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Effect of Addition Pattern on the Electrochemical and Spectroscopic Properties of Neutral and Reduced 1,2- and 1,4-$(C_6H_5CH_2)_2C_{60}$ Isomers

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The spectral and electrochemical properties of isomeric 1,2- and 1,4-adducts of fullerenes of the type R_2C_{60} have been examined in their neutral, singly and/or doubly reduced forms. The first reduction potentials of 1,2- and 1,4-$(C_6H_5CH_2)_2C_{60}$ in PhCN containing 0.1 M TBAP are the same within experimental error but the second and third reductions of the two isomers differ by 50 mV, with the 1,2-isomer being easier to reduce. Much larger differences, however, are seen in the near-IR spectra of the singly and doubly reduced organofullerene isomers. The monoanion of 1,2-R_2C_{60} possesses an absorption band at about 1000 nm, while the dianion has a band at around 900 nm. The 1,4-R_2C_{60} derivatives also show bands at similar wavelengths in their monoanionic and dianionic forms, but there is a second near-IR band at 1500 (monoanion) or 1300 nm (dianion).

Introduction

The addition of two identical groups onto a C_{60} molecule will most often generate two different types of isomers.[1,2] One isomer is a 1,2-adduct which is obtained if the addition occurs between two hexagons (Figure 1a), while the other is a 1,4-adduct that is formed when the addition occurs across a six-membered ring (Figure 1b). Organofullerenes obtained by 1,2-addition retain the electronic structure of C_{60}, i.e., all the double bonds are located within the six-membered rings, but this is not the case for the 1,4-adducts of C_{60} which possess one double bond in a pentagon (see b_{5-6} in Figure 1b).

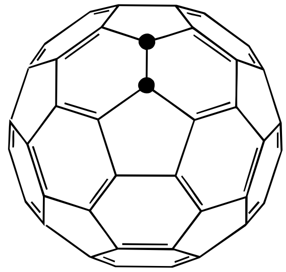
The introduction of a double bond into a pentagon of the 1,4-adduct of C_{60} increases the energy of the C_{60} cage by about 8 kcal/mol compared with the case of the 1,2-adduct.[3,4] However, this unfavorable energy increase would be compensated for by a decrease in steric hindrance when bulky groups are added to the cage and located in the 1,4-position. Thus, 1,4-adducts are the dominant products when bulky groups are added to C_{60}.[5−7]

It has been shown that the 1,2- and 1,4-adducts of C_{60} are characterized by two different types of absorption spectra. The 1,2-adducts display a weak spike around 432 nm[8] while the 1,4-adducts exhibit a broad absorption band at about 445 nm,[5b,6,7] although the origin for these absorptions is not clear.

To our knowledge, there are no reports in the literature on isolation of a C_{60} derivative involving a 1,2-addition of two bulky groups. As part of our efforts to prepare organofullerenes by electrosynthesis,[5] we have synthesized, isolated, and characterized 1,2-$(C_6H_5CH_2)_2C_{60}$, which is described in the present paper. This is the first example of a 1,2-adduct of C_{60} which has two bulky groups close to each other.

Electrochemistry[5,9−24] and spectroelectrochemistry[5,25−36] have been used to characterize fullerenes as well as organofullerenes.

(a) 1,2-R_2C_{60}



(b) 1,4-R_2C_{60}

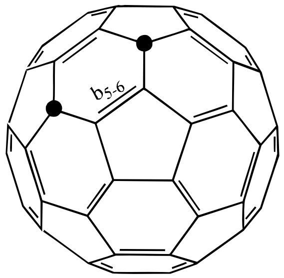


Figure 1. Schematic illustration of (a) 1,2-R_2C_{60} and (b) 1,4-R_2C_{60}.

The derivatives of C_{60} may have electrochemical properties similar to those of C_{60} but the former compounds are generally less electron deficient than the latter due to the loss of one or more double bonds in the electronic structure of the organofullerene. This is evident from reduction potentials which, in the case of most organofullerenes, are shifted cathodically compared to $E_{1/2}$ values for C_{60}.[14−24] Although it is known that both 1,2- and 1,4-adducts of C_{60} can be isolated in a stable form, there have been few reports in the literature on how the two isomers will differ in their electrochemical and spectroscopic

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properties.[1,15] This point is examined in the present paper, which compares the electrochemical and spectroscopic (UV−vis, near-IR, and NMR) properties of 1,2- and 1,4-$(C_6H_5CH_2)_2C_{60}$ in their neutral, singly reduced, and doubly reduced forms.

