J. Org. Chem. **1999,** *64,* 5913−5920

Photoinduced Electron-Transfer Reactions of [60]Fullerene with Triethylamine

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Received March 8, 1999

Fullerene molecules undergo efficient photochemical reactions with tertiary amines to form complex mixtures of addition products. The separation and identification of several monoadducts from photochemical reactions of C_{60} with triethylamine under different experimental conditions are reported. According to molecular spectroscopic results, the photoaddition of triethylamine to C_{60} is initiated via photoinduced electron transfer between the excited singlet C_{60} and the amine, similar to photochemical reactions of conventional aromatic molecules with tertiary amines. However, the reaction products with fullerene are completely different. Mechanistic implications of the results are discussed.

Introduction

[60]Fullerene (C_{60}) is an excellent electron acceptor, undergoing nucleophilic addition reactions with amines.[1−3] In fact, additions of primary and secondary amines to C_{60} are among the earliest reactions investigated in fullerene chemistry.[4−6] It was found in the early work that fullerene−amine reactions yield complex mixtures of polyaminofullerene products, the separation of which represents a significant challenge. Since then, successful separation and identification of addition products from several fullerene−amine reactions have been reported.[7−11] For example, Kampe et al. studied reactions of C_{60} with *N,N′*-dimethylethylenediamine, piperazine, and homopiperazine and isolated exclusively dehydrogenated 1,2-diamino-C_{60} cycloadducts.[8] Amination reactions were also used in the incorporation of fullerene cages into polymeric structures.[12−14] For the reactions of C_{60} with an excess of secondary amines morpholine and piperidine in air-saturated solution, Schick et al. found that the reaction products are exclusively dehydrogenated diamino-C_{60} and tetraamino-C_{60} adducts with a preferred 1,4-addition pattern and also a large percentage of aminated fullerene dimer with a single inter-fullerene linkage.[10] Mechanistically, single electron transfer from amine to C_{60} to form a fullerene radical anion was suggested to be the first reaction step according to results from carefully monitored C_{60}−amine reactions with electron spin resonance (ESR) and electronic absorption spectroscopy.[10,15] The fact that only dehydrogenated products were obtained prompted a proposal that the initially formed intermediates, such as aminated fullerene radical anions or zwitterions, are oxidized by oxygen, presumably singlet molecular oxygen, to form aminated fullerene radicals.[10] The addition products were attributed to aminated fullerene radical recombination and related processes. In such a mechanistic explanation, oxygen plays an important role in determining addition patterns of the secondary amines to the fullerene cage.

Addition reactions of secondary amines to C_{60} are much more efficient photochemically.[14,16,17] For example, photoirradiating a solution of C_{60}−*N,N′*-dimethylethylenediamine in toluene for an hour results in the same C_{60} conversion as that achieved in the thermal reaction for 5 days.[8,16,17] The photochemical C_{60}−diamine reactions produce the same dehydrogenated 1,2-diamino−C_{60} cycloadducts, but with much higher yields than those obtained in the corresponding thermal reactions. It appears that the formation of exclusively dehydrogenated cycloadducts is not a function of dissolved molecular oxygen because the same products were obtained from the photochemical C_{60}−amine reactions in a carefully deoxygenated solution.[17] Without the oxidation effect that may otherwise be used to account for the special fullerene−amine addition patterns, there are no simple

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10.1021/jo9904112 CCC: $18.00

explanations for the formation of dehydrogenated products in the framework of the classical mechanism for photochemical reduction of aromatic compounds by primary and secondary amines.[18−21] In the classical mechanism, the one-photon photoreduction is due to a photoinduced sequential electron transfer, proton transfer, and radical recombination process, which yields hydrogenated aminoadducts.[18−21] The mechanism appears not to be applicable to the C_{60} photoaddition reactions with amines such as *N,N′*-dimethylethylenediamine, where no hydrogenated products have been observed. However, it is possible that the photoreduction of fullerene by amines is a reaction that involves multiple photons and several intermediate products, with each reaction step still generally following the same mechanistic process as that for the photoreduction of aromatic compounds, which is well-established in the literature. The formation of exclusively dehydrogenated adducts might be because the photochemical reaction is multistep, reflecting a tendency for the aminated C_{60} to lose the methine hydrogen on the cage in subsequent photoinduced electron-transfer−proton-transfer processes.[10]

Aromatic systems can also be reduced photochemically by tertiary amines.[20,21] In fact, photoaddition reactions of aromatic compounds with tertiary amines have been studied extensively because they are mechanistically important to an understanding of photoinduced electron transfer and subsequent processes. For example, Lewis and co-workers carried out systematic investigations of trans-stilbene−tertiary amine photochemical reactions.[20] The reactions follow a well-established mechanism that involves sequential single electron transfer, proton transfer, and radical recombination, which is similar to that for the photoreduction of aromatic compounds by primary and secondary amines.[18−21]

Fullerene molecules also undergo efficient photochemical reactions with tertiary amines under ambient conditions to form a complex mixture of addition products.[22−26] Mechanistically, the photochemical fullerene−tertiary amine additions represent an interesting class of fullerene reactions that involve photoinduced electron transfer and related processes. However, the complex reaction products make any mechanistic elucidation a significant challenge. Here we report the separation and identification of several monoadducts from photochemical reactions of C_{60} with triethylamine under different experimental conditions as an initial step toward an understanding of photoinduced fullerene−tertiary amine electron transfer and subsequent processes. The results allow a direct comparison between the fullerene and conventional aromatic systems in photochemical reactions with a tertiary amine. Mechanistic implications of the results are discussed.

Experimental Section

Materials. C_{60} was purchased from MER Co. (purity > 99.5%), Southern Chemical Group (purity > 99.5%), and BuckyUSA (purity > 99%). The sample purity was checked by UV−vis absorption, ^{13}C NMR, and matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) MS methods. Triethylamine (TEA) was obtained from Burdick & Jackson and was distilled before use. Reagent grade solvents for chromatography separation were purified by fraction distillation. Spectrophotometry grade solvents were used as received in absorption and emission measurements because no interference from impurity was observed in the applicable wavelength region according to spectroscopic measurements of the solvents. Deuterated solvents and tetramethylsilane for NMR experiments were purchased from Cambridge Isotope Laboratory.

