Splitting of Degenerate Orbitals of Dibenzyl and Tetrabenzyl Adducts of C_{60}: ESR of the Radical Anions and the Rotation Barriers of Benzyl Groups

Shunichi Fukuzumi,*,[†] Tomoyoshi Suenobu,[†] Xiang Gao,[‡] and Karl M. Kadish*,[‡]

Department of Material and Life Science, Graduate School of Engineering, Osaka University,
CREST, Japan Science and Technology Corporation, Suita, Osaka 565-0871, Japan, and
Department of Chemistry, University of Houston, Houston, Texas 77204-5641

Received: November 4, 1999; In Final Form: January 18, 2000

The degenerate $^2E_{1u}$ ground state and the thermally accessible low-lying $^2A_{2u}$ excited state of $C_{60}^{\bullet-}$ give a broad ESR signal ($\Delta H_{msl} = 30.9$ G at 213 K) which has a smaller g value (1.9984) as compared to the free spin value (2.0023) and linewidth which decreases with decreasing temperature ($\Delta H_{msl} = 6.5$ G at 133 K). The I_h symmetry of the parent C_{60} is lowered by the introduction of two benzyl groups to C_{60} to give 1,4-$(C_6H_5CH_2)_2C_{60}$, which leads to the larger g value (2.0004) of 1,4-$(C_6H_5CH_2)_2C_{60}^{\bullet-}$ than that of $C_{60}^{\bullet-}$ ($g = 1.9984$) and a much smaller linewidth ($\Delta H_{msl} = 2.5$ G at 213 K) which is independent of temperature. An even smaller ΔH_{msl} value (0.17 G) and a larger g value (2.0011) are observed in the tetrabenzyl C_{60} adduct radical anion, 1,4,10,24-$(C_6H_5CH_2)_4C_{60}^{\bullet-}$. This is ascribed to a large splitting of the degenerate t_{1u} orbitals caused by introduction of four benzyl groups to C_{60}. In this case, a hyperfine structure due to two nonequivalent protons of only one benzyl group (aH$_1$ = 0.31 G, aH$_2$ = 0.11 G) is observed and this is consistent with the predicted localized spin density at the C2 position next to the C1 carbon to which a benzyl group is attached. The observation of two nonequivalent hyperfine coupling constants due to the benzyl methylene protons indicates that rotation of the benzyl group at the C1 position is slow on the ESR time scale. The slow rotation rates of the benzyl groups in 1,4-dibenzyl adducts of C_{60} and the activation parameters were determined from a line broadening of the methylene protons in the ^{1}H NMR spectra with increasing temperature.

Introduction

Buckminsterfullerene, C_{60}, has I_h symmetry and the t_{1u} LUMO (lowest unoccupied molecular orbital) and t_{1g} LUMO+1 orbitals are both triply degenerate.[1,2] Placing one electron into the triply degenerate LUMO gives a species whose ESR spectrum shows a very broad signal with a g value (1.9984) which is significantly lower than the free spin value (2.0023).[3−5] Although Jahn-Teller distortion lowers the symmetry of $C_{60}^{\bullet-}$ to D_{5d}, the SOMOs (singly occupied molecular orbitals) of the monoanion are still doubly degenerate, causing the low g value and the large linewidth.[3−5] A strong NIR band is seen at $\lambda_{max} = 1080$ nm for $C_{60}^{\bullet-}$, and this absorption band is ascribed to the symmetry allowed $t_{1u}-t_{1g}$ transition[6] and predicted to be about 1 eV.[7] The symmetry of derivatized C_{60} radical anions is reduced from that of $C_{60}^{\bullet-}$, and this is expected to affect both the NIR (Near Infrared) and ESR spectra. The introduction of more than two groups to C_{60} at proximate positions may also lead to a hindered rotation of the addends. However, no systematic study has yet been reported as to the effects of addends on the ESR spectra of derivatized C_{60} radical anions nor is there any information in the literature on the hindered rotation of the addends.

We recently reported that a series of dialkyl and tetraalkyl derivatives of C_{60} could be formed by the reaction of C_{60}^{2-} with alkyl halides (RX).[8,9] The present paper reports the first systematic study on how splitting of the degenerate LUMO and LUMO+1 C_{60} orbitals is caused by introduction of two or four benzyl groups to C_{60} and this leads to ESR spectra of the organofullerene radical anions that are quite different from those of the parent C_{60} radical anion. The hindered rotation of the addends on R_2C_{60} is also examined by measuring the temperature dependence of the ^{1}H NMR spectra.

Experimental Section

Materials. C_{60} (>99.95% pure) was purchased from Science Laboratories Co., Ltd., Japan, and used as received. Benzonitrile (PhCN) was purchased from Wako Pure Chemical Ind. Ltd., Japan, and distilled over P_2O_5 prior to use.[10] All alkyl halides, naphthalene, trifluoroacetic acid, and sodium were obtained commercially from Aldrich and Wako Pure Chemical Ind. Ltd., Japan in special grade. CS_2, hexanes, toluene, acetonitrile, methanol, and silica gel from EM Science (Gibbstown, NJ) were used without further treatment. Toluene-d_8 for NMR measurements was purchased from EURI SO-TOP, CEA, France and used as received. *tert*-Butyl iodide (t-BuI) from Wako Pure Chemical Ind. Ltd. was distilled in the dark under a reduced pressure of 100 mmHg at 333 K. Tetrahydrofuran (THF) was dried by refluxing under nitrogen with sodium prior to use. Tetra-n-butylammonium perchlorate (TBAP) was recrystallized from ethanol and dried under vacuum at 313 K. The sodium salt of the naphthalene radical anion (2.4×10^{-1} M in THF) was prepared by reduction of naphthalene (5.5 mmol) with sodium (5.0 mmol) under deaerated conditions in distilled THF at 298 K. The dimeric 1-benzyl-1,4-dihydronicotinamide [$(BNA)_2$] was prepared according to procedures described in the literature.[11,12]

The examined 1,4-R_2C_{60} derivatives (R = $C_6H_5CH_2$, 2-$BrC_6H_4CH_2$, 3-$BrC_6H_4CH_2$, and 4-$BrC_6H_4CH_2$) were prepared by a reaction of electrogenerated C_{60}^{2-} with RBr as described

---

[†] Osaka University.
[‡] University of Houston.

