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Electrogeneration and Characterization of $(C_6H_5CH_2)_2C_{70}$

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$(C_6H_5CH_2)_2C_{70}$ was electrosynthesized from C_{70}^{2-} and $C_6H_5CH_2Br$ and purified by HPLC. Mass spectral results for the largest HPLC fraction confirm formation of the compound, while ^1H NMR spectroscopy suggests that three isomers are present in this fraction, all of which are 1,4-addition products. The isomers are proposed to be the 22,25-, 22,41-, and 22,45-isomers on the basis of ^1H NMR data and the fact that bulky benzyl groups on C_{60} form preferentially 1,4- rather than 1,2-addition products. $(C_6H_5CH_2)_2C_{70}$ was examined as to its electrochemical properties, and two sets of reduction processes were observed, one of which is assigned to the 22,25- and 22,41-isomers that exhibit identical electrochemical properties and the other to the 22,45-isomer of $(C_6H_5CH_2)_2C_{70}$. The vis−near-IR spectrum of $(C_6H_5CH_2)_2C_{70}^{\bullet-}$ in benzonitrile shows a strong band at 776 nm which is not seen for $C_{70}^{\bullet-}$ as well as two more bands in the near-IR region (1062 and 1250 nm) which are blue-shifted with respect to the near-IR absorption band of $C_{70}^{\bullet-}$ that appears at 1368 nm.

Introduction

The methods for producing C_{60} and C_{70} in macroscopic amounts were discovered at the same time,[1] and despite numerous published studies on C_{60}, the chemistry of C_{70} has remained much less explored due to the relatively low abundance of the latter compound. C_{70} has been shown to have electrochemical properties and reactivity similar to those of C_{60}. The compound exhibits six reversible one-electron reductions at potentials which are slightly shifted in a positive direction with respect to the six one-electron reductions of C_{60}.[2] Both C_{60} and C_{70} can undergo reactions with diazo compounds,[3−6] nucleophiles,[7,8] electron-rich metal complexes,[9−12] hydrogen,[13−16] and nitrile compounds.[17,18] However, the two fullerenes have different geometries; there are only two types of bonds in C_{60} (labeled as b_1 and b_2 in Figure 1a) as compared to eight types of bonds in C_{70} (labeled as b_i, $i = 1-8$, in Figure 1b). This makes the regiochemistry of C_{70} organofullerene derivatives much more complicated than that of C_{60}.

Cahill and co-workers have demonstrated by both theoretical and experimental means that the 1,9- and 7,8-adducts of C_{70} (see Taylor's numbering structure[19] in Figure 1b) are the two most stable 1,2-addition products for $C_{70}H_2$.[14] They also predicted, using hydrogen as a model, that the 1,7- and 22,41-adducts would be the most stable 1,4-addition products.[14] However, to date, no 1,4-disubstituted C_{70} derivatives with covalent C−C bonds have ever been isolated.

We have earlier demonstrated that organofullerenes with either 1,4- or 1,2-addition patterns could be electrochemically generated *via* a reaction between the dianion of C_{60} and $C_6H_5CH_2Br$,[20,21] and this electrosynthesis technique can also be used to obtain organofullerene derivatives of C_{70}. The reaction between C_{70}^{2-} and $C_6H_5CH_2Br$ yielded a mixture of three $(C_6H_5CH_2)_2C_{70}$ isomers whose electrosynthesis, isolation, and characterization are reported in the present paper. A stable alkyl adduct of C_{70} is also generated by addition of $C_6H_5CH_2Br$ to a photolyzed solution containing C_{70} and 4-*tert*-butyl-1-benzyl-

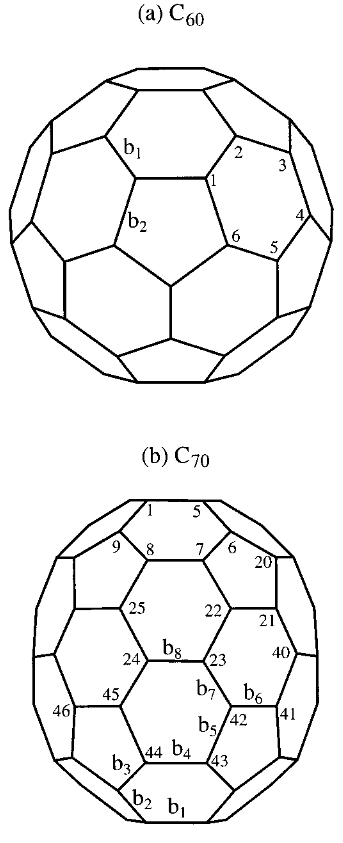

Figure 1. Schematic representation of (a) C_{60} and (b) C_{70} including the labeling of different types of bonds and the numbering of some carbon atoms on both molecules. The numbering of carbons for C_{70} is taken from ref 19.