Photochemical Apparatus. Photochemical reactions were carried out using an ACE-7861 type immersion-well photochemical reaction assembly acquired from Ace Glass Inc. The light source is a 450-W Hanovia medium-pressure mercury lamp. The circulating cooling water jacket serves as a filter for absorbing near-IR irradiation of the lamp. The sample container has inlet and outlet openings for continuous bubbling of nitrogen or argon gas during photoirradiation. The setup was modified such that an additional jacket was added between the water jacket and the sample container to allow the use of a solution filter.

Measurements. Proton and ^{13}C NMR spectra were obtained on Bruker AF-200 and AC-300 NMR spectrometers and a JEOL Eclipse +500 NMR spectrometer. Chromium (III) acetylacetonate ($Cr(acac)_3$) obtained from Lancaster was used as paramagnetic relaxation reagent in some ^{13}C NMR measurements to decrease the nuclear relaxation times, so as to increase the number of scans in a given time duration.[27]

MALDI-TOF MS analyses were performed on a Kratos Kompact-III mass spectrometer equipped with a nitrogen laser. α-Cyano-4-hydroxycinnamic acid, 3,5-dimethoxy-4-hydroxycinnamic acid, 2,5-dihydroxybenzoic acid, pyrene, and 9-nitroanthracene were used as matrix materials.

Absorption spectra were measured using a computer-controlled Shimadzu UV-2101PC UV−vis spectrophotometer. Emission spectra were recorded on a Spex Fluorolog-2 photon-counting emission spectrometer equipped with a 450-W xenon source, a Spex 340S dual-grating and dual-exit emission monochromator, and two detectors. The two gratings are blazed at 500 nm (1200 grooves/mm) and 1000 nm (600 grooves/mm). The room-temperature detector consists of a Hamamatsu R928P photomultiplier tube operated at −950 V, and the thermoelectrically cooled detector consists of a near-infrared-sensitive Hamamatsu R5108 photomultiplier tube operated at −1500 V. In fluorescence measurements, a Schott 540 nm (GG-540) or 610 nm (RG-610) color glass sharp-cut filter was placed before the emission monochromator to eliminate the excitation scattering. Minor distortion at the blue onset of the observed fluorescence spectra caused by the filter was corrected using the transmittance profile of the filter. Unless specified otherwise, fluorescence spectra were corrected for nonlinear instrumental response by use of predetermined correction factors.

Fluorescence decays were measured using time-correlated single photon counting (TCSPC) method. The TCSPC setup consists of a Hamamatsu Stabilized Picosecond Light Pulser (PLP-02) as the excitation source, which produces 33 ps (full width at half-maximum (fwhm)) light pulses at 632 nm with

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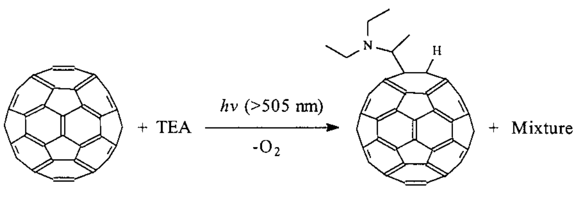
Scheme 1



I

a repetition rate of 1 MHz. Fluorescence decays were monitored via a 695 nm color glass sharp-cut filter. The detector consists of a Philips XP2254B photomultiplier tube operated at −2 kV using an EG&G Ortec 556 high-voltage power supply. The detector electronics from EG&G Ortec include two 9307 discriminators, a 457 biased time-to-amplitude converter, and a 916A multichannel analyzer. The instrument response function of the setup has a fwhm of ~1 ns. Fluorescence lifetimes were determined from observed decay curves and instrument response functions via deconvolution by use of the Marquardt nonlinear least-squares method.

Results and Discussion

Photochemical reactions of C_{60} with TEA were carried out in room-temperature solutions under both deoxygenated and air-saturated conditions. The products obtained from C_{60}-TEA reactions without and with dissolved molecular oxygen were quite different.

C_{60}−TEA in Deoxygenated Solution. The reaction was carried out by photoirradiating a deoxygenated toluene solution of C_{60} and TEA. In a typical experiment, a 300 mL solution of C_{60} in toluene (1 mg/mL) was deoxygenated by bubbling the solution with dry argon gas for 45 min. A condenser was used in the deoxygenation process to minimize solvent loss. To the solution was added 13 mL of TEA (94 mmol). The TEA concentration in the solution (0.31 M) was selected such that thermal reactions between C_{60} and TEA were negligible in the duration of photoirradiation.[23] The solution was then deoxygenated again via bubbling with dry argon gas for 10 min. The deoxygenated solution was irradiated in the immersion-well photochemical apparatus for 30 min. An aqueous potassium chromate solution (0.5 M) was used as a cutoff filter (505 nm). During the photoirradiation, the C_{60}−TEA solution was bubbled with a slow stream of dry N_2 gas to prevent a recontamination of oxygen and also to provide the required agitation. Following the photoirradiation, the solvent toluene and residual TEA were evaporated on a rotatory evaporator. The reaction mixture thus obtained was fractionated in terms of the solubility in room-temperature toluene. The toluene-soluble fraction contains unreacted C_{60} and at least two reaction products according to TLC analyses.

The unreacted C_{60} and reaction products were separated on a silica gel column using a 1:1 (v/v) toluene−hexane mixture as eluent. Under the chromatography condition, only one fraction was moving after unreacted C_{60}. It was collected and further purified by washing the solid sample with neat acetonitrile. The molecular structure of the photoreaction product **I** (in ~10% yield on the basis of reacted C_{60}) was identified using ^{1}H and ^{13}C NMR methods (Scheme 1).

The proton spectrum of **I** consists of eight signals (Figure 1). Application of total correlation spectroscopy (TOCSY) reveals two separate spin systems. One of them includes two methylene signals at δ 3.02 and 2.88 ppm, and a methyl signal at δ 1.04 ppm. These protons can be easily assigned to an ethylamino group. Their integrated intensities of 2, 2, and 6 indicate that there are two equivalent ethyl groups attached to the nitrogen atom. The two protons attached to the same methylene carbon are diastereotopic and give two separate signals. Protons contributing to the five other signals form the second spin system. These signals can be assigned to the methine proton next to the nitrogen (1H, δ 4.75, dd, J 4.7, 12.6 Hz), the methine proton next to the methyl group (1H, δ 3.575, m), two inequivalent methylene protons at δ 2.72 (1H, q, J 12.5 Hz) and 2.56 (1H, dt, J 4.7, 4.7, 11.9 Hz), and the methyl protons (3H, δ 1.79, d, J 6.9 Hz). The connectivity between the protons was established with double quantum filtered-correlation spectroscopy (DQF−COSY). The heteronuclear single quantum coherence (HSQC) spectrum confirms that the two methylene protons are attached to the same carbon atom. It is interesting that the first methylene signal appears as almost a perfect quartet. This proton couples with three different protons in one geminal coupling ^2J and two vicinal couplings ^3J. The "quartet" structure of the signal shows that all three coupling constants are approximately the same. The coincidence of the vicinal couplings suggests that the two methine protons are in the same orientation relative to the methylene protons. The results suggest that the NEt_2 and methyl groups are cis with respect to the five-member ring.

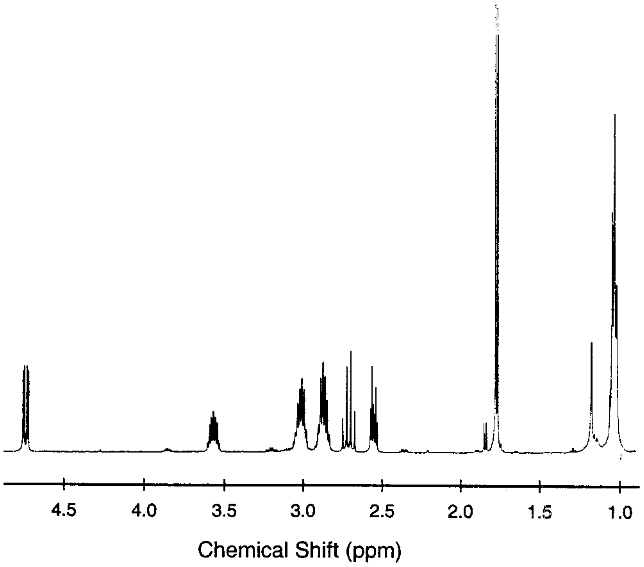


Figure 1. The ^{1}H spectrum (500 MHz) of **I** in CS_2 with C_6D_6 as lock and trimethylsilane (TMS) as internal standard.

The ^{13}C NMR spectrum of **I** shows 58 resonances in the fullerene region,[28] as expected for a mono-functionalized C_{60} derivative with C_1 symmetry.[29] The two bridgehead quaternary carbons appear at δ 74.0 and 76.8 ppm. Signals of protonated carbons at δ 76.7 (CH−N), 46.2 (CH), 45.7 (CH_2−N), 34.9 (CH_2), 17.6 (**C**H_3−CH), and

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[28] ^{13}C NMR (125.8 MHz, CS_2/C_6D_6, 30 mM Cr(acac)$_3$) δ 157.39, 157.13, 154.78, 154.47, 148.22, 147.69, 147.33, 147.12, 146.56 (2C), 146.40, 146.30, 146.23, 146.19, 146.15, 146.06, 146.02, 145.98, 145.85, 145.69, 145.42 (2), 145.40, 145.31, 145.27, 145.21, 145.17, 145.08, 144.76, 144.62, 144.54, 144.40, 143.30, 143.17, 142.75 (2C), 142.68, 142.66, 142.52, 142.47, 142.33, 142.27, 142.23, 142.14, 141.99, 141.97, 141.94, 141.81 (2C), 141.73, 140.14, 139.98, 139.66 (2C), 136.64, 135.61, 135.00, 134.19, 76.8, 76.7, 74.0, 46.2, 45.7 (broad), 34.9, 17.6, 14.4.

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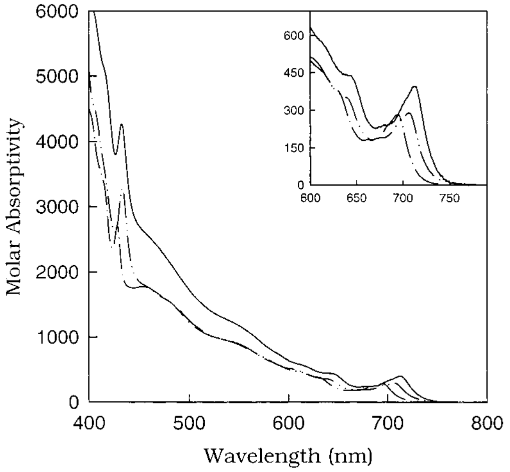

Figure 2. UV−vis absorption spectra of **I** (—), **II** (-..-..-), and **III** (-.-.-.-) in room-temperature toluene.

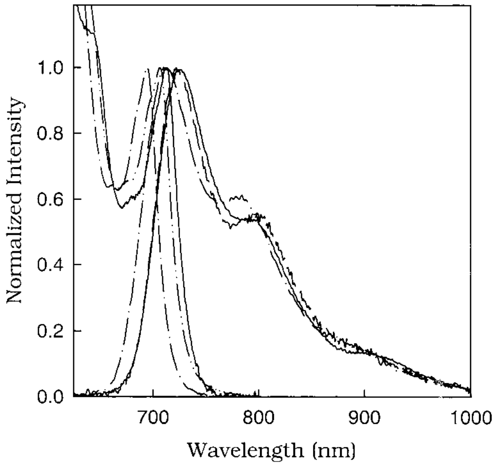

Figure 3. Fluorescence spectra of **I** (—), **II** (-..-..-), and **III** (-.-.-.-) in room-temperature toluene. Corresponding absorption spectra at the red onset are also shown for comparison.

