Electrosynthesis and Structural Characterization of Two $(C_6H_5CH_2)_4C_{60}$ Isomers

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Abstract: The structural, spectral, and electrochemical properties of two $(C_6H_5CH_2)_4C_{60}$ isomers are reported. One is designated as the 1,4;1,4-$(C_6H_5CH_2)_4C_{60}$ isomer and the other as the 1,4;1,2-isomer of $(C_6H_5CH_2)_4C_{60}$. The two isomers were isolated by HPLC from the products obtained by a reaction between $[(C_6H_5CH_2)_2C_{60}]^{2-}$ and $C_6H_5CH_2Br$. X-ray data show that the two $(C_6H_5CH_2)_4C_{60}$ isomers differ from one another by the position of only one benzyl group and that, in each compound, the four benzyl addends are in close proximity. Both $(C_6H_5CH_2)_4C_{60}$ isomers undergo three one-electron reductions in PhCN containing 0.1 M tetra-*n*-butylammonium perchlorate (TBAP) and have $E_{1/2}$ values which are more negative than values for either C_{60} or 1,4-$(C_6H_5CH_2)_2C_{60}$. The monoanions of 1,4;1,4- and 1,4;1,2-$(C_6H_5CH_2)_4C_{60}$ were electrogenerated by bulk controlled-potential electrolysis in PhCN containing 0.2 M TBAP and characterized as to their spectral properties in both the visible and near-infrared regions.

Introduction

The regiochemistry of organofullerenes with two 1,2-additions on the C_{60} molecule has been studied in detail and is now well-understood.[1] For example, in the case of methanofullerenes, Hirsch and co-workers[1] have shown that the *e* and *trans*-3 positions[2] are preferential sites of addition when two bulky addends on the C_{60} cage comprise bis-adducts. However, the preferential addition pattern is of the type *cis*-1[2] when there is no steric hindrance between the addends.[1] The major H_4C_{60} product generated by addition of hydrogen to H_2C_{60} has a *cis*-1 pattern.[3] Bergosh et al.[4] have examined the multiple addition of hydrogen to C_{60} and reported that compounds with *e* and *trans*-3 addition patterns were the major reaction products.

In contrast to the well-known regiochemistry for multiple 1,2-adducts of C_{60}, the regiochemistry of R_4C_{60} involving 1,4-addition to the C_{60} cage has not yet been elucidated. Only a few examples of organofullerenes with multiple addends involving a 1,4-addition pattern have been reported.[5−8] Our groups have previously reported the HPLC trace of the crude reaction product generated by mixing the dianion of 1,4-$(C_6H_5CH_2)_2C_{60}$ with benzyl bromide and shown that it consists of several fractions, one of which was characterized as $(C_6H_5CH_2)_4C_{60}$ by both spectroscopic and electrochemical methods.[8] The present paper reports a structural characterization of this compound in addition to the structural, spectral, and electrochemical characterization of a second $(C_6H_5CH_2)_4C_{60}$ isomer. The monoanions of each $(C_6H_5CH_2)_4C_{60}$ isomer were also generated by bulk controlled-potential electrolysis in PhCN containing 0.2 M TBAP, and their visible and near-IR spectra were examined.

Experimental Section

Chemicals. The synthesis of 1,4-$(C_6H_5CH_2)_2C_{60}$ has been reported elsewhere.[8] Electrochemical grade tetra-*n*-butylammonium perchlorate (TBAP), purchased from Fluka, was recrystallized from absolute ethanol and dried under vacuum at 313 K prior to use. Benzonitrile (PhCN) was distilled over P_2O_5 under vacuum at 305 K prior to use. $C_6H_5CH_2Br$ (98%) and tetramethylsilane (TMS) (99.9+%) were purchased from Aldrich and used as received. CS_2, hexanes, toluene, and methanol from EM Science (Gibbstown, NJ) were used without further treatment. CD_2Cl_2 for NMR measurements was purchased from Cambridge Isotope Laboratories (Andover, MA) and used as received.

Instrumentation. ^{1}H NMR spectra were recorded on a Bruker AMX-600 spectrometer in CD_2Cl_2 and referenced to TMS. UV−visible spectra of the neutral $(C_6H_5CH_2)_4C_{60}$ isomers were recorded on a Hewlett-Packard model 8453 diode array spectrophotometer. Near-IR spectra were obtained with both a Hewlett-Packard model 8453 diode array and a Perkin Elmer model 330 spectrophotometer. Cyclic voltammetry (CV) and controlled-potential bulk electrolyses were carried out using

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Table 1. Crystal Data and X-ray Experimental Details

	1,4,10,24-$(C_6H_5CH_2)_4C_{60}$ (1,4;1,4-isomer)	1,2,4,15-$(C_6H_5CH_2)_4C_{60}$ (1,4;1,2-isomer)
empirical formula	$C_{88}H_{28}{\cdot}CS_2{\cdot}{}^1/_2C_6H_{14}$	$C_{88}H_{28}{\cdot}2CS_2$
temp of data collcn, K	223	223
crystal dimens, mm	0.40 × 0.15 × 0.08	0.35 × 0.32 × 0.16
crystal color	brown	brown
space group	$P2_1/c$	$P2_1/c$
a, Å	9.8961(6)	17.4959(9)
b, Å	19.5227(11)	18.2567(9)
c, Å	27.4677(16)	18.5325(10)
β, deg	92.177(1)	113.857(1)
fw	1204.32	1237.36
radiation (λ, Å)	Mo Kα (0.710 73)	Mo Kα (0.710 73)
D_c, g/cm^3	1.508	1.518
no. of measd reflns	21 818	22 220
no. of unique reflns	7674	7822
no. of obsd reflns ($I > 4\sigma(I)$)	3659	4218
type of refinement	F^2	F^2
no. of params in refinement	848	847
$R(F)$	0.0621	0.0634
$R_w(F)$	0.1580	0.1630

an EG&G Princeton Applied Research (PAR) model 263 potentiostat/galvanostat. A conventional three-electrode cell was used for CV measurements and consisted of a glassy carbon working electrode, a platinum counter electrode, and a saturated calomel reference electrode (SCE). The SCE was separated from the bulk of the solution by a fritted-glass bridge of low porosity which contained the solvent/supporting electrolyte mixture. Controlled-potential bulk electrolyses were performed in a glovebox from Vacuum Atmospheres Co. (Hawthorne, CA) using an H-type cell which consisted of two platinum gauze electrodes (working and counter electrodes) separated by a sintered-glass frit. Solutions containing about 2×10^{-4} M of the desired $(C_6H_5CH_2)_4C_{60}$ anionic species were obtained by setting the applied potential at values 150−250 mV more negative than the $E_{1/2}$ of the $[(C_6H_5CH_2)_4C_{60}]^{n-}$/$[(C_6H_5CH_2)_4C_{60}]^{(n+1)-}$ ($n = 0$ or 1) redox couple in the given solvent/supporting electrolyte system. Cyclic voltammetry measurements were carried out in the glovebox immediately after bulk electrolysis to determine the stability of the electrogenerated species on the bulk electrolysis time scale. The electrogenerated anions of $(C_6H_5CH_2)_4C_{60}$ were then transferred from the bulk cell to a 1 cm quartz cuvette, and the cuvette was removed from the glovebox after being capped with a rubber septum and sealed with Parafilm. Near-IR measurements of the electrogenerated anions were made under an N_2 atmosphere.

MALDI (matrix-assisted laser desorption ionization) mass spectra were acquired at the UT-Houston Medical School, using a Perseptive Voyager Elite time-of-flight mass spectrometer equipped with a delayed-extraction apparatus and a nitrogen laser. The sample was dissolved in toluene or carbon disulfide. A saturated solution of 2,5-dihydroxybenzoic acid in 0.1% trifluoroacetic acid was used as a matrix. A solution containing 0.5 μL of matrix and 0.5 μL of sample was placed on the target. The sample was allowed to dry at room temperature and was protected from light.

Purification of $(C_6H_5CH_2)_4C_{60}$ by HPLC was performed using a preparatory Buckyclutcher I column (Regis, Morton Grove, IL) with a 55:45 v/v mixture of hexanes/toluene as the eluent and a flow rate of 8 mL/min. The eluted fractions were monitored by a UV−visible detector set at $\lambda = 365$ nm.

Synthesis of $(C_6H_5CH_2)_4C_{60}$. Figure 1 shows the HPLC trace of the crude product obtained after the reaction between electrogenerated $[1,4\text{-}(C_6H_5CH_2)_2C_{60}]^{2-}$ and $C_6H_5CH_2Br$ in PhCN containing 0.2 M TBAP was allowed to proceed for 60 min. The formation of doubly reduced 1,4-$(C_6H_5CH_2)_2C_{60}$ was obtained at −1.15 V vs SCE as described in the literature.[8] Fractions 7 and 9 in Figure 1 were isolated, purified as described in ref 8, and characterized as the 1,4;1,4- and 1,4;1,2-isomers of $(C_6H_5CH_2)_4C_{60}$, respectively. The synthesis and spectroscopic characterization of fraction 7 have already been reported.[8] Fraction 9 is another product formed during the synthesis of fraction 7, but it was not isolated and characterized in our previous study. The HPLC trace also showed several other peaks, but the products corresponding to these fractions rapidly decomposed after collection in hexanes/toluene and were not characterized further.

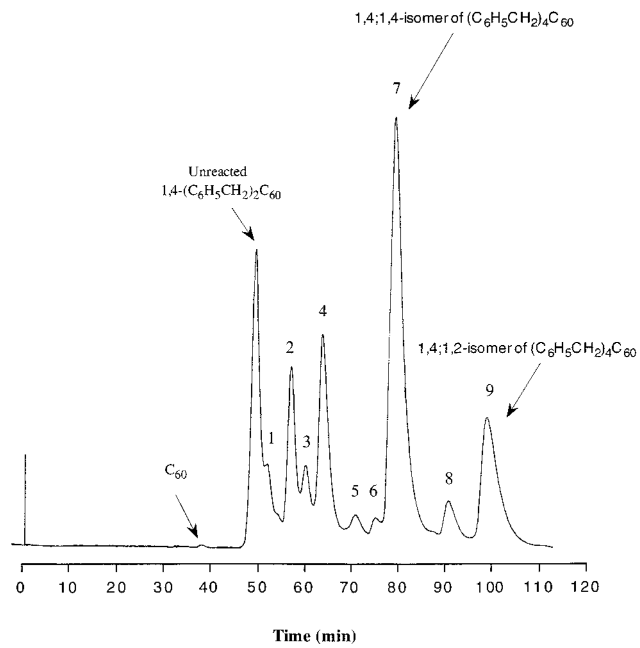

Figure 1. HPLC trace of the $[(C_6H_5CH_2)_2C_{60}]^{2-}/C_6H_5CH_2Br$ reaction product eluted by 55:45 v/v hexanes/toluene using a preparative Buckyclutcher I column at a flow rate of 8 mL/min.

X-ray Single-Crystal Diffraction. Single crystals suitable for X-ray diffraction measurements were obtained by slowly diffusing hexanes into a CS_2 solution of fractions 7 and 9 at −10 °C. All measurements were made with a Siemens SMART platform diffractometer equipped with a 1K CCD area detector. A hemisphere of data (1271 frames at 5 cm detector distance) was collected using a narrow-frame method with scan widths of 0.30° in ω and exposure times of 30 s/frame for crystals of fraction 7 and 40 s/frame for crystals of fraction 9. The first 50 frames were measured again at the end of the data collection to monitor instrument and crystal stability, and the maximum correction on I was <1%. The data were integrated using the Siemens SAINT program with the intensities corrected for Lorentz factor, polarization, air absorption, and absorption due to variation in the path length through the detector faceplate. A ψ-scan absorption correction based on the entire data set was applied. Redundant reflections were averaged. Final cell constants were refined using 6177 reflections having $I > 10\sigma(I)$ for crystals of fraction 7 and 8192 reflections having $I > 10\sigma(I)$ for crystals of fraction 9. These, along with other information pertinent to data collection and refinement, are listed in Table 1. The Laue symmetry was determined to be $2/m$, and from the systematic absences noted, the space group was shown unambiguously to be $P2_1/c$ for both isomers.

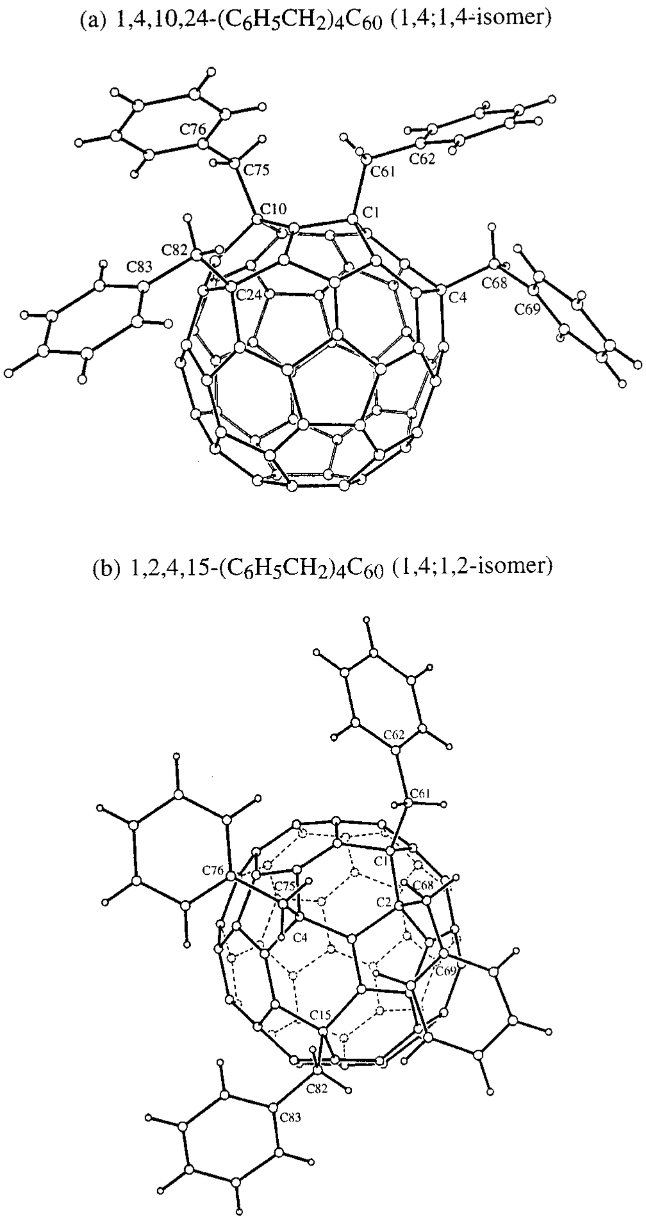

Figure 2. Crystal structures of the $(C_6H_5CH_2)_4C_{60}$ isomers.

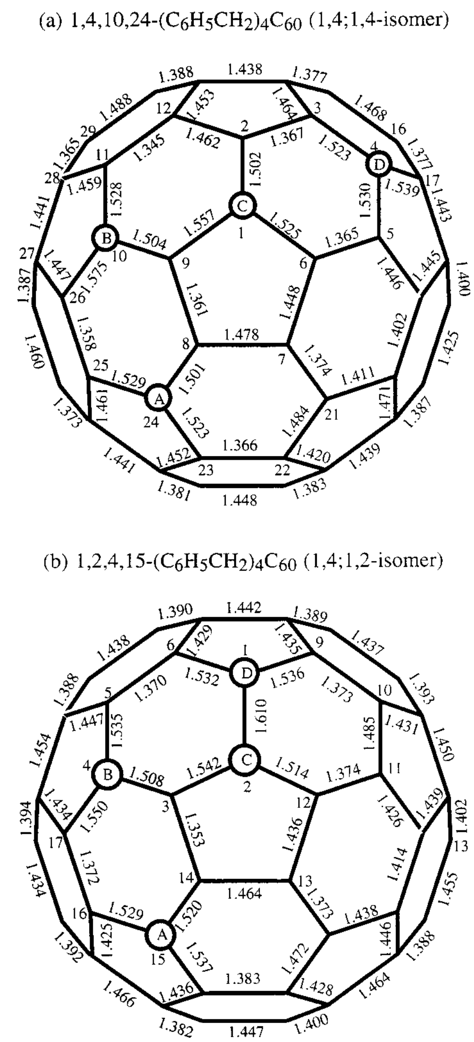

Figure 3. Schematic representations of the $(C_6H_5CH_2)_4C_{60}$ isomers. The positions of addition on the C_{60} molecule are indicated by circles A, B, C, and D. The number next to each C−C bond represents the C−C bond length in angstroms. Selected carbon atoms are labeled using IUPAC numbering.

Both solvent molecules were found to refine best using partial occupancies, but all chemical calculations are based on full occupancy under the assumption that some solvent was lost during handling. The crystals of fraction 7 were composed of a 50:50 mixture of two mirror-image enantiomers which are designated as 1,4,10,24 and 1,4,14,31 in IUPAC terminology.[9] The crystals of fraction 9 were also composed of a 50:50 mixture of two mirror-image enantiomers, which are designated as 1,2,4,15 and 1,3,4,11 using IUPAC terminology.[9] The asymmetric unit was arbitrarily chosen to contain the former configuration, and all atom numbers were adjusted accordingly. Refinement of F^2 were performed against all reflections. The weighted R factor, R_w, and goodness of fit, S, are based on F^2; conventional R factors, R, are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 4\sigma(F^2)$ is used only for calculating R factors etc. and is not relevant to the choice of reflections for refinement. R factors based on F^2 are statistically about twice as large as those based on F, and R factors based on all data are even larger.

Results and Discussion

Structural Characterization. The X-ray crystal structure of the isomers are shown in Figure 2, while schematic representations of the compounds are shown in Figure 3. Each isomer has four benzyl groups on the C_{60} cage, with a 1,4;1,4-addition pattern for one compound (Figure 2a) and a 1,4;1,2-addition pattern for the other (Figure 2b). The positions of the two benzyl groups in the starting compound are labeled as “A” and “B”, while the two added benzyl groups in the products are labeled as “C” and “D” (see Figure 3).

Each compound possesses four benzyl groups in close proximity (see Figure 2), and this result confirms our previous suggestion as to the arrangement of the benzyl groups on the C_{60} molecule which was made on the basis of ^{1}H NMR data.[8] The structures shown in Figure 2 differ in the position of a single benzyl addend which is labeled as “D” in Figure 3. The structural data thus suggest that both isomers could be generated via a common tribenzyl-addended C_{60} intermediate in which the third benzyl group is located at the C position, a result consistent with our mechanism for synthesis of R_4C_{60} from R_2C_{60} proposed previously.[8]

Position C in Figure 3 is located on a six-membered ring adjacent to the six-membered ring which possesses the two benzyl groups of 1,4-$(C_6H_5CH_2)_2C_{60}$; it is also two bonds away from position B.[10] It should be noted that the carbon labeled as “12” in Figure 3a also fits the above description of position C.