10.1021/jp993899j CCC: $19.00

previously.[13] This method was also utilized to prepare $(C_6H_5CH_2)_4C_{60}$ starting from 1,4-$(C_6H_5CH_2)_2C_{60}$.[9,14] The reaction between electrogenerated $(C_6H_5CH_2)_2C_{60}^{2-}$ and $C_6H_5CH_2Br$ in benzonitrile was allowed to proceed for 60 min. Benzonitrile was removed from the solution by a rotary evaporator after which the solid residue was washed with methanol and filtered to eliminate the TBAP supporting electrolyte and excess $C_6H_5CH_2Br$. The crude solid was mixed with a hexanes/toluene mixture (55:45 v/v) and then analyzed by HPLC. Some material could not be eluted with the hexanes/toluene mixture and required pure toluene to be eluted. The crystal structure of one fraction eluted with the hexanes/toluene mixture was determined as a 1,4;1,4-isomer of $(C_6H_5CH_2)_4C_{60}$, which is designated as 1,4,10,24-$(C_6H_5CH_2)_4C_{60}$.[14] Preparation of 1-*tert*-butyl-4-benzyl-1,4-dihydro[60]fullerene 1,4-(*t*-Bu)$(C_6H_5CH_2)C_{60}$ was accomplished by a reaction between chemically generated C_{60}^{2-} and *t*-BuI (1.66 mL) to give *t*-BuC_{60}^{-}, which reacts further with $C_6H_5CH_2Br$ to yield the final product.[9]

ESR Measurements. In a typical experiment for ESR measurements, a deaerated benzonitrile solution containing C_{60}, 1,4-R_2C_{60} derivatives (R = $C_6H_5CH_2$, 2-$BrC_6H_4CH_2$, 3-$BrC_6H_4CH_2$ and 4-$BrC_6H_4CH_2$), 1,4-(*t*-Bu)$(C_6H_5CH_2)C_{60}$ or 1,4,10,-24-$(C_6H_5CH_2)_4C_{60}$ (2.8×10^{-4} M), and $(BNA)_2$ (1.4×10^{-3} M) was added to a 3 mm quartz ESR tube under an atmospheric pressure of Ar. The samples containing $(BNA)_2$ and C_{60} or the C_{60} derivative were then irradiated in the cavity of the ESR spectrometer with the focused light of a 1000 W high-pressure Hg lamp through an aqueous filter. The ESR spectra of the radical anions of 1,4-$(C_6H_5CH_2)_2C_{60}$ or 1,4,10,24-$(C_6H_5CH_2)_4C_{60}$ formed by the photochemical reactions with $(BNA)_2$ were measured at various temperatures (133 to 233 K) with a JEOL X-band spectrometer (JES−RE1XE) using an attached VT (variable temperature) apparatus. The radical anion of 1,4-$(C_6H_5CH_2)_2C_{60}$ was also obtained by electron-transfer reduction with an equivalent amount of naphthalene radical anion which was prepared by reduction of naphthalene radical anion with Na.[12] The ESR spectra were recorded under nonsaturating microwave power conditions. The magnitude of modulation was chosen to optimize the resolution and the signal-to-noise (*S*/*N*) ratio of the observed spectra, when the maximum slope line-width (ΔH_{msl}) of the ESR signals was unchanged with larger modulation. The *g* values and hyperfine coupling constants were calibrated with an Mn^{2+} marker.

NMR Measurements. ^1H NMR spectra of 1,4-R_2C_{60} derivatives (R = $C_6H_5CH_2$, 2-$BrC_6H_4CH_2$, 3-$BrC_6H_4CH_2$, and 4-$BrC_6H_4CH_2$) and 1,4-(*t*-Bu)$(C_6H_5{-}CH_2)C_{60}$ in toluene-d_8 were recorded on either a Bruker AMX-600 or a JEOL GSX-400 (400 MHz) spectrometer at different temperatures. Chemical shifts were expressed in parts per million downfield from tetramethylsilane as an internal standard ($\delta = 0$).

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.[15] 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 a keyword "PRECISE". To estimate the rotation barrier of the benzyl groups on 1,4-$(C_6H_5CH_2)_2C_{60}$, the ΔH_f values were calculated by optimizing the total molecular energy with respect to all structural variables except for the torsion angle which was varied.

