun.* **1990**, 1423.

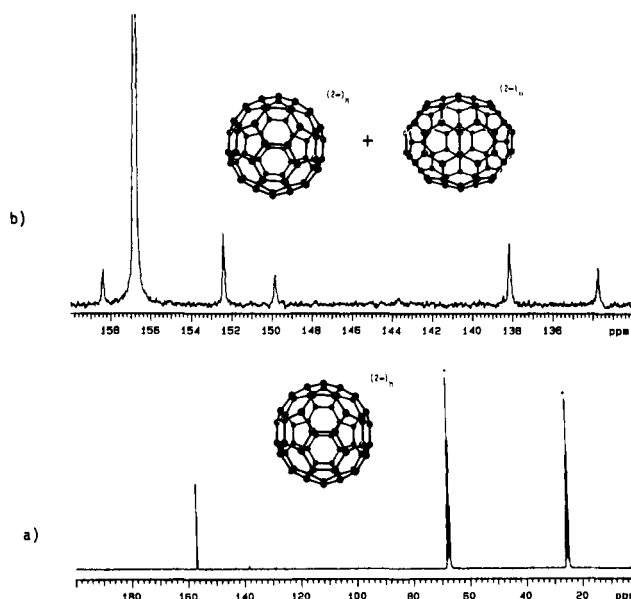


Figure 1. (a) Room temperature 75-MHz ^{13}C NMR spectrum of C_{60} polyanion in THF-d_8 [(*) peaks due to solvent]; (b) 75-MHz ^{13}C NMR spectrum of a mixture of C_{60} and C_{70} polyanions in THF-d_8 at -80°C .

The fullerenes C_{60} and C_{70} were separated by Kroto⁶ via column chromatography and their structures characterized by ^{13}C NMR spectroscopy. The ^{13}C NMR spectrum of C_{60} in benzene consists of a single line at 142.7 ppm confirming the icosahedral structure 1. The ^{13}C NMR spectrum for C_{70} in benzene consists of five lines (150.7, 148.1, 147.4, 145.4, and 130.9 ppm in a 1:2:1:2:1 ratio, respectively) confirming a highly symmetrical egg-shaped structure⁸ 2 (C_{5h} symmetry).

In view of our interest in cage compounds and persistent organic ions, we undertook a study of the anion(s) and cation(s) of the C_{60} and C_{70} fullerenes. Theory predicts an extremely high electron affinity (facile reduction) for both fullerenes.^{4a,k} Initial experimental support for the ease of reduction of C_{60} was the formation of $\text{C}_{60}\text{H}_{36}$ via a Birch reduction.⁹ Further cyclic voltammetry studies⁹ indicated that C_{60} undergoes reversible two-electron reduction. More recently, Wudl, Diederich, and co-workers^{10a} carried out cyclic voltammetry studies on pure samples of C_{60} and C_{70} , which showed that each fullerene undergoes reversible three-electron reduction (down to -1.5 V vs Ag/AgCl electrode).^{10b}

We reduced a mixture of fullerenes C_{60} and C_{70} (in an approximately 85:15 ratio generated by using a carbon arc)^{5b,11a} using Li metal (reduction potential of $\text{Li}^0 \sim -3.0$ V) in THF-d_8 with the aid of ultrasound.^{11b} The fullerenes C_{60} and C_{70} are only slightly soluble in THF; however, the reduced fullerenes are highly soluble and generate a deep red-brown solution after sonication.¹² The ^{13}C NMR spectrum¹³ at room temperature (see Figure 1a)

(7) Johnson, R. D.; Meijer, G.; Bethune, D. S. *J. Am. Chem. Soc.* **1990**, *112*, 8983.

(8) (a) Kroto, H. W. *Nature (London)* **1987**, *329*, 529. (b) Schmalz, T. G.; Seitz, W. A.; Klein, D. J.; Hite, G. E. *J. Am. Chem. Soc.* **1988**, *110*, 1113.

(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) (a) Allemand, P. M.; Koch, A.; Wudl, F.; Rubin, Y.; Diederich, F.; Alvarez, M. M.; Anz, S. J.; Whetten, R. L. *J. Am. Chem. Soc.*, submitted for publication. (b) It is likely that under optimal cyclic voltammetric conditions C_{60} and C_{70} can be reduced further. For example, the tetraanion of 9,9'-bianthryl can be electrochemically generated if the appropriate solvent-electrolyte system (THF , NaBPh_4) is used. See: Mortensen, J.; Heinze, J. *J. Electroanal. Chem.* **1984**, *175*, 333.

(11) (a) Bae, Y. K.; Lorents, D. L.; Malhotra, R.; Becker, C. H.; Tse, D.; Jusinsky, L. *MRS Proc.*, in press. (b) The polyanions were prepared in a 5-mm NMR tube with ~ 20 mg of the fullerene mixture and excess lithium metal (~ 20 mg) in 0.9 mL of dry THF-d_8 under an argon atmosphere. The sonication (~ 4 h) was carried out at room temperature by using a SONICATOR ultrasonic processor probe from HeatSystems-Ultrasonics, Inc.

(12) Initial sonication generates a cloudy green-colored solution. Further vigorous sonication results in a deep red-brown solution.