

**Figure 2.** HPLC profiles on a chiral HPLC column (Chiral Pak AS, Daicel Chemicals Co.) for compound 5: (A) authentic *S* enantiomer, (B) a 1:1 mixture of *S* and *R* enantiomers, (C) a 1:1 mixture of *S* and *R* enantiomers with authentic *S* enantiomer added, and (D) a reaction mixture obtained with an (antibody 2):(compound 3):NaBH<sub>4</sub> ratio of 1:2:60. Chromatography conditions were as follows: mobile phase, *n*-hexane-ethanol (50:50, v/v); flow rate, 1.0 mL/min; UV detection at 340 nm.

kindly provided by Professor C. Herdeis, Universitat Wurzburg. It has been confirmed by using the authentic sample of (*S*)-5 that the peak with the longer retention time is due to the *S* enantiomer. See Figure 2C. Enantiomeric excesses were determined by measuring the peak intensity for the *R* and *S* enantiomers. A maximum enantiomeric excess of 36% was obtained with a substrate:NaBH<sub>4</sub> molar ratio of 1:30.

Saturation of the antibody combining site with compound 1, which possesses a stronger affinity to the antibody 2 than compound 3, abolished the enantiomeric excess. This result indicates that the stereoselective reduction has actually occurred in the antibody combining site.

Use of the active site of proteins as chiral auxiliaries for stereoselective reactions has attracted considerable attention. It was reported that use of pyruvate kinase for the stereoselective reduction by NaBH<sub>4</sub> of pyruvate to lactate in the presence of Mg<sup>2+</sup> as a cofactor resulted in a stereoselective reduction of pyruvate, giving a 19% enantiomeric excess of D-lactic acid.<sup>7</sup> The present method is more general in that the dansyl group may be used as an anchor for other types of stereoselective reactions in the hydrophobic subsite of the same antibody. In addition, it was possible to isolate and identify the reduction product on an HPLC chiral column. The stereoselective reaction reported in the present communication is stoichiometric rather than catalytic in nature. However, detailed analyses of the conformation and the mechanism of stereoselective reactions of hapten side chains will become

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of increasing importance, for example, for the design of catalytic antibodies.<sup>8</sup>

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### Statistical Incorporation of <sup>13</sup>C<sub>2</sub> Units into C<sub>60</sub>

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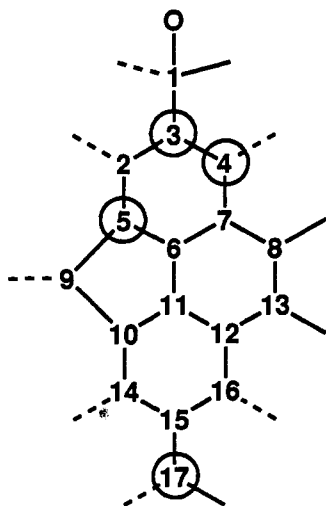
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Partially <sup>13</sup>C enriched C<sub>60</sub> (buckminsterfullerene) can be prepared by the laser<sup>1</sup> or contact-arc<sup>2</sup> vaporization of heterogeneous mixtures of solid <sup>12</sup>C and <sup>13</sup>C. Mass spectral analysis of the partially enriched C<sub>60</sub> suggests that the <sup>13</sup>C is statistically distributed among the clusters.<sup>1,3</sup> Rather than <sup>12</sup>C<sub>60</sub> and <sup>13</sup>C<sub>60</sub> being formed predominately, <sup>13</sup>C<sub>*n*</sub><sup>12</sup>C<sub>(60-*n*)</sub> mixtures form with a distribution consistent with isotopic scrambling via C<sub>*m*</sub> units where *m* is small. While the mass spectrum indicates the isotope distribution between the carbon clusters, it does not address the isotope distribution within the carbon clusters. <sup>13</sup>C NMR can potentially indicate the distribution of <sup>13</sup>C's within a carbon cluster by the degree of <sup>13</sup>C-<sup>13</sup>C coupling.<sup>4,5</sup> The 1D <sup>13</sup>C NMR spectrum of enriched C<sub>70</sub> qualitatively implies carbon atom mixing on an atomic scale during fullerene formation in that the spectrum consists of "predominantly singlets", rather than "predominantly multiplets due to coupling of adjacent <sup>13</sup>C atoms."<sup>5</sup> In this paper, we quantitatively examine the <sup>13</sup>C distribution within enriched C<sub>60</sub>. Buckminsterfullerene cannot be analyzed directly, however, as <sup>13</sup>C<sub>*n*</sub><sup>12</sup>C<sub>(60-*n*)</sub> shows a single <sup>13</sup>C NMR peak<sup>6</sup> and therefore no coupling information. In contrast, osmylated buckminsterfullerene<sup>7</sup> resolves into 17 peaks and the associated couplings.<sup>8</sup> Here, we measure the degree of <sup>13</sup>C-<sup>13</sup>C coupling for four types of carbons in C<sub>60</sub>(OsO<sub>4</sub>)(4-*tert*-butylpyridine)<sub>2</sub>, calculate the expected degrees of <sup>13</sup>C-<sup>13</sup>C coupling for these carbons given a random distribution of <sup>13</sup>C's within the clusters, and find that the two sets of numbers agree within experimental error.