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The addition of a benzyl group at this position would yield a different tribenzyl-C_{60} intermediate but would give the same 1,4;1,4-product by a follow-up 1,4-addition at C29. However, a follow-up 1,2-addition at C11 from this proposed intermediate would yield a 1,4;1,2-tetrakis-adduct in which three of the four benzyl groups would be next to each other, i.e., the ones at C10, C11, and C12. Also, two of the three benzyl groups in this tetrakis-adduct would have a 5,6-closed addition pattern, that is, the ones at C10 and C11. Both factors should make this type of 1,4;1,2-tetrakis-adduct of C_{60} very unstable.[11−13] However, such a compound might still be formed during the reaction and may be one of the seven unidentified fractions in the HPLC trace of Figure 2. In summary, two different pathways can, in principle, yield the 1,4;1,4-isomer shown in Figure 2a but the 1,4;1,2-isomer in Figure 2b can be obtained by only a single reaction pathway.

On the basis of theoretical calculations, Cahill and co-workers proposed that 1,2,4,15-H_4C_{60} should be the second most stable isomer of H_4C_{60}.[12] However, to our knowledge, no organofullerene with this type of addition pattern has ever been reported in the literature and the 1,4;1,2-isomer characterized in the present work is therefore the first example of an organofullerene with this type of configuration. Noteworthy is the fact that the benzyl groups, which are bulky addends as compared to hydrogen, should not favor a configuration in which a 1,2-addition is involved.[8] In fact, the 1,4;1,2-isomer shows an average distance of only 2.15 Å between the two pairs of face-to-face methylene protons of the benzyl groups at the 1,2-positions (on C61 and C68 in Figure 2b) and this distance is much shorter than the sum of the van der Waals radii of two free hydrogen atoms (2.4 Å).[14] This result suggests that there is a large steric hindrance between these two benzyl groups, but any instability resulting from this steric hindrance would likely be compensated for by the electronic structure brought about by this addition pattern.[3]

The average bond length is 1.538 Å between the sp^3 and sp^2 carbons for the 5,6-bond involving three 1,4-additions. This value is larger than the average 1.510 Å for bond lengths between the sp^3 and sp^2 carbons of the 6,6-bond. The above 5,6-bonds are noticeably longer than those for the 1,2-adducts of C_{60} (1.49 Å).[15] The average sp^2-sp^2 6,6-bond length within the addended six-membered rings is 1.365 Å, a value almost identical to the 1.360 Å for the sp^2-sp^2 5,6-bonds within the addended six-membered ring.

The distance between the two sp^3 carbons (C1−C2) in Figure 3b is 1.610 Å, and this value is identical to the reported distance between the two bridged carbon atoms of methanofullerenes.[15] Also, the average bond length is 1.531 Å between the four sp^3 and sp^2 carbons involving 1,2-addition, i.e., C1−C6, C1−C9, C2−C3, and C2−C12, a value which is larger than the 1.49 Å reported for the same type of carbon−carbon bonds in methanofullerenes.[15] The average bond length is 1.372 Å for the three sp^2-sp^2 6,6-bonds within the six-membered rings which contain addends involving the 1,2-addition, i.e., C5−C6, C9−C10, and C11−C12, and this is in good agreement with a value of 1.39 Å reported for the same type of bonds in 1,2-adducts of C_{60}.[15]

Table 2. Selected Bond Angles and Deviations from Ideal Bond Values for a Tetrahedral Geometry

1,4;1,4-isomer[a]			1,4;1,2-isomer[a]		
atoms	angle, deg	δ,[b] deg	atoms	angle, deg	δ,[b] deg
C2−C1−C6	107.9(4)	−1.6	C2−C1−C6	112.4(4)	2.9
C2−C1−C9	110.2(5)	0.7	C2−C1−C9	112.7(4)	3.2
C6−C1−C9	101.4(4)	−8.1	C6−C1−C9	99.2(4)	−10.3
C3−C4−C5	107.5(4)	−2.0	C1−C2−C3	113.8(4)	4.3
C3−C4−C17	108.9(5)	−0.6	C1−C2−C12	114.5(4)	5.0
C5−C4−C17	100.8(4)	−8.7	C3−C20−C12	100.2(4)	−9.3
C9−C10−C11	109.6(5)	0.1	C3−C4−C5	108.0(4)	−1.5
C9−C10−C26	108.1(5)	−1.4	C3−C4−C17	107.2(4)	−2.3
C11−C10−C26	100.7(5)	−8.8	C5−C4−C17	99.8(4)	−9.7
C8−C24−C23	109.6(5)	0.1	C14−C15−C16	107.1(4)	−2.4
C8−C24−C25	107.4(5)	−2.1	C14−C15−C32	108.6(4)	−0.9
C23−C24−C25	101.9(5)	−7.6	C16−C15−C32	100.5(5)	−9.0
C62−C61−C1	115.4(5)	5.9	C62−C61−C1	116.1(5)	6.6
C69−C68−C4	112.6(5)	3.1	C69−C68−C2	115.7(4)	6.2
C76−C75−C10	114.9(5)	5.4	C76−C75−C4	113.5(4)	4.0
C83−C82−C24	112.1(5)	2.6	C83−C82−C15	111.5(5)	2.0

[a] See Table 1 for the complete formulas. [b] δ is the difference between the observed bond angles and the ideal bond value (109.5°) for a tetrahedral geometry.

Noteworthy, the distance between C11 and C12 in Figure 3a (1.345 Å) compares well with the shortest bond length (1.350 Å) reported for organofullerenes where only carbon−carbon bonds are formed upon addition of adducts to the C_{60} cage.[6] Finally, all of the bond lengths and bond angles involving carbons located far from the addition sites are within the range of values reported for C_{60}.[16]

Table 2 summarizes the carbon−carbon bond angles centered at each sp^3 carbon on the C_{60} cage and each methylene carbon for the two isomers of $(C_6H_5CH_2)_4C_{60}$. The bond angles centered at the sp^3 carbons of C_{60} for 1,4-addition are closer to the ideal value (109.5°) for a tetrahedral geometry than those for 1,2-addition, thus indicating that the 1,4-addition has a greater effect in relaxing the strain of the C_{60} cage than does the 1,2-addition. Table 2 also shows that the bond angles centered at the methylene carbons deviate significantly from the ideal value for tetrahedral geometry. Most importantly, the larger the deviation of the bond angle (δ) from 109.5°, the greater the strain of the benzyl groups. The bond angles which have the largest δ values in the 1,4;1,4-isomer are those centered at C61 and C75, while the bond angles with the largest δ values in the 1,4;1,2-isomer are those centered at C61 and C68 (see Table 2). The data thus imply that the benzyl groups attached at the C1 and C10 atoms (1,4;1,4-isomer) and at the C1 and C2 atoms (1,4;1,2-isomer) (see Figure 2) are more strained than the other benzyl groups, a result which is consistent with their close proximity.