Experimental Section

Chemicals. The electrosynthesis of 1,4-$(C_6H_5CH_2)_2C_{60}$ and 1,4-$C_6H_5CH_2(t\text{-Bu})C_{60}$ has been described in the literature.[5b,c] 1,2-$(C_6H_5CH_2)_2C_{60}$ was generated as an additional product in the synthesis of 1,4-$(C_6H_5CH_2)_2C_{60}$,[5b] but it has not previously been isolated and characterized. Electrochemical grade tetra-*n*-butylammonium perchlorate (TBAP), purchased from Fluka, was recrystallized from absolute ethanol and dried in a 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. ^1H NMR spectra were recorded on either a GE QE 300-MHz or a Bruker AMX 600-MHz spectrometer in CD_2Cl_2 or $CS_2/CDCl_3$ and referenced to TMS. ^{13}C NMR spectra were recorded on either a GE QE 75-MHz or a Bruker AMX 150-MHz spectrometer in $CS_2/CDCl_3$ and referenced to the solvent. UV−visible spectra of neutral $(C_6H_5CH_2)_2C_{60}$ were recorded on a Hewlett-Packard model 8453 diode array spectrophotometer. UV−visible and near-IR spectra for the anionic species of the 1,2-$(C_6H_5CH_2)_2C_{60}$ and 1,4-$(C_6H_5CH_2)_2C_{60}$ from 500 to 1100 nm were obtained with a Hewlett-Packard model 8453 diode array spectrophotometer while spectra from 900 to 1600 nm were obtained with a Perkin-Elmer model 330 spectrophotometer. Cyclic voltammetry (CV) and controlled-potential bulk electrolyses were carried out on 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 Atmosphere Co. 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 monoanion and dianion of 1,2-$(C_6H_5CH_2)_2C_{60}$ and 1,4-$(C_6H_5CH_2)_2C_{60}$ were obtained by setting the applied potential at values 150 to 250 mV more negative than $E_{1/2}$ of the $[(C_6H_5CH_2)_2C_{60}]^{(n+1)-}/(C_6H_5CH_2)_2C_{60}{}^{n-}$ ($n = 0$ or 1) redox couple in PhCN containing 0.2 M TBAP. Cyclic voltammetric measurements were carried out in the glovebox immediately after bulk electrolysis. The electrogenerated monoanion and dianion of $(C_6H_5CH_2)_2C_{60}$ 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 compounds were carried out under an N_2 atmosphere.

Purification of the 1,2- and 1,4-$(C_6H_5CH_2)_2C_{60}$ isomers was achieved by HPLC using an analytical "Buckyclutcher I" column (Regis, Morton Grove, IL) with a 3:1 v/v mixture of hexanes/toluene as eluent and a flow rate of 3.6 mL/min. The eluted fractions were monitored by a UV−visible detector set at $\lambda = 365$ nm.

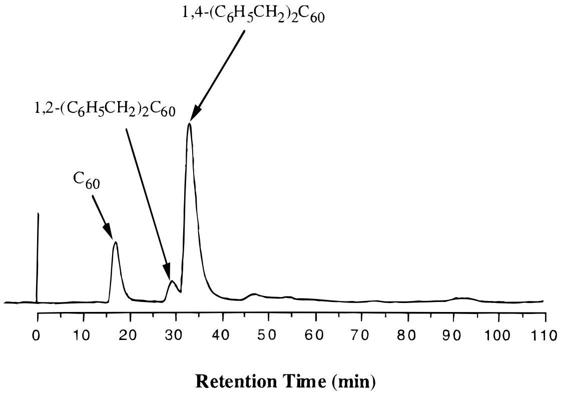


Figure 2. HPLC trace of the crude reaction products formed between $C_{60}{}^{2-}$ and $C_6H_5CH_2Br$. The compound was eluted by a 3:1 v/v hexanes/toluene mixture with an analytical Buckyclutcher I column at a flow rate of 3.6 mL/min.

Both negative and positive 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 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.

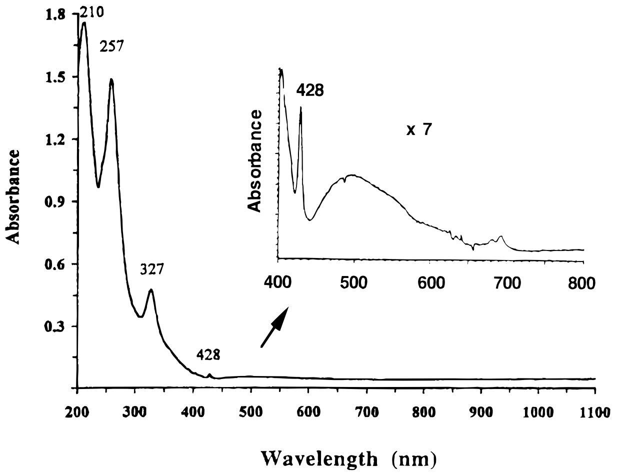
1,2-$(C_6H_5CH_2)_2C_{60}$: ^{13}C NMR ($CDCl_3/CS_2$, 295 K, 150 Hz) $\delta = 149.9$ (2 C), 147.8 (2 C), 145.9 (2 C), 145.8 (2 C), 145.5 (2 C), 145.4 (4 C), 145.4 (2 C), 145.1 (1 C), 145.0 (4 C), 144.9 (1 C), 144.7 (2 C), 144.5 (2 C), 144.1 (2 C), 144.0 (2 C), 143.4 (2 C), 143.3 (6 C), 143.3 (2 C), 143.0 (2 C), 142.6 (2 C), 142.5 (2 C), 142.4 (2 C), 141.4 (2 C), 141.2 (2 C), 138.8 (2 C), 136.8 (2 C), 133.3 (2 C), 131.5 (4 C, Ph), 129.1 (4 C, Ph), 128.8 (2 C, Ph), 75.5 (2 C), 43.8 (2 C, CH_2). Negative MALDI MS: 811 $(M - C_6H_5CH_2)^-$, 720 $(M - 2C_6H_5CH_2)^-$. Positive MALDI MS: 811 $(M - C_6H_5CH_2)^+$, 720 $(M - 2C_6H_5CH_2)^+$.