Natural-abundance carbon rods were cored, packed with 99% <sup>13</sup>C powder, and converted to C<sub>60</sub> in a Smalley-type contact arc

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**Figure 1.** Seventeen types of cluster carbons in  $C_{60}(\text{OsO}_4)(4\text{-tert-butylpyridine})_2$ .<sup>8</sup> Dashed lines indicate bonds between symmetry-related carbons. Circles indicate carbon types with integratable satellites.

**Table I.** Experimental and Calculated Ratios of Satellite Integration to Central Peak Integration in  $^{13}\text{C}$ -Enriched  $C_{60}(\text{OsO}_4)(4\text{-tert-butylpyridine})_2$

carbon type	experimental ratio	statistical ratio
3	0.22	0.24
4	0.18	0.16
5	0.22	0.24
17	0.14	0.16

vaporization apparatus.<sup>3</sup> Mass spectral analysis of the  $C_{60}$ -indicated 5.0 mol %  $^{13}\text{C}$ . This material was converted to  $C_{60}(\text{OsO}_4)(4\text{-tert-butylpyridine})_2$ <sup>7</sup> and analyzed by  $^{13}\text{C}$  NMR. Carbon types 3, 4, 5, and 17 in  $C_{60}(\text{OsO}_4)(4\text{-tert-butylpyridine})_2$  are well separated from the other peaks,<sup>8</sup> and the  $^{13}\text{C}$  satellites could be integrated relative to the central peaks (Figure 1, Table I).<sup>9</sup> The observed satellite peaks are composed of doublets, quartets, and one-half of the triplet pattern, while the central peak corresponds to singlets plus one-half of the triplet pattern.

If the  $^{13}\text{C}$ 's are randomly distributed in  $C_{60}$ , the ratio of the satellite integration to the central peak integration is described by eq 1, where  $s_n$ ,  $d_n$ ,  $t_n$ , and  $q_n$  correspond to the singlet, doublet, triplet, and quartet signals per  $^{13}\text{C}_n^{12}\text{C}_{(60-n)}$  molecule, and  $I_n$  corresponds to the intensity of the  $m/z$   $720 + n$  peak in the mass spectrum. Carbon types 3 and 5 each couple with three adjacent nonequivalent carbons, and carbon types 4 and 17 each couple with two adjacent nonequivalent carbons. Assuming random  $^{13}\text{C}$  distributions,  $s_n$ ,  $d_n$ ,  $t_n$ , and  $q_n$  are given by eqs 2-5 for carbon types 3 and 5 and by eqs 6-9 for carbon types 4 and 17 ( $x = 2$  for type 17, and  $x = 4$  for type 4). The satellite to central peak ratios calculated for random  $^{13}\text{C}$  distribution within the carbon clusters using eqs 1-9 and the mass spectrum<sup>10</sup> agree very well with the experimental values (Table I). In contrast, if the  $^{13}\text{C}$ 's were incorporated into  $C_{60}$  as intact  $C_m$  units with  $m \geq 2$ , these ratios would be much larger, approximately 4 for carbon types 3 and 5, and approximately 1.5 for carbon types 4 and 17.