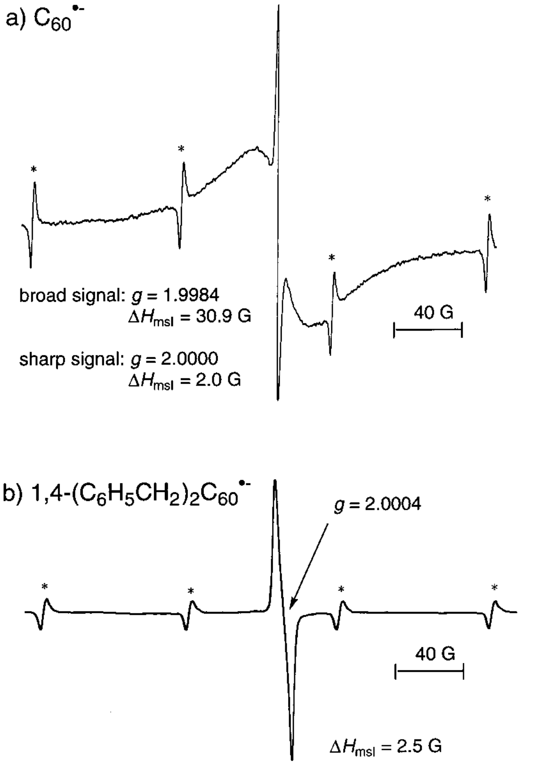
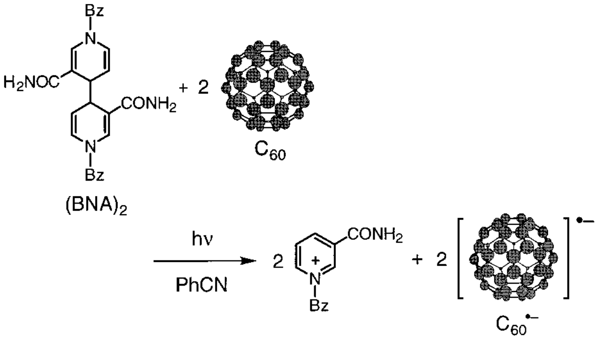


Figure 1. ESR spectra of (a) $C_{60}^{\bullet-}$ generated in the photoinduced electron transfer from $(BNA)_2$ (1×10^{-4} M) to C_{60} (2×10^{-4} M) in deaerated benzonitrile under irradiation of UV−vis light from Xe lamp and (b) 1,4-$(C_6H_5CH_2)_2C_{60}^{\bullet-}$ generated in the electron-transfer reduction of 1,4-$(C_6H_5CH_2)_2C_{60}$ (2×10^{-4} M) by naphthalene radical anion (2×10^{-4} M) in deaerated PhCN observed in frozen benzonitrile at 213 K. Asterisk (*) denotes an Mn^{2+} marker.

Results and Discussion

ESR Spectra of Radical Anions of C_{60} Derivatives. When the dimeric 1-benzyl-1,4-dihydronicotinamide [$(BNA)_2$] is used as an electron donor, irradiation of a PhCN solution containing $(BNA)_2$ and C_{60} with visible light results in the complete one-electron reduction of C_{60} to $C_{60}^{\bullet-}$ (eq 1).[9] The formation of $C_{60}^{\bullet-}$ detected by ESR spectroscopy after the photochemical reaction of C_{60} with $(BNA)_2$ is shown in Figure 1a; there is a characteristic broad signal of $C_{60}^{\bullet-}$ ($g = 1.9984$, $\Delta H_{msl} = 30.9$ G) observed at 213 K together with a sharp "spike" signal ($g = 2.0000$, $\Delta H_{msl} = 2.0$ G) which is always seen in the ESR spectrum of $C_{60}^{\bullet-}$.[3−5,16−19] The percentage of the spike signal is just less than 1% of the major broad signal of $C_{60}^{\bullet-}$. Essentially, the same ESR signals are obtained for $C_{60}^{\bullet-}$ produced by the reduction of C_{60} with naphthalene radical anion.



(1)

The radical anion of 1,4-$(C_6H_5CH_2)_2C_{60}$[20] shows a much sharper signal than $C_{60}^{\bullet-}$ and has a larger *g* value ($g = 2.0004$,

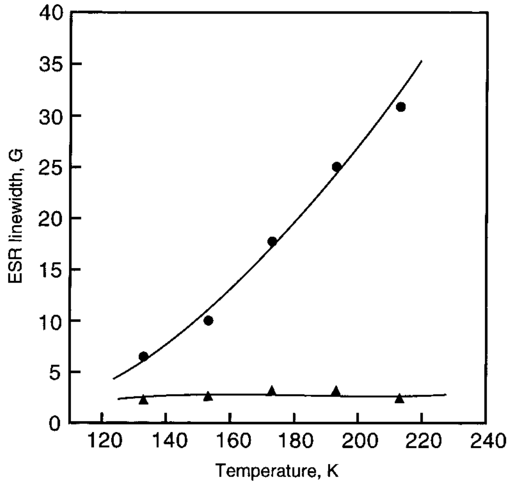


Figure 2. Temperature dependence of linewidth of ESR spectra for $C_{60}^{\bullet-}$ (●) and 1,4-$(C_6H_5CH_2)_2C_{60}^{\bullet-}$ (▲) in frozen benzonitrile.

ΔH_{msl} = 2.5 G) as illustrated in Figure 1b. In addition, no additional broader or narrower signals are observed. Hyperfine structure due to methylene protons of the benzyl groups is also not observed, even at a much smaller modulation (0.2 G), and this could be due to the fact that the hyperfine coupling constants may be too small to detect with this linewidth (2.5 G).

