4456 *J. Phys. Chem. A* **1998,** *102,* 4456−4461

Photophysical Properties of $C_{60}H_{18}$ and $C_{60}H_{36}$: A Laser Flash Photolysis and Pulse Radiolysis Study

Dipak K. Palit, Hari Mohan, and Jai P. Mittal*,†

Chemistry Division, Bhabha Atomic Research Centre, Mumbai 400 085, India

Received: November 13, 1997; In Final Form: March 17, 1998

Spectroscopic and photophysical properties of two hydrogenated fullerenes, namely, $C_{60}H_{18}$ and $C_{60}H_{36}$, have been studied in benzene solution using laser flash photolysis and pulse radiolysis techniques. Samples of $C_{60}H_{18}$ and $C_{60}H_{36}$ used were prepared by the reduction of C_{60} with Zn/concentrated HCl in benzene or toluene at normal (for $C_{60}H_{36}$) or at high (for $C_{60}H_{18}$) temperature and pressure. It is reported that $C_{60}H_{18}$ and $C_{60}H_{36}$ prepared by these methods have tetrahedral (T) symmetry containing four highly delocalized benzenoid rings, and a crown structure with C_{3v} symmetry, respectively. Owing to hydrogenation, the fluorescence band of C_{60} shifts toward the blue and both the fluorescence quantum yields and the singlet-state (S_1) lifetimes of the more hydrogenated species increase compared with those of the parent fullerene molecule. Triplet quantum yields reduce considerably (e.g., ϕ_T for $C_{60}H_{18}$ and $C_{60}H_{36}$ is 0.15 and 0.1, respectively) compared with unity for C_{60}. Also the singlet−singlet and triplet−triplet absorption spectra show considerable differences from those of C_{60}. Owing to successive hydrogenation of C_{60}, the intensity of the near-IR band (at ca. 880 nm) in the singlet−singlet absorption spectra decreases and that in the visible (at ca. 500 nm) becomes more prominent. In the triplet−triplet absorption spectrum, the major band, which is seen at 740 nm for C_{60}, gradually shifts to the blue in the more hydrogenated species. The spectroscopic properties of the hydrogenated fullerenes used by us have been seen to be different in many aspects compared with those reported by Bensasson et al. (*Chem. Phys.* **1997**, *215*, 111), possibly owing to the different symmetries of these derivatives prepared by different hydrogenation methods.

Introduction

The highly symmetric structure and unique properties of the all-carbon molecule C_{60} has been the subject of immense research because of its possible applications in different fields. Hence, one aspect of research has been the preparation of new derivatives of fullerenes by the addition of different kinds of groups or molecules[1,2] that distort the highly symmetric cage structure of C_{60} differently and hence that modify its intrinsic properties.[3] Suitably functionalized fullerene derivatives are used in a number of important applications in fields ranging from optical limiting[4] to various topics in biological chemistry.[5] The site and degree of functionalization severely affect the physicochemical properties of these fullerene derivatives, and this effect has been rationalized in terms of perturbation of the fullerenes' π system.[6] Recently, several attempts have been made to synthesize water-soluble derivatives of C_{60} [7] and to charactreize their photophysical and redox properties in connection with their potential biological applications.[8] Also, the recent studies on larger carbon allotropes (say, C_{76}, C_{78}, and C_{84}) have shown that they should be better electron acceptor and donor moieties than C_{60} and can serve as photosensitizers or electron relays in photoinduced electron-transfer reactions.[9] The presence of more than one isomer for these higher fullerenes results in considerable complications in the separation process of these isomers and in the characterization of their properties.[10] Speculations regarding the possible use of the fullerene hydrides in batteries appearing in numerious media reports led the various groups to prepare the hydrogenated derivatives of the fullerene by adopting different methods of hydrogenation. Although theoretical calculations and symmetry considerations have indicated that the most stable isomers in the $C_{60}H_{12n}$ series should be $C_{60}H_{36}$ and $C_{60}H_{48}$,[11] it has been shown that $C_{60}H_{18}$ and $C_{60}H_{36}$ (and not $C_{60}H_{48}$) are the most stable hydrogenated derivatives of the fullerene. Probably the former one is the more stable of the two because it is often formed by degradation of $C_{60}H_{36}$ and is more prominent in the mass spectrum than the latter at high temperature.[12] It has been reported that the structure and symmetry of the highly hydrogenated product $C_{60}H_{36}$ should be dependent on the method of synthesis. For example, Smalley and co-workers prepared $C_{60}H_{36}$ using Birch reduction[2] and suggested the tetrahedral (T_h) symmetry for the molecule. Although it has been predicted that there are more than 10^{14} different isomeric forms of $C_{60}H_{36}$,[13] only four isomers have been proposed to be stable and show possible existence.[14] Among them, the isomer with T_h symmetry is the most symmetrical one in which the 12 carbon−carbon double bonds, one in each isolated pentagon, are arranged as far apart as possible on its surface, with no aromatic six-membered rings in the molecule.[3a,15]

Attalla and co-workers[16] prepared $C_{60}H_{36}$ using hydrogen radical species ($H^\bullet$) at elevated temperatures (400 °C) and high hydrogen pressures (6.9 MPa). They assigned the most likely structure to D_{3d} or C_{3i} (S_6) symmetry, either of which has two aromatic six-membered rings at the 3-fold axis poles of the molecule, with the other six carbon−carbon double bonds isolated in six pentagons—these double bonds either point

---

* To whom correspondence should be addressed.