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1,4-dihydronicotinamide (*t*-BuBNAH). The reaction proceeds via formation of the *tert*-butylated C_{70} anion (t-BuC_{70}^-) as was also reported for the photochemical reaction of C_{60}.[22,23]

Experimental Section

Chemicals. C_{70} was obtained from TechnoCarbo, France, and used as received. 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. $C_6H_5CH_2Br$ (98%) and tetramethylsilane (TMS) (99.9+%) were purchased from Aldrich and used as received. The *tert*-butylated BNAH (*t*-BuBNAH) was prepared by a Grignard reaction with BNA^+Cl^-.[24,25] Benzonitrile (PhCN) was distilled over P_2O_5 under a vacuum at 305 K prior to use. 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.

Synthesis. The dianion of C_{70} was generated by bulk controlled-potential electrolysis of C_{70} at −0.9 V vs SCE, a potential which is located between $E_{1/2}$ for the second and third reductions of C_{70}. A 5-fold excess of $C_6H_5CH_2Br$ was then added to the solution after the potentiostat was switched off. The reaction was allowed to proceed for 1 h, after which the solvent was evaporated and CH_3OH added to wash the residue and precipitate the crude product. Purification of the crude product was performed using an analytical "Buckyclutcher I" column and a 2:1 v/v hexanes/toluene mixture as eluent. The most abundant fraction of the HPLC trace was collected and characterized by MS, ^1H NMR, UV−vis spectroscopy and electrochemistry, while the singly reduced product of $(C_6H_5CH_2)_2C_{70}$ was characterized by vis−near-IR spectroscopy.

The *tert*-butylated C_{70} anion was prepared by the following procedure. Typically, to a solution of C_{70} (0.25 mg, 0.0003 mmol) in deaerated PhCN (3 mL) under an atmospheric pressure of argon was added *t*-BuBNAH (0.081 mg, 0.0003 mmol). The solution was irradiated for 1 h with a Xe lamp ($\lambda > 370$ nm) equipped with a Toshiba UV-37 cutoff filter. The addition of $C_6H_5CH_2Br$ to the photolyzed PhCN solution of C_{70} and *t*-BuBNAH yielded *tert*-butylbenzyldihydro[70]fullerene (t-$Bu(C_6H_5CH_2)C_{70}$). The final product was isolated and characterized by FAB-mass spectrometry. FAB-MS: mass calcd for $C_{81}H_{16}$ 989.0, found 988.8.

Instrumentation. ^1H NMR spectra were recorded on a GE QE 300 MHz spectrometer in CD_2Cl_2 and referenced to TMS. UV−vis spectra of neutral $(C_6H_5CH_2)_2C_{70}$ 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 spectrophotometer and a Perkin-Elmer model 330 spectrophotometer. Cyclic voltammetry (CV) and controlled-potential bulk electrolyses were carried out using 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 monoanion of $(C_6H_5CH_2)_2C_{70}$ were obtained by setting the applied potential at values 150−250 mV more negative than $E_{1/2}$ of the $(C_6H_5CH_2)_2C_{70}^-/(C_6H_5CH_2)_2C_{70}$ 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 of $(C_6H_5CH_2)_2C_{70}$ was then transferred from the bulk cell to a 1 cm quartz cuvette and the cuvette removed from the glovebox after being capped with a rubber septum and sealed with Parafilm. Vis−near-IR measurements of the compound were carried out under a N_2 atmosphere.