Figure 2 shows plots of the linewidth (ΔH_{msl}) for the broad signal of $C_{60}^{\bullet-}$ and the sharp signal of 1,4-$(C_6H_5CH_2)_2C_{60}^{\bullet-}$ as a function of temperature. The ΔH_{msl} value of $C_{60}^{\bullet-}$ increases significantly with temperature as was earlier reported,[3-5,21] while the ΔH_{msl} value of 1,4-$(C_6H_5CH_2)_2C_{60}^{\bullet-}$ remains unchanged at 2.5 G, irrespective of temperature. The broad ESR signal, the temperature dependence of the ΔH_{msl} value of $C_{60}^{\bullet-}$, and its small *g* value as compared to the free spin value (2.0023) have been ascribed to a degenerate $^2E_{1u}$ ground state and a thermally accessible low-lying $^2A_{2u}$ excited state, both of which would arise from Jahn−Teller distortion of $C_{60}^{\bullet-}$ along the principal axis in D_{5d} symmetry.[18,22,23] Since 1,4-$(C_6H_5CH_2)_2C_{60}$ has much lower symmetry (C_s symmetry), the triply degenerate t_{1u} orbitals in the parent C_{60} would no longer be degenerate in 1,4-$(C_6H_5CH_2)_2C_{60}$. In such a case, there would be no thermally accessible low-lying excited state in 1,4-$(C_6H_5CH_2)_2C_{60}^{\bullet-}$. A lower *g* value and larger linewidth results from a spin−orbit coupling which arises because of the existence of a low-lying excited state.[24] The linewidth of 1,4-$(C_6H_5CH_2)_2C_{60}^{\bullet-}$ therefore becomes much smaller than that of $C_{60}^{\bullet-}$ and should be independent of temperature while the *g* value (2.0004) becomes larger than that of $C_{60}^{\bullet-}$ (g = 1.9984). A relatively narrow ESR signal (ΔH_{msl} = 0.5−3 G) was also reported for $C_{76}^{\bullet-}$ which has low symmetry (D_2) with a *g* value close to the free spin value.[25] The radical anion of C_{84} which has D_{2d} symmetry also gives a *g* value close to the free spin value with a relatively small linewidth (ΔH_{msl} = 2.3 G).[26]

The introduction of two additional benzyl addends to the dibenzyl adduct of C_{60} may result in much larger splitting of the triply degenerate t_{1u} orbitals than is seen in the parent C_{60}. An X-ray structure of the major product isolated in a reaction of the dianion of 1,4-$(C_6H_5CH_2)_2C_{60}$ with $C_6H_5CH_2Br$ reveals formation of 1,4,10,24-$(C_6H_5CH_2)_4C_{60}$ which has no symmetry (C_1).[14,27] The optimized structure of 1,4,10,24-$(C_6H_5CH_2)_4C_{60}$ was obtained by PM3 MO calculations and is shown in Figure 3, agreeing well with the X-ray structure.[14]

The radical anion of 1,4,10,24-$(C_6H_5CH_2)_4C_{60}$ produced by the photochemical reaction with $(BNA)_2$ shows a much sharper ESR signal as compared to 1,4-$(C_6H_5CH_2)_2C_{60}^{\bullet-}$, and this spectrum is illustrated in Figure 4a where the hyperfine structure is observed with a small modulation (0.2 G). The *g* value of 2.0010 for 1,4,10,24-$(C_6H_5CH_2)_4C_{60}^{\bullet-}$ becomes closer to the free spin value (g = 2.0023) and is quite different from the *g* value of $C_{60}^{\bullet-}$ (g = 1.9984). Figure 4b shows the computer

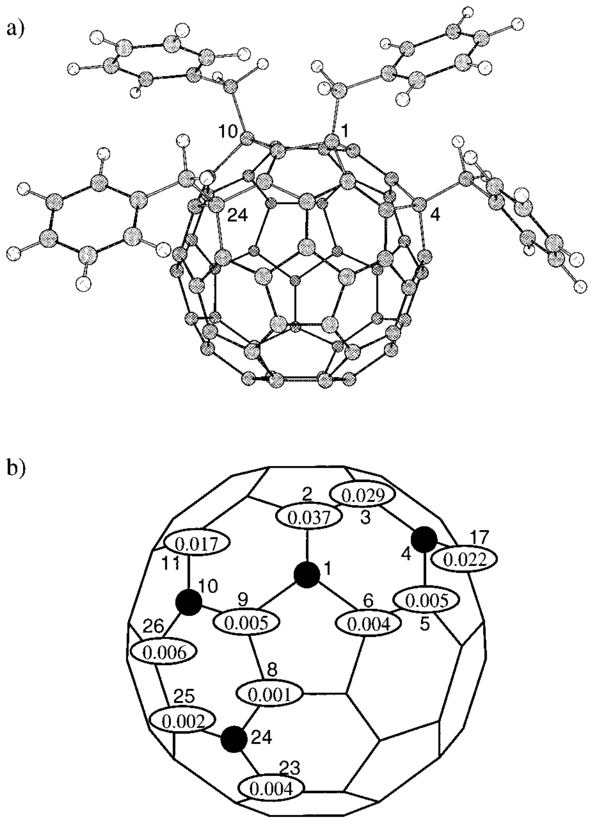


Figure 3. (a) The MO calculation optimized structure and (b) the schematic representation of 1,4,10,24-$(C_6H_5CH_2)_4C_{60}$. The position of substitution on the C_{60} molecule is indicated by the solid circles at 1, 4, 10, 24. The number in the open ellipse represents the sum of the square of the carbon 2p orbital coefficients $[(2p_x)^2 + (2p_y)^2 + (2p_z)^2]$ for the LUMO orbital. Selected carbon atoms are labeled using IUPAC numbering.

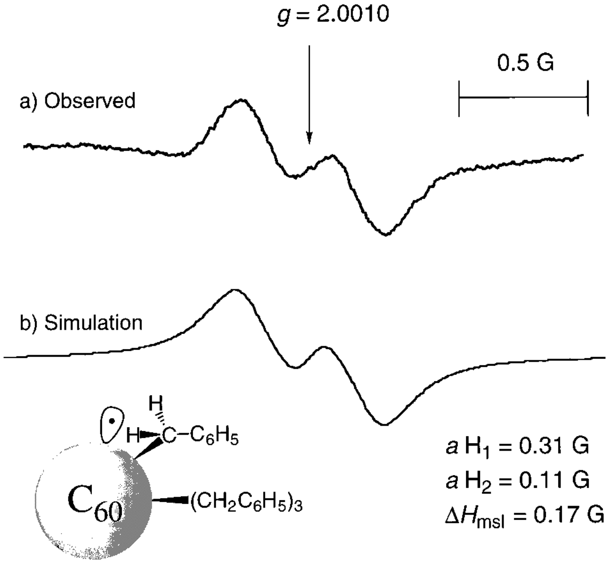


Figure 4. ESR spectrum of (a) 1,4,10,24-$(C_6H_5CH_2)_4C_{60}^{\bullet-}$ generated in the photochemical reduction of 1,4,10,24-$(C_6H_5CH_2)_4C_{60}$ (2×10^{-4} M) with $(BNA)_2$ (2×10^{-4} M) in deaerated PhCN observed at 298 K and (b) the computer simulation spectrum.

simulation spectrum of the tetrabenzyl C_{60} adduct monoanion and gives $aH_1 = 0.31$ G, $aH_2 = 0.11$ G, and $\Delta H_{msl} = 0.17$ G, which agree with the experimental results in Figure 4a.[28]

The much smaller ΔH_{msl} value (0.17 G) and larger g value (2.0011) of 1,4,10,24-$(C_6H_5CH_2)_4C_{60}^{\bullet -}$ as compared to $C_{60}^{\bullet -}$ ($\Delta H_{msl} = 30.9$ G and $g = 1.9984$) are ascribed to a large splitting of degenerate t_{1u} orbitals caused by introduction of four benzyl groups to C_{60}. The hyperfine structure in Figure 4 arises from interaction of the single unpaired electron with two nonequivalent protons of only one of the four benzyl groups in 1,4,10,24-$(C_6H_5CH_2)_4C_{60}^{\bullet -}$. The magnitude of the proton hyperfine coupling constant may be proportional to the spin density on the carbon that is located next to the carbon to which the benzyl group is attached. The square of the coefficient (C_i^2) of the p π atomic orbital of the ith carbon atom in the LUMO of 1,4,10,24-$(C_6H_5CH_2)_4C_{60}$ may correspond to the spin density in the radical anion. MO calculations of the radical anion of 1,4,10,24-$(C_6H_5CH_2)_4C_{60}$ with the unrestricted Hartree−Fock (UHF) formalism would have been preferred but unfortunately the SCF field could not be obtained in the calculation. Thus, a PM3 semiempirical MO calculation of 1,4,10,24-$(C_6H_5CH_2)_4C_{60}$ was made with the restricted Hartree−Fock (RH) formalism to give the C_i^2 values of the p π atomic orbital of carbons in the LUMO orbitals and only the C_i^2 values for the carbons next to those to which benzyl groups are attached are shown in Figure 3b.[29] It is found that the C2 position next to the C1 carbon to which a benzyl group is attached has the largest value (0.037).[30] This suggests that the unpaired electron in 1,4,10,24-$(C_6H_5CH_2)_4C_{60}^{\bullet -}$ is much more localized as compared to the completely delocalized unpaired electron in $C_{60}^{\bullet -}$. The observation of two nonequivalent hyperfine coupling constants due to the benzyl methylene protons of tetrabenzyl adduct anion radical indicates that rotation of the benzyl group at the C1 position is slow on the ESR time scale. Rotation of the other three benzyl groups may also be slow due to the steric effects of the bulky benzyl groups located close to each other. Rotation rates of the benzyl groups in the neutral 1,4-dibenzyl adducts of C_{60} were also examined on the NMR time scale which is much slower than an ESR time scale and this is discussed below.

Hindered Rotation of Benzyl Groups in Neutral Compounds. The ^{1}H NMR signals due to the benzyl methylene protons of each R_2C_{60} derivative (R = 2-$BrC_6H_4CH_2$, 3-$BrC_6H_4CH_2$, or 4-$BrC_6H_4CH_2$) in $CS_2/CDCl_3$ have been reported to show an AB quartet between 3.68 and 4.16 ppm.[13] The two methylene protons of each benzyl group in the 1,4-disubstituted C_{60} derivative are not equivalent due to the C_s symmetry of each compound and these two protons are therefore diastereotopic to give an AB quartet when rotation is slow on the NMR time scale.[31] The difference in chemical shifts of the two methylene proton resonances of 1,4-$(C_6H_5CH_2)_2C_{60}$, which is defined as $\Delta\delta$, decreases with increasing temperature as shown in Figure 5. The slow rotation at 298 K gives rise to AB quartet signals from individual diastereotopic protons. However, as the temperature increases, the rotation rate of the two benzyl groups increases, the signals broaden and a smaller $\Delta\delta$ value begins to coalesce (Figure 5). The temperature dependence of $\Delta\delta$ values for each 1,4-R_2C_{60} derivative (R = 2-$BrC_6H_4CH_2$, 3-$BrC_6H_4CH_2$, or 4-$BrC_6H_4CH_2$) and 1,4-(t-Bu)$(C_6H_5CH_2)C_{60}$ is shown in Figure 6. In the case of 1,4-(2-$BrC_6H_4CH_2)_2C_{60}$ and 1,4-(t-Bu)$(C_6H_5CH_2)C_{60}$, coalescence of these methylene proton signals that have larger $\Delta\delta$ values than 1,4-$(C_6H_5CH_2)_2C_{60}$ was not reached up to 370 K, at which point the signals of 1,4-$(C_6H_5CH_2)_2C_{60}$ already coalesced (Figure 5). At the higher temperature the compound starts to decompose.

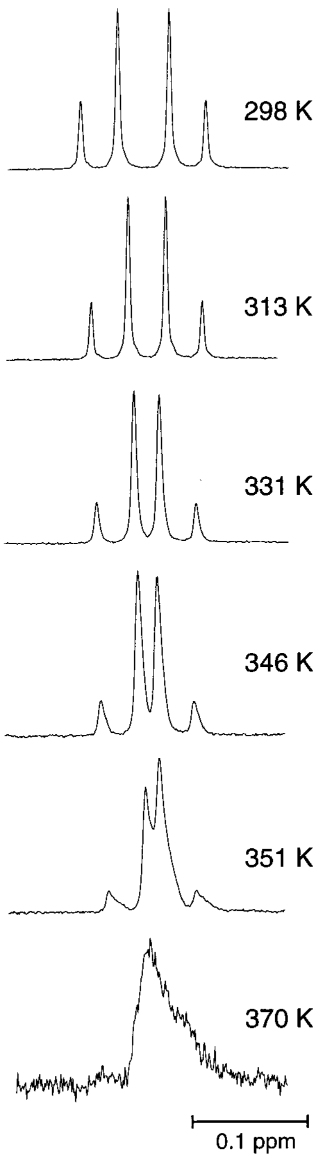


Figure 5. Temperature dependence of the NMR spectra of 1,4-$(C_6H_5CH_2)_2C_{60}$ in toluene-d_8 at various temperatures.

The rotation rate constant (k) can be derived from the $\Delta\delta$ value using eq 2,[32]

$$k = [(\Delta\delta_0^{\ 2} - \Delta\delta^2)\nu_0^{\ 2}]^{1/2}/(2\sqrt{2}) \qquad (2)$$

where $\Delta\delta_0$ is the value without rotation and ν_0 is the resonance frequency (400 MHz). The rotation rate constants (k) thus obtained are plotted as a function of temperature for each 1,4-R_2C_{60} derivative using the Eyring equation, eq 3. The

$$\ln(k/T) = -\Delta H^{\ddagger}/RT + \Delta S^{\ddagger}/R + \ln(k_B/h) \qquad (3)$$

enthalpies and entropies of activation ($\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$) for the rotational barrier in each molecule (k_B is the Boltzman constant, h is Planck's constant, and R is the universal gas constant in eq 3) are obtained from the Eyring plots in Figure 7 and the activation parameters thus obtained are listed in Table 1.[33]

The $\Delta H^{\ddagger}$ values are in the range 2.2−2.8 kcal mol^{-1}, while the $\Delta S^{\ddagger}$ values are highly negative and range from −45 to −48 cal K^{-1} mol^{-1}. The largest $\Delta H^{\ddagger}$ value (2.8 kcal mol^{-1}) is obtained for 1,4-(t-Bu)$(C_6H_5CH_2)C_{60}$ due to the large steric interaction between the bulky t-Bu group and $C_6H_5CH_2$ group

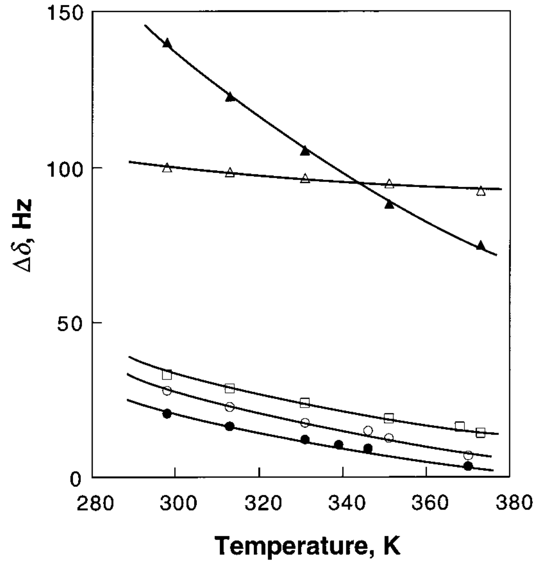


Figure 6. Temperature dependence of the difference in chemical shifts (Δδ) of two benzyl protons of 1,4-$(C_6H_5CH_2)_2C_{60}$ (○), 1,4-*t*-Bu$(C_6H_5CH_2)C_{60}$ (△), 1,4-(3′-$BrC_6H_4CH_2)_2C_{60}$ (□), 1,4-(4′-$BrC_6H_4CH_2)_2C_{60}$ (●), and 1,4-(2′-$BrC_6H_4CH_2)_2C_{60}$ (▲) (2.0×10^{-4} M).

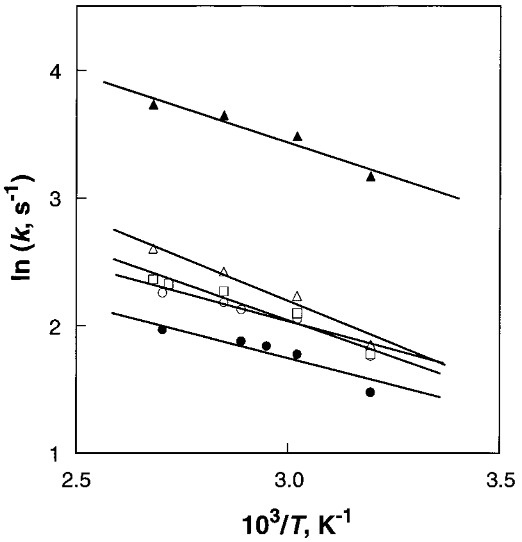


Figure 7. Arrhenius plots of rotation rate constants (*k*) vs T^{-1} of benzyl group for 1,4-$(C_6H_5CH_2)_2C_{60}$ (○), 1,4-*t*-Bu$(C_6H_5CH_2)C_{60}$ (△), 1,4-(3′-$BrC_6H_4CH_2)_2C_{60}$ (□), 1,4-(4′-$BrC_6H_4CH_2)_2C_{60}$ (●), and 1,4-(2′-$BrC_6H_4CH_2)_2C_{60}$ (▲) (2.0×10^{-4} M).

TABLE 1: Activation Parameters of Rotation of Benzyl or Substituted Benzyl Groups in 1,4-Dialkylated C_{60}

compound	$\Delta H^{\ddagger\,a}$ kcal mol^{-1}	$\Delta S^{\ddagger\,b}$ cal K^{-1} mol^{-1}
(*t*-Bu)$(C_6H_5CH_2)C_{60}$	2.8	−46
$(C_6H_5CH_2)_2C_{60}$	2.3	−48
$(2\text{-}BrC_6H_4CH_2)_2C_{60}$	2.2	−45
$(3\text{-}BrC_6H_4CH_2)_2C_{60}$	2.2	−48
$(4\text{-}BrC_6H_4CH_2)_2C_{60}$	2.7	−47

[a] The experimental error is ±0.2 kcal mol^{-1}. [b] The experimental error is ±2 cal K^{-1} mol^{-1}.

as compared to other dibenzyl adducts. The small $\Delta H^{\ddagger}$ value for 1,4-$(C_6H_5CH_2)_2C_{60}$ is consistent with the maximum change (1.5 kcal mol^{-1}) in the heat of formation of 1,4-$(C_6H_5CH_2)_2C_{60}$ ($\Delta\Delta H_f$) with variation of the dihedral angle (θ) taken as the torsion angle shown in Figure 8 (see Experimental Section). All other structural variables including the geometry of the other benzyl group were optimized in the calculation. The calculation indicates that rotation of the two proximate benzyl groups in 1,4-$(C_6H_5CH_2)_2C_{60}$ highly correlates to each other. This may be the reason for the largely negative $\Delta S^{\ddagger}$ values observed in the hindered rotation of the benzyl groups in the compounds listed in Table 1.

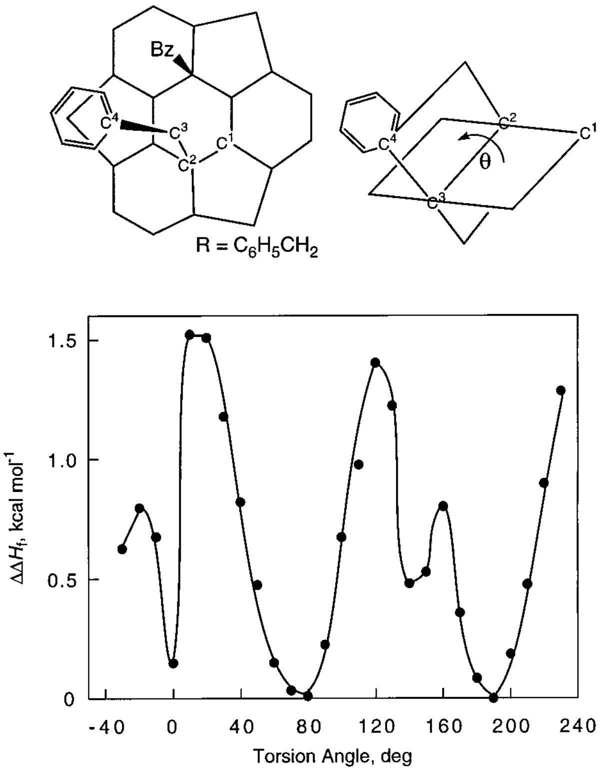


Figure 8. Plot of change in the calculated heat of formation ($\Delta\Delta H_f$) vs torsion angle (θ) defined as the dihedral angle for the rotation of benzyl group in 1,4-$(C_6H_5CH_2)_2C_{60}$.

Acknowledgment. We thank an International Scientific Research Program (11694079) and a Grant-in-Aid for Scientific Research Priority Area (nos. 11133232 and 11166241) from the Ministry of Education, Science, Culture and Sport, Japan and the Robert A. Welch Foundation (K.M.K., Grant E-680) and the Petroleum Research Fund (K.M.K., Grant ACS-PRF27598-AC5) for financial support. We also thank Prof. C. A. Reed for a preprint of his excellent review article (ref 3).

References and Notes

(1) Hirsch, A. *The Chemistry of the Fullerenes*; Georg Thieme Verlag: New York, 1994.

(2) Bilow, U.; Jansen, M. *J. Chem. Soc., Chem. Commun.* **1994**, 403.

(3) Reed, C. A.; Bolskar, R. D. *Chem. Rev.*, **2000**, *100*, in press.

(4) Eaton, S. S.; Eaton, G. R. *Appl. Magn. Reson.* **1996**, *11*, 155.

(5) (a) Allemand, P.-M.; Srdanov, G.; Koch, A.; Khemani, K.; Wudl, F.; Rubin, Y.; Diederich, F.; Alvarez, M. M.; Anz, S. J.; Whetten, R. L. *J. Am. Chem. Soc.* **1991**, *113*, 2780. (b) Dubois, D.; Kadish, K. M.; Flanagan, S.; Haufler, R. E.; Chibante, L. P. F.; Wilson, L. J. *J. Am. Chem. Soc.* **1991**, *113*, 4364.

(6) (a) Greaney, M. A.; Gorun, S. M. *J. Phys. Chem.* **1991**, *95*, 7142. (b) Gasyna, Z.; Andrews, L.; Schatz, P. N. *J. Phys. Chem.* **1992**, *96*, 1525. (c) Kato, T.; Kodama, T.; Shida, T.; Nakagawa, T.; Matsui, Y.; Suzuki, S.; Shiromaru, H.; Yamauchi, K.; Achiba, Y. *Chem. Phys. Lett.* **1991**, *180*, 446.

(7) (a) Larsson, S.; Volosov, A.; Rosen, A. *Chem. Phys. Lett.* **1987**, *137*, 501. (b) Negri, F.; Orlandi, G.; Zerbetto, F. *Chem. Phys. Lett.* **1988**, *144*, 31.

(8) Subramanian, R.; Kadish, K. M.; Vijayashree, M. N.; Gao, X.; Jones, M. T.; Miller, M. D.; Krause, K. L.; Suenobu, T.; Fukuzumi, S. *J. Phys. Chem.* **1996**, *100*, 16327.

(9) Fukuzumi, S.; Suenobu, T.; Hirasaka, T.; Arakawa, R.; Kadish, K. M. *J. Am. Chem. Soc.* **1998**, *120*, 9220.

(10) Perrin, D. D.; Armarego, W. L. F. *Purification of Laboratory Chemicals*; Butterworth-Heinemann: Oxford, 1988.

(11) Patz, M.; Kuwahara, Y.; Suenobu, T.; Fukuzumi, S. *Chem. Lett.* **1997**, 567.

(12) Fukuzumi, S.; Suenobu, T.; Patz, M.; Hirasaka, T.; Itoh, S.; Fujitsuka, M.; Ito, O. *J. Am. Chem. Soc.* **1998**, *120*, 8060.

(13) Kadish, K. M.; Gao, X.; Van Caemelbecke, E.; Hirasaka, T.; Suenobu, T.; Fukuzumi, S. *J. Phys. Chem.* **1998**, *102*, 3898.

(14) Kadish, K. M.; Gao, X.; Van Caemelbecke, E.; Suenobu, T.; Fukuzumi, S. *J. Am. Chem. Soc.* **2000**, *122*, 563.

(15) Stewart, J. J. P. *J. Comput. Chem.* **1989**, *10*, 209, 221.

(16) Dubois, D.; Jones, M. T.; Kadish, K. M. *J. Am. Chem. Soc.* **1992**, *114*, 6446.

(17) Greaney, M. A.; Gorun, S. M. *J. Phys. Chem.* **1991**, *95*, 7142.

(18) (a) Stinchcombe, J.; Pénicaud, A.; Bhyrappa, P.; Boyd, P. D. W.; Reed, C. A. *J. Am. Chem. Soc.* **1993**, *115*, 5212. (b) Stinchcombe, J.; Pénicaud, A.; Bhyrappa, P.; Boyd, P. D. W.; Reed, C. A. *J. Am. Chem. Soc.* **1994**, *116*, 6484.

(19) For discussion about the “spike” in the ESR spectrum of $C_{60}^{\bullet-}$, see ref 3 and references therein.

(20) The X-ray structure confirms that the dibenzyl adduct of C_{60} is the 1,4-isomer; see ref 8.

(21) Boulas, P. L.; Subramanian, R.; Jones, M. T.; Kadish, K. M. *Appl. Magn. Reson.* **1996**, *11*, 239.

(22) Kato, T.; Kodama, T.; Oyama, M.; Okazaki, S.; Shida, T.; Nakagawa, T.; Matsui, Y.; Suzuki, S.; Shiromaru, H.; Yamauchi, K.; Achiba, Y. *Chem. Phys. Lett.* **1991**, *186*, 35.

(23) Volkel, G.; Poppl, A.; Simon, J.; Hoentsch, J.; Orlinskii, S.; Klos, H.; Gotschy, B. *Phys. Rev. B* **1995**, *52*, 10188.

(24) Wertz, J. E.; Bolton, J. R. *Electron Spin Resonance Elementary Theory and Practical Applications*; McGraw-Hill: New York, 1972.

(25) Azamar-Barrios, J. A.; Muñoz P.; E.; Pénicaud, A. *J. Chem. Soc., Faraday Trans.* **1997**, *93*, 3119.

(26) Boulas, P. L.; Jones, M. T.; Ruoff, R. S.; Lorents, D. C.; Malhotra, R.; Tse, D. S.; Kadish, K. M. *J. Phys. Chem.* **1996**, *100*, 7573.

(27) The X-ray structure of the minor product has revealed that the tetrabenzyl adduct of C_{60} is 1,2,4,15-$(C_6H_5CH_2)C_{60}$; see ref 14.

(28) The aH_2 value is the best fit value in Figure 4. Although it is diffucult to determine the aH_2 value accuratetly, it is certain that $aH_1 > aH_2$.

(29) MO calculations at the ab initio level were unsuccessful due to the excessive computational time at that level.

(30) Although the exact assignment of the two nonequivalent protons has yet to be made, the calculation indicates the nonequivalence of eight benzyl methylene protons.

(31) (a) Sanders, J. K. M.; Hunter, B. K. *Modern NMR Spectroscopy*; Oxford University Press: Oxford, 1986; pp 209−302. (b) Richards, S. A. *Laboratory Guide to Proton NMR Spectroscopy*; Blackwell Scientific Publications: Oxford, 1988; pp 82-92.

(32) Carrington, A.; McLachlan, A. D. *Introduction to Magnetic Resonance*; Harper & Row Publishers: New York, 1967.

(33) The $\Delta\delta_0$ values were taken from the $\Delta\delta$ values determined at the lowest temperature. The exact $\Delta\delta_0$ values without rotation may be larger than the values used to evaluate k in eq 2. This may be the reason for the nonlinear behavior of the data in Figure 7. In such a case, the $\Delta H^{\ddagger}$ values evaluated from the plots in Figure 7 may be larger than the actual values. However, the experimetal errors may not be so large since the activation free energy ($\Delta G^{\ddagger} = 20.1$ kcal mol^{-1}) evaluated from the coalescence temperature of 1,4-$(C_6H_5CH_2)_2C_{60}$ agrees well with the value (20.1 kcal mol^{-1}) derived from the $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ values in Table 1.