14.4 ppm ($\mathbf{C}H_3-CH_2$) were assigned using HSQC 2D-spectroscopy. The signal at 45.7 ppm is broad both in a diamagnetic solution and in the presence of paramagnetic relaxation reagent. The broadening is probably a result of some rate processes involving the amino group, e.g., inversion at the nitrogen atom. Although the proton spectrum obtained at 20 °C shows no exchange broadening, the exchange broadening for methyl and methylene protons of the diethylamino group was observed at lower temperatures.

The MALDI-TOF MS analysis of the compound using α-cyano-4-hydroxycinnamic acid as matrix material further confirms the structural assignment, with a molecular weight of 847 for **I**.

The UV−vis absorption spectrum of **I** in toluene is shown in Figure 2. The spectral features are similar to those of pyrrolidino-C_{60} derivatives,[30−32] with the 0−0 absorption band at ~700 nm. The fluorescence spectrum of **I** has a mirror-image relationship with the red onset portion of the absorption spectrum (Figure 3).

In addition to the reaction product identified above as **I**, there is a significant fraction that does not move on the silica gel column with the 1:1 (v/v) toluene−hexane mixture as eluent. The fraction, which was washed down the column using a 10:1 (v/v) toluene−acetonitrile mixture, is a complex mixture of compounds according to thin-layer chromatography (TLC) analyses. The separation and purification of these compounds for their structural characterizations remain a challenging task in further investigations.

C_{60}−TEA in Air-Saturated Solution. The C_{60}−TEA photoreaction in air-saturated toluene solution yields different reaction products. In a typical reaction, a solution of 200 mg (0.28 mmol) C_{60} in 230 mL toluene was prepared. To the solution was added 9 mL of TEA (6.5 mmol). Then, the solution was irradiated in the immersion-well photochemical apparatus for 30 min. An aqueous potassium chromate solution (0.5 M) was used as a cutoff filter (505 nm) in the photoirradiation. Upon the removal of toluene and residual TEA on a rotatory evaporator, the reaction mixture was fractionated in terms of the solubility in room-temperature toluene. According to TLC analyses, the toluene-soluble portion contains two reaction products in addition to unreacted C_{60}.

The unreacted C_{60} and reaction products were separated on a silica gel column using toluene as eluent. The fraction moving after unreacted C_{60} was a single compound. It was characterized using ^{1}H and ^{13}C NMR and MALDI-TOF MS methods. The ^{1}H spectrum in CS_2 solution with C_6D_6 as internal lock shows methine protons at δ 4.81 (2H, q, J 6.5 Hz), methyls at δ 1.84 ($2\times CHC\mathbf{H}_3$, 6H, d, J 6.5 Hz), methyl at δ 1.48 ($CH_2C\mathbf{H}_3$, 3H, t, J 7.1 Hz), and two methylene protons at δ 3.27 (H_a, 1H, dq, J 7.4, 11.9 Hz) and δ 2.91 (H_b, 1H, dq, J 6.9, 11.9 Hz). Results from the selective homonuclear decoupling experiment indicate that the methylene protons H_a and H_b are coupled to each other and to the methyl protons at δ 1.48. Because there are no signals corresponding to methine protons on the fullerene cage, the ^{1}H NMR spectrum can be assigned to the pyrrolidino-C_{60} structure **II** (in 10−15% yield on the basis of reacted C_{60}).[24] The inequivalence of the methylene protons indicates that methyl substituents at the tertiary carbons are trans with respect to the five-member ring.[24] The ^{13}C spectrum was obtained using the same solution, but in the presence of 0.04 M Cr(acac)$_3$. The results further support the structural assignment of **II**.[33] The signal at δ 74.36 (2C) as a result of the fullerene bridgehead sp^3 carbons indicates that the compound has a 6,6-closed cage addition pattern.[29] The structural assignment is also consistent with the number and intensity pattern of the signals in the fullerene region,[33] which correspond to an effectively C_2 symmetry[24,29] (Scheme 2).

The molecular weight of **II** (819) was confirmed by MALDI-TOF MS analysis. The UV−vis absorption spec-

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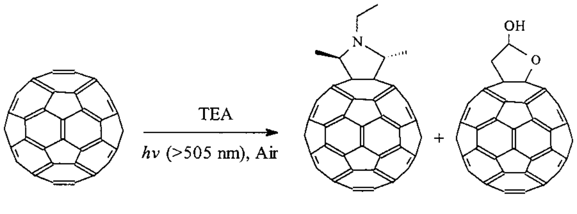
[33] ^{13}C NMR (125.8 MHz, CS_2/C_6D_6, 30 mM Cr(acac)$_3$) δ 155.85 (2C), 153.39 (2C), 146.95 (2C), 146.30 (2C), 146.01 (2C), 145.95 (2 × 2C), 145.71 (2 × 2C), 145.32 (2C), 145.15 (2C), 145.01 (2C), 144.98 (2C), 144.87 (2C), 144.27 (2C), 144.25 (2C), 142.85 (2C), 142.38 (2C), 142.32 (2C), 141.99 (2C), 141.89 (2C), 141.82 (2 × 2C), 141.52 (2C), 141.42 (2C), 139 91 (2C), 139.51 (2C), 136.79 (2C) and 135.84 (2C); 74.36 (2C), 65.43, 40.77, 15.10 (2C), 14.16.

Scheme 2



II **III**

trum and fluorescence spectrum of **II** in toluene are also shown in Figures 2 and 3, respectively.

