Enhanced Reactivity of C_{70} in the Photochemical Reactions with NADH and NAD Dimer Analogues As Compared to C_{60} via Photoinduced Electron Transfer

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Visible light irradiation of a benzonitrile solution containing C_{70} and an NADH analogue, 4-*tert*-butyl-1-benzyl-1,4-dihydronicotinamide (*t*-BuBNAH), results in efficient formation of the *tert*-butylated anion (*t*-BuC$_{70}^{-}$) accompanied by the oxidation of *t*-BuBNAH to BNA^{+}. The transient formation of $C_{70}^{\bullet-}$ ($\lambda_{max} = 1374$ nm) has been detected, accompanied by the decay of the triplet−triplet absorption band of $^{3}C_{70}^{*}$ at 960 nm in laser flash photolysis of the *t*-BuBNAH-C_{70} system. The initial electron transfer from *t*-BuBNAH to $^{3}C_{70}^{*}$ to produce *t*-BuBNAH$^{\bullet+}$ and $C_{70}^{\bullet-}$ is followed by fast C−C bond cleavage in *t*-BuBNAH$^{\bullet+}$ to give *t*-Bu$^{\bullet}$ which is coupled with $C_{70}^{\bullet-}$ to yield *t*-BuC$_{70}^{-}$. The limiting quantum yield for formation of *t*-BuC$_{70}^{-}$ ($\Phi_{\infty} = 0.45$) is significantly larger than the value ($\Phi_{\infty} = 0.21$) of *t*-BuC$_{60}^{-}$ produced when C_{70} is replaced by C_{60}. When *t*-BuBNAH is replaced by 1-benzyl-1,4-dihydronicotinamide (BNAH) or the dimeric form [(BNA)$_2$], the selective one-electron reduction of C_{70} to $C_{70}^{\bullet-}$ is attained through photoinduced electron transfer from BNAH or (BNA)$_2$ to the triplet excited state of C_{70}. The limiting quantum yields for formation of $C_{70}^{\bullet-}$ in the photoreduction of C_{70} by BNAH and (BNA)$_2$ exceed unity; $\Phi_{\infty} = 2.0$ and 1.9, both of which are also larger than the corresponding values for formation of $C_{60}^{\bullet-}$ ($\Phi_{\infty} = 1.3$ and 0.80, respectively). The enhanced reactivity of C_{70} as compared to C_{60} is ascribed to a more localized unpaired electron and negative charge in $C_{70}^{\bullet-}$ due to loss of symmetry which facilitates the follow-up reaction in competition with the back electron transfer to the ground-state reactant pair. In the case of 4-isopropyl-1-benzyl-1,4-dihydronicotinamide (*i*-PrBNAH), the photochemical reaction with C_{70} yields not only $C_{70}^{\bullet-}$ but also the isopropylated anion (*i*-PrC$_{70}^{-}$).

Introduction

Buckminsterfullerene (C_{60}) is known to act as an electrophile and thus much attention has been focused on its functionalization with various nucleophiles via the thermal and photochemical reactions.[1−5] As the accessibility of higher fullerenes such as C_{70} and beyond has gradually improved, higher fullerenes, in particular C_{70}, have been functionalized in many ways.[6,7] Loss of symmetry when going from I_h symmetry in C_{60} to D_{5h} symmetry in C_{70} increases the number of different carbon atoms from one in C_{60} to five in C_{70} and the number of chemically different C−C bonds from two in C_{60} to eight in C_{70}.[8] This leads to a growing number of possible adduct isomers derived from C_{70} as compared to C_{60}. The regioselectivity in the functionalization of higher fullerenes has now been explored extensively.[9,10] However, it remains unclear whether C_{70} is more reactive than C_{60},[11] since the larger aromaticity of C_{70} is suggested to result in a lower reactivity,[12] but slightly lower LUMO energies for C_{70} than for C_{60} may result in an increased reactivity of C_{70} as compared to C_{60}.[13,14] A direct comparison of the reactivity of C_{70} and C_{60} in the reactions with the same series of substrates is certainly required in order to disclose the effect of lowering symmetry on the reactivity of fullerenes.

We have recently reported that the photoinduced electron transfer from 4-*tert*-butyl-1-benzyl-1,4-dihydronicotinamide (*t*-BuBNAH) and 1-benzyl-1,4-dihydronicotinamide (BNAH) to the triplet excited state of C_{60} ($^{3}C_{60}^{*}$) in benzonitrile leads to formation of the *tert*-butylated C_{60} anion (*t*-BuC$_{60}^{-}$) and stable $C_{60}^{\bullet-}$, respectively.[15] The photoinduced electron transfer from the dimeric 1-benzyl-1,4-dihydronicotinamide [(BNA)$_2$] to $^{3}C_{60}^{*}$ also yields $C_{60}^{\bullet-}$ selectively.[15] We report herein that the photoinduced electron transfer from *t*-BuBNAH to the triplet excited state of C_{70} ($^{3}C_{70}^{*}$) yields the *tert*-butylated C_{70} anion (*t*-BuC$_{70}^{-}$) and that from BNAH and (BNA)$_2$ to $^{3}C_{70}^{*}$ results in formation of stable $C_{70}^{\bullet-}$ selectively. We also report that the photochemical reaction of C_{70} with 4-isopropyl-1-benzyl-1,4-dihydronicotinamide (*i*-PrBNAH) yields not only the isopropylated anion (*i*-PrC$_{70}^{-}$) but also $C_{70}^{\bullet-}$. Determination of the quantum yields and direct detection of transient formation of $C_{70}^{\bullet-}$ by laser flash photolysis in this study provide an excellent opportunity to compare the reactivity of C_{70} with C_{60} in the same series of photochemical reactions via photoinduced electron transfer.

Experimental Section

Materials. C_{70} (>99.9% pure) was purchased from Science Laboratories Co., Ltd., Japan, and used as received. The *tert*-butylated BNAH (*t*-BuBNAH) and isopropylated BNAH (*i*-PrBNAH) were prepared by the Grignard reaction with

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BNA^+Cl^-.[16,17] Preparation of 1-benzyl-1,4-dihydronicotinamide (BNAH) and the BNA dimer was described previously.[15,18,19] Benzonitrile (PhCN; 99.9% pure) was purchased from Tokyo Kasei Kogyo Co., Ltd., and further purified by successive distillation over P_2O_5 prior to use. Benzyl bromide ($PhCH_2Br$) and trifluoroacetic acid were obtained commercially from Aldrich and Wako Pure Chemical Ind., Ltd., Japan, respectively.

Reaction 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), and the solution was irradiated with a Xe lamp ($\lambda > 370$ nm) equipped with Toshiba UV-37 cut filter for 1 h. The successive reaction with CF_3COOH (0.0003 mmol) in deaerated PhCN at room temperature yields *tert*-butyldihydro[70]fullerene (*t*-$BuC_{70}H$). *t*-$BuC_{70}H$ along with unreacted C_{70} was obtained. FAB-MS: Mass calcd for $C_{74}H_{10}$, 898.9: found 899.1.

Addition of $PhCH_2Br$ instead of CF_3COOH to the photolyzed PhCN solution of C_{70} and *t*-BuBNAH gave *tert*-butylbenzyldihydro[70]fullerene [*t*-$Bu(PhCH_2)C_{70}$]. 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.

Electrospray Mass Ionization Spectrometry. Electrospray mass ionization spectrometry (ESI-MS) was used to identify RC_{70}^- (R = *t*-Bu and *i*-Pr) and $C_{70}^{\bullet -}$ in PhCN. Mass spectra were recorded on a JEOL JNX-DX303 HF mass spectrometer or a Shimadzu GCMS-QP2000 gas chromatograph mass spectrometer. A sector-type mass spectrometer (JEOL-D300) connected with a homemade ESI (electrospray ionization) interface was used to obtain ESI mass spectra. The interface is similar to that of the ESI ion source designed by Fenn.[20] The sample solution was sprayed at the tip of a needle applied at a current 3.5 kV higher than that of the counter electrode. This electrode consisted of a 12 cm long capillary pipe of stainless steel. Heated N_2 gas (70 °C) flowed between the needle and the capillary electrode to aid the desolvation of charged droplets sprayed. Ions entered the vacuum system through the first and the second skimmer to a mass spectrometer. The flow rate of a sample solution was $1-2\ \mu L\ min^{-1}$. The voltage of the first skimmer was 50 V higher than that of the second, and that of the capillary electrode is 50 V higher than that of the first. For measurements of ESI mass spectra, all of the samples were dissolved in freshly distilled PhCN to prepare a sample concentration of ca. 0.1 mM. ESI-MS: Mass calcd for *t*-BuC_{70}^- ($C_{74}H_9$), 897.1; found 897. *i*-PrC_{70}^- ($C_{73}H_7$), 883.1; found 883. $C_{70}^{\bullet -}$, 840.0; found 840.

Quantum Yield Determinations. A standard actinometer (potassium ferrioxalate)[21] was used for the quantum yield determination of the photochemical reactions of C_{70} with NADH analogues. Square quartz cuvettes (10 mm × 10 mm) which contained a deaerated PhCN solution (3.0 mL) of C_{70} (1.0×10^{-4} M) with NADH and the dimer analogues at various concentrations were irradiated with monochromatized light of $\lambda = 546$ nm from a Shimadzu RF-5000 fluorescence spectrophotometer. Under the conditions of actinometry experiments, the actinometer and C_{70} absorbed essentially all the incident light of $\lambda = 546$ nm. The light intensity of monochromatized light of $\lambda = 546$ nm was determined as 1.41×10^{-9} einstein s^{-1} with the slit width of 5 nm. The photochemical reaction was monitored using a Hewlett-Packard 8453 diode-array spectrophotometer or a Shimadzu UV-3100 PC UV−Vis−NIR scanning spectrophotometer. The quantum yields were determined from the increase in absorbance due to the C_{70} adducts at 472 nm or $C_{70}^{\bullet -}$ at 1374 nm. To avoid the contribution of light absorption of the products, only the initial rates were determined for determination of the quantum yields.

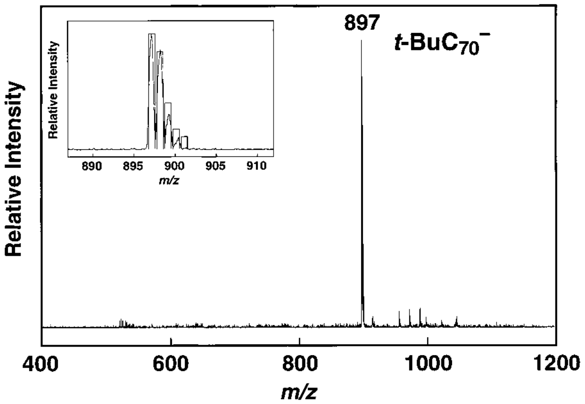


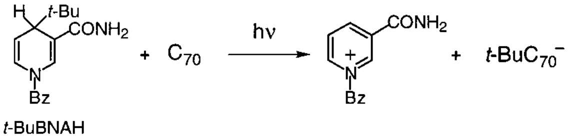
Figure 1. Negative ion ESI-MS of *t*-BuC_{70}^- in deaerated PhCN at 298 K.

Laser Flash Photolysis. The C_{70} solution (1.0×10^{-4} M) was excited by a Nd:YAG laser (Quanta-Ray, GCR-130, 6 ns fwhm) at 532 nm with the power of 7 mJ. A pulsed xenon flash lamp (Tokyo Instruments, XF80-60, 15 J, 60 ms fwhm) was used for the probe beam, which was detected with a Ge-APD module (Hamamatsu, C5331-SPL) after passing through the photochemical quartz vessel (10 mm × 10 mm) and a monochromator. The output from Ge-APD module was recorded with a digitizing oscilloscope (HP 54510B, 300 MHz). Since C_{70} in benzonitrile containing an NADH analogue disappeared by each laser shot (532 nm; 7 mJ), the transient spectra were recorded using fresh solutions in each laser excitation. All experiments were performed at 295 K. The solution was deoxygenated by argon purging for 10 min prior to the measurements.

Cyclic Voltammetry. Cyclic voltammetry measurements were performed at 298 K on a BAS 100W electrochemical analyzer in deaerated PhCN containing 0.1 M NBu_4ClO_4 as supporting electrolyte. A conventional three-electrode cell with a gold working electrode (surface area of 0.3 mm^2) and a platinum wire as the counter electrode were utilized. The Pt working electrode (BAS) was polished with a BAS polishing alumina suspension and rinsed with acetone before use. The measured potentials were recorded with respect to the Ag/$AgNO_3$ (0.01 M) reference electrode. All potentials (vs Ag/Ag^+) were converted to values vs SCE by adding 0.29 V. All electrochemical measurements were carried out under an atmospheric pressure of argon.

Results and Discussion

Formation of *t*-BuC_{70}^-. Visible light irradiation of a benzonitrile solution containing C_{70} and 4-*tert*-butyl-1-benzyl-1,4-dihydronicotinamide (*t*-BuBNAH) results in efficient formation of the *tert*-butylated anion (*t*-BuC_{70}^-), accompanied by the oxidation of *t*-BuBNAH to BNA^+ (eq 1).



(1)

Formation of *t*-BuC_{70}^- was confirmed by the electrospray ionization mass (ESI-MS) spectrum as shown in Figure 1, where peaks appear clearly at the mass number of *t*-BuC_{70}^- (897).

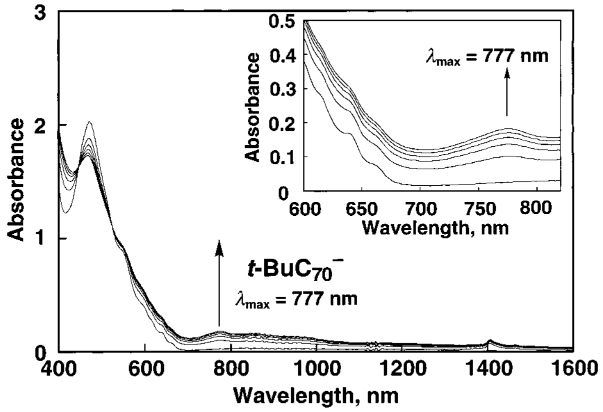


Figure 2. Electronic absorption spectra observed in the photochemical reaction of C_{70} (1.0×10^{-4} M) with t-BuBNAH (1.0×10^{-4} M) in deaerated PhCN under irradiation of visible light ($\lambda > 540$ nm) at 298 K.

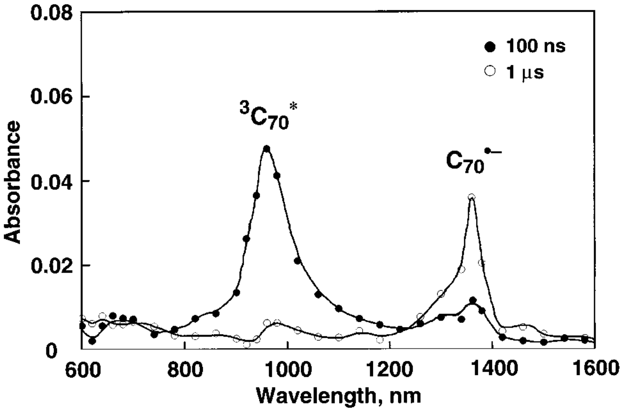


Figure 3. Transient absorption spectra observed in the photoreduction of C_{70} (1.0×10^{-4} M) by t-BuBNAH (2.0×10^{-3} M) at 100 ns (●) and 1 μs (○) after laser excitation in deaerated PhCN at 295 K.

The natural isotope abundance patterns agree well with the simulated values and these are shown as histograms in the inset of Figure 1. The vis–NIR spectral change observed in the photochemical reaction of C_{70} with t-BuBNAH in deaerated PhCN is shown in Figure 2, where a new absorption band at 777 nm is assigned as due to t-BuC$_{70}^-$.

The subsequent trap of t-BuC$_{70}^-$ by CF_3COOH and $PhCH_2Br$ gave t-BuC$_{70}$H and t-Bu($PhCH_2$)C_{70}, respectively (see Experimental Section) as reported for the reactions of t-BuC$_{60}^-$ with electrophiles.[15]

The transient formation of $C_{70}^{•-}$ is detected as a reactive intermediate in the photochemical reaction of C_{70} with t-BuBNAH to yield t-BuC$_{70}^-$ by the laser flash photolysis of a deaerated PhCN solution of C_{70} in the presence of t-BuBNAH as shown in Figure 3. The transient absorption band at 960 nm appearing immediately after nanosecond laser pulse excitation is attributed to the triplet–triplet absorption band of $^3C_{70}^*$.[22,23] The decay of the absorption band of $^3C_{70}^*$ is accompanied by appearance of a new absorption band at 1374 nm which is diagnostic of $C_{70}^{•-}$.[23,24] The decay of the absorbance at 960 nm due to $^3C_{70}^*$ obeys pseudo-first-order kinetics, coinciding with the rise of the absorbance at 1374 nm due to $C_{70}^{•-}$ as shown in Figure 4. Thus, it is confirmed that the reaction of $^3C_{70}^*$ with t-BuBNAH occurs by electron transfer from t-BuBNAH to $^3C_{70}^*$ to produce $C_{70}^{•-}$.

The pseudo-first-order decay rate constant of $^3C_{70}^*$ increases linearly with an increase in the concentration of t-BuBNAH. From the slope of the linear dependence, the rate constant (k_{et}) for electron transfer from t-BuBNAH to $^3C_{70}^*$ was determined as 2.3×10^9 M^{-1} s^{-1} which is nearly equal to the corresponding k_{et} value for $^3C_{60}^*$ (2.1×10^9 M^{-1} s^{-1})[15] in Table 1. The free energy change of electron transfer (ΔG^0_{et}) is calculated from the one-electron oxidation potential of t-BuBNAH (E^0_{ox} vs SCE = 0.71 V)[16] and the one-electron reduction potential of $^3C_{70}^*$

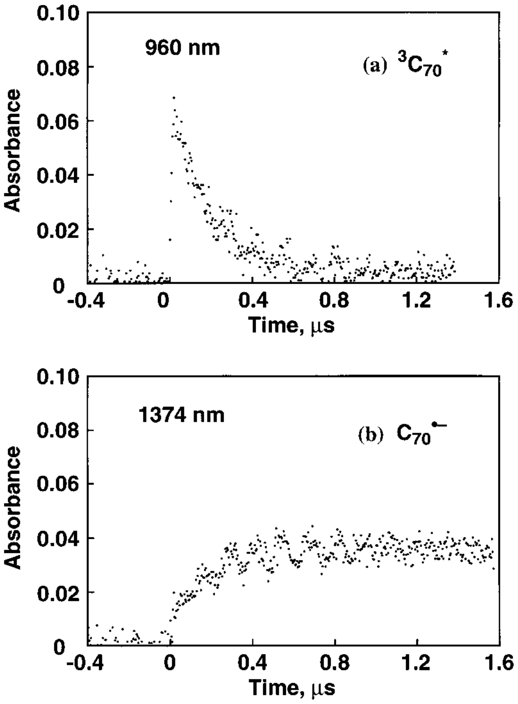
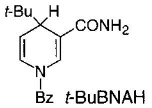
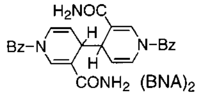
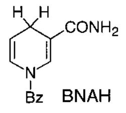
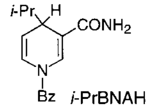


Figure 4. Decay of the absorbance at 960 nm due to $^3C_{70}^*$ (a) and the rise of the absorbance at 1374 nm due to $C_{70}^{•-}$ (b) observed in the photoreduction of C_{70} (1.0×10^{-4} M) by t-BuBNAH (2.0×10^{-3} M) after laser excitation in deaerated PhCN at 295 K.

TABLE 1: Free Energy Change (ΔG^0_{et}) of Photoinduced Electron Transfer from Electron Donors to $^3C_{70}$, Rate Constants (k_{et}) and Limiting Quantum Yields (Φ_∞) for the Photoreduction of C_{70} by Electron Donors in PhCN at 298 K

electron donor	E^0_{ox} vs SCE, V	ΔG^0_{et},[a] kcal mol^{-1}	k_{et}, M^{-1} s^{-1}	Φ_∞
 t-BuBNAH	0.71	-9.2 (-9.9)[b]	2.3×10^9 (2.1×10^9)[b]	0.45 (0.21)[b]
 (BNA)$_2$	0.26	-19.6 (-20.3)[b]	3.3×10^9 (3.4×10^9)[b]	2.00 (1.30)[b]
 BNAH	0.57	-12.5 (-13.1)[b]	3.0×10^9 (2.9×10^9)[b]	1.88 (0.80)[b]
 i-PrBNAH	0.72	-9.0 (-9.7)[b]	2.5×10^9 (1.9×10^9)[b]	1.36 (0.68)[b]

[a] Obtained from the E^0_{ox} values of electron donors and the E^0_{red} value of $^3C_{70}^*$ (1.11 V vs SCE) by using equation; $\Delta G^0_{et} = F(E^0_{ox} - E^0_{red})$.[15,16]

[b] Values in parentheses are those of ΔG^0_{et}, k_{et} and Φ_∞ for C_{60}.[15]

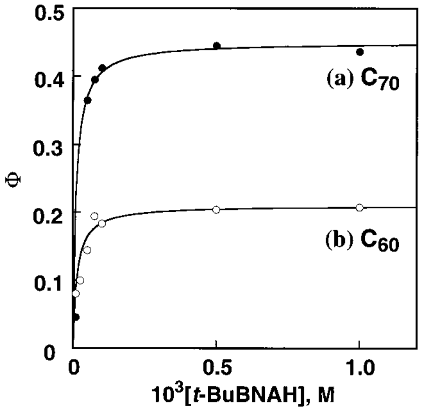


Figure 5. Dependence of the quantum yields Φ on [*t*-BuBNAH] for the photoreduction of C_{70} (1.0×10^{-4} M) (a) and C_{60} (2.8×10^{-4} M) (b) by *t*-BuBNAH in deaerated PhCN at 298 K.

(E^0_{red} vs SCE = 1.11 ± 0.03 V) which is obtained from the E^0_{red} value (-0.42 V)[25] and the triplet energy (1.53 ± 0.03 eV)[26] as -0.40 eV. The ΔG^0_{et} value of $^3C_{60}$* is essentially the same as that of $^3C_{70}$*, since the E^0_{red} value of C_{60} (-0.43 V)[27] and the triplet energy of $^3C_{60}$* (1.56 eV)[28] are nearly the same as the value of C_{70} and $^3C_{70}$*, respectively.[29] Thus, there is no difference in the reactivity between $^3C_{70}$* and $^3C_{60}$* for the electron-transfer reactions.

The quantum yields (Φ) for the photochemical formation of *t*-BuC_{70}^- were determined from an increase in absorbance due to *t*-BuC_{70}^- under irradiation of monochromatized light of $\lambda = 546$ nm. The Φ value increases with an increase in the concentration of *t*-BuBNAH to reach a limiting value (Φ_∞) as shown in Figure 5. A similar dependence of Φ on [*t*-BuBNAH] has been reported in the case of the photochemical reaction of C_{60} with *t*-BuBNAH as also shown in Figure 5 for comparison.[15] The Φ_∞ value (0.45) for C_{70} is significantly larger than the value of C_{60} (0.21) as listed in Table 1. The reaction mechanism for the photochemical reaction of C_{70} with *t*-BuBNAH is essentially the same as that of C_{60} as shown in Scheme 1.[15] The photochemical reaction is started by the photoinduced electron transfer from *t*-BuBNAH to $^3C_{70}$* to give the radical ion pair of *t*-BuBNAH$^{\bullet+}$ and $C_{70}^{\bullet-}$. This is followed by the facile C(4)−C bond cleavage of *t*-BuBNAH$^{\bullet+}$ by the nucleophilic radical reaction with $C_{70}^{\bullet-}$ to yield the final product (*t*-BuC_{70}^-) in competition with the back electron transfer (Scheme 1). The lowered symmetry of $C_{70}^{\bullet-}$ as compared to $C_{60}^{\bullet-}$ may result in the more localized unpaired electron in $C_{70}^{\bullet-}$, thus facilitating the nucleophilic radical reaction to give a larger Φ_∞ value for C_{70} than C_{60}.

By applying the steady-state approximation to the reactive species: $^3C_{70}$* and the radical ion pair in Scheme 1, the dependence of Φ on [*t*-BuBNAH] can be derived as given by eq 2,

$$\Phi = \Phi_\infty k_{et}\tau_T[t\text{-BuBNAH}]/(1 + k_{et}\tau_T[t\text{-BuBNAH}]) \quad (2)$$

which agrees with the observed dependence of Φ on [*t*-BuBNAH] in Figure 5. The simulation based on eq 2 using the τ_T (38 μs for $^3C_{70}$*) and k_{et} values determined from the laser flash photolysis is shown as solid lines in Figure 5, which demonstrates excellent agreement between the simulation and the experimental results for both C_{70} and C_{60}. Such an agreement confirms the validity of Scheme 1.

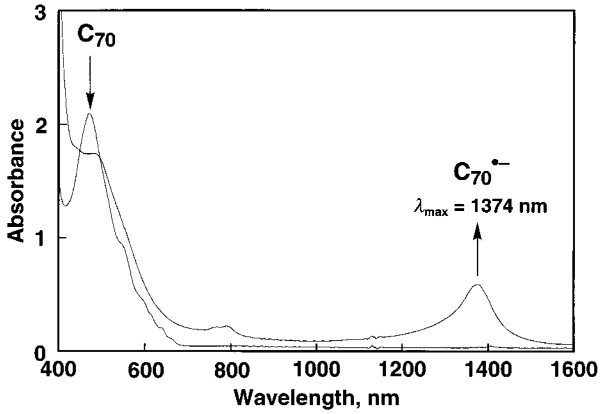
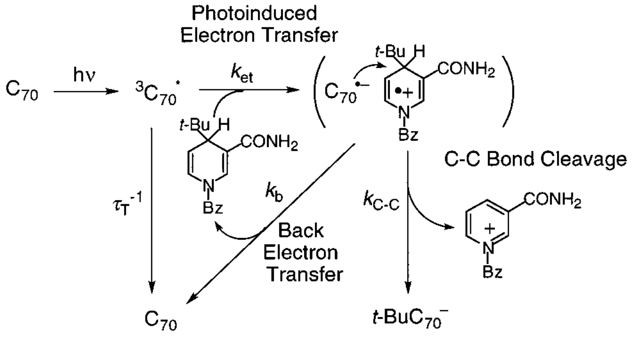
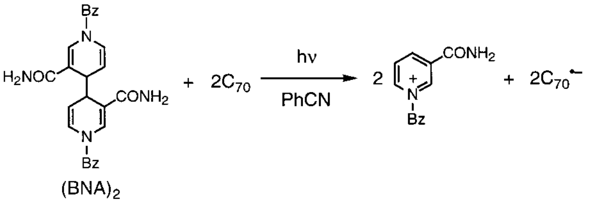


Figure 6. Electronic absorption spectra observed in the photochemical reaction of C_{70} (1.0×10^{-4} M) with $(BNA)_2$ (1.0×10^{-2} M) in deaerated PhCN under irradiation of visible light ($\lambda > 540$ nm) at 298 K.

SCHEME 1

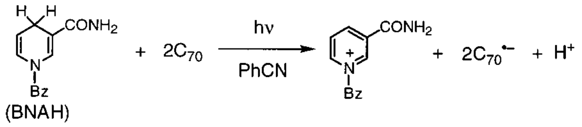


Selective One-Electron Reduction of C_{70} via Photoinduced Electron Transfer. When a dimeric NADH analogue [$(BNA)_2$] is used as an electron donor, irradiation of a PhCN solution containing $(BNA)_2$ and C_{70} with even daylight results in efficient one-electron reduction of C_{70} to $C_{70}^{\bullet-}$ (eq 3):



(3)

No reaction occurs in the dark. The formation of $C_{70}^{\bullet-}$ is detected by the typical NIR spectrum as shown in Figure 6 (λ_{max} = 1374 nm).[23,24] The $C_{70}^{\bullet-}$ generated in the photochemical reaction is stable in deaerated PhCN, and the stoichiometry of the reaction is established as shown in eq 3, where $(BNA)_2$ acts as a two-electron donor to reduce two equivalents of C_{70} to $C_{70}^{\bullet-}$. Similarly the photochemical reaction of C_{70} with the monomeric NADH analogue, 1-benzyl-1,4-dihydronicotinamide (BNAH), occurs to yield $C_{70}^{\bullet-}$ efficiently (eq 4).



(4)

The quantum yields (Φ) for the one-electron photoreduction of C_{70} were determined from an increase in absorbance due to $C_{70}^{\bullet-}$ under irradiation of monochromatized light of $\lambda = 546$ nm. The Φ value for the photoreduction of C_{70} by $(BNA)_2$ in PhCN increases with an increase in the concentration of $(BNA)_2$ to reach a limiting value (Φ_∞) as shown in Figure 7. It should be noted that the Φ_∞ value for formation of $C_{70}^{\bullet-}$ exceeds unity;

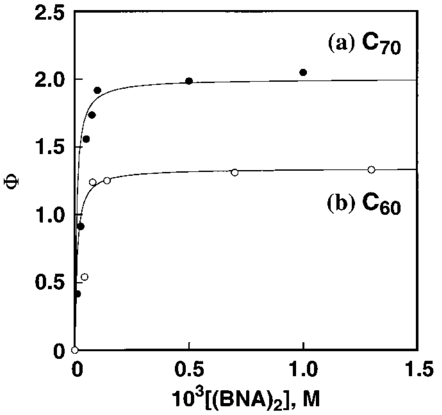
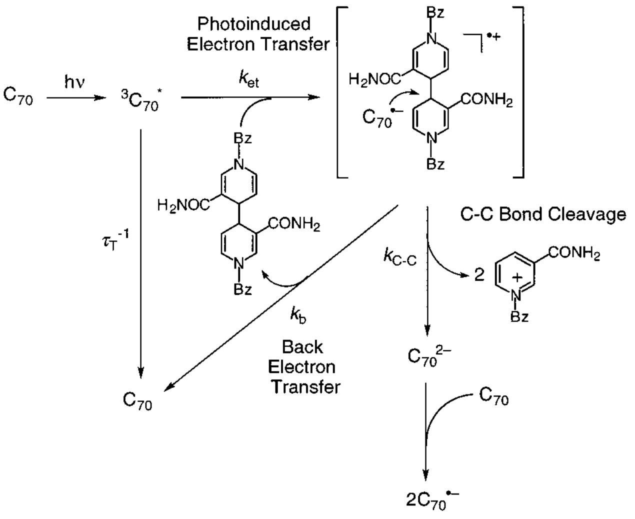


Figure 7. Dependence of the quantum yields Φ on $[(BNA)_2]$ for the photoreduction of C_{70} (1.0×10^{-4} M) (a) and C_{60} (2.8×10^{-4} M) (b) by $(BNA)_2$ in deaerated PhCN at 298K.

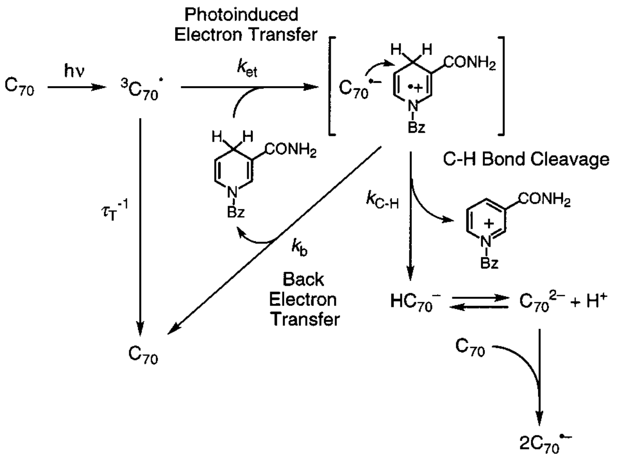
SCHEME 2



$\Phi_\infty = 2.0$ which is even larger than the value ($\Phi_\infty = 1.3$) for formation of $C_{60}^{\bullet -}$ in the photochemical reaction of C_{60} with $(BNA)_2$ as also shown in Figure 7 for comparison.[15] Such a large quantum yield exceeding unity is consistent with the stoichiometry in eq 4, where $(BNA)_2$ can reduce two equivalents of C_{70}. The dependence of Φ on the BNAH concentration was also examined, and the Φ_∞ values for $(BNA)_2$ and BNAH are listed in Table 1.

The reaction mechanism for the selective one-electron photoreduction of C_{70} by $(BNA)_2$ may be essentially the same as for the photochemical reaction of C_{70} with *t*-BuBNAH (Scheme 1) except for the final product as shown in Scheme 2. First photoinduced electron transfer from $(BNA)_2$ to $^3C_{70}^*$ occurs to give the radical ion pair: $(BNA)_2^{\bullet +}$ and $C_{70}^{\bullet -}$, followed by the facile C(4)−C bond cleavage of $(BNA)_2^{\bullet +}$ by the nucleophilic radical reaction with $C_{70}^{\bullet -}$ to yield C_{70}^{2-} and two equivalents of BNA^+ in competition with the back electron transfer (Scheme 2). In the case of *t*-BuC_{70}^- in Scheme 1, no dissociation of *t*-BuC_{70}^- to *t*-Bu^+ and C_{70}^{2-} occurs since the one-electron oxidation potential (E^0_{ox}) of C_{70}^{2-} which is equivalent to the one-electron reduction potential (E^0_{red}) of $C_{70}^{\bullet -}$ (−0.83 V) is much lower than the E^0_{red} value of *t*-Bu^+ which is equivalent to E^0_{ox} of *t*-$Bu^\bullet$ (0.08 V).[30] In such a case, even if the dissociation occurred to give *t*-Bu^+ and C_{70}^{2-}, the back electron transfer from C_{70}^{2-} to *t*-Bu^+ should regenerate *t*-BuC_{70}^- which is stable in benzonitrile. In contrast to this, the E^0_{ox} value of C_{70}^{2-} (−0.83 V) is higher than the E^0_{red} value of BNA^+ (−1.08 V),[18] when no adduct between BNA^+ and C_{70}^{2-} would be formed. In this case, the facile electron transfer from C_{70}^{2-} to C_{70} occurs to produce two equivalents of $C_{70}^{\bullet -}$ (Scheme 2).

SCHEME 3



According to Scheme 2, the dependence of Φ on $[(BNA)_2]$ can be derived as given by eq 2, where [*t*-BuBNAH] is replaced by $[(BNA)_2]$, agreeing with the observed dependence of Φ on $[(BNA)_2]$ in Figure 7. The k_{et} value for electron transfer from $(BNA)_2$ to $^3C_{70}^*$ (3.3×10^9 M^{-1} s^{-1}) obtained from the dependence of Φ on $[(BNA)_2]$ in Figure 7 is nearly the same as the corresponding value of C_{60} (3.4×10^9 M^{-1} s^{-1}),[15] as expected from the similar ΔG^0_{et} values in Table 1. The limiting quantum yield Φ_∞ is given by eq 5:

$$\Phi_\infty = 2\Phi_T k_{C-C}/(k_{C-C} + k_b) \qquad (5)$$

where Φ_T is the quantum yield for generation of the triplet excited state. Thus, the observed Φ_∞ value (2.0) indicates that the Φ_T value for formation of $^3C_{70}^*$ is unity[31] and that the C−C bond cleavage in $(BNA)_2^{\bullet +}$ (k_{C-C}) by $C_{70}^{\bullet -}$ is much faster than the back electron-transfer process (k_b):$k_{C-C} \gg k_b$. In the case of C_{60}, the Φ_T value for formation of $^3C_{60}^*$ is also known to be unity.[28] However, the rate of the C−C bond cleavage in $(BNA)_2^{\bullet +}$ (k_{C-C}) by $C_{60}^{\bullet -}$ may be slower than that by $C_{70}^{\bullet -}$ because of the more delocalized negative charge in $C_{60}^{\bullet -}$, becoming comparable with the back electron-transfer process (k_b). In such a case, the Φ_∞ value for formation of $C_{60}^{\bullet -}$ in the photochemical reaction of C_{60} with $(BNA)_2$ is less than 2.0 as listed in Table 1 ($\Phi_\infty = 1.3$). The rate of back electron transfer of $C_{70}^{\bullet -}$ may be the same as that of $C_{60}^{\bullet -}$, since the E^0_{ox} values of $C_{70}^{\bullet -}$ and $C_{60}^{\bullet -}$ (equivalent to the E^0_{red} values of C_{70} and C_{60}) are essentially the same (vide supra).

The one-electron photoreduction of C_{70} by BNAH may also proceed via photoinduced electron transfer from BNAH to $^3C_{70}^*$, as shown in Scheme 3. In this case, the C−H bond cleavage of $BNAH^{\bullet +}$ by $C_{70}^{\bullet -}$ occurs to give HC_{70}^- and BNA^+ instead of the C−C bond cleavage in the case of *t*-$BuBNAH^{\bullet +}$ (Scheme 1) and $(BNA)_2^{\bullet +}$ (Scheme 2). The subsequent facile electron transfer from C_{70}^{2-} being in equilibrium with HC_{70}^- to C_{70} leads to formation of two equivalents of $C_{70}^{\bullet -}$. The k_{et} value for electron transfer from BNAH to $^3C_{70}^*$ (3.0×10^9 M^{-1} s^{-1}) obtained from the dependence of Φ on [BNAH] is also nearly the same as the corresponding value of C_{60} (2.9×10^9 M^{-1} s^{-1})[15] as expected from the similar ΔG^0_{et} values in Table 1. As the case of *t*-BuBNAH and $(BNA)_2$, the limiting quantum yield for the reduction of C_{70} ($\Phi_\infty = 1.88$) exceeding unity is significantly larger than the corresponding value of C_{60} ($\Phi_\infty = 0.80$)[15] in Table 1. This indicates that the rate of C−H bond

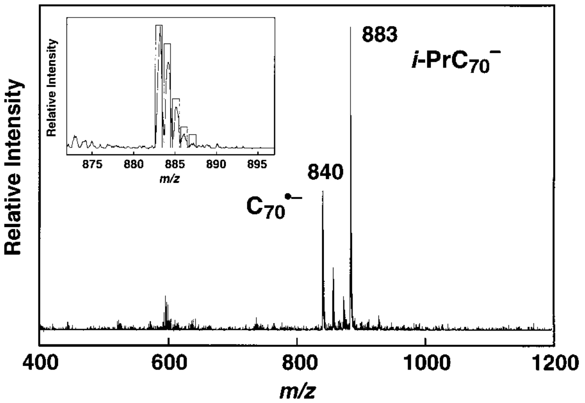


Figure 8. Negative ion ESI-MS of i-PrC$_{70}^-$ and $C_{70}^{\bullet-}$ in deaerated PhCN at 298 K.

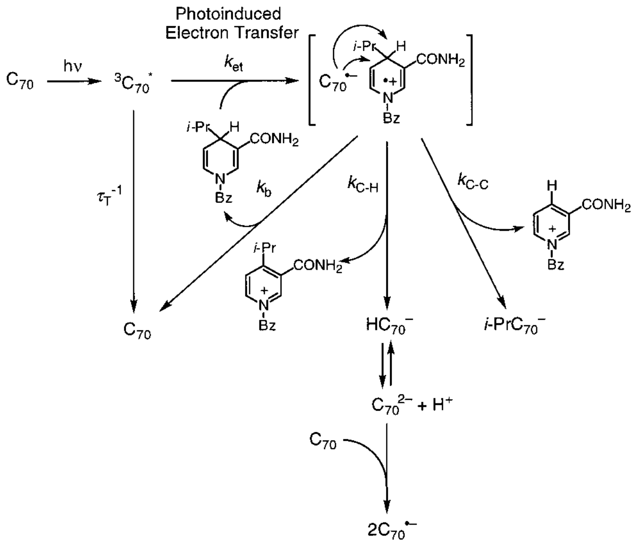
cleavage of BNAH$^{\bullet+}$ by $C_{70}^{\bullet-}$ is faster than the rate by $C_{60}^{\bullet-}$ due to a more localized negative charge in $C_{70}^{\bullet-}$ as compared to the highly delocalized negative charge in $C_{60}^{\bullet-}$.

C−C vs C−H Bond Cleavage in the Photochemical Reaction of C_{70} with *i*-PrBNAH. When BNAH is replaced by 4-isopropyl-1-benzyl-1,4-dihydronicotinamide (i-PrBNAH), the photochemical reaction with C_{70} results in efficient formation of not only $C_{70}^{\bullet-}$ but also the isopropylated anion (i-PrC$_{70}^-$). The formation of both $C_{70}^{\bullet-}$ and i-PrC$_{70}^-$ is confirmed by the electrospray ionization mass (ESI-MS) spectrum of the product mixture as shown in Figure 8, where leading peaks appear at the mass number of i-PrC$_{70}^-$ (883) and $C_{70}^{\bullet-}$ (840). The natural isotope abundance pattern of i-PrC$_{70}^-$ agrees well with the simulated values, and this is shown as histograms in the inset of Figure 8. The vis−NIR spectral change observed in the photochemical reaction of C_{70} with i-PrBNAH in deaerated PhCN exhibited appearance of absorption bands due to $C_{70}^{\bullet-}$ (54% yield) and i-PrC$_{70}^-$ (46% yield) at 1374 and 777 nm, respectively.

We have previously reported that cleavage of the C(9)−C bond of radical cation of an NADH analogue, 9-*tert*-butyl-10-methyl-9,10-dihydroacridine (AcrH(t-Bu)), occurs selectively rather than the cleavage of the C(9)−H bond in the electron-transfer oxidation of AcrH(t-Bu) by Fe^{3+} complexes but that cleavage of both the C(9)−C bond and C(9)−H bond occurs when the *tert*-butyl group is replaced by an isopropyl group.[32] Savéant and co-workers have also reported that the electrochemical oxidation of t-BuBNAH results in the selective C(4)−C bond cleavage of t-BuBNAH$^{\bullet+}$.[33] In this case as well, cleavage of both the C(4)−C bond and C(4)−H bond in i-PrBNAH$^{\bullet+}$ occurs when the *tert*-butyl group of t-BuBNAH is replaced by an isopropyl group.[16] Since the photochemical reaction of C_{70} with i-PrBNAH occurs via photoinduced electron transfer from i-PrBNAH to $^3C_{70}^*$ to produce i-PrBNAH$^{\bullet+}$, cleavage of both the C(4)−C bond and C(4)−H bond in i-PrBNAH$^{\bullet+}$ occurs leading to yield both i-PrC$_{70}^-$ and $C_{70}^{\bullet-}$ as shown in Scheme 4 which is the combination of Scheme 1 and Scheme 3.

The k_{et} value for electron transfer from i-PrBNAH to $^3C_{70}^*$ is also determined from the dependence of Φ on [i-PrBNAH] as 2.5×10^9 M^{-1} s^{-1}, which is nearly the same as the value for t-BuBNAH but smaller than the values for BNAH and (BNA)$_2$, being consistent with the ΔG^0_{et} values in Table 1. The limiting quantum yield for generation of $C_{70}^{\bullet-}$ and i-PrC$_{70}^-$ is determined as $\Phi_\infty = 1.36$, which is also significantly larger than the corresponding value of C_{60} ($\Phi_\infty = 0.68$) as shown in Table 1, which also exceeds unity because of formation of two equivalents of $C_{70}^{\bullet-}$, but is smaller than the value for BNAH ($\Phi_\infty = 1.88$) because of the accompanied formation of one equivalent of i-PrC$_{70}^-$.

SCHEME 4



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