1,4-$(C_6H_5CH_2)_2C_{60}$: ^{13}C NMR ($CDCl_3/CS_2$, 295 K, 150 Hz) $\delta = 157.6$ (2 C), 151.5 (2 C), 148.4 (4 C), 147.0 (1 C), 146.7 (2 C), 146.7 (2 C), 145.9 (2 C), 145.3 (2 C), 144.9 (2 C), 144.6 (1 C), 144.5 (2 C), 144.4 (2 C), 144.2 (2 C), 144.1 (2 C), 143.9 (2 C), 143.8 (2 C), 143.5 (2 C), 143.0 (2 C), 142.9 (6 C), 142.8 (2 C), 142.5 (2 C), 142.4 (1 C), 142.3 (2 C), 141.9 (2 C), 141.8 (2 C), 140.4 (1 C), 138.6 (2 C), 137.7 (2 C), 136.0 (2 C, Ph), 130.9 (4 C, Ph), 128.4 (4 C, Ph), 127.4 (2 C, Ph), 60.4 (2 C), 48.5 (2 C, CH_2). Negative MALDI MS: 811 $(M - C_6H_5CH_2)^-$, 720 $(M - 2C_6H_5CH_2)^-$. Positive MALDI MS: 811 $(M - C_6H_5CH_2)^+$, 720 $(M - 2C_6H_5CH_2)^+$.

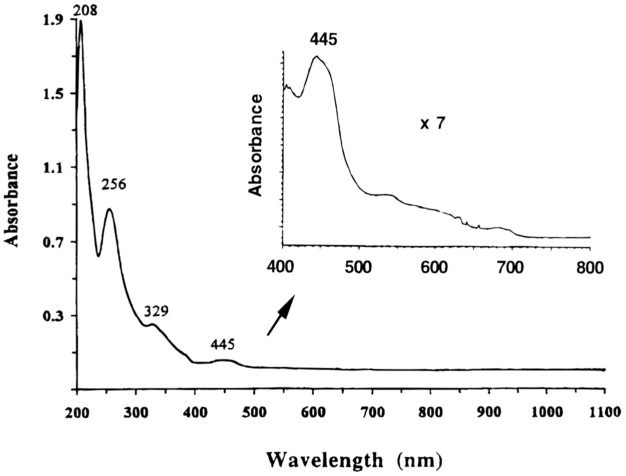
Results and Discussion

HPLC of $(C_6H_5CH_2)_2C_{60}$. Figure 2 illustrates an HPLC trace of the crude reaction product between $C_{60}{}^{2-}$ and $C_6H_5CH_2Br$. The 1,4-$(C_6H_5CH_2)_2C_{60}$ adduct is the dominant product of the two resulting $(C_6H_5CH_2)_2C_{60}$ isomers. Only a small amount of the 1,2-adduct is seen in the HPLC trace and this can be accounted for by the likely instability of the compound caused by steric hindrance between the two bulky benzyl groups. The structure of 1,4-$(C_6H_5CH_2)_2C_{60}$ has early been confirmed by single-crystal X-ray diffraction[5a] but the 1,2-adduct has not previously been isolated for characterization.

UV−Visible Spectra. A solution of 1,2-$(C_6H_5CH_2)_2C_{60}$ in a mixture of hexanes/toluene has a pink color which is similar to that of C_{60}, while 1,4-$(C_6H_5CH_2)_2C_{60}$ is yellow under the same solution conditions. Figure 3 shows the UV−visible spectra of



(a) 1,2-($C_6H_5CH_2$)$_2$C$_{60}$



(b) 1,4-($C_6H_5CH_2$)$_2$C$_{60}$

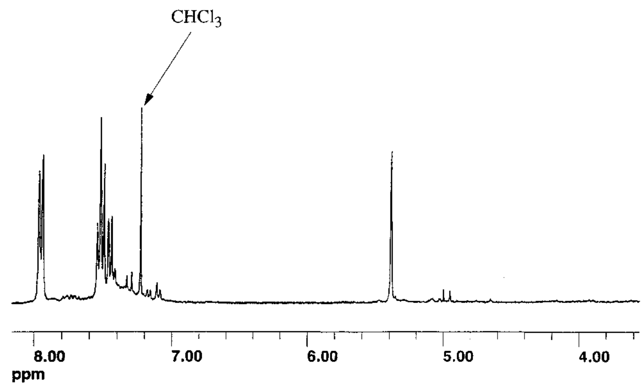
Figure 3. UV−visible spectrum of (a) 1,2-($C_6H_5CH_2$)$_2$C$_{60}$ and (b) 1,4-($C_6H_5CH_2$)$_2$C$_{60}$ in hexanes. Insets are the expanded region from 400 to 800 nm.