† Also affiliated as Honorary Professor with The Jawaharlal Nehru Centre for Advanced Scientific Research, Bangalore, India.

S1089-5639(98)00190-X CCC: $15.00

approximately toward (for C_{3i} or S_6 structure) or are at right angles to the poles (for D_{3d} structure).

Detailed investigations of the vibrational and electronic spectra and structure of $C_{60}H_{36}$, prepared by the technique of transfer hydrogenation method,[17] has revealed that the most probable symmetry of the isomer is C_{3i} (S_6), but the presence of the lowest energy tetrahedral (T_h) as well as the D_{3d} isomers could not be excluded.[18]

Recently, Darwish et al. has developed a method of reduction of C_{60} with Zn/concentrated HCl in either benzene or toluene solution, resulting in rapid and quantitative conversion of C_{60} into mainly $C_{60}H_{36}$.[19] According to their report, $C_{60}H_{36}$ prepared by this method is the lowest energy isomer having T symmetry structure, which has no center of symmetry, and the C=C double bonds in this structure are located in four isolated aromatic six-membered highly delocalized benzenoid rings.[12,19]

On the other hand, the calculation of Clare and Kepert[20] reveals that there are 27 isomers that should be stable among the possible 1.5×10^{13} isomers of $C_{60}H_{18}$ estimated by Balasubramanian.[13] The most stable structure found for this molecule has C_{3v} symmetry containing $C_{18}H_{18}$ crown with an isolated C_6 ring at the center of the crown. The spectral characteristics of $C_{60}H_{18}$ prepared by the reduction of C_{60} at high temperature and pressure are consistent with the proposed structure of the most stable isomer.

In this paper we report the results of our detailed and systematic investigations of the photophysical and photochemical properties of $C_{60}H_{18}$ and $C_{60}H_{36}$, which are the samples prepared and characterized by Darwish et al.[19] in benzene solutions. Recently, Bensasson et al.[18] published their results on the spectroscopic and photophysical properties of the ground and triplet state of $C_{60}H_{18}$ and $C_{60}H_{36}$, both of which have been prepared by transfer hydrogenation methods.. Our present results differ from those of Bensasson et al. and have been assigned owing to differences in structures and symmetries of these molecules.

Experimental Section

The hydrogenated fullerenes were a kind gift from the Fullerene Science Centre, University of Sussex, U.K., and the methods of preparation and characterization are available in detail elsewhere.[11,16] In brief, $C_{60}H_{36}$ was obtained by the reduction of C_{60} with Zn/concentrated HCl in benzene or toluene solution, leading to rapid and quantiative conversion of C_{60} into $C_{60}H_{36}$. $C_{60}H_{36}$ is soluble in dimethylformamide and carbondisulfide, but it undergoes rapid light-catalyzed degradation in the presence of oxygen.[19] However, it is sparingly soluble in hydrocarbon solvents, say benzene and cyclohexane, and reasonably stable. Spectroscopic grade benzene and cyclohexane were obtained from Spectrochem, India and used without any further purification. All other chemicals were of Analar grade purity. Iolar grade N_2 (Indian Oxygen, 99.9% purity) was used to deaerate the samples prior to pulsed experiments. Steady-state optical absorption and fluorescence spectra were recorded on a Shimadzu model UV-160A spectrophotometer and Hitachi model F-4010 spectrofluorometer, respectively. Flurorescence lifetimes were determined using the time-domain fluorescence spectrometer model 199 (Edinburgh Instruments, U.K.), which uses a hydrogen discharge flash lamp (pulse width of 1 ns) for excitation of the sample and single-photon-counting fluorescence detection technique to record the fluorescence decay.

Laser Flash Photolysis. For picosecond laser flash photolysis experiments, the third (355 nm, 5 mJ) harmonic output pulses of 35 ps duration from an active−passive mode-locked Nd:YAG laser (Continuum, model 501-C-10) were used for excitation and continuum probe pulses in the 400−920 nm region were generated by focusing the residual fundamental in a H_2O/D_2O mixture (50:50).[21] The probe pulses were delayed with respect to the pump pulses using a 1 m long linear-motion translation stage, and the transient absorption spectra at different delay times (up to 6 ns) were recorded by an optical multichannel analyzer (Spectroscