

Dodecylated Large Fullerenes: An Unusual Class of Solids

Arnab Mukherjee, Lawrence B. Alemany, Jayanta Chattopadhyay, Soma Chakraborty, Wenhua Guo, Sandy M. Yates, and W. E. Billups*

Department of Chemistry and The Richard E. Smalley Institute for Nanoscale Science and Technology, Rice University, 6100 Main Street, Mail Stop 60, Houston, Texas 77005

Received March 12, 2008. Revised Manuscript Received June 18, 2008

The large fullerenes that are formed during the synthesis of C_{60} by the arc discharge technique can be solubilized by reductive alkylation. The mass range of dodecylated large fullerenes determined by laser desorption ionization, time-of-flight mass spectrometry was found to be 650–3500 amu. The solubility of the dodecylated large fullerenes in chloroform is 15.7 g/L as measured by near-infrared spectroscopy. High-resolution transmission electron microscopy images show the expected nontubular, ring-shaped contrast resembling large fullerenes attached to dodecyl groups. The dodecylated large fullerenes have distinctly different behavior than regular organic molecules in dipolar dephasing, magic angle spinning nuclear magnetic resonance (^{13}C MAS NMR) experiments. Thermal gravimetric analysis and ^{13}C MAS NMR experiments indicate that there is 1 dodecyl group for every 23 sp^2 fullerene carbon atoms, that the quaternary aliphatic carbons generated upon dodecylation give signals considerably more shielded than those in alkylated C_{60} and C_{70} but similar to the quaternary aliphatic signals in dodecylated single-walled carbon nanotubes, and that the dodecyl groups in the dodecylated large fullerenes exhibit widely varying degrees of motional freedom. The last characteristic was unexpected and apparently results from a combination of dodecyl groups in void spaces of varying size and dodecyl groups on molecules that tumble at various rates.

Introduction

Due to their globular and irregularly shaped carbon structures, the large fullerenes are of special interest to the scientific community.^{1–3} Soluble derivatives of the large fullerenes that are formed during the synthesis of HiPco single-walled carbon nanotubes (SWNTs) have been isolated as fluorinated derivatives.⁴ Large fullerenes have also been functionalized by dodecyl radicals, generated by decomposing benzoyl peroxide in the presence of dodecyl iodide, and investigated microscopically.^{4,5} Other reports have dealt with the extraction of fullerene soot using high-boiling-point solvents.^{6–10} In this paper, we report an efficient route to soluble derivatives of the large fullerenes that are formed

during the commercial synthesis of C_{60} by the arc discharge process.^{11,12} Spectroscopic and microscopic studies of the dodecylated derivatives have been performed.

Experimental Methods

The large fullerenes are present in the carbon soot (raw large fullerenes) produced by the MER Corp. (Tucson, AZ) during the production of C_{60} from graphite via the arc discharge method. The carbon soot contains more than 90 wt % large fullerenes after extraction of C_{60} and C_{70} . High-resolution transmission electron microscopy (HRTEM) images show the presence of <1 wt % graphitic nanoshells. The derivatization reactions were carried out by adding the raw large fullerenes (4.2 mmol) under an atmosphere of argon to a dry 100 mL, three-neck, round-bottomed flask fitted with a dry ice condenser. Ammonia (80 mL) was then condensed into the flask followed by the addition of lithium metal (42 mmol). Dodecyl iodide (6.3 mmol) was then added and the mixture stirred for 12 h. The ammonia was then allowed to evaporate, and the flask was cooled in an ice bath. The reaction mixture was quenched by the slow addition of ethanol (30 mL) followed by water (30 mL). The reaction mixture was acidified with 10% HCl, and the dodecylated large fullerenes were extracted into hexane and washed several times with water. The hexane layer was then filtered through a 0.2 μm PTFE membrane and washed with hexane and ethanol to remove unreacted starting material. The dodecylated large fullerenes were dried overnight in vacuo at 80 $^{\circ}\text{C}$.

* To whom correspondence should be addressed. E-mail: billups@rice.edu. Phone: (713) 348-5694.

- (1) Kroto, H. W.; Heath, J. R.; O'Brien, S. C.; Curl, R. F.; Smalley, R. E. *Nature* **1985**, *318*, 162–163.
- (2) Krätschmer, W.; Fostiropoulos, K.; Huffman, D. R. *Chem. Phys. Lett.* **1990**, *170*, 167–170.
- (3) Krätschmer, W.; Lamb, L. D.; Fostiropoulos, K.; Huffman, D. R. *Nature* **1990**, *347*, 354–358.
- (4) Ramesh, S.; Brinson, B.; Pontier Johnson, M.; Gu, Z.; Saini, R. K.; Willis, P.; Marriott, T.; Billups, W. E.; Margrave, J. L.; Hauge, R. H.; Smalley, R. E. *J. Phys. Chem. B* **2003**, *107*, 1360–1365.
- (5) Sadana, A. K.; Liang, F.; Brinson, B.; Arepalli, S.; Farhat, S.; Hauge, R. H.; Smalley, R. E.; Billups, W. E. *J. Phys. Chem. B* **2005**, *109*, 4416–4418.
- (6) Diederich, F.; Ettl, R.; Rubin, Y.; Whetten, R. L.; Beck, R.; Alvarez, M.; Anz, S.; Sensharma, D.; Wudl, F.; Khemani, K. C.; Koch, A. *Science* **1991**, *252*, 548–551.
- (7) Smart, C.; Eldridge, B.; Reuter, W.; Zimmerman, J. A.; Creasy, W. R.; Riviera, N.; Ruoff, R. S. *Chem. Phys. Lett.* **1992**, *188*, 171–176.
- (8) Creasy, W. R.; Zimmerman, J. A.; Ruoff, R. S. *J. Phys. Chem.* **1993**, *97*, 973–979.
- (9) Shinohara, H.; Sato, S.; Saito, Y.; Izuoka, A.; Sugawara, T. *J. Phys. Chem.* **1991**, *95*, 8449–8451.

- (10) Parker, D. H.; Wurz, P.; Chatterjee, K.; Lykke, K. L.; Pellin, M. J.; Hemminger, J. C.; Gruen, D. M.; Stock, L. M. *J. Am. Chem. Soc.* **1991**, *113*, 7499–7503.
- (11) Liang, F.; Sadana, A. K.; Peera, A.; Chattopadhyay, J.; Gu, Z.; Hauge, R. H.; Billups, W. E. *Nano Lett.* **2004**, *4*, 1257–1260.
- (12) Chattopadhyay, J.; Sadana, A. K.; Liang, F.; Beach, J. M.; Xiao, Y.; Hauge, R. H.; Billups, W. E. *Org. Lett.* **2005**, *7*, 4067–4069.

Solubility in chloroform was determined by near-infrared (NIR) spectroscopy.¹³ A study by solid-state, dipolar dephasing, magic angle spinning nuclear magnetic resonance (¹³C MAS NMR) of the dodecylated large fullerenes focused on some unusual motional behavior.

Fourier-transform infrared (FTIR) spectra were obtained using a Nicolet spectrometer with an ATR accessory. Raman spectra were collected from samples using a Renishaw 1000 micro-Raman system with a 785 nm laser source. Thermogravimetric analysis (TGA) data were obtained under argon using a model SDT 2960 TA instrument. Samples were degassed at 80 °C, then heated at 10 °C/min to 700 °C, and held there for 20 min.

Mass spectra were acquired using a Reflex IV (Bruker Daltonics Inc., Billerica, MA) matrix-assisted, laser desorption ionization, time-of-flight (MALDI-TOF) instrument equipped with pulsed ion extraction and a pulsed nitrogen laser (337 nm). Samples for mass analysis were prepared using a solution of dodecylated large fullerenes in toluene (approximately 1 mg/mL) and applying 0.350 μ L of it on the polished stainless steel MALDI target plate. This droplet was allowed to air-dry prior to loading the plate into the instrument. During the acquisition of the spectra, the MALDI target plate was constantly moved to irradiate new regions within the sample spot, as the deposited sample would be rapidly exhausted by the laser irradiation. The laser energy was set to be slightly greater than the threshold required for obtaining the spectra, in an attempt to mitigate fragmentation of the dodecylated large fullerenes during the acquisition of the spectra. Postacquisition analyses of the spectra were performed using the Data Analysis software suite (version 3.4.179, Bruker Daltonics Inc.). The instrument was operated in reflectron mode with an accelerating voltage of 20 kV. NIR absorbance spectra were measured on a Shimadzu UV-3101 PC spectrometer in 1 mm path length Starna cells with Teflon closures. Light absorbance in the range of 900–1500 nm scales linearly with the concentration. This Beer's law behavior yields calibration curves for measuring the concentration of dodecylated large fullerenes in organic solvents. The raw and dodecylated large fullerenes were further examined by HRTEM. A drop of large fullerenes (both raw and dodecylated) in chloroform was placed on a TEM grid (mesh size 200 μ m), dried, and examined. HRTEM images are taken using a high-resolution transmission electron microscope (JEM-2010F) operated at an accelerating voltage of 200 kV.

Solid-state ¹³C MAS NMR spectra were acquired on a Bruker AVANCE-200 NMR spectrometer (50.3 MHz, ¹³C; 200.1 MHz, ¹H) using standard Bruker pulse programs, as described previously.¹⁴ Critical parameters are given in the figure captions. In the dipolar dephasing experiment, the total dephasing interval includes the 8.6 μ s 180° ¹³C refocusing pulse and 1 μ s intervals immediately following CP and immediately preceding FID acquisition. Thus, the total dephasing interval is 10.6 μ s longer than the nominal dephasing time specified (e.g., 60.6 μ s if a pair of 25 μ s dephasing periods are used). MAS at 7.6 kHz displaced the spinning sidebands outside the centerband region in the CP experiments, as the spinning sidebands were ± 151 ppm from the corresponding centerband. At this spinning speed, one rotor period equals 131.6 μ s. The basic

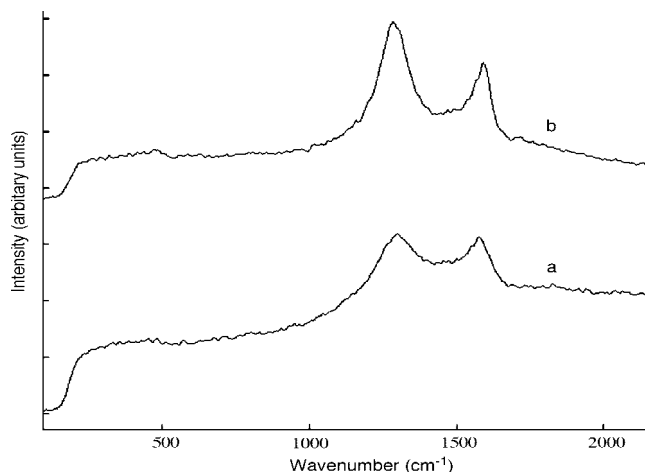
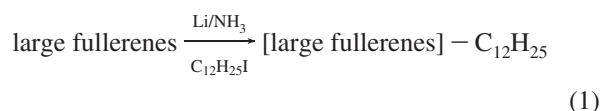


Figure 1. Raman spectra (785 nm) of (a) raw large fullerenes and (b) dodecylated large fullerenes obtained by dodecylation.

CP experiment and the 14 dipolar dephasing experiments were done in one 18 day period to try to minimize any long-term instrumental variations, although two liquid nitrogen fills of the magnet had to be done between experiments. Probe tuning with a spinning rotor was checked before and after each liquid nitrogen fill and slightly adjusted if necessary. Each of these experiments lasted 25 h, except for the experiment with the longest dephasing time, lasting 42 h because of the additional scans taken to increase the S/N of the very weak aliphatic signals.

Results and Discussion

“Large fullerene salts” prepared by treating raw large fullerenes with lithium in liquid ammonia react readily with dodecyl iodide to give large fullerenes functionalized by dodecyl groups. The dodecylated large fullerenes are soluble in chloroform, tetrahydrofuran, dimethylformamide, and hexane.^{11,12} An FTIR spectrum obtained using an ATR accessory exhibits C–H stretching absorptions associated with the dodecyl group at 2910 and 2840 cm^{-1} .



TGA analysis of the raw large fullerenes shows a small weight loss ($\sim 2\%$) over the temperature range 200–350 °C, whereas a 30% weight loss is observed for the dodecylated large fullerenes over the same temperature range. This leads to a level of functionalization of about 1 dodecyl group for every 23 sp^2 fullerene carbon atoms. The extent of functionalization can also be inferred from the exceptionally strong disorder peak in the Raman spectrum (Figure 1) As shown in Figure 1a, the Raman spectrum of the raw large fullerenes exhibits a tangential mode (G band) at 1590 cm^{-1} and a disorder band (D band) at 1290 cm^{-1} . The broad shoulder in the G band arises from residual C_{60} and corresponds to the highest frequency first-order Raman mode [$\text{H}_g(8)$] of C_{60} at 1577 cm^{-1} .^{15,16} The D band probably arises

- (13) Rai, P. K.; Pinnick, R. A.; Parra-Vasquez, A. N. G.; Davis, V. A.; Schmidt, H. K.; Hauge, R. H.; Smalley, R. E.; Pasquali, M. *J. Am. Chem. Soc.* **2006**, *128*, 591–595.
- (14) (a) Peng, H.; Alemany, L. B.; Margrave, J. L.; Khabashesku, V. N. *J. Am. Chem. Soc.* **2003**, *125*, 15174–15182. (b) Liang, F.; Alemany, L. B.; Beach, J. M.; Billups, W. E. *J. Am. Chem. Soc.* **2005**, *127*, 13941–13948. (c) Ashcroft, J. M.; Hartman, K. B.; Mackeyev, Y.; Hofmann, C.; Pheasant, S.; Alemany, L. B.; Wilson, L. J. *Nanotechnology* **2006**, *17*, 5033–5037. (d) Alemany, L. B.; Zhang, L.; Zeng, L.; Edwards, C. L.; Barron, A. R. *Chem. Mater.* **2007**, *19*, 735–744.

- (15) Dong, Z.-H.; Zhou, P.; Holden, J. M.; Eklund, P. C.; Dresselhaus, M. S.; Dresselhaus, G. *Phys. Rev. B* **1993**, *48*, 2862–2865.
- (16) Dresselhaus, M. S.; Dresselhaus, G.; Eklund, P. C. *J. Raman Spectrosc.* **1996**, *27*, 351–371.

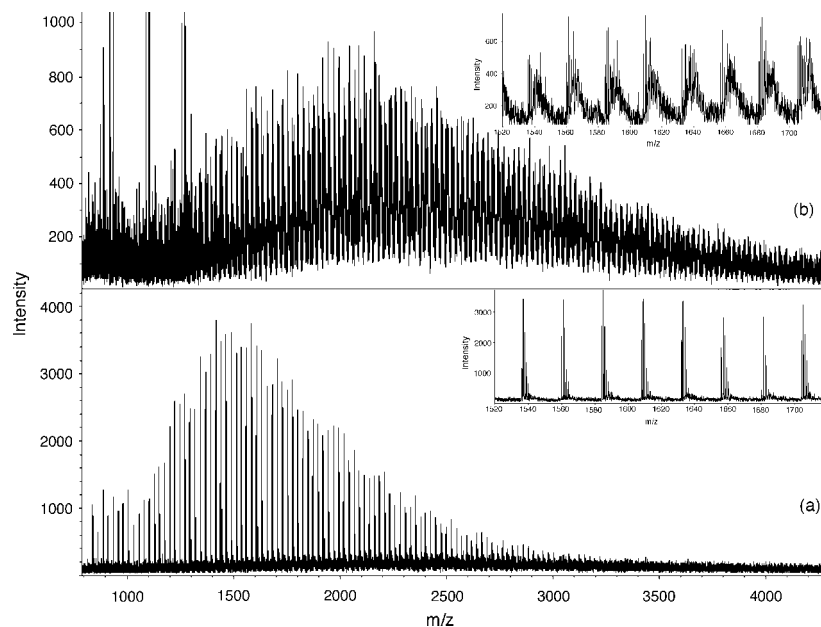


Figure 2. LDI-TOF mass spectra of (a) raw large fullerenes and (b) dodecylated large fullerenes.

from the structural changes that occur during either the synthesis or the purification of the raw large fullerenes.¹⁷ After functionalization, the relative intensity of the D band was observed to increase (Figure 1b), confirming that covalent attachment of the dodecyl groups had occurred.

Laser desorption/ionization, time-of-flight (LDI-TOF) mass spectra are shown in Figure 2. These spectra are representative of the LDI spectra for (a) raw large fullerenes and (b) dodecylated large fullerenes. Several runs of raw large fullerenes showed a spectral range from 650 to 3500 amu (C_{54} – C_{290}). The observed ion abundance distribution exhibited a broad maximum at m/z 1400–1600 (C_{110} – C_{130}) for raw large fullerenes and a monotonic decrease in ion abundance at increasing mass. The insets of Figure 2 are representative of a region in the LDI spectra for (a) raw large fullerenes and (b) dodecylated large fullerenes.

The LDI mass spectra of the raw large fullerenes showed features that were typical of higher mass fullerenes having ions with m/z ratio spacing due to C_2 units.¹⁸ The mass spectra representing putative derivatized large fullerenes exhibit features that are consistent with dodecylated large fullerenes.

The low molecular weight large fullerenes are more susceptible to functionalization than the higher ones.¹⁹ Hence, the unresolved features at higher m/z ratios originate from multiply dodecylated large fullerenes having low molecular weight, as the Reflex IV had a mass resolving power of approximately 8500 (fwhm) at m/z 1660 under the LDI conditions used. This is illustrated in Figure 3, where the ion abundances were calculated using the isotope pattern simulation function within the Data Analysis software suite.

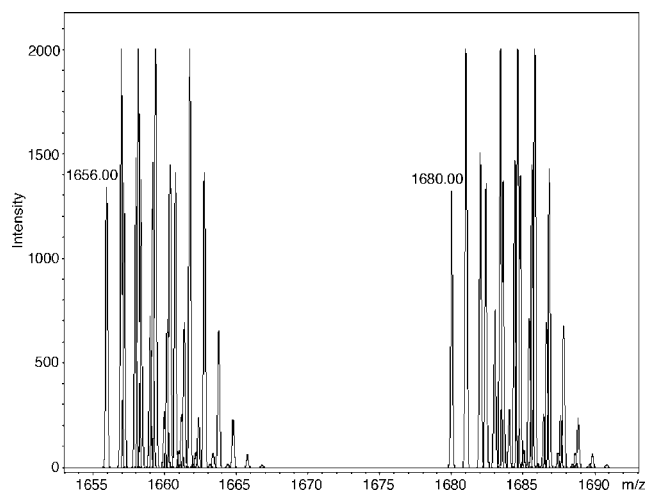


Figure 3. Simulated mass spectra of dodecylated large fullerenes using isotopic abundance calculation.

Each species was calculated with a monoisotopic base peak intensity of 2000. Thus, no relative intensity information for the peaks should be inferred for the various dodecylated large fullerenes. As indicated by the calculated isotope distribution, the unresolved ion peaks would occur at higher m/z ratios with respect to the raw large fullerenes by fractional masses. This is a consequence of the fact that the dodecylated large fullerenes contain hydrogen with a positive mass defect of approximately +0.0078 amu. Thus, the ion signals for dodecylated large fullerenes will be unresolved at a higher m/z ratio than the proximate C_2 ion signal.

Thermal gravimetric analysis of dodecylated large fullerenes in the 200–800 °C range with online monitoring of the volatile products by a mass spectrometer operating in electron impact ionization mode provides further evidence of covalent functionalization by dodecyl groups. The groups liberated from 200–350 °C were shown by TGA–MS to contain a major peak at m/z 169 corresponding to the dodecyl group. No additional peaks were observed.

- (17) Scott, C. D.; Ugarov, M.; Hauge, R. H.; Sosa, E. D.; Arepalli, S.; Schultz, J. A.; Yowell, L. *J. Phys. Chem. C* **2007**, *111*, 36–44.
- (18) (a) O'Brien, S. C.; Heath, J. R.; Curl, R. F.; Smalley, R. E. *J. Chem. Phys.* **1988**, *88*, 220–230. (b) Ulmer, G.; Campbell, E. E. B.; Kuhnle, R.; Busmann, H. G.; Hertel, I. V. *Chem. Phys. Lett.* **1991**, *182*, 114–119.
- (19) Rai, P. K.; Parra-Vasquez, A. N. G.; Peng, H.; Hauge, R. H.; Pasquali, M. *J. Phys. Chem. C* **2007**, *111*, 17966–17969.

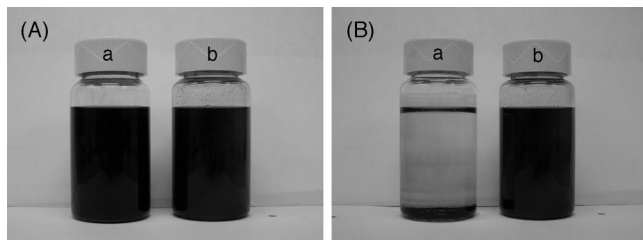


Figure 4. Photographs of (a) raw large fullerenes and (b) dodecylated large fullerenes in chloroform (CHCl_3): (A) immediately after sonication, (B) after 15 min.

Stable solutions of the dodecylated large fullerenes in organic solvents are formed after sonication for a few minutes. Although solutions of raw and dodecylated large fullerenes in chloroform appear to be identical immediately after sonication (Figure 4), the raw large fullerenes precipitate after a few minutes.

Solubility measurements of the dodecylated large fullerenes were made by nIR absorbance studies.¹³ Figure 5a shows the nIR absorption spectra of the dodecylated large fullerenes in chloroform (CHCl_3) at four different concentrations. The peak at 1430 nm is due to the change in detector. Figure 5b shows the corresponding calibration lines at 1000 and 1500 nm. The two independent measurements of the absorbance of the most concentrated solution fall on the calibration curves. The maximum concentration of dodecylated large fullerenes obtained by extrapolation of the calibration lines at 1000 nm ($\epsilon = 0.3103 \text{ mL mg}^{-1} \text{ cm}^{-1}$) and 1500 nm ($\epsilon = 0.1925 \text{ mL mg}^{-1} \text{ cm}^{-1}$) was found to be 15.7 g/L.

The TEM micrograph recorded at a magnification of 1 200 000 (accelerating voltage 200 kV) is shown in Figure 6a, where spherical closed shell structures resembling large fullerenes with an average diameter of 1.1 nm are observed. A magnified view of a closed end of a large fullerene is shown in Figure 6b. As expected, large fullerenes appeared as simple ring-shaped contrast in HRTEM images.²⁰ The sample was found to contain no SWNTs, but the presence of graphitic shell particles resembling functionalized carbon onion-type structures that are formed during the synthesis of the fullerenes can be seen in Figure 6c. Lattice spacing between the fringes in the closed shell onion-type structure was found to be 3.4 Å. Figure 6d shows a large fullerene possibly functionalized by a dodecyl group as shown in the magnified view in the inset of Figure 6d. Structural instability and continuous movement of the large fullerenes on exposure to the electron beam were also observed. This resulted in detachment of the functional groups (from the large fullerene surface) and deformation of the fullerene molecules in most cases.

Solution-state and solid-state NMR studies of the dodecylated large fullerenes were undertaken to obtain additional information. However, the dodecylated large fullerenes were not sufficiently soluble in CDCl_3 to obtain ^1H and ^{13}C spectra (500 MHz spectrometer) with significant useful information. Signals consistent with the presence of long chain alkyl groups were clearly evident in the ^1H and ^{13}C spectra, but

no other information could readily be obtained. In contrast, solid-state ^{13}C MAS NMR studies of the dodecylated large fullerenes provided important additional information. Three types of experiments were done: direct ^{13}C pulse experiments with different relaxation delays, ^1H – ^{13}C cross-polarization experiments with different contact times, and ^1H – ^{13}C cross-polarization followed by variable delays before FID acquisition (the dipolar dephasing experiment) to attenuate signals experiencing strong ^{13}C – ^1H dipole–dipole interactions.

Direct ^{13}C pulse experiments were done with relaxation delays ranging from 10 to 150 s to assess relative relaxation rates and obtain a spectrum with meaningful relative sp^2 and sp^3 signal intensities. Lengthening the relaxation delay from 10–20 to 40–60 to 90 s showed a steady increase in the sp^2 signal intensity; increasing the relaxation delay to 150 s resulted in no significant change in the relative sp^2 and sp^3 signal intensities (Figure 7). With relaxation complete, the relative centerband areas indicate the presence of 1 dodecyl group for every 23 sp^2 carbons. (The spinning sidebands are extremely weak with 12 kHz MAS.)

The sp^2 centerband is devoid of fine structure, but the sp^3 centerband clearly shows signals for dodecyl methyl carbons (14 ppm) and internal methylene carbons (30 ppm), with an upfield shoulder for C-11 methylene carbons (23 ppm). Of particular significance, as the relaxation delay increased, the downfield aliphatic region also became significantly more intense, which we attribute to an increasing contribution from slowly relaxing quaternary aliphatic carbons. Previous work^{14b} has indicated that the quaternary aliphatic carbons in dodecylated SWNTs could reasonably be expected to give signals near 40 ppm. This is considerably upfield of the region (from about 55–65 ppm) where signals are commonly found for the quaternary aliphatic carbons of alkylated C_{60} and C_{70} .^{14b,21–24} The quaternary aliphatic carbons in the dodecylated large fullerenes and dodecylated SWNTs presumably exhibit this significant upfield shift (much more like that given by the quaternary aliphatic carbons in dialkylidihydro derivatives of large planar condensed aromatic hydrocarbons^{14b}) for the same reason: dodecylated large

(20) Goel, A.; Howard, J. B.; Vander Sande, J. B. *Carbon* **2004**, 42, 1907–1915.

- (21) (a) Caron, C.; Subramanian, R.; D'Souza, F.; Kim, J.; Kutner, W.; Jones, M. T.; Kadish, K. M. *J. Am. Chem. Soc.* **1993**, 115, 8505–8506. (b) Allard, E.; Rivière, L.; Delaunay, J.; Dubois, D.; Cousseau, J. *Tetrahedron Lett.* **1999**, 40, 7223–7226. (c) Al-Matar, H.; Abdul Sada, A. K.; Avent, A. G.; Taylor, R.; Wei, X.-W. *J. Chem. Soc., Perkin Trans. 2* **2002**, 1251–1256.
- (22) (a) Wang, G.-W.; Murata, Y.; Komatsu, K.; Wan, T. S. M. *Chem. Commun.* **1996**, 2059–2060. (b) Allard, E.; Rivière, L.; Delaunay, J.; Rondeau, D.; Dubois, D.; Cousseau, J. *Proc.—Electrochem. Soc.* **2000**, 2000–10, 88–93. (c) Allard, E.; Delaunay, J.; Cousseau, J. *J. Org. Lett.* **2003**, 5, 2239–2242.
- (23) (a) Abdul-Sada, A. K.; Avent, A. G.; Birkett, P. R.; Kroto, H. W.; Taylor, R.; Walton, D. R. M. *J. Chem. Soc., Perkin Trans. 1* **1998**, 393–395. (b) Meier, M. S.; Bergosh, R. G.; Gallagher, M. E.; Spielmann, H. P.; Wang, Z. *J. Org. Chem.* **2002**, 67, 5946–5952.
- (24) (a) Kadish, K. M.; Gao, X.; Van Caemelbecke, E.; Hirasaka, T.; Suenobu, T.; Fukuzumi, S. *J. Phys. Chem. A* **1998**, 102, 3898–3906. (b) Fukuzumi, S.; Suenobu, T.; Hirasaka, T.; Arakawa, R.; Kadish, K. M. *J. Am. Chem. Soc.* **1998**, 120, 9220–9227. (c) Kadish, K. M.; Gao, X.; Van Caemelbecke, E.; Suenobu, T.; Fukuzumi, S. *J. Phys. Chem. A* **2000**, 104, 3878–3883. (d) Zheng, M.; Li, F.; Shi, Z.; Gao, X.; Kadish, K. M. *J. Org. Chem.* **2007**, 72, 2538–2542. (e) Toganoh, M.; Suzuki, K.; Udagawa, R.; Hirai, A.; Sawamura, M.; Nakamura, E. *Org. Biomol. Chem.* **2003**, 1, 2604–2611. (f) Wang, G.-W.; Zhang, T.-H.; Wang, F. *Org. Biomol. Chem.* **2004**, 2, 1160–1163. (g) Matsuo, Y.; Nakamura, E. *J. Am. Chem. Soc.* **2005**, 127, 8457–8466.

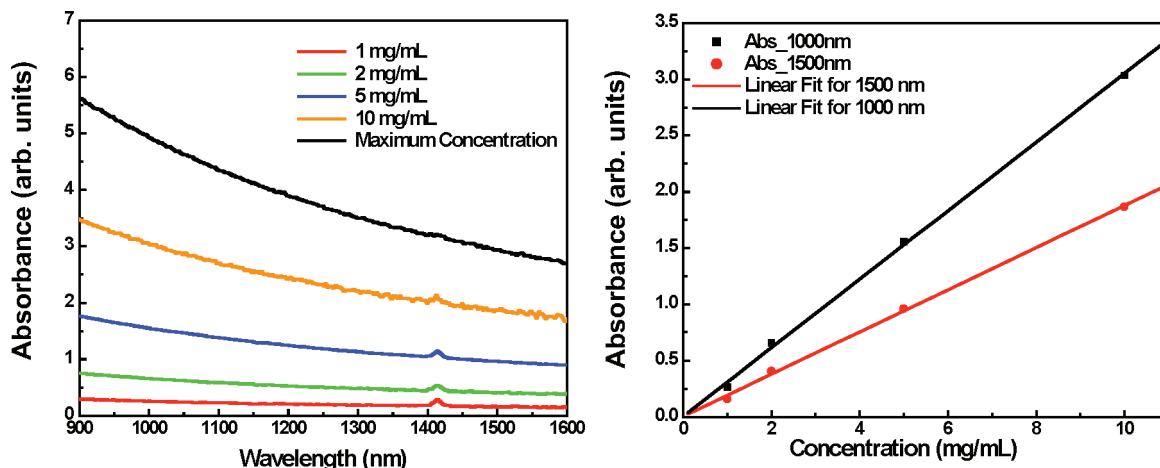


Figure 5. (a, left) nIR absorbance spectra of dodecylated large fullerenes in chloroform (CHCl_3) at different concentrations and (b, right) the corresponding calibration line at 1000 and 1500 nm.

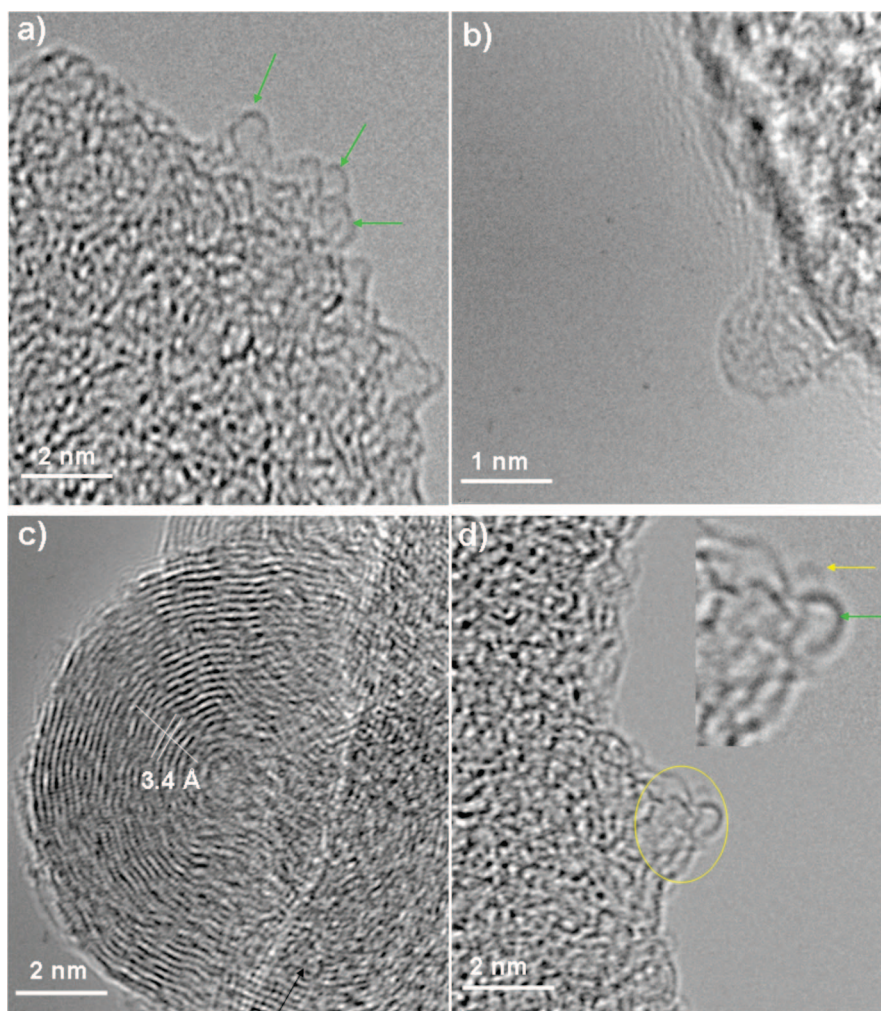


Figure 6. HRTEM images of raw large fullerenes. (a) Arrows indicate nearly spherical 1–1.5 nm closed shell structures. (b) Magnified view of raw large fullerenes. (c) Carbon onions showing graphitic fringes. (d) Dodecylated large fullerenes. The inset shows both the fullerene and functional group. The green arrow points at the fullerene, and the yellow arrow points at the dodecyl group.

fullerenes and dodecylated SWNTs are less curved than C_{60} or C_{70} , and the chemical shift is very sensitive to changes in the bond lengths and bond angles.^{14b,25}

Additional support for attributing part of the signal intensity near 40 ppm to quaternary aliphatic carbon comes from a series of ^1H – ^{13}C cross-polarization experiments

obtained with contact times (t_{cp}) ranging from 0.5 to 10 ms. In general, methyl and quaternary aliphatic carbons are known to cross-polarize more slowly than methine or methylene carbons,²⁶ and at the longer contact times, the amount of aliphatic signal intensity from the methyl and δ 40 signals is proportionately much higher than at shorter

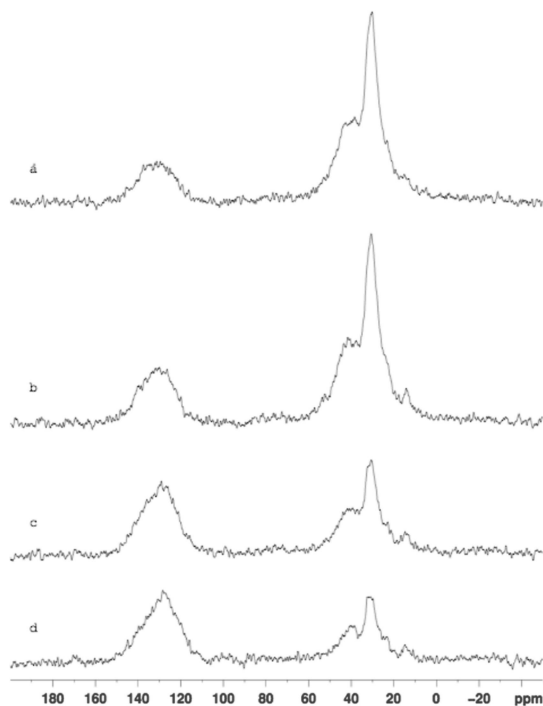


Figure 7. Centerband region of the direct ^{13}C pulse MAS spectra of the dodecylated large fullerenes: (a) 10 s relaxation delay, 8600 scans, (b) 90 s relaxation delay, 3144 scans. Other parameters: 12 kHz MAS, $4.3 \mu\text{s}$ 90° ^{13}C pulse, 20.54 ms FID, line broadening 20 Hz (0.4 ppm).

contact times (Figure 8). Proton spin–lattice relaxation in the rotating frame, characterized by the time constant $T_{1\rho}(\text{H})$, clearly attenuates all signals at longer contact times.²⁶ This effect is most noticeable for the methylene signals, which cross-polarize the fastest.