The third fraction in the silica gel column separation was also a single compound. It was further purified by washing the solid sample repeatedly with neat acetonitrile to eliminate nonfullerene impurities. The MALDI-TOF MS analysis of the compound using α-cyano-4-hydroxycinnamic acid as matrix material yielded a molecular weight value of 780. The sample was further characterized using high-resolution fast atom bombardment (FAB) MS analysis, which yielded molecular weight 780.0228.[34] For a fullerene derivative, the molecular formula closely matching the experimental molecular weight value is $C_{62}O_2H_4$ (780.0211).

The ^{1}H NMR spectrum of the compound in CS_2 solution with C_6D_6 as internal lock is shown in Figure 4. The spectrum is unusual and deserves a detailed discussion. There are only four signals with chemical shifts 6.29 (1H, ddd), 3.7−3.9 (2H, AB-system modulated by couplings with two other protons), and 2.86 ppm (1H, m). With the known molecular formula, the ^{1}H NMR spectrum is assigned to the derivatized fullerene structure **III** (in 6−10% yield on the basis of reacted C_{60}). The upfield proton signal shows behavior typical of a hydroxyl proton, namely that (a) it disappears after the solution is treated with CD_3OD as a result of deuterium exchange; (b) it shifts downfield at a lower temperature and in the presence of donor solvents; and (c) its chemical shift and line width depend on the sample concentration and purity (the fine structure can be observed only for a fresh, carefully purified sample). Results from selective homonuclear decoupling experiments reveal the unusual feature of this spin system. Each proton in **III**, including O**H**, exhibits measurable couplings with three other protons. A computer simulation of the spectrum allows the determination of the coupling constants (Table 1). Because exchangeability normally prevents hydroxyl proton peaks from showing fine structures, the hydrogen exchange in **III** must have a considerably lower rate than those in common organic compounds. Surprisingly, the long-range coupling constant $^4J_{OH-CH(B)}$ is also large.

The structural assignment of **III** is further supported by the ^{13}C NMR results.[35] The carbon spectrum consists of 58 signals in the fullerene region and two signals as a result of bridgehead sp^3 carbons, indicative of a 6,6-closed addition pattern on the fullerene cage. The chemical shifts of 99.5 and 67.2 ppm for the sp^3 carbons are typical of the bridgehead carbons attached to oxygen and carbon atoms, respectively.[36] Only two signals from protonated carbons at δ 99.9 (CH) and 49.7 ppm (CH_2) were observed, and numbers of attached protons were independently confirmed in distortionless enhancement by polarization transfer (DEPT) experiments. In a paramagnetic solution containing 30 mM $Cr(acac)_3$, the CH signal shows broadening. The broadening may be explained in terms of the close proximity of this protonated carbon to paramagnetic chromium ions in intermolecular outer-sphere complexes formed between **III** and $Cr(acac)_3$, because it is well known that substrates with hydroxyl groups form hydrogen bonds with $Cr(acac)_3$.[37] Thus, relaxation properties of the carbons close to the OH group are strongly affected by the paramagnetic reagent.

The isolation and identification of monoadducts from the photochemical C_{60}−TEA reactions under different experimental conditions represent an important step toward a mechanistic understanding of the photoinduced electron transfer and subsequent processes. To examine the role of intramolecular electron transfer with amine-functionalized C_{60} cage in determining the product distribution via secondary reactions, electron-transfer properties of **I** in the excited singlet state were studied using molecular spectroscopic methods.

Photoinduced Electron Transfer in I. Fluorescence properties of **I** are sensitive to solvent polarity. The results provide strong evidence for intramolecular electron transfer in the excited singlet state of **I** in a polar or polarizable solvent environment.

The UV−vis absorption spectra of **I** in hexane and a series of polar solvents are essentially the same as that in toluene (Figure 2). The fluorescence spectral profile of **I** is also insensitive to solvent changes. Shown in Figure 5 are fluorescence spectra of **I** in room-temperature hexane and methylene chloride solutions. Despite the significant difference in their relative intensities, the spectra upon normalization are similar. The results show that there are no other emission contributions for **I** in a polar solvent such as methylene chloride.[16] However, fluorescence quantum yields of **I** in nonpolar and polar solvents are different. The fluorescence yield of **I** in room-temperature hexane was determined in reference to that of C_{60} in the same solvent ($\Phi_F = 3.3 \times 10^{-4}$).[38] **I** is more fluorescent than C_{60}, with the fluorescence quantum yield larger than that of C_{60} by approximately a factor of 3.5, which is typical for mono-functionalized C_{60} derivatives.[30,39,40] The fluorescence of **I** becomes significantly weaker in more polarizable and polar solvents (Table 2). For example, the yield in toluene (5.1×10^{-4}) is less than half of that in hexane. In polar solvents, fluorescence yields are much lower (Table 2). The solvent polarity dependence of fluorescence quantum yields is more

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[34] The high-resolution FAB was performed by Steven Mullens at the Mass Spectrometry Laboratory, School of Chemical Sciences, University of Illinois.

[35] ^{13}C NMR (125.8 MHz, $CS_2/CDCl_3$, 30 mM $Cr(acac)_3$) δ 156.28, 155.51, 151.61, 148.89, 148.13, 147.51, 146.51 (2C), 146.46, 146.40, 146.32, 146.20, 146.18 (2C), 146.10, 146.04, 145.78, 145.75, 145.53, 145.46, 145.40, 145.35, 145.32 (3C), 145.26 (2C), 145.19, 144.88, 144.84, 144.78, 144.48, 143.10, 143.07, 142.83, 142.81, 142.75 (2C), 142.65, 142.64, 142.44, 142.37, 142.35, 142.32 (2C), 142.13 (2C), 142.04, 141.86, 141.72, 140.21, 140.14, 139.78, 139.66, 138.03, 137.89, 137.23, 135.47, 99.8, 99.5, 67.2, 49.6.

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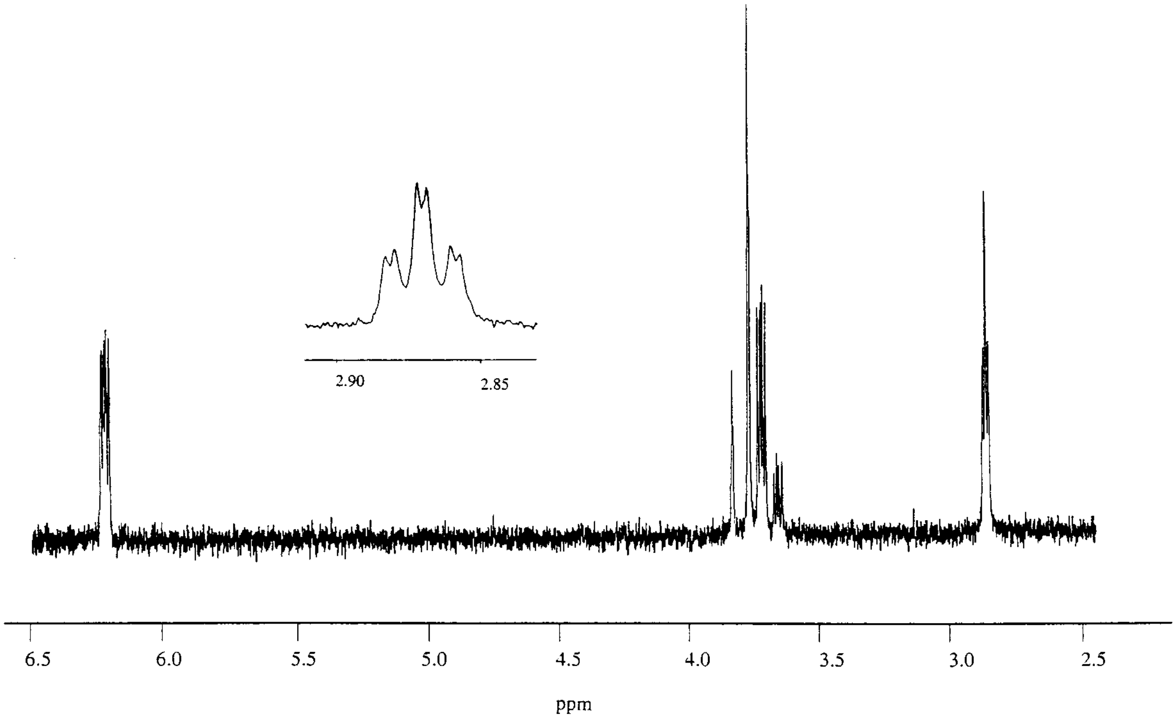


Figure 4. The ^{1}H NMR spectrum (200 MHz) of **III** in CS_2 with C_6D_6 as lock and TMS as internal standard.

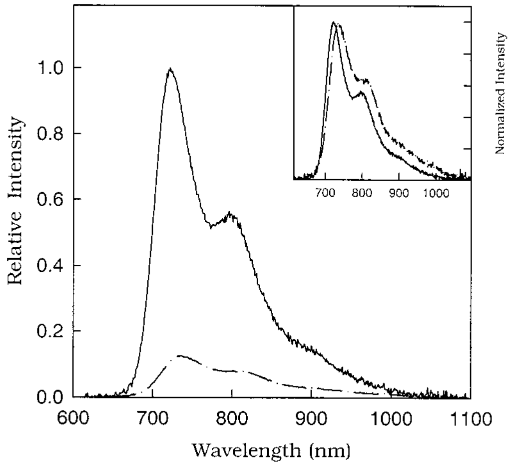


Figure 5. Fluorescence spectra of **I** in hexane (—) and methylene chloride (-.-.-.-) at room temperature. Shown in the inset are the normalized spectra.

Table 1. Coupling Constants from the Computer Simulation for the Proton Spin System in III

			coupling constant, Hz			
proton	type	δ, ppm	1	2	3	4
1	CH	6.29	–	0.4	4.1	2.1
2	CH_2 (A)	3.82	0.4	–	12.6	0.5
3	CH_2 (B)	3.73	4.1	12.6	–	2.3
4	OH	2.86	2.1	0.5	2.3	–

clearly demonstrated by the results of **I** in a series of hexane–methylene chloride mixtures. As the methylene chloride volume fraction in the mixtures increases from 0 to 40%, the fluorescence quantum yield of **I** decreases monotonically from 12×10^{-4} to 4.2×10^{-4} (Table 2).

Fluorescence decays of **I** in room-temperature hexane and methylene chloride were measured. The decay curve in hexane can be deconvoluted well from the instrumental response function using a monoexponential equation, yielding a fluorescence lifetime of 1.25 ns. The result is similar to that of other mono-functionalized C_{60} derivatives.[30–32,39,40] However, the fluorescence decay of **I** in methylene chloride can only be deconvoluted using a biexponential equation with lifetimes for the short- and long-lived components of 0.18 and 1.05 ns, respectively (Table 2).

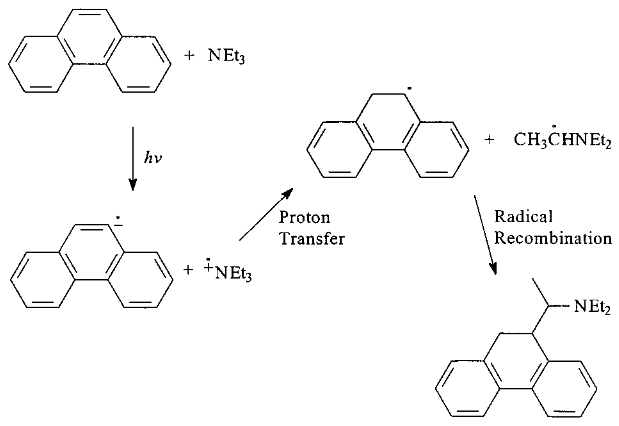
Photophysical properties of **I** are affected strongly by the presence of acid in sample solutions. For **I** in methylene chloride, the addition of 1% (v/v) trifluoroacetic acid (TFA) results in blue-shifts of both absorption and fluorescence spectra, although the spectral profiles are barely affected. The addition of TFA to the solution of **I** in methylene chloride also significantly changes the fluorescence quantum yield and lifetime of the compound. In the presence of 1% (v/v) TFA, the fluorescence quantum yield of **I** becomes 11×10^{-4}, which is close to that in neat hexane (Table 2). Although the fluorescence decay of **I** in methylene chloride solution is biexponential, the decay becomes monoexponential in the solution with 1% (v/v) TFA. The fluorescence lifetime of **I** in the methylene chloride–TFA (1% v/v) mixture is 1.3 ns, which is also quite similar to that in hexane (Table 2).