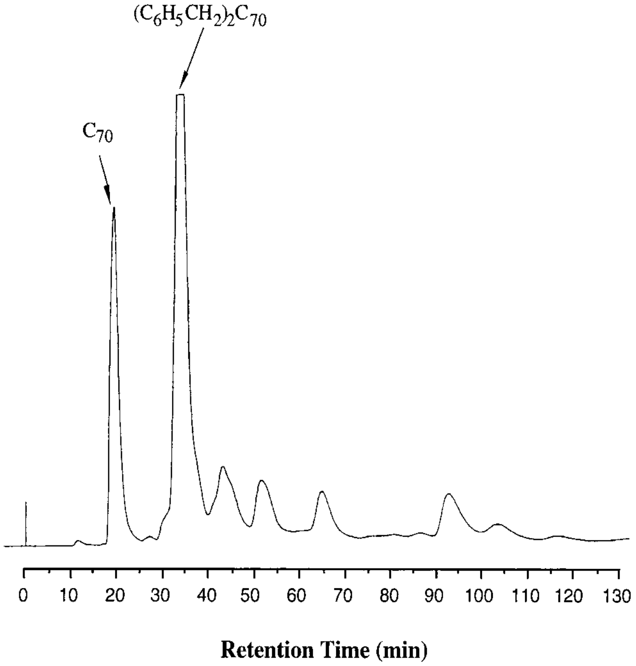


Figure 2. HPLC trace of the crude mixture obtained by reaction between C_{70}^{2-} and $C_6H_5CH_2Br$ using an analytical Buckyclutcher I column eluted by a 2:1 v/v hexanes/toluene mixture with a flow rate of 3.6 mL/min.

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 delayed extraction 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. Electrospray mass ionization spectra (ESI-MS) of t-BuC_{70}^- in PhCN were recorded on a JEOL JNX-DX303 HF mass spectrometer. ESI-MS: mass calcd for t-BuC_{70}^- ($C_{74}H_9$) 897.1, found 897.

Theoretical Calculations. Theoretical calculations were performed using the MOPAC program (version 6) which is incorporated in the MOLMOLIS program by Daikin Industries, Ltd. The PM3 Hamiltonian was used for the semiempirical MO calculations.[26] Final geometries and energetics were obtained by optimizing the total molecular energy with respect to all structural variables. The heats of formation (ΔH_f) were calculated with the restricted Hartree−Fock (RHF) formalism using the keyword "PRECISE".

Results and Discussion

Electrosynthesis of $(C_6H_5CH_2)_2C_{70}$. The HPLC trace of the reaction between C_{70}^{2-} and $C_6H_5CH_2Br$ is shown in Figure 2 and displays several fractions in addition to that corresponding to unreacted C_{70}. The largest fraction in the HPLC trace was

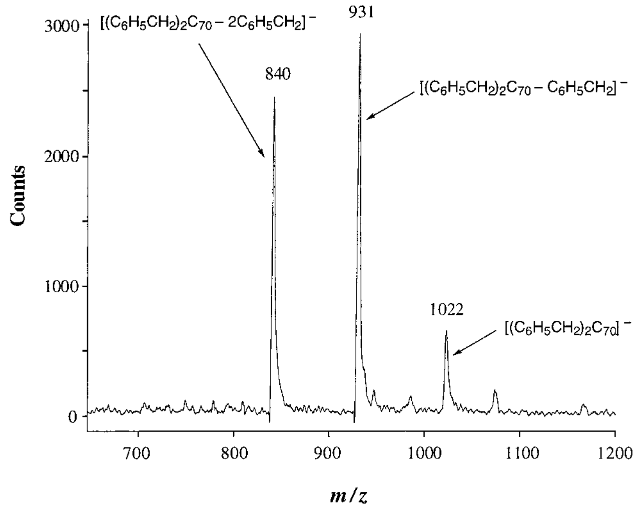
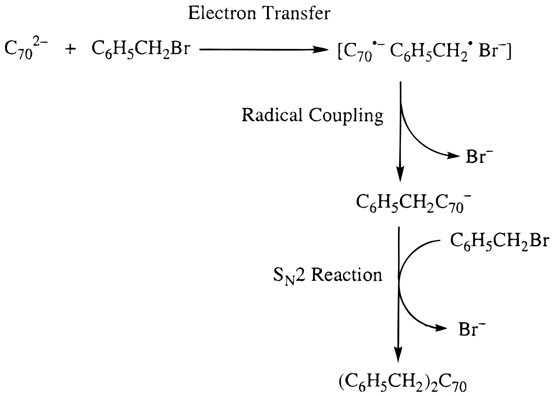


Figure 3. Negative MALDI mass spectrum of $(C_6H_5CH_2)_2C_{70}$.