1,2- and 1,4-($C_6H_5CH_2$)$_2$C$_{60}$ in hexanes. Both isomers have similar bands at 208−210, 256−257, and 327−329 nm and similar bands are also observed in the UV−visible spectrum of C$_{60}$.[37] The 1,4-($C_6H_5CH_2$)$_2$C$_{60}$ isomer also exhibits a broad absorption band centered at 445 nm, while the 1,2-($C_6H_5CH_2$)$_2$C$_{60}$ isomer displays a spike at 428 nm and a broad absorption around 500 nm (see Figure 3 inset). The absorption spectra of the two ($C_6H_5CH_2$)$_2$C$_{60}$ isomers thus have features similar to those of other 1,4-adducts[5−7] and 1,2-adducts[8] of C$_{60}$.

NMR Spectra. The ^{1}H NMR spectra of 1,2-($C_6H_5CH_2$)$_2$C$_{60}$ and 1,4-($C_6H_5CH_2$)$_2$C$_{60}$ are illustrated in Figure 4. The methylene protons of 1,2-($C_6H_5CH_2$)$_2$C$_{60}$ are characterized by a singlet at 5.28 ppm, while an AB quartet centered at 3.73 ppm is assigned to the methylene protons of 1,4-($C_6H_5CH_2$)$_2$C$_{60}$. The *sp*^{3} carbons of C$_{60}$ are nonchiral for 1,2-($C_6H_5CH_2$)$_2$C$_{60}$ due to the C_{2v} symmetry of the molecule (see Figure 1a), and the two methylene protons are thus identical, resulting in a singlet.[37,38] In contrast, the *sp*^{3} carbons of 1,4-($C_6H_5CH_2$)$_2$C$_{60}$ are chiral due to the C_s symmetry of the molecule (see Figure 1b), and the methylene protons thus display an AB quartet.[37,38] Resonances from the aromatic protons of both isomers are also observed in Figure 4 and this is consistent with the structure of the compounds.

Figure 5 illustrates the *sp*^{3} carbon resonances of 1,2-($C_6H_5CH_2$)$_2$C$_{60}$ and 1,4-($C_6H_5CH_2$)$_2$C$_{60}$ in CS$_2$/CDCl$_3$, while Figure 6 shows the *sp*^{2} carbon resonances of the two ($C_6H_5CH_2$)$_2$C$_{60}$ isomers under the same solvent conditions. Two resonances for each isomer are seen in Figure 5. One is for the two methylene carbons of the benzyl groups and the other is for the two *sp*^{3} carbons of C$_{60}$. The methylene carbons of 1,2-($C_6H_5CH_2$)$_2$C$_{60}$ have a resonance at 43.8 ppm, while the methylene carbons of 1,4-($C_6H_5CH_2$)$_2$C$_{60}$ have a resonance at 48.5 ppm. The resonance for the *sp*^{3} carbons of 1,2-($C_6H_5CH_2$)$_2$C$_{60}$ is located at 75.5 ppm, while the resonance for the *sp*^{3} carbons of 1,4-($C_6H_5CH_2$)$_2$C$_{60}$ is seen at 60.4 ppm. Noteworthy, the *sp*^{3} carbons of 1,2-(C_6H_5-

(a) 1,2-($C_6H_5CH_2$)$_2$C$_{60}$



(b) 1,4-($C_6H_5CH_2$)$_2$C$_{60}$

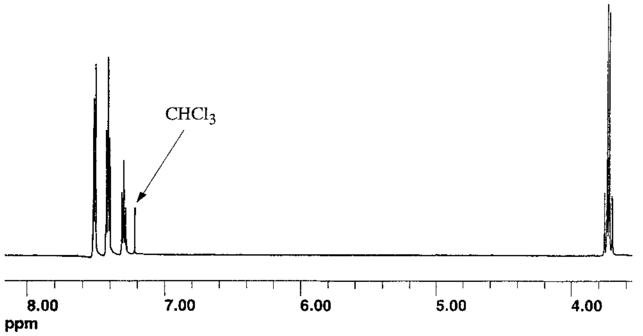
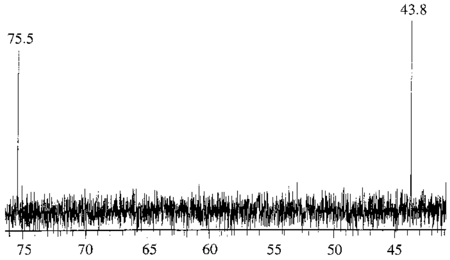


Figure 4. ^{1}H NMR spectrum of (a) 1,2-($C_6H_5CH_2$)$_2$C$_{60}$ and (b) 1,4-($C_6H_5CH_2$)$_2$C$_{60}$ in CS$_2$/CDCl$_3$.