Mechanistic Consideration. Interestingly, photochemical reactions of C_{60} with TEA form exclusively cyclic monoadducts (**I**–**III**). The formation of cycloadducts is obviously unique to the reactions involving fullerene molecules. In the photochemical reduction of nonfullerene aromatic compounds by tertiary amines such as TEA, no cycloadducts were observed.[20,21] Mechanistically, photoreduction reactions of aromatic compounds with tertiary amines are similar to those with primary and secondary amines, involving photoinduced sequential electron transfer, proton transfer, and radical recombination processes.[18–21] The classical mechanistic scheme using phenanthrene as an example can be described in Scheme 3.

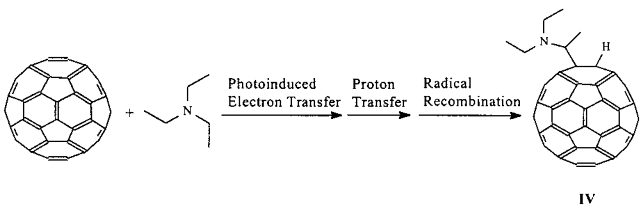
Table 2. Fluorescence Parameters of I under Different Solvent Conditions

solvent	dielectric constant	Φ_F ($\times 10^{-4}$)	τ_{F1} (ns)	τ_{F2} (ns)
hexane	1.89	12	1.25	
toluene	2.38	5.1	0.35	0.85
o-xylene	2.57	5.8		
1,2,4-trimethylbenzene	2.26	8.1		
1,2,3,5-tetramethylbenzene	2.29	8.6		
carbon disulfide	2.64	6.9		
chloroform	4.81	4.0		
THF	7.58	0.92		
methylene chloride	8.93	1.5	0.18	1.05
methylene chloride + 1% TFA		11	1.3	
dichlorobenzene	9.93	2.6		
hexane + 5% (v/v) methylene chloride		11		
hexane + 10% (v/v) methylene chloride		9.2		
hexane + 20% (v/v) methylene chloride		6.7		
hexane + 30% (v/v) methylene chloride		5.3		
hexane + 40% (v/v) methylene chloride		4.2		

Scheme 3



Scheme 4



For C_{60} and TEA in a toluene solution at room temperature, there are definitely photoinduced electron-transfer processes according to results from fluorescence quenching experiments.[23] The excited singlet state of C_{60} is quenched by TEA in a rather efficient fashion, with a Stern–Volmer quenching constant of 3.47 M^{-1}. Thus, a bimolecular quenching rate constant of 2.9×10^9 $M^{-1}s^{-1}$ can be obtained by using the well-established fluorescence lifetime of 1.2 ns for C_{60} in toluene.[23] The electron-transfer nature of the fluorescence quenching is confirmed by the results of solution acidity effects.[41] The fluorescence quenching becomes negligible in a toluene solution of C_{60} and TEA in the presence of 1–2% (v/v) TFA, which indicates that the n-electrons in TEA are responsible for the fluoresence quenching. If the same mechanistic scheme is applied, photochemical reactions of C_{60} with TEA should yield a monoadduct **IV** (Scheme 4).

According to Liou and Cheng, monoadducts of the **IV** type were indeed observed as initial products in photochemical reactions of C_{60} with trimethylamine (TMA) and *N*,*N*-dimethylaniline (DMA).[26] In the C_{60}–TEA photochemical reactions reported here, **IV** was not observed in the reaction mixtures. Because the photoinduced electron transfer is an excited singlet state process, dissolved molecular oxygen in air-saturated solution should have no effects on the interactions between excited singlet C_{60} and TEA. The fluorescence lifetime of C_{60} (1.2 ns in the absence of TEA) is too short to be quenched by the low concentration molecular oxygen in the solution. Thus, the formation of C_{60} radical anion–TEA radical cation pair should be the first step of the photochemical reactions in solutions both with and without dissolved molecular oxygen. The different products from the C_{60}–TEA reactions in deoxygenated and air-saturated toluene solutions might be due to oxygen effects on the subsequent steps following radical ion pair formation. However, the **IV** type products in the photochemical reactions of C_{60} with TMA and DMA reported by Liou and Cheng were obtained under ambient reaction conditions;[26] oxygen was not rigorously excluded from the toluene solutions used in their reactions. On the basis of the results reported by Liou and Cheng, it seems logical to conclude that the **IV** type simple adducts should be the initial products formed in C_{60}–tertiary amine photochemical reactions regardless of whether the solutions are deoxygenated or air-saturated. The fact that **IV** was not found in the C_{60}–TEA reaction mixtures is not sufficient to rule out the possibility that **IV** may indeed be the initial product. The different monoadducts obtained from the C_{60}–TEA photochemical reactions under deoxygenated and air-saturated conditions are probably secondary products from a common initially formed species such as **IV**. In this regard, it is possible that the same mechanistic characteristics are shared by the fullerene–TEA and nonfullerene aromatic compound–TEA photochemical reactions following the absorption of a single photon.