A ^1H – ^{13}C CPMAS spectrum with much higher S/N than those shown in Figure 8 exhibits a weak intensity near 80 ppm, as well as the much more prominent aliphatic signals further upfield and fullerene sp^2 signals further downfield (Figure 9). The multiple contact time CP experiments show that the signals near 80 ppm cross-polarize relatively slowly, with maximum intensity generated with $t_{\text{cp}} = 3.0$ ms. The possibility of ether or epoxide functionality had to be considered as the source of these weak signals. A characterization procedure specific to epoxides²⁷ indicated that these weak signals were, indeed, from epoxides. Specifically, treatment of a larger batch of dodecylated large fullerenes with $\text{CH}_3\text{ReO}_3/\text{H}_2\text{O}_2$ and $\text{P}(\text{C}_6\text{H}_5)_3$ resulted in the formation of $\text{O}=\text{P}(\text{C}_6\text{H}_5)_3$ and the complete disappearance of the band near 80 ppm in ^1H – ^{13}C CPMAS (36 000 scans, $t_{\text{cp}} = 1.0$ ms, 5 s relaxation delay) and direct ^{13}C pulse MAS (10 600 scans, 60 s relaxation delay) spectra exhibiting high S/N. The disappearance of this band results from the conversion of epoxides into alkenes.

The aliphatic intensity in the ^1H – ^{13}C CPMAS spectrum obtained with $t_{\text{cp}} = 1.0$ ms (Figure 9) is proportionately much higher than in any of the direct ^{13}C pulse MAS spectra

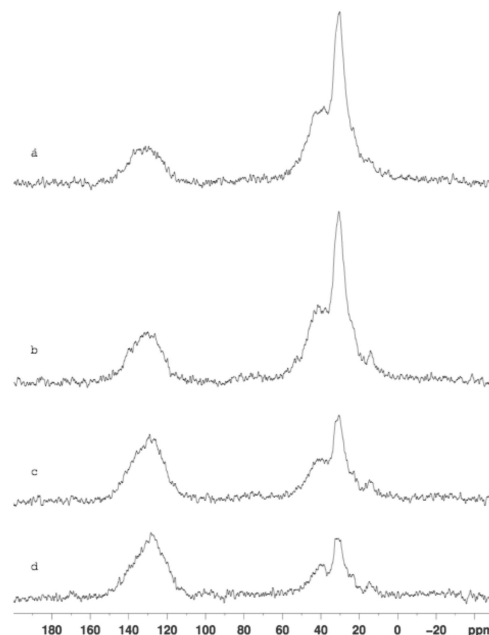


Figure 8. Centerband region of the ^1H – ^{13}C CPMAS spectra of the dodecylated large fullerenes obtained under identical conditions except for the contact time (t_{cp}): (a) $t_{\text{cp}} = 0.5$ ms, (b) $t_{\text{cp}} = 1.0$ ms, (c) $t_{\text{cp}} = 4.5$ ms, (d) $t_{\text{cp}} = 7.5$ ms. Other parameters: 7.6 kHz MAS, $2.93 \mu\text{s}$ 90° ^1H pulse, 29.35 ms FID, 5 s relaxation delay, 2000 scans, line broadening 20 Hz (0.4 ppm).

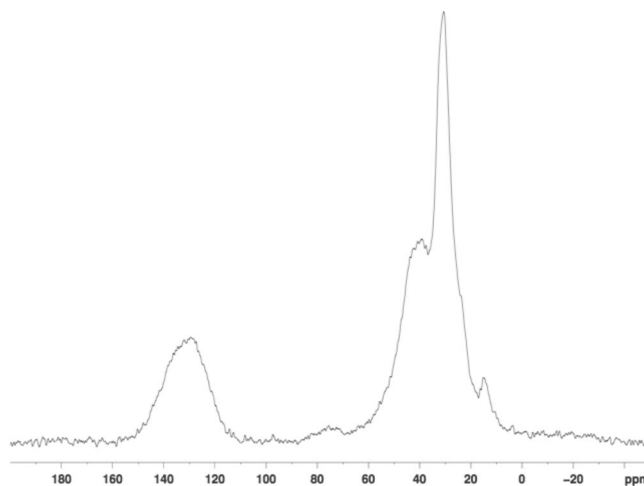


Figure 9. Centerband region of the ^1H – ^{13}C CPMAS spectrum of the dodecylated large fullerenes: $t_{\text{cp}} = 1.0$ ms, 18 000 scans. Other parameters are as in Figure 8.

(Figure 7). A 1 ms contact time is often adequate for generating meaningful relative signal intensities if all of the carbons efficiently cross-polarize and greatly reduces the amount of signal attenuation caused by $T_{1\rho}(\text{H})$ relaxation when much longer contact times are used.²⁶ However, the CPMAS spectrum discriminates against carbons far from protons. With only 1 dodecyl group on average for every 23 sp^2 carbons, some sp^2 carbons clearly are far from protons in the same or nearby molecules and thus cross-polarize much more slowly and to only a limited extent. The absolute intensity of the sp^2 centerband reaches a maximum at $t_{\text{cp}} \approx 3.0$ – 4.5 ms. Comparing the CP spectra in Figure 8 against the direct ^{13}C pulse spectra in Figure 7 shows the slow and incomplete CP of the sp^2 carbons.

(25) (a) Grant, D. M. *Encyclopedia of Nuclear Magnetic Resonance*; Wiley: London, 1996; Vol. 2, pp 1298–1321. (b) Nossal, J.; Saini, R. K.; Sadana, A. K.; Bettinger, H. F.; Alemany, L. B.; Scuseria, G. E.; Billups, W. E.; Saunders, M.; Khong, A.; Weisemann, R. *J. Am. Chem. Soc.* **2001**, *123*, 8482–8495.

(26) Alemany, L. B.; Grant, D. M.; Pugmire, R. J.; Alger, T. D.; Zilm, K. W. *J. Am. Chem. Soc.* **1983**, *105*, 2133–2141.

(27) Ogrin, D.; Chattopadhyay, J.; Sadana, A. K.; Billups, W. E.; Barron, A. R. *J. Am. Chem. Soc.* **2006**, *128*, 11322–11323.