(a) 1,2-($C_6H_5CH_2$)$_2$C$_{60}$



(b) 1,4-($C_6H_5CH_2$)$_2$C$_{60}$

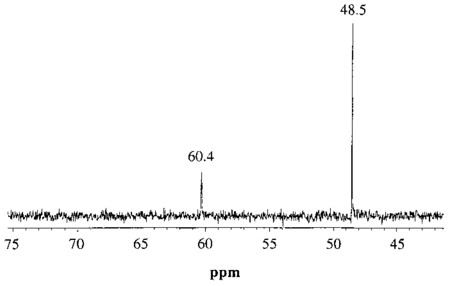
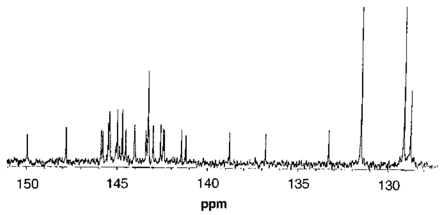


Figure 5. ^{13}C NMR spectrum of (a) 1,2-($C_6H_5CH_2$)$_2$C$_{60}$ and (b) 1,4-($C_6H_5CH_2$)$_2$C$_{60}$ in CS$_2$/CDCl$_3$ for the region of the *sp*^{3} carbons.

(a) 1,2-$(C_6H_5CH_2)_2C_{60}$



(b) 1,4-$(C_6H_5CH_2)_2C_{60}$

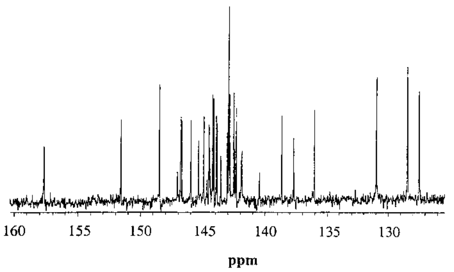


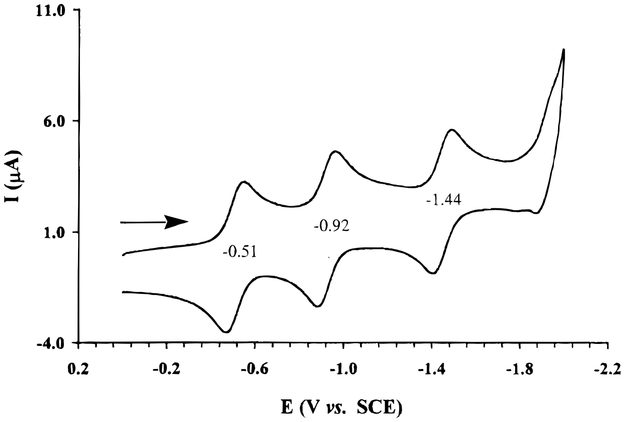
Figure 6. ^{13}C NMR spectrum of (a) 1,2-$(C_6H_5CH_2)_2C_{60}$ and (b) 1,4-$(C_6H_5CH_2)_2C_{60}$ in $CS_2/CDCl_3$ for the region of the *sp*^{2} carbons.

$CH_2)_2C_{60}$ have a chemical shift similar to that of $C_{61}H_2$ (71.0 ppm), a 1,2-adduct of C_{60} which has been previously characterized.[8a]

As seen in Figure 6, each isomer of $(C_6H_5CH_2)_2C_{60}$ is characterized by four phenyl-carbon resonances which are located at 128.8, 129.1, 131.5, and 136.8 ppm for 1,2-$(C_6H_5CH_2)_2C_{60}$ and at 127.4, 128.4, 130.9, and 136.0 ppm for 1,4-$(C_6H_5CH_2)_2C_{60}$. All of the resonances from 133.3 to 149.9 ppm in Figure 6a except the one at 136.8 ppm are assigned as originating from the *sp*^{2} carbons of 1,2-$(C_6H_5CH_2)_2C_{60}$, while all the resonances from 137.7 to 157.6 ppm in Figure 6b are assigned as originating from the *sp*^{2} carbons of 1,4-$(C_6H_5CH_2)_2C_{60}$. The assignments of the phenyl carbon resonances in 1,2-$(C_6H_5CH_2)_2C_{60}$ and 1,4-$(C_6H_5CH_2)_2C_{60}$ are based on carbon resonances of substituted phenyl compounds such as $C_6H_5CH_2Cl$ and $C_6H_5CH_2Br$.[40] The *o*-, *m*-, and *p*-phenyl carbon resonances of benzyl derivatives appear within a relatively fixed region, independent of the substituents, but the chemical shift of the phenyl carbon which is bonded to the methylene carbon of a benzyl group will vary greatly depending on the substituent attached to the methylene carbon.[40] The peak at 136.8 ppm in Figure 6a is assigned to this phenyl carbon in 1,2-$(C_6H_5CH_2)_2C_{60}$, while the resonance for this phenyl carbon in 1,4-$(C_6H_5CH_2)_2C_{60}$ is assigned as being associated with the peak at 136.0 ppm. The two $(C_6H_5CH_2)_2C_{60}$ isomers have virtually the same chemical shift for this phenyl carbon resonance (136.8 and 136.0 ppm, see Experimental Section) and this is expected on the basis of the compounds' molecular structures. The assignments are also in good agreement with the values assigned for 1,2-$H(C_6H_5CH_2)C_{60}$.[8b]