SCHEME 1



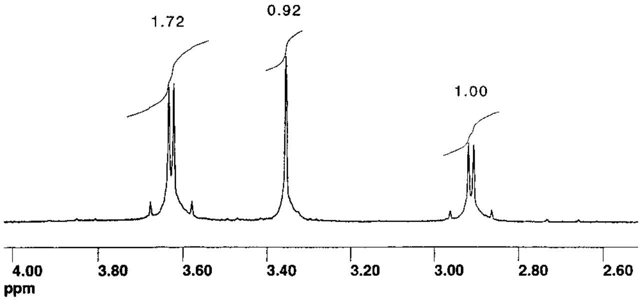
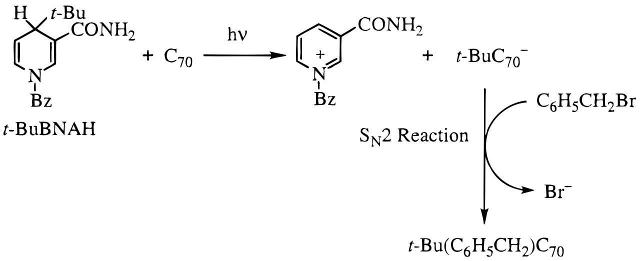


Figure 4. ^{1}H NMR for the major fraction of the HPLC trace of $(C_6H_5CH_2)_2C_{70}$ in CS_2/CD_2Cl_2. Only the region corresponding to the methylene proton resonances is shown.

SCHEME 2



isolated, and its negative MALDI mass spectrum is illustrated in Figure 3. This spectrum exhibits the $(C_6H_5CH_2)_2C_{70}^{\bullet-}$ molecular ion peak at $m/z = 1022$ along with two fragment ions corresponding to the stepwise loss of the two $C_6H_5CH_2$ groups, *i.e.*, $[(C_6H_5CH_2)_2C_{70} - C_6H_5CH_2]^-$ at $m/z = 931$ and $[(C_6H_5CH_2)_2C_{70} - 2C_6H_5CH_2]^-$ at $m/z = 840$. The MS data are therefore consistent with formation of $(C_6H_5CH_2)_2C_{70}$.

A reaction mechanism for generation of $(C_6H_5CH_2)_2C_{60}$ from C_{60}^{2-} and benzyl bromide has been reported in the literature,[20,21] and a similar sequence of steps is proposed for the formation of $(C_6H_5CH_2)_2C_{70}$ from C_{70}^{2-} and benzyl bromide. An electron transfer from electrogenerated C_{70}^{2-} to benzyl bromide gives a radical ion pair $[C_{70}^{\bullet-}C_6H_5CH_2^{\bullet}Br^-]$ in which the radical coupling between $C_{70}^{\bullet-}$ and $C_6H_5CH_2^{\bullet}$ yields $C_6H_5CH_2C_{70}^-$ and this is followed by an S_N2 reaction of $(C_6H_5CH_2)C_{70}^-$ with benzyl bromide to yield $(C_6H_5CH_2)_2C_{70}$ (Scheme 1).

The formation of stable C_{70} mono- and dialkyl adducts can be achieved by the photochemical reaction of C_{70} with 4-*tert*-butyl-1-benzyl-1,4-dihydronicotinamide (*t*-BuBNAH) as was the case for C_{60}.[22] Visible light irradiation of a benzonitrile solution containing C_{70} and 4-*tert*-butyl-1-benzyl-1,4-dihydronicotinamide (*t*-BuBNAH) results in formation of the *tert*-butylated anion ($t\text{-}BuC_{70}^-$) and a simultaneous oxidation of *t*-BuBNAH to BNA^+ as shown in Scheme 2. The formation of stable $t\text{-}BuC_{70}^-$ was confirmed by the electrospray ionization mass (ESI-MS) spectrum which shows a peak at the mass number expected for $t\text{-}BuC_{70}^-$ (897). The vis−near-IR spectrum of $t\text{-}BuC_{70}^-$ has an absorption band at 777 nm. The subsequent S_N2 reaction of $t\text{-}BuC_{70}^-$ with $C_6H_5CH_2Br$ (Scheme 2) gives $t\text{-}Bu(C_6H_5CH_2)C_{70}$ (Scheme 2) as was reported for the reaction of $t\text{-}BuC_{60}^-$ with electrophiles.[21]