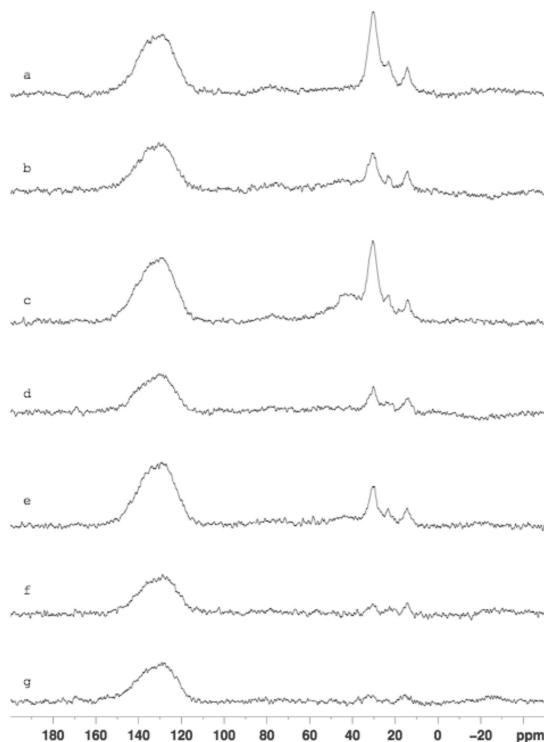


Figure 10. Centerband region of the ^1H – ^{13}C CPMAS spectra of the dodecylated large fullerenes obtained with various dephasing delays before FID acquisition: (a) $2 \times 25 \mu\text{s}$, (b) $2 \times 60.5 \mu\text{s}$ (1.0 rotor period), (c) $2 \times 126.3 \mu\text{s}$ (2.0 rotor periods), (d) $2 \times 192.1 \mu\text{s}$ (3.0 rotor periods), (e) $2 \times 257.9 \mu\text{s}$ (4.0 rotor periods), (f) $2 \times 553.9 \mu\text{s}$ (8.5 rotor periods), (g) $2 \times 817.1 \mu\text{s}$ (12.5 rotor periods). The same phasing parameters were used as in the basic ^1H – ^{13}C CPMAS spectrum shown in Figure 9. Other parameters are also as in Figure 9, except for 30 000 scans in (g).

The dipolar dephasing spectra^{14b,28} were remarkable in that they exhibited exceptionally slowly decaying aliphatic signals. The decay rate of the methylene signals clearly was not constant but, rather, indicated the presence of dodecyl groups with widely varying degrees of motional freedom.

A $50 \mu\text{s}$ dephasing period is usually sufficient to greatly attenuate, if not completely eliminate, methine and methylene carbon signals,^{14b,28} but significant non-methyl aliphatic intensity clearly remained when a $60.6 \mu\text{s}$ dephasing period was applied to the dodecylated large fullerenes (Figure 10a). The observed peak maxima are entirely reasonable for the methyl, C-11 methylene, and internal methylene signals of the various dodecyl groups. Compared to those of the basic CP spectrum (Figure 9), the dodecyl methyl carbon signal at 14 ppm is better resolved and the shoulder for the dodecyl C-11 methylene carbons at 23 ppm is more visible. It is reasonable for the methyl signal to be only moderately attenuated after a total dephasing time of $60.6 \mu\text{s}$. However, it is unusual for so much methylene intensity to remain after a dephasing time of this length, which indicates that some of the methylene groups have an unusual amount of motional freedom, as this would result in considerably weaker ^{13}C – ^1H dipole–dipole interactions.

In contrast, the aliphatic signal downfield of about 38 ppm in the basic CP spectrum has almost entirely decayed after a total dephasing time of $60.6 \mu\text{s}$. The large decrease in aliphatic intensity downfield of about 38 ppm indicates that this region results in part from methylene carbons experiencing strong ^{13}C – ^1H dipole–dipole interactions. The methylene carbon directly bonded to the fullerene would have the least motional freedom, and thus, its signal would be expected to decay the fastest. Unfortunately, no ^{13}C chemical shift information appears to be available on relevant model systems. For the more highly curved 1,4-disubstituted derivatives of C_{60} bearing $-(\text{CH}_2)_6\text{X}$ ($\text{X} = \text{Cl}$ or I) substituents, the methylene carbon adjacent to the fullerene appears to give a signal at δ 43.6.^{22b} We are not aware of any ^{13}C shift data for *cis*-dialkyldihydro derivatives of polycyclic aromatic compounds with C_2 or longer alkyl groups. The C-2 and C-3 ^{13}C NMR signals would presumably be upfield of the C-1 signal.

The quaternary aliphatic signals of the epoxides (near 80 ppm) and the signals from the fullerene sp^2 carbons undergo, as expected, little change with only a $60.6 \mu\text{s}$ dephasing period.

An additional, but much smaller, amount of the CH_2 intensity is eliminated after a total dephasing time of $131.6 \mu\text{s}$ (corresponding to 1.0 rotor period), Figure 10b. For some of the methylene signals to still be present indicates that these methylene groups have a remarkable amount of motional freedom. As expected,²⁶ the methylene signals clearly decayed more rapidly than the methyl signal.

The CH_2 and CH_3 signals remaining after a dephasing time corresponding to 1.0 rotor period subsequently exhibit an exceptionally slow decay indicative of exceptionally large motional freedom. Dephasing times were chosen to correspond to integral numbers or half-integral numbers of rotor periods (1.0, 1.5, 2.0, 2.5, 3.0, 3.5, 4.0, 4.5, 5.5, 6.5, 8.5, 10.5, and 12.5) in an attempt to detect rotational echoes at dephasing times corresponding to 2.0 and 4.0 rotor periods.

Comparing the spectrum obtained with a total dephasing time of 2.0 rotor periods (Figure 10c) to those obtained with a total dephasing time of 1.5 or 2.5 rotor periods (not shown) shows a strong rotational echo after 2.0 rotor periods.^{28b} Not only do the signals for fullerene sp^2 and interior CH_2 groups clearly increase in intensity, but the signal intensity is restored from about δ 38 to δ 60. For a signal in this region to so strongly decay and then reappear at a rotational echo suggests that this signal results principally from methylene rather than quaternary aliphatic carbon. In any event, the slowly decaying methylene and methyl signals prevent seeing any negative signals from dipolar modulation. The weak, broad signal from about δ 70 to δ 90 also shows a modest increase in intensity because of the rotational echo.

Lengthening the dephasing period to $394.8 \mu\text{s}$ (3.0 rotor periods) still did not eliminate the internal and C-11 methylene signals (Figure 10d), although the intensity of all the signals was less than that after a dephasing interval corresponding to 1.0 rotor period (Figure 10b). The methylene signals continue to decay more rapidly than the methyl signal.

- (28) (a) Opella, S. J.; Frey, M. H. *J. Am. Chem. Soc.* **1979**, *101*, 5854–5856. (b) Alemany, L. B.; Grant, D. M.; Alger, T. D.; Pugmire, R. J. *J. Am. Chem. Soc.* **1983**, *105*, 6697–6704.
- (29) (a) Johnson, R. D.; Yannoni, C. S.; Dorn, H. C.; Salem, J. R.; Bethune, D. S. *Science* **1992**, *255*, 1235–1238. (b) Tycko, R.; Dabbagh, G.; Vaughan, G. B. M.; Heiney, P. A.; Strongin, R. M.; Cichy, M. A.; Smith, A. B., III *J. Chem. Phys.* **1993**, *99*, 7554–7564.

Comparing the spectrum obtained with a total dephasing time of 4.0 rotor periods (Figure 10e) to those obtained with a total dephasing time of 3.5 or 4.5 rotor periods (not shown) shows a much weaker rotational echo after 4.0 rotor periods. In general, comparing spectra with dephasing times differing by 2.0 rotor periods (i.e., 1.5 and 3.5, 2.0 and 4.0, and 2.5 and 4.5 rotor periods) shows in each case a clear overall decrease in intensity, particularly for the CH₂ signals, as expected.