$$\frac{\text{satellite integration}}{\text{central peak integration}} = \frac{\sum_n \left( d_n + \frac{t_n}{2} + q_n \right) I_n}{\sum_n \left( s_n + \frac{t_n}{2} \right) I_n} \quad (1)$$

(9) Since there is no NOE and the acquisition parameters were optimized for the approximately 4 s  $T_1$  of carbon types 2-17, the integration is quite reliable. The ratios of the integrals of carbon types 3, 4, 5, and 17 (including the  $^{13}\text{C}$  satellites) are within 3% of the expected ratios, i.e., 4:4:4:2.

(10) MS:  $m/z$  (intensity) 720 (21 693), 721 (24 094), 722 (20 970), 723 (17 726), 724 (13 672), 725 (10 780), 726 (7205), 727 (5285), 728 (3362), 729 (2137), 730 (1341), 731 (813), 732 (495), 733 (246), 734 (311), 735 (155).

$$s_n(3,5) = \frac{4n}{60} - d_n(3,5) - t_n(3,5) - q_n(3,5) \quad (2)$$

$$d_n(3,5) = \frac{12n}{60} \left( \frac{n-1}{59} \right) \left( 1 - \frac{n-2}{58} \right) \left( 1 - \frac{n-2}{57} \right) \quad (3)$$

$$t_n(3,5) = \frac{12n}{60} \left( \frac{n-1}{59} \right) \left( \frac{n-2}{58} \right) \left( 1 - \frac{n-3}{57} \right) \quad (4)$$

$$q_n(3,5) = \frac{4n}{60} \left( \frac{n-1}{59} \right) \left( \frac{n-2}{58} \right) \left( \frac{n-3}{57} \right) \quad (5)$$

$$s_n(4,17) = \frac{xn}{60} - d_n(4,17) - t_n(4,17) \quad (6)$$

$$d_n(4,17) = \frac{2xn}{60} \left( \frac{n-1}{59} \right) \left( 1 - \frac{n-2}{58} \right) \quad (7)$$

$$t_n(4,17) = \frac{xn}{60} \left( \frac{n-1}{59} \right) \left( \frac{n-2}{58} \right) \quad (8)$$

$$q_n(4,17) = 0 \quad (9)$$

From the examination of mass spectral data, Heath concluded, "The chemical species initially ejected from the graphite rods in the carbon arc are...atoms and possibly dimers."<sup>3</sup> From this study, we conclude that if the initially ejected species are dimers, the carbon atoms of the  $C_2$  units must scramble either before or after condensation into the  $C_{60}$  cluster, as they do not remain connected in the isolated  $C_{60}$ .

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### Potential-Dependent Surface Raman Spectroscopy of Buckminsterfullerene Films on Gold: Vibrational Characteristics of Anionic versus Neutral $C_{60}$

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We report here real-time surface-enhanced Raman (SER) spectra for films of buckminsterfullerene ( $C_{60}$ ) on gold in acetonitrile observed during cyclic voltammetric potential excursions. The results provide the first vibrational spectra for the  $C_{60}$  monoanion; they indicate that reduction induces significant perturbations in the bonding and symmetry characteristics of  $C_{60}$ .

Several Raman and infrared studies have been reported for neutral  $C_{60}$ .<sup>1-3</sup> Most findings are in harmony with the predicted

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