^{1}H NMR Spectrum of $(C_6H_5CH_2)_2C_{70}$. Figure 4 shows the ^{1}H NMR spectrum of $(C_6H_5CH_2)_2C_{70}$ in the region for methylene protons, while Table 1 summarizes the position of resonances for the methylene protons in this spectral region. The spectrum which was recorded in a mixture of CS_2/CD_2Cl_2 is characterized by two AB quartets with different integrated intensities (1.00 and 1.72) centered at 2.91 and 3.63 ppm (referenced to TMS) and a singlet (with an integrated intensity of 0.92) centered at 3.35 ppm. The AB quartets are caused by the diastereotopic methylene protons of the benzyl groups as was observed for $(C_6H_5CH_2)_2C_{60}$, thus indicating that the sp^3 carbons of C_{60} and C_{70} which are bonded to the benzyl groups are chiral centers.[27,28] The coupling constants of 13.0−13.3 Hz between protons of the AB quartets (see Table 1) are within the normal range for coupling constants between geminal protons.[29] However, the fact that the two AB quartets in Figure 4 have different intensities suggests that the signals originate from two different isomers of $(C_6H_5CH_2)_2C_{70}$. Each isomer should possess a C_s or C_2 symmetry since both compounds exhibit an AB quartet; a similar spectral pattern has been reported for 1,4-$(C_6H_5CH_2)_2C_{60}$,[20] a molecule which has C_s symmetry.

Earlier studies on $(C_6H_5CH_2)_2C_{60}$ have shown that a 1,4-addition to C_{60} is preferred over a 1,2-addition due to the bulky size of the benzyl groups,[20] and a similar result is true for addition of the two bulky benzyl groups to C_{70} as discussed below. Underivatized C_{70} with D_{5h} symmetry has five sets of carbon atoms such as C(5), C(6), C(7), C(22), and C(23) arranged radially about the symmetry axis. The most probable sites for nucleophilic attack have been suggested to be C(22) or C(7), followed by C(5), on the basis of the semiempirical MO calculations of enthalpies of formation for the five isomers of HC_{70}^-, MeC_{70}^-, and $t\text{-}BuC_{70}^-$.[30] Our semiempirical MO calculations of $C_6H_5CH_2C_{70}^-$ indicate that the addition of one benzyl group to C_{70} would occur preferentially at the C(7), C(22), or C(5) position to produce 7-, 22-, or 5-$C_6H_5CH_2C_{70}^-$, all three of which are thermodynamically more stable than the other two isomers as shown in Table 2.

TABLE 1: ^{1}H NMR Resonances for Methylene Protons of the Three Proposed Isomers of $(C_6H_5CH_2)_2C_{70}$ in $CS_2/CDCl_2$

			chemical shift (ppm)		coupling constant (Hz)		
proposed 1,4-isomer	resonance	intensity	H_a	H_b	J_1	J_2	$\Delta\delta$ (Hz)[a]
22,41-adduct	AB quartet	1.00	2.88	2.94	13.0	13.0	16.6
22,25-adduct	AB quartet	1.72	3.60	3.66	13.0	13.3	16.4
22,45-adduct	singlet	0.92	3.35				

[a] $\Delta\delta$ is the separation (Hz) between the centers of two doublets for an AB quartet.

TABLE 2: Heat of Formation of All Five Possible $C_6H_5CH_2C_{70}^-$ Isomers and Some $(C_6H_5CH_2)_2C_{70}$ Isomers Calculated by the PM3 Method

$C_6H_5CH_2C_{70}^-$ isomer	ΔH_f (kcal mol^{-1})	$C_6H_5CH_2C_{70}^-$ isomer	ΔH_f (kcal mol^{-1})
7-$C_6H_5CH_2C_{70}^-$	810.1	6-$C_6H_5CH_2C_{70}^-$	817.0
22-$C_6H_5CH_2C_{70}^-$	811.0	23-$C_6H_5CH_2C_{70}^-$	830.3
5-$C_6H_5CH_2C_{70}^-$	812.9		