In an attempt to determine how much time would be needed to completely eliminate the aliphatic signals, still longer dephasing periods not corresponding to rotational echoes were chosen. Even after a dephasing period of 1118.4 μ s (8.5 rotor periods), weak signals remained for the dodecyl internal methylene, C-11 methylene, and methyl carbons (Figure 10f). Since the intensity of the signal near 30 ppm from all the internal methylene carbons was comparable to the intensity of the signal near 14 ppm from the methyl carbon, the signals for the methylene carbons were still decaying more rapidly.

The aliphatic signals still remained after a dephasing period corresponding to 10.5 rotor periods but were so weak as to be barely detectable above the baseline noise. A final experiment with a dephasing period corresponding to 12.5 rotor periods (1644.8 μ s) and with 30 000 scans (not 18 000 scans as in all the previous experiments) still gave detectable signals for the internal methylene carbons and the methyl carbon (Figure 10g).

The wide range of decay rates for the methylene carbon signals indicates the presence of dodecyl groups with widely varying degrees of motional freedom. It is reasonable to conclude that the most mobile dodecyl groups either are rather freely moving in large void spaces remaining after some very large fullerene molecules pack together or are on relatively rapidly tumbling molecules. Dodecyl groups trapped in smaller void spaces created by the packing of some not quite so large fullerene molecules have less volume in which to reorient; accordingly, their signals decay more rapidly in a series of dipolar dephasing experiments. Dodecyl groups on molecules tumbling less rapidly would also give signals decaying more rapidly in a series of dipolar dephasing experiments. Dodecyl groups trapped in still smaller void spaces created by the packing of still smaller fullerene molecules have even less volume in which to reorient—in some cases, perhaps essentially no free volume—and thus behave like a normal solid in a series of dipolar dephasing experiments. Dodecyl groups on molecules tumbling rather slowly would also give signals decaying very rapidly in a series of dipolar dephasing experiments. Thus, a continuum of degrees of motional freedom exists for the dodecyl side chains. It is relevant to note that the rotator phase of C₆₀ is known to tumble exceptionally rapidly.^{29a} Below the phase transition temperature of C₆₀, a second phase (the ratchet phase) also is present, with slower tumbling.^{29a} C₇₀ exhibits rapid, nearly isotropic rotation above 330 K in the face-centered cubic phase and less rapid, anisotropic rotation about the 5-fold symmetry axis at lower temperatures in the

rhombohedral and monoclinic phases.^{29b} We are not aware of any similar reports for larger fullerenes or for alkylated fullerenes.

Another solid that has methylene carbons exhibiting unusually slow dipolar dephasing rates because of unusually large molecular motion is the noncrystalline component of a melt-quenched polyethylene, a complex solid consisting of a crystalline component, a noncrystalline component, and a third component.³⁰ Furthermore, the noncrystalline component itself clearly has two different types of structures with dipolar dephasing rates differing by an order of magnitude (a typical fast rate and the atypical slow rate). The authors³⁰ indicated that the transition rate between trans and gauche conformers in this component is very high and that the dephasing time is a measure of molecular motion.

Similarly, dipolar dephasing experiments on some low-rank coals have provided evidence for segmental motion thought to arise from methylene groups associated with hydroaromatic and/or polymethylene structural units.^{31a} Dipolar dephasing rates differing by up to an order of magnitude were observed for the signal at 30 ppm in the nonmobile and mobile components.^{31a} A similar study on another coal also provided evidence for segmental motion associated with the moieties giving rise to the signal at 30 ppm.^{31b}

A few small, nearly spherical molecules (frozen norbornadiene,³² 1-bromoadamantane,³³ and 1-chloroadamantane³⁴) have also been shown to give exceptionally slowly decaying signals for proton-bearing carbons in dipolar dephasing experiments because rapid, nearly isotropic rotation greatly reduces the effective ¹³C—¹H dipole—dipole interaction. The data for the melt-quenched polyethylene,³⁰ coals,³¹ and dodecylated large fullerenes clearly show that this phenomenon, while rare, is not limited to small, nearly spherical molecules.

Finally, we note that to verify that this unexpectedly slow decay with the dodecylated large fullerenes was real (i.e., not an unrecognized experimental artifact), the commercially available model compound 1,4-didodecylbenzene was again^{14b} studied under the same conditions except for a slightly slower spinning speed (7.0 kHz) and dephasing intervals up to only 3.5 rotor periods. The results were entirely reasonable. Spectra with very high S/N showed the expected^{14b,28} rapid decay of the CH and CH₂ signals, the intermediate rate of decay of the CH₃ signal, and the slow rate of decay of the quaternary aromatic signal. Superimposed on these decays were dipolar and rotational modulation effects that were particularly noticeable for the protonated carbons. The rotational echo was particularly strong after 2.0 rotor periods,^{28b,31b} with very weak signals evident for

(30) Chen, Q.; Yamada, T.; Kurosu, H.; Ando, I.; Shionon, T.; Doi, Y. *J. Polym. Sci., B: Polym. Phys.* **1992**, *30*, 591–601.

(31) (a) Soderquist, A.; Burton, D. J.; Pugmire, R. J.; Beeler, A. J.; Grant, D. M.; Durand, B.; Huk, A. Y. *Energy Fuels* **1987**, *1*, 50–55. (b) Wilson, M. A.; Pugmire, R. J.; Karas, J.; Alemany, L. B.; Woolfenden, W. R.; Grant, D. M.; Given, P. H. *Anal. Chem.* **1984**, *56*, 933–943.

(32) Alla, M.; Lippmaa, E. *Chem. Phys. Lett.* **1976**, *37*, 260–264.

(33) Huang, Y.; Gilson, D. F. R.; Butler, I. S.; Morin, F. *J. Phys. Chem.* **1991**, *95*, 2151–2156.

(34) Huang, Y.; Paroli, R. M.; Gilson, D. F. R.; Butler, I. S. *Can. J. Chem.* **1993**, *71*, 1890–1897.

all of the methylene carbons. In contrast, no methylene carbon signals were detected with dephasing intervals corresponding to 1.5, 2.5, 3.0, or 3.5 rotor periods. Lengthening the dephasing interval from 1.5 to 3.5 rotor periods reduced by about a factor of 2 the S/N for the quaternary aromatic and methyl signals.

Further discussion on the dipolar dephasing spectra of the dodecylated large fullerenes and related materials under study will appear elsewhere.

In conclusion, we describe an efficient route (yield of soluble large fullerenes 34%) for functionalizing large fullerenes by dodecylation in a single step and solubilizing them in common organic solvents. The maximum concentration of dodecylated large fullerenes that can be solubilized using our technique is 15.7 g/L, which is a relatively high solubility for such compounds. ^{13}C MAS NMR experiments

on the dodecylated large fullerenes indicated that there is 1 dodecyl group for every 23 sp^2 fullerene carbon atoms, that the quaternary aliphatic carbons generated upon dodecylation give signals considerably more shielded than those in alkylated C_{60} and C_{70} but similar to the quaternary aliphatic signals in dodecylated SWNTs, and that the dodecyl groups in the dodecylated large fullerenes exhibit widely varying degrees of motional freedom. Thus, we describe an unusual class of solids formed by the dodecylation of large fullerenes that are soluble in common organic solvents and show some unusual NMR characteristics in the solid state.

Acknowledgment. We thank the Robert A. Welch Foundation (Grant C-0490), the National Science Foundation (Grant CHE-0450085), and NASA for support of this work.

CM800737Z