A significant difference between fullerenes and nonfullerene aromatic compounds such as phenanthrene is that upon monofunctionalization the fullerene cage is still an excellent electron acceptor with photoirradiation in the same wavelength region as that for the parent C_{60}.[30,39] The secondary photochemical reactions for the formation of the observed products **I**–**III** are probably complicated. For **II**, it seems logical to assume that the initial product **IV** may undergo both photoinduced intramolecular and intermolecular electron transfers. The subsequent proton transfer and radical recombination processes result in the formation of the cycloadduct **II** in the presence of

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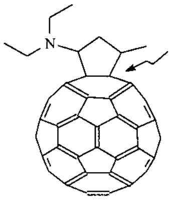
(41) Sun, Y.-P.; Bunker, C. E.; Ma, B.; Lawson, G. E., unpublished results.

Scheme 5



oxygen.[24] Although mechanistic details on the role of oxygen are not clear, we suspect that there is an oxidation process similar to that observed in the photocyclization reaction of *cis*-stilbene, in which phenanthrene instead of dihydrophenanthrene is formed in the presence of oxygen.[42]

There is no readily available explanation for the formation of **I**. In any case, the breaking of carbon−nitrogen bond is required for the product. Although carbon−nitrogen bond breaking and formation are rarely observed, they are not unprecedented in photochemical reactions involving fullerene molecules. In the photoaddition reactions of sarcosine ester to C_{60}, Gan and co-workers reported the isolation of products that can only be produced via breaking and re-forming carbon−nitrogen bonds.[11] The formation of cycloadducts with a five-member ring was cited as the driving force for the unusual photochemical carbon−nitrogen bond breaking and forming processes.[11] It is probably no coincidence that **I** is also a five-member ring cycloadduct. In addition, a positively charged amino group is a known leaving group (Hoffman elimination, for example), which may be substituted by the electron-deficient fullerene cage. Thus, the end connected to the fullerene bridgehead carbon (marked by an arrow in the **I** molecular structure) is likely the one broken away from the carbon−nitrogen bond (Scheme 5).

It is more difficult to derive a mechanistic explanation for the formation of **III**. As an oxidation product, it requires carbon−nitrogen bond breaking for carbon−oxygen bond formation. Interestingly, **III** is also a five-member ring cycloadduct. In addition to the dissolved molecular oxygen, dissolved carbon dioxide in the reaction solution was suspected as a potential oxygen source. In control experiments, however, **III** was absent in the reaction mixtures when the C_{60}−TEA photochemical reactions were carried out in a carbon-dioxide-saturated toluene solution. It is thus concluded that the oxidation for the formation of **III** is due to dissolved molecular oxygen in the air-saturated solution.

Photoinduced electron transfer processes are most likely responsible for the initiation of the secondary reactions for the observed products. Monofunctionalized C_{60} derivatives are capable of undergoing photoinduced intermolecular electron transfers with amines as electron donors.[30,39] For photoinduced intramolecular electron transfers, **I** serves as a model compound. Fluorescence results of **I** in different solvents clearly show that there is substantial quenching of the fullerene excited state by the intramolecular tertiary amine group via electron transfer interactions in a polar or polarizable solvent environment. The involvement of the n-electrons in electron transfer is made evident by the acid effects on fluorescence properties. The acid effects are most likely associated with the protonation of the amino group in **I**, which effectively shuts off the n-π^* electron transfer process. More quantitatively, the electron transfer rate constant in a polar solvent may be estimated by assuming that fullerene excited singlet state processes other than the electron transfer are essentially solvent independent (with changes within error margins of fluorescence measurements).[16]

$$k_{\mathrm{ET}} = 1/\tau_{\mathrm{F},1} - 1/\tau_{\mathrm{F,hexane}} \qquad (1)$$

where $\tau_{\mathrm{F},1}$ denotes observed fluorescence lifetimes of the vertical excited singlet state. The electron-transfer rate constants k_{ET} thus obtained are $\sim 2 \times 10^9$ and 4.8×10^9 s^{-1} in toluene and methylene chloride, respectively. These rate constants are comparable to that obtained in the electron-transfer quenching of C_{60} fluorescence by TEA in room-temperature toluene.[23] The results suggest that the secondary reactions of the initially formed C_{60}−TEA adducts are subject to competitions between intramolecular and intermolecular processes. Such competitions may also be responsible for the complex product distributions in the C_{60}−TEA photochemical reactions.

In summary, fullerene C_{60} undergoes efficient photochemical reactions with TEA to form a complex mixture of addition products under ambient and deoxygenated conditions. The reactions are initiated via photoinduced electron transfer between the excited singlet C_{60} and the amine. The monoadducts isolated and identified in this work are completely different from those expected on the basis of the photoinduced sequential electron transfer, proton transfer, and radical combination mechanism, which is well-established in reactions of conventional aromatic molecules with tertiary amines. The complexity in the reactions involving fullerene is attributed to the fact that the functionalized fullerene molecules remain electron acceptors for both inter- and intramolecular electron-transfer reactions. The existence of these electron-transfer processes is made evident by molecular spectroscopic results. Thus, the observed C_{60}−TEA photoreaction products are likely from multistep processes, each of which may involve either inter- or intramolecular photoinduced electron transfer. Further isolation and identification of other products in the complex reaction mixture are required for a more detailed mechanistic understanding.

Acknowledgment. We thank Dr. C. E. Bunker for measuring the fluorescence lifetimes, R. Guduru for experimental assistance, and Professor R. A. Abramovitch for helpful discussion. Y.-P.S. acknowledges the financial support from the National Science Foundation (CHE-9727506) and, in part, the Center for Advanced Engineering Fibers & Films, a NSF/ERC at Clemson University. We also thank the National Science Foundation (CHE-9700278) for the acquisition of the 500-MHz NMR instrument.

Supporting Information Available: The HSQC 2D-spectrum (500 MHz) of **I** in CS_2 with C_6D_6 as lock and TMS as internal standard. This material is available free of charge via the Internet at http://pubs.acs.org.

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