Twenty-five resonances are seen for the *sp*^{2} C_{60} carbons of 1,2-$(C_6H_5CH_2)_2C_{60}$ (Figure 6a, see Experimental Section for assignment), a number which is higher than the theoretically predicted 16 resonances for a 1,2-adduct of C_{60} with two identical addends.[8a] This appears to be inconsistent with the singlet ^1H NMR signal for methylene protons of 1,2-$H(C_6H_5CH_2)C_{60}$ due to the C_{2v} symmetry (Figure 4). The two bulky benzyl groups in the 1,2-adduct of $(C_6H_5CH_2)_2C_{60}$ are so close to each other that their rotation is partially hindered. A steric hindrance between benzyl groups has also been observed in the recently solved crystal structure of 1,4;1,2-$(C_6H_5CH_2)_2C_{60}$.[41] Thus, the symmetry of 1,2-$(C_6H_5CH_2)_2C_{60}$ may be reduced from the C_{2v} symmetry depending on the conformation of the two benzyl groups. The ^{13}C NMR signals of the *sp*^{2} C_{60} carbons of 1,2-$(C_6H_5CH_2)_2C_{60}$ may be sensitive to the slight reduction from the C_{2v} symmetry due to the conformational change, leading to more signals than those expected from the exact C_{2v} symmetry. On the other hand, the ^1H NMR signals for methylene protons of 1,2-$(C_6H_5CH_2)_2C_{60}$ may be insensitive to the slight change in the symmetry as compared to the ^{13}C NMR signals of the *sp*^{2} C_{60} carbons of 1,2-$(C_6H_5CH_2)_2C_{60}$, retaining the singlet peak. However, a detailed assignment of the ^{13}C NMR signals of the *sp*^{2} C_{60} carbons of 1,2-$(C_6H_5CH_2)_2C_{60}$ has yet to be made.

(a) 1,2-$(C_6H_5CH_2)_2C_{60}$



(b) 1,4-$(C_6H_5CH_2)_2C_{60}$

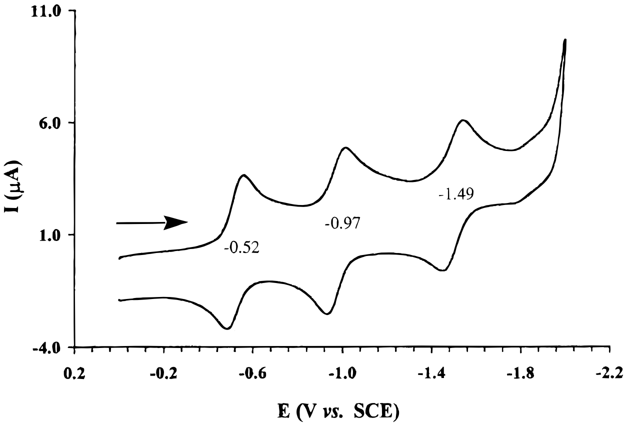


Figure 7. Cyclic voltammogram of (a) 1,2-$(C_6H_5CH_2)_2C_{60}$ and (b) 1,4-$(C_6H_5CH_2)_2C_{60}$ in PhCN containing 0.1 M TBAP.

TABLE 1: Reduction Potentials of C_{60}, 1,2-$(C_6H_5CH_2)_2C_{60}$, and 1,4-$(C_6H_5CH_2)_2C_{60}$ in PhCN Containing 0.1 M TBAP

compound	$E_{1/2}$ (V vs SCE) 1st	2nd	3rd
C_{60}	−0.41	−0.84	−1.33
1,2-$(C_6H_5CH_2)_2C_{60}$	−0.51	−0.92	−1.44
1,4-$(C_6H_5CH_2)_2C_{60}$	−0.52	−0.97	−1.49

1,4-$(C_6H_5CH_2)_2C_{60}$ has 28 *sp*^{2} resonances (see Figure 6b and Experimental Section), a number which is smaller than the theoretically predicted 31[6,7] due to the fact that some of the resonances are overlapped. In summary, the ^1H and ^{13}C NMR spectra shown in Figures 4−6 are consistent with the molecular structures of both 1,2- and 1,4-$(C_6H_5CH_2)_2C_{60}$ isomers.

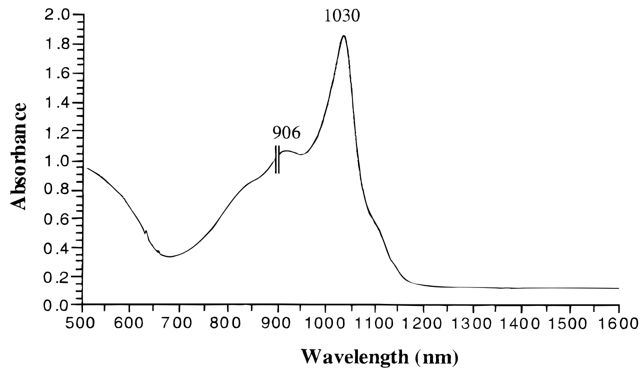
Electrochemistry. Cyclic voltammograms of 1,2-$(C_6H_5CH_2)_2C_{60}$ and 1,4-$(C_6H_5CH_2)_2C_{60}$ in PhCN containing 0.1 M TBAP are shown in Figure 7. Both isomers exhibit three well-defined reversible one-electron reductions between 0.0 and −2.0

TABLE 2: Spectral Data for Mono- and Dianions of Several 1,2-R_2C_{60} and 1,4-R_2C_{60} Derivatives in PhCN Containing 0.2 M TBAP[a]

compound	λ_{max}, nm (ϵ, M^{-1} cm^{-1}) monoanion		dianion		ref
1,2-$(C_6H_5CH_2)_2C_{60}$	1030 (5900)		905 (8100)		tw
1,2-$(CH_3)_2C_{60}$	997		874		36
(*o*-xylyl)C_{60}	1006		868		36
1,2-H(*t*-Bu)C_{60}	995		880		tw
1,4-$(C_6H_5CH_2)_2C_{60}$	989 (1900)	1498 (1500)	903 (5200)	1294 (4800)	5b
1,4-$(2\text{-}BrC_6H_4CH_2)_2C_{60}$	988 (1800)	1505 (1300)	903 (5800)	1300 (4800)	5b
1,4-$(3\text{-}BrC_6H_4CH_2)_2C_{60}$	992 (1500)	1501 (900)	904 (6100)	1300 (4700)	5b
1,4-$(4\text{-}BrC_6H_4CH_2)_2C_{60}$	994 (1500)	1495 (900)	904 (5800)	1299 (5000)	5b
1,4-$C_6H_5CH_2$(*t*-Bu)C_{60}	984 (2800)	1512 (2200)	904 (5700)	1308 (4400)	tw

[a] The average uncertainty in ϵ measurement is ca. 20%; tw = this work.

(a) $[1,2\text{-}(C_6H_5CH_2)_2C_{60}]^{-\bullet}$



(b) $[1,4\text{-}(C_6H_5CH_2)_2C_{60}]^{-\bullet}$

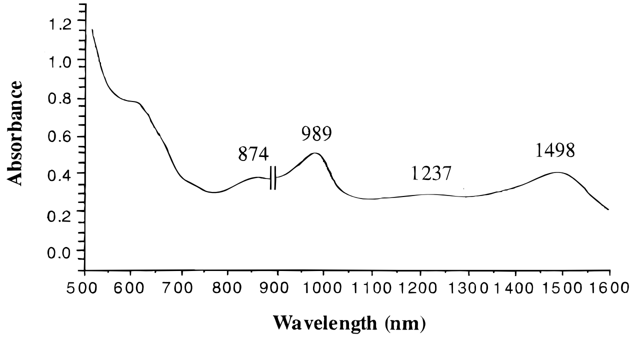
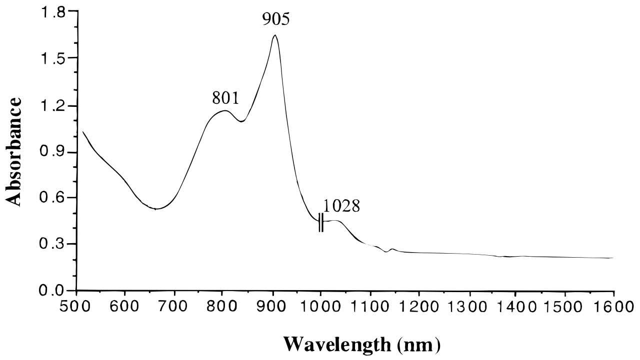


Figure 8. Visible and near-IR spectra of (a) $[1,2\text{-}(C_6H_5CH_2)_2C_{60}]^{\bullet-}$ (3.1×10^{-4} M) and (b) $[1,4\text{-}(C_6H_5CH_2)_2C_{60}]^{\bullet-}$ (2.7×10^{-4} M) in PhCN containing 0.2 M TBAP. The spectra were recorded on an HP 8453 spectrophotometer from 500 to 900 nm and on a Perkin-Elmer 330 spectrophotometer from 900 to 1600 nm.

(a) $[1,2\text{-}(C_6H_5CH_2)_2C_{60}]^{2-}$



(b) $[1,4\text{-}(C_6H_5CH_2)_2C_{60}]^{2-}$

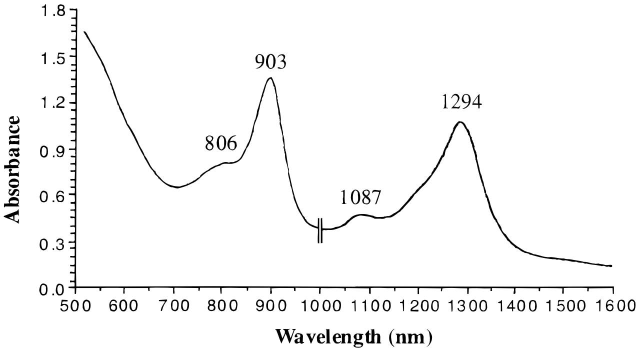


Figure 9. Visible and near-IR spectra of (a) $[1,2\text{-}(C_6H_5CH_2)_2C_{60}]^{2-}$ (2.0×10^{-4} M) and (b) $[1,4\text{-}(C_6H_5CH_2)_2C_{60}]^{2-}$ (2.7×10^{-4} M) in PhCN containing 0.2 M TBAP. The spectra were recorded on an HP 8453 spectrophotometer from 500 to 1000 nm and on a Perkin-Elmer 330 spectrophotometer from 1000 to 1600 nm.

V. The $E_{1/2}$ values for these processes are noted in Figure 7 and summarized in Table 1, which also lists half-wave potentials for the first three reductions of C_{60}. The first one-electron reduction of each $(C_6H_5CH_2)_2C_{60}$ isomer is the same within experimental error but this is not the case for the second and third reductions of the two compounds where 1,2-$(C_6H_5CH_2)_2C_{60}$ is easier to reduce than 1,4-$(C_6H_5CH_2)_2C_{60}$ by 50 mV. Since the two organofullerenes have the same substituents on the C_{60} molecule, the differences in electrochemistry between the two isomers must be accounted for by differences in the addition pattern.

Previously reported electrochemistry of 1,2-$(CH_3)_2C_{60}$ and 1,4-$(CH_3)_2C_{60,}$[1] methanofullerenes and methanofulleroid isomers,[14] as well as 1,2- and 1,4-silicated C_{60} derivatives[15] has shown that these isomers have virtually identical values of $E_{1/2}$ for the first three reductions, independent of the addition pattern. 1,2- and 1,4-$(C_6H_5CH_2)_2C_{60}$ are thus the only known organofullerenes to show significant differences in reduction potentials as a function of the isomer type. A similar phenomenon has also been observed for the 1,4;1,4- and 1,4;1,2-$(C_6H_5CH_2)_4C_{60}$ isomers,[41] where the molecules have different addition patterns. The oxidation of the two $(C_6H_5CH_2)_2C_{60}$ isomers was also examined by cyclic voltammetry but no reversible processes were found.

Visible and Near-IR Spectra of Singly and Doubly Reduced Compounds. Figure 8 shows the visible and near-IR spectra of $[1,2\text{-}(C_6H_5CH_2)_2C_{60}]^{\bullet-}$ and $[1,4\text{-}(C_6H_4CH_2)_2C_{60}]^{\bullet-}$, while Figure 9 shows the visible and near-IR spectra of $[1,2\text{-}(C_6H_5CH_2)_2C_{60}]^{2-}$ and $[1,4\text{-}(C_6H_5CH_2)_2C_{60}]^{2-}$. The $[1,2\text{-}(C_6H_5CH_2)_2C_{60}]^{\bullet-}$ isomer exhibits a strong near-IR absorption band at 1030 nm and a weaker band at 906 nm, while the $[1,4\text{-}(C_6H_5CH_2)_2C_{60}]^{\bullet-}$ isomer exhibits two well-defined absorption bands at 1498 and 989 nm and also two much weaker bands at 874 and 1237 nm. Doubly reduced 1,2-$(C_6H_5CH_2)_2C_{60}$ shows one strong absorption band at 905 nm and one weaker band at 801, while doubly reduced 1,4-$(C_6H_5CH_2)_2C_{60}$ displays two strong absorption bands at 1294 and 903 nm and two much weaker bands at 806 and 1087 nm. Although the doubly reduced forms of the two isomers differ in their absorption spectra, both have one major near-IR absorption band at almost the same wavelength (903 and 905 nm). The major near-IR absorption bands of both isomers are blue-shifted upon going from the monoanion to the dianion, a result which parallels what has been observed for the mono- and dianions of C_{60}.[26]

Table 2 summarizes the near-IR spectral data of $[1,2\text{-}(C_6H_5CH_2)_2C_{60}]^{n-}$ and $[1,4\text{-}(C_6H_5CH_2)_2C_{60}]^{n-}$ ($n = 1$ or 2) along with data for the mono- and dianions of several related derivatives. As shown in this table, the singly and doubly reduced 1,2-adducts of C_{60} each exhibits a single near-IR band at 995−1030 nm (monoanion) and 868−905 nm (dianion), while the singly and doubly reduced 1,4-adducts of C_{60} display bands at similar wavelengths plus one additional absorption at ca. 1500 (monoanion) or ca. 1300 (dianion) nm. The spectral data in Table 2 are similar to the visible and near-IR spectral data of previously characterized mono- and bis-adducts of methanofullerenes in their anionic forms[25,42] and are also consistent with the spectral data of other singly and doubly reduced R_4C_{60} derivatives.[41] Thus, the visible and near-IR spectral data of R_2C_{60} anions can be used as a means to differentiate between 1,2- and 1,4-adducts.

Conclusions

1,2-$(C_6H_5CH_2)_2C_{60}$ is the first isolated and characterized 1,2-R_2C_{60} adduct with two bulky groups on the C_{60} cage. The spectroscopic and electrochemical properties of 1,2-$(C_6H_5CH_2)_2C_{60}$ were compared with data for 1,4-$(C_6H_5CH_2)_2C_{60}$, a compound whose structure was earlier determined by single-crystal X-ray diffraction. The 1,2-R_2C_{60} and 1,4-R_2C_{60} visible and near-IR spectra differ from one another for both the singly and doubly reduced forms of the compounds and this result can be used as a diagnostic criterion to differentiate the two types of R_2C_{60} adducts.

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