Mass Spectra. Figure 4 shows mass spectra of the two isomers, while Table 3 lists the m/z values for the observed fragments and adducts. Both isomers show a protonated molecular ion at $m/z = 1085$, but the relative intensity of this peak is much smaller for the 1,4;1,2-isomer.

The 1,4;1,2-isomer of $(C_6H_5CH_2)_4C_{60}$ reacts with oxygen from the matrix, as evidenced by the presence of peaks at m/z = 736, 752, and 768 in Figure 4b. They are assigned to oxygen adducts of C_{60}, i.e., $(O)_nC_{60}$ where n = 1, 2, or 3. Al-Matar et

(10) The discussion applies only to one of the enantiomers, i.e., 1,4,-10,24 for the 1,4;1,4-isomer and 1,2,4,15 for the 1,4;1,2-isomer. For the other enantiomer, the position of the third benzyl group should be at the mirror-image position of "C" shown in Figure 3.

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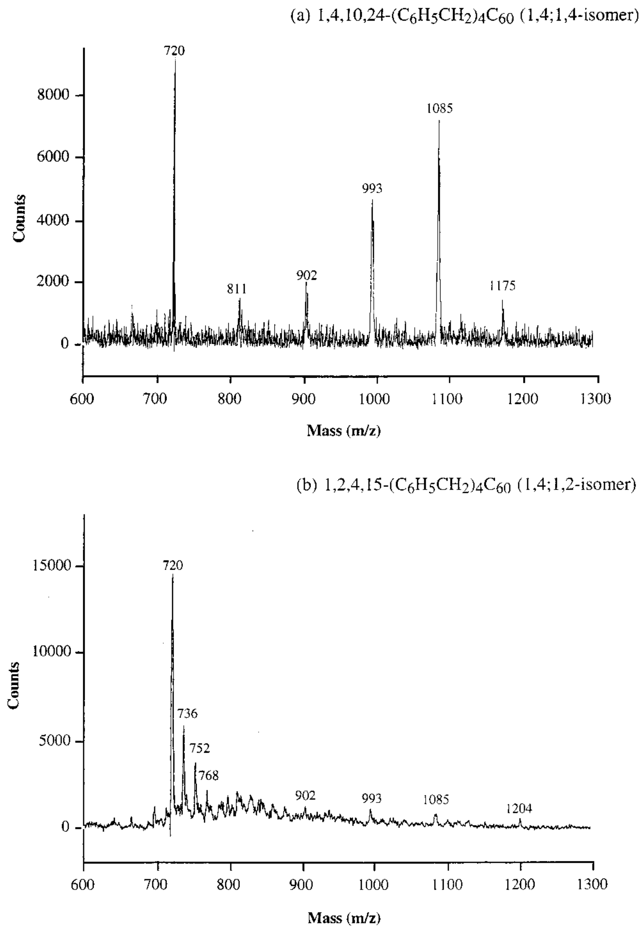

Figure 4. MALDI mass spectra of the $(C_6H_5CH_2)_4C_{60}$ isomers.

Table 3. Theoretical *m/z* Values for Fragment Ions and Gas-Phase Adducts of $(C_6H_5CH_2)_4C_{60}$

species	*m/z*
$[(C_6H_5CH_2)_4C_{60} - 4C_6H_5CH_2]^+$	720
$[(C_6H_5CH_2)_4C_{60} - 4C_6H_5CH_2 + O]^+$	736
$[(CH_5CH_2)_4C_{60} - 4C_6H_5CH_2 + 2O]^+$	752
$[(C_6H_5CH_2)_4C_{60} - 4C_6H_5CH_2 + 3O]^+$	768
$[(C_6H_5CH_2)_4C_{60} - 3C_6H_5CH_2]^+$	811
$[(C_6H_5CH_2)_4C_{60} - 2C_6H_5CH_2]^+$	902
$[(C_6H_5CH_2)_4C_{60} - C_6H_5CH_2]^+$	993
$[(C_6H_5CH_2)_4C_{60} + H]^+$	1085
$[(C_6H_5CH_2)_4C_{60} + C_6H_5CH_2]^+$	1175
$[(C_6H_5CH_2)_4C_{60} + C_6H_3COOH]^+$	1204

al.[17] have reported that $(CH_3)_2C_{60}$ can also yield several oxygen adducts under ambient conditions, but the reactions we have observed occur only in the gas phase. The small peak at $m/z = 1204$ in Figure 4b is due to formation of $[(C_6H_5CH_2)_4C_{60} + C_6H_3COOH]^+$ where $C_6H_3COOH^+$ comes from the matrix of 2,5-dihydroxybenzoic acid.

^{1}H NMR Spectra. ^{1}H NMR spectroscopy is an effective method to characterize organofullerenes. The addended C_{60} carbon atoms become chiral centers when there is no symmetry along the sp^3 carbons of R_2C_{60} or R_4C_{60}.[8a] The methylene protons are thus diastereotopic and exhibit an AB quartet.[18,19] Therefore, the molecule must possess a C_1 symmetry and have four benzyl groups covalently bonded to C_{60} when four AB quartets are seen in the ^{1}H NMR spectrum of $(C_6H_5CH_2)_4C_{60}$. This is the case for both $(C_6H_5CH_2)_4C_{60}$ isomers, as seen in Table 4 and Figure 5, the latter of which illustrates ^{1}H NMR spectra recorded in CD_2Cl_2.

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Table 4. ^{1}H NMR Data for the Two Isomers in CD_2Cl_2

AB quartet[a]	chem shift, ppm H_a	chem shift, ppm H_b	coupling const, Hz J_1	coupling const, Hz J_2	$\Delta\delta$,[b] Hz
		1,4;1,4-Isomer			
I (aa)	2.69	2.62	13.2	13.2	38.9
II (bb)	3.39	3.31	13.2	13.2	42.4
III (cc)	3.80	3.42	13.2	13.2	229.1
IV (dd)	4.03	3.85	13.2	13.2	107.9
		1,4;1,2-isomer			
I (aa)	3.47	3.65	13.3	13.3	108.8
II (bb)	4.40	4.65	12.8	12.2	152.9
III (cc)	4.47	4.51	12.2	12.8	26.4
IV (dd)	4.55	4.57	12.8	12.2	6.4

[a] See Figure 5 and text for the assignments of aa, bb, cc, and dd. [b] $\Delta\delta$ is the separation between the two centers of two doublets for an AB quartet.

The 1,4;1,4-isomer (Figure 5a) displays four AB quartets (labeled as aa, bb, cc, and dd) centered at 2.66, 3.35, 3.61, and 3.94 ppm, which are assigned to diastereotopic methylene protons. The average coupling constant for the methylene protons is 13.2 Hz (see Table 4), and this value falls in the range for geminal protons.[20] Resonances due to phenyl groups are also seen between 7.12 and 7.65 ppm but are not shown in the figure.

The methylene protons of the 1,4;1,2-isomer (Figure 5b) give four sets of AB quartets also labeled as aa, bb, cc, and dd (overlapped), thus confirming that this organofullerene also has C_1 symmetry. The average ^{1}H−^{1}H coupling constant for the methylene protons is 12.7 Hz (see Table 4), a value similar to values found for methylene protons of the 1,4;1,4-isomer. The 1,4;1,2-isomer shows a large separation between the doublets of two AB quartets (aa and bb in Figure 5b), and a similar pattern is observed for the other two AB quartets of the 1,4;1,4-isomer (cc and dd in Figure 5a). This result suggests that, for each isomer, two phenyl groups have a larger steric interaction than the other two,[21] and this agrees with the X-ray data discussed above. The 1,4;1,2-isomer also exhibits phenyl resonances between 7.15 and 7.70 ppm which are not shown in Figure 5.

UV−Visible Spectra. Figure 6 shows the UV−visible spectra of the $(C_6H_5CH_2)_4C_{60}$ isomers in hexanes. The spectrum of the 1,4;1,4-isomer lacks the 455 nm band seen for 1,4-$(C_6H_5CH_2)_2C_{60}$,[8a] while the spectrum of the 1,4;1,2-isomer lacks the characteristic 432 nm band for 1,2-adducts of C_{60}.[22] The UV−visible spectra of 1,4-$(C_6H_5CH_2)_2C_{60}$ and C_{60} both show a strong absorption band at 210 nm[8a,23] but a shoulder at this wavelength is seen in the UV−visible spectra of the two $(C_6H_5CH_2)_4C_{60}$ isomers. Finally, it should be noted that the 1,4;1,4- and 1,4;1,2-isomers exhibit well-defined absorption bands at 248 and 250 nm, respectively. These bands are blue-shifted with respect to the 256 and 257 nm absorption bands of 1,4-$(C_6H_5CH_2)_2C_{60}$[8a] and C_{60}.[23]

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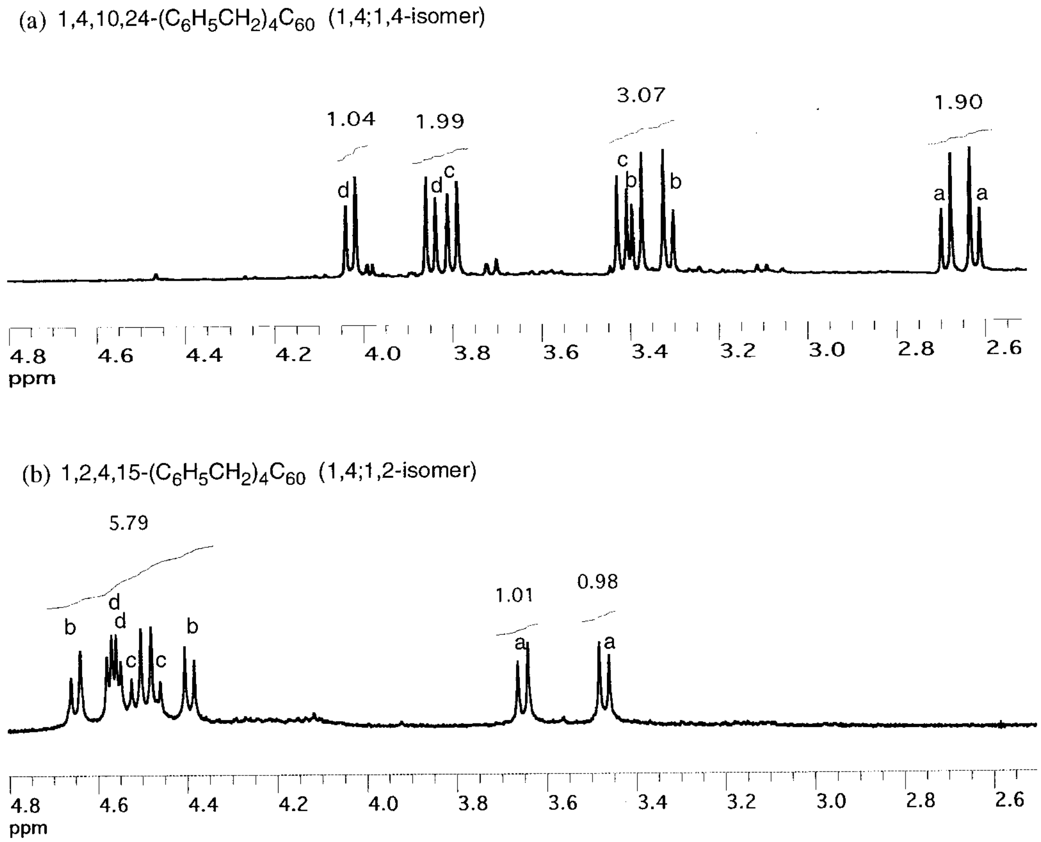

Figure 5. [1]H NMR spectra of the ($C_6H_5CH_2$)$_4$$C_{60}$ isomers in CD_2Cl_2.

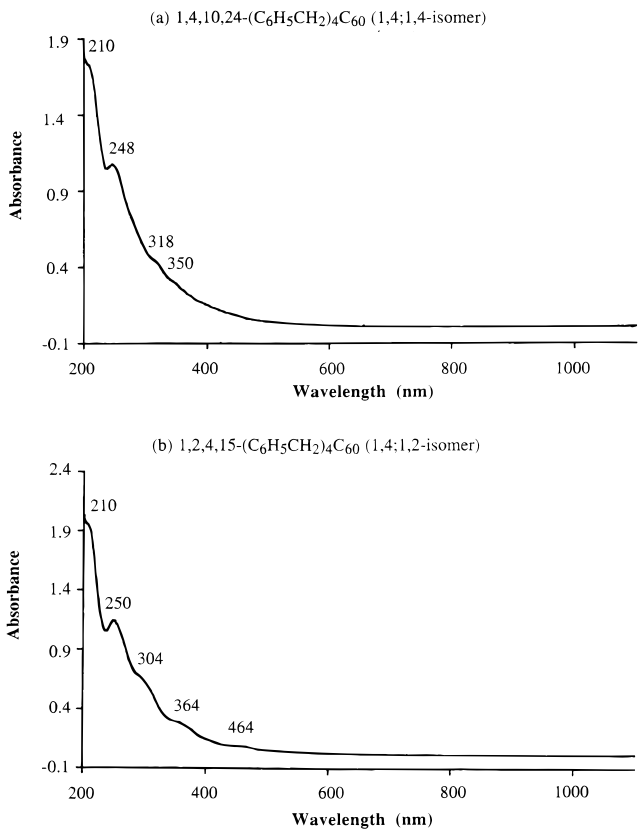

Figure 6. UV−visible spectra of the ($C_6H_5CH_2$)$_4$$C_{60}$ isomers in hexanes.

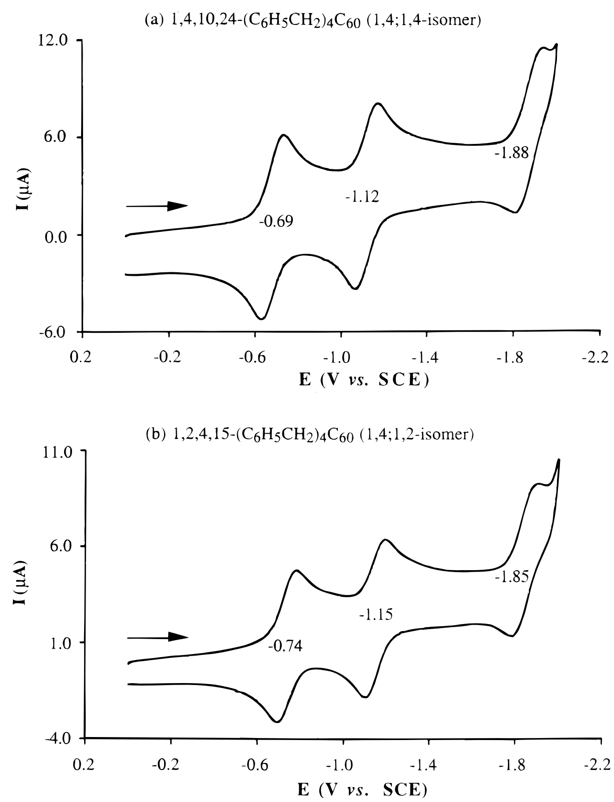

Figure 7. Cyclic voltammograms of the ($C_6H_5CH_2$)$_4$$C_{60}$ in PhCN containing 0.2 M TBAP.

Electrochemistry. Cyclic voltammograms of the two ($C_6H_5CH_2$)$_4$$C_{60}$ isomers in PhCN containing 0.1 M TBAP are illustrated in Figure 7, and Table 5 summarizes the redox potentials of the two compounds along with those of C_{60} and 1,4-($C_6H_5CH_2$)$_2$$C_{60}$. Both isomers of ($C_6H_5CH_2$)$_4$$C_{60}$ undergo three reversible one-electron reductions within the potential range of the solvent, but $E_{1/2}$ of each reduction varies with the

Table 5. $E_{1/2}$ Values for Reduction of C_{60} and Its Benzyl-Addended Derivatives in PhCN Containing 0.1 M TBAP

compd	$E_{1/2}$ (V *vs.* SCE) 1st	2nd	3rd	Fc^+/Fc	Δ_{1-2},[a] V	Δ_{2-3},[b] V
C_{60}	−0.41	−0.84	−1.33	0.50	0.43	0.49
1,4-$(C_6H_5CH_2)_2C_{60}$	−0.52	−0.97	−1.49	0.50	0.45	0.52
1,4,10,24-$(C_6H_5CH_2)_4C_{60}$	−0.69	−1.12	−1.88	0.50	0.43	0.76
1,2,4,15-$(C_6H_5CH_2)_4C_{60}$	−0.74	−1.15	−1.85	0.50	0.41	0.70

[a] Δ_{1-2} is the potential difference between the first and second reductions. [b] Δ_{2-3} is the potential difference between the second and third reductions.

position of the addends on the C_{60} cage. This contrasts with results from previous studies of methanofullerenes with bis-addends where the $E_{1/2}$ values were shown to be independent of the positions of addends.[24] For instance, the first reduction of the 1,4;1,4-isomer of $(C_6H_5CH_2)_4C_{60}$ is easier than the first reduction of the 1,4;1,2-isomer but an opposite trend is observed for the third reduction (see Figure 7).

Table 5 also lists the potential differences between two successive reductions of the isomers, given as Δ_{1-2} and Δ_{2-3}. All of the compounds have virtually the same Δ_{1-2}, but Δ_{2-3} varies from 0.49 V for C_{60} to 0.76 V for the 1,4;1,4-isomer (1,4,10,24-$(C_6H_5CH_2)_4C_{60}$) and is 0.70 V for the 1,4;1,2-isomer (1,2,4,15-$(C_6H_5CH_2)_4C_{60}$). This result can be explained by a splitting of the degenerate t_{1u} orbitals of C_{60} due to a decrease in symmetry upon going from C_{60} with I_h symmetry to the tetrakis-adducts which have C_1 symmetry.[8a]

Electrochemical data are available in the literature for multiadducts of methanofullerenes.[24] It is noteworthy to point out that $E_{1/2}$ for the first reduction of the 1,4;1,4-isomer is within the range of values seen for bis-adducts of methanofullerenes, while $E_{1/2}$ for the first reduction of the 1,4;1,2-isomer falls within the range of values observed for tris-adducts and tetrakis-adducts.[24a,c]

A facile and reversible oxidation process is observed for bis-adducts of methanofullerenes,[24c] but this process is not seen in the case of the two $(C_6H_5CH_2)_4C_{60}$ isomers.

Visible and Near-IR Spectra of Singly Reduced Species. Figure 8 illustrates visible and near-IR spectra of the two singly reduced isomers, while Table 6 summarizes the visible and near-IR absorption spectral data for the monoanions of the two isomers along with those for $C_{60}^{\bullet-}$ and $[1,4\text{-}(C_6H_5CH_2)_2C_{60}]^{\bullet-}$. Unlike the 1,4;1,4-isomer, which is stable as both a monoanion and a dianion,[8a] only the monoanionic form of the 1,4;1,2-isomer could be spectrally characterized, since the dianion of this compound decomposed during bulk electrolysis in PhCN containing 0.2 M TBAP. As shown in Figure 8 and Table 6, the monoanion of the 1,4;1,4-isomer possesses absorptions at both 801 and 1374 nm, and this result contrasts with the case of the monoanion of the 1,4;1,2-isomer, which exhibits only a single absorption band at 1084 nm (Figure 8b). The 1084 nm absorption band has a molar absorptivity which is larger than that of either absorption band of the 1,4;1,4-isomer (see Table 6). This result can be rationalized by the number of absorption bands in the spectra of the two isomers, i.e., two bands for the 1,4;1,4-isomer and only one band for the 1,4;1,2-isomer. Guldi et al.[25] have reported that monoanions of bis- and tris-adducts of C_{60} exhibit absorption bands which are all blue-shifted with respect to the bands of C_{60}[26] and could be accounted for by destruction of the π system in the C_{60} adducts. The present work

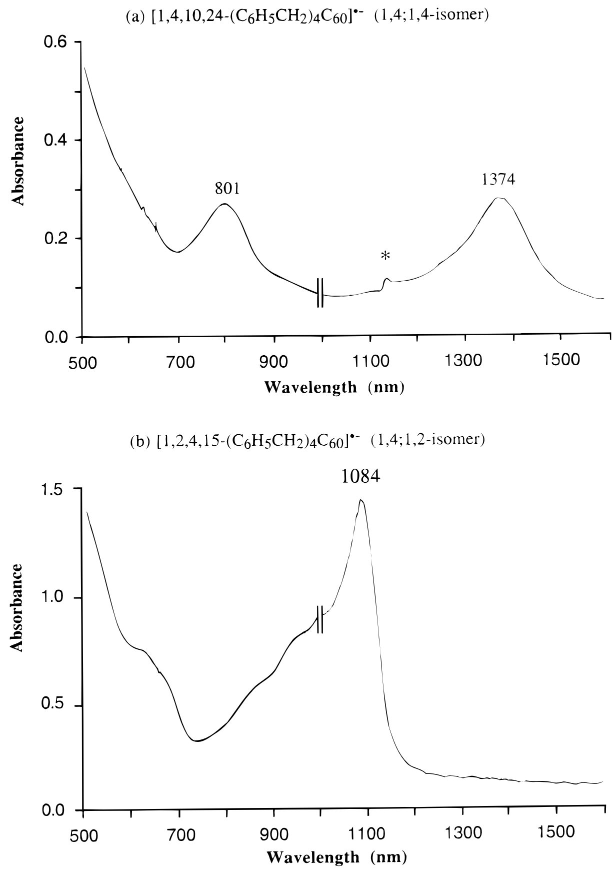

Figure 8. Visible and near-IR spectra for the monoanions of (a) the 1,4;1,4-isomer (1.6×10^{-4} M) and (b) the 1,4;1,2-isomer (4.5×10^{-4} M) in PhCN containing 0.2 M TBAP. The spectra from 500 to 1000 nm were recorded on an HP 8453 diode array spectrophotometer, while absorptions from 1000 to 1600 nm were measured with a Perkin-Elmer 330 UV−visible−near-IR spectrophotometer. The peak marked with an asterisk is due to an artifact caused by the instrument.

Table 6. Spectral Data for Monoanions of C_{60}, $(C_6H_5CH_2)_2C_{60}$, and $(C_6H_5CH_2)_4C_{60}$ in PhCN Containing 0.2 M TBAP

species	λ_{max}, nm (ϵ,[a] M^{-1} cm^{-1})
$C_{60}^{\bullet-}$	1078 (12 000)[b]
$[1,4\text{-}(C_6H_5CH_2)_2C_{60}]^{\bullet-}$	1498 (1500)[c] 989 (1900)[c]
$[1,4,10,24\text{-}(C_6H_5CH_2)_4C_{60}]^{\bullet-}$	1374 (1700) 801 (1300)
$[1,2,4,15\text{-}(C_6H_5CH_2)_4C_{60}]^{\bullet-}$	1084 (3100)

[a] The average uncertainty in ϵ measurements is ca. 20%. [b] Value taken from ref 26. [c] Value taken from ref 8a.

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does not support such a proposal, since the monoanionic forms of the two isomers of $(C_6H_5CH_2)_4C_{60}$ both exhibit absorption bands which are red-shifted with respect to the bands of $C_{60}^{\bullet -}$.[26]

Conclusions

In summary, we have shown that two stable isomers of $(C_6H_5\text{-}CH_2)_4C_{60}$ can be isolated from a mixture of products obtained by a reaction between $C_6H_5CH_2Br$ and $[1,4\text{-}(C_6H_5CH_2)_2C_{60}]^{2-}$. The structural data reveal that one of the products is a 1,4;1,4-isomer and the other a 1,4;1,2-isomer. The two isomers have three benzyl groups at identical positions. The regiochemistry of the two isomers can be rationalized by the initial formation of a $[(C_6H_5CH_2)_3C_{60}]^-$ intermediate followed by either a 1,4- or 1,2-addition relative to the third benzyl group. The two isomers differ in their $E_{1/2}$ values, and the magnitude of the negative potential shift upon going from C_{60} to R_4C_{60} is not proportional to the number of cleaved π bonds. The monoanions of the two isomers of $(C_6H_5CH_2)_4C_{60}$ were electrochemically generated and were shown to display different visible and near-IR spectra.

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Supporting Information Available: Tables of atomic coordinates, equivalent isotropic displacement parameters, and bond lengths and angles, figures showing labeled schematic diagrams and packings in the unit cells, and X-ray crystallographic files, in CIF format, for 1,4,10,24-$(C_6H_5CH_2)_4C_{60}$ and 1,2,4,15-$(C_6H_5CH_2)_4C_{60}$ (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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