A 1,4-addition to 7-$C_6H_5CH_2C_{70}^-$ would lead to the 1,7- or 7,24-isomers,[14] neither of which would show AB quartets or a singlet in the NMR spectrum since the two adducts both have C_1 symmetry. A 1,4-addition to 5-$C_6H_5CH_2C_{70}^-$ would produce the 5,8-isomer which is equivalent to the 1,7-isomer. On the other hand, a 1,4-addition to 22-$C_6H_5CH_2C_{70}^-$ would produce the 22,25- or 22,41-isomer, both of which would exhibit AB quartets since they have a C_s and a C_2 symmetry, respectively. The AB quartet of 1,4-$(C_6H_5CH_2)_2C_{60}$[20a] is located at 3.73 ppm, and the curvature of the C_{70} molecule resembles that of C_{60} at the 22,25-positions.[12] Thus, we assign the AB quartet centered at 3.63 ppm to the 22,25-adduct, while the AB quartet centered at 2.91 ppm is assigned to the 22,41-adduct. The 22,41-isomer of $C_{70}H_2$ is known to be theoretically the most stable among the 1,4-adducts.[14] The monoalkyl precursor of the $(C_6H_5CH_2)_2C_{70}$ isomers which should give two AB quartets may therefore be 22-$C_6H_5CH_2C_{70}^-$ rather than the 7- or 5-isomer of $C_6H_5CH_2C_{70}^-$.

The two benzylmethylene groups of $(C_6H_5CH_2)_2C_{70}$ can give singlet signals when the isomer has a symmetry higher than C_{2v} or when two benzyl groups attached to equivalent carbons are well-separated from each other and can rotate freely on the NMR time scale. The 23,40-$(C_6H_5CH_2)_2C_{70}$ species is the only isomer which has C_{2v} symmetry.[31] The precursor of 23,40-$(C_6H_5CH_2)_2C_{70}$ should be 23-$C_6H_5CH_2C_{70}^-$. However, 23-$C_6H_5CH_2C_{70}^-$ is the most thermodynamically unstable monobenzyl adduct anion as shown in Table 2, and it has been suggested that a nucleophilic attack at the equator of C_{70} does not occur.[30] Thus, the only case in which the ^{1}H NMR signals of the two benzylmethylene groups of $(C_6H_5CH_2)_2C_{70}$ would exhibit a singlet seems to be when the two benzyl groups are located far enough away from each other that a free rotation of the two benzyl groups becomes possible. The only isomer derived from 22-$C_6H_5CH_2C_{70}^-$ which satisfies these conditions is 22,45-$(C_6H_5CH_2)_2C_{70}$, which has a C_2 symmetry. In this case, the expected AB quartet which originates from such a molecule can be seen as a singlet. This type of addition may occur at the 1- and 4-positions of a butadiene moiety buried in four six-membered (pyrene-type) rings which are not found in the C_{60} skeleton but are involved in C_{70}.

The ^{13}C NMR spectrum of $(C_6H_5CH_2)_2C_{70}$ which exhibits resonances assigned to three methylene groups and three sp^3 C_{70} carbons and the ^{1}H$-$^{1}H COSY data show that the three sets of resonances do not correlate with each other.[32] Both results are consistent with the presence of three $(C_6H_5CH_2)C_{70}$ isomers in the major fraction of the HPLC trace in Figure 2. It was recently reported that the analytical Buckyclutcher I column is not able to separate C_{70} adducts of $(Ph_3P)_2PtC_{60}$,[33] and this appears also to be the case for the three examined isomers of $(C_6H_5CH_2)_2C_{70}$.

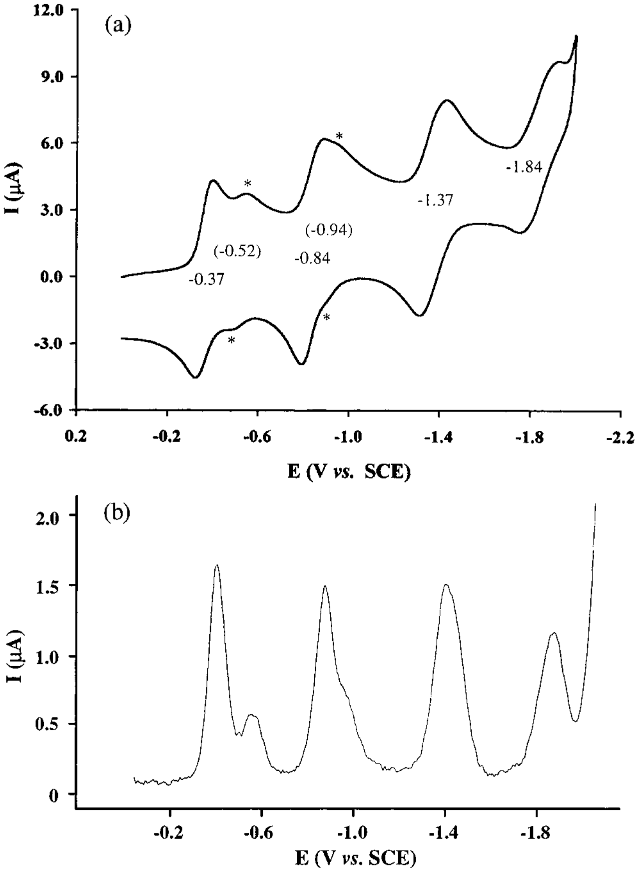


Figure 5. (a) Cyclic voltammogram (scan rate 0.10 V s^{-1}) and (b) differential pulse voltammogram (scan rate 0.01 V s^{-1}, modulation amplitude 25 mV) of $(C_6H_5CH_2)_2C_{70}$ in PhCN containing 0.1 M TBAP. Peaks marked with asterisks are assigned as the first two reductions of the minor $(C_6H_5CH_2)_2C_{70}$ isomer, and $E_{1/2}$ values for these reductions are given in parentheses.

TABLE 3: Reduction Potentials of C_{70} and $(C_6H_5CH_2)_2C_{70}$ in PhCN Containing 0.1 M TBAP[a]

	$E_{1/2}$ (V *vs* SCE)			
species	1st	2nd	3rd	4th
C_{70}	−0.42	−0.83	−1.27	−1.70
$(C_6H_5CH_2)_2C_{70}$ major component[b]	−0.37	−0.84	−1.37	−1.84
$(C_6H_5CH_2)_2C_{70}$ minor component[c]	−0.52	−0.94	−1.37	−1.84

[a] The Fc$^+$/Fc couple was 0.49 V *vs* SCE under the same conditions. [b] Proposed mixture of 22,41- and 22,25-adducts. [c] Proposed 22,45-adduct.

Cyclic Voltammetry of $(C_6H_5CH_2)_2C_{70}$. Figure 5 shows a cyclic voltammogram and differential pulse voltammogram of the three unresolved $(C_6H_5CH_2)_2C_{70}$ isomers in PhCN containing 0.1 M TBAP, while Table 3 lists the $E_{1/2}$ values for reduction of C_{70} and the $(C_6H_5CH_2)_2C_{70}$ isomers under the same solution conditions. The voltammetric data show only two sets of electrochemical processes rather than three as seen in the ^{1}H

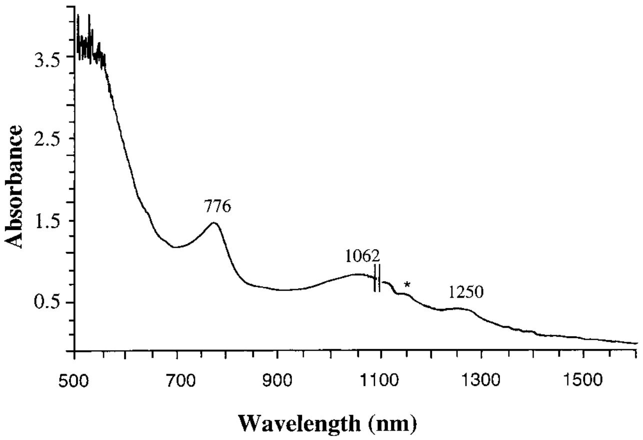


Figure 6. Visible and near-IR spectra of $(C_6H_5CH_2)_2C_{70}^{\bullet -}$ (3.1×10^{-4} M) in PhCN containing 0.2 M TBAP. The spectrum from 500 to 1000 nm was recorded on a HP 8453 diode array spectrophotometer, while absorptions from 1000 to 1600 nm were measured with a Perkin-Elmer 330 UV−vis−near-IR spectrophotometer. The peak marked with an asterisk is due to an artifact caused by the instrument.

NMR data of Figure 4. The major electroactive component of the $(C_6H_5CH_2)_2C_{70}$ mixture undergoes four reversible one-electron reductions at $E_{1/2} = -0.37$, -0.84, -1.37, and -1.84 V, and those values can be compared to $E_{1/2} = -0.42$, -0.83, -1.27, and -1.70 V for reduction of C_{70}. The first reduction of $(C_6H_5CH_2)_2C_{70}$ is thus shifted *anodically* by 50 mV with respect to the first reduction of C_{70}, and this result contrasts with the reductions of derivatives of C_{60} and C_{70}, which are usually shifted *cathodically* by about 100 mV with respect to reductions of the parent compound.[20]

The two electron-transfer processes at $E_{1/2} = -0.52$ and -0.94 V in Figure 5a are shown more clearly by the differential pulse voltammogram in Figure 5b. The peak currents for these processes are smaller than those of the four major electrode processes. If the electron-transfer processes at $E_{1/2} = -0.52$ and -0.94 V involve reduction of the minor 22,45-isomer of $(C_6H_5CH_2)_2C_{70}$, the expected third and fourth reductions would be overlapped with the third and fourth reductions of the two major isomeric fractions, which seem to be electrochemically indistinguishable from each other. In such a case, the ratio of peak currents for the reduction of combined 22,41- and 22,25-adducts at -0.37 and the 22,45-adduct at -0.52 V (76:24) should correspond to the ratio of isomers shown by the ratios of integrated intensities given in Table 1. The ratio of peak currents for the process at -0.37 and -0.52 V agrees well with the ^{1}H NMR combined intensity ratio (68:23) of the two AB quartets (22,41- and 22,25-isomers) and the singlet (22,45−isomer), thus suggesting these assignments as indicated in Table 3.

The $E_{1/2}$ values for the first two reductions of the smaller isomeric fraction (-0.52 and -0.94 V) differ from $E_{1/2}$ values for the first two reductions of the major $(C_6H_5CH_2)_2C_{70}$ component (-0.37 and -0.84 V) (see Figure 5 and Table 3), but this may be consistent with the fact that the minor and major fractions of $(C_6H_5CH_2)_2C_{70}$ have different types of addition patterns.

Vis−Near-IR Spectra of $(C_6H_5CH_2)_2C_{70}^-$. The anions of C_{60} and C_{70} both exhibit distinctive absorption bands in the visible and near-IR regions.[34,35] Anions of R_2C_{60} derivatives also show near-IR spectral features, and a similar result is expected for the anions of R_2C_{70}. However, no vis−near-IR data of any 1,4-R_2C_{70} derivative in its monoanionic form are available in the literature. Figure 6 shows the visible and near-IR spectra of $(C_6H_5CH_2)_2C_{70}^{\bullet -}$ in PhCN containing 0.2 M TBAP, while Table 4 lists the absorption maxima and molar absorptivities for absorption bands of $(C_6H_5CH_2)_2C_{70}^{\bullet -}$, $C_{70}^{\bullet -}$, and t-BuC_{70}^-.[23] The monoanion of the organofullerene, $(C_6H_5CH_2)_2C_{70}^{\bullet -}$, has a strong absorption band at 776 nm along with two weaker absorption bands at 1062 and 1250 nm which cannot be assigned to a specific isomer. These absorption maxima, however, can be compared to the absorption maxima of $C_{70}^{\bullet -}$ which exhibit one strong absorption band around 1368 nm and one very weak absorption band around 790 nm.[23,34,35] It is perhaps interesting to point out that t-BuC_{70}^- also has a band at 777 nm whose intensity is weaker than that of $(C_6H_5CH_2)_2C_{70}^{\bullet -}$ but stronger than that of $C_{70}^{\bullet -}$.[23] Efforts were also made to electrogenerate $(C_6H_5CH_2)_2C_{70}^{2-}$ to examine the spectral properties of the compound, but this was unsuccessful owing to an instability of the dianionic species during the bulk electrolysis time scale.

TABLE 4: Spectral Data for $(C_6H_5CH_2)_2C_{70}^{\bullet -}$, $C_{70}^{\bullet -}$, and t-BuC_{70}^- in PhCN Containing 0.2 M TBAP

	λ_{max} (nm) (ϵ (M^{-1} cm^{-1}))[a]	
species	vis	near-IR
$(C_6H_5CH_2)_2C_{70}^{\bullet -}$	776 (4500)	1062 (2400), 1250 (1160)
$C_{70}^{\bullet -}$	790 (1300)	1368 (4000)[b]
t-BuC_{70}^-	777 (1800)	none

[a] The average uncertainty in ϵ measurement is ca. 20%. [b] Values are taken from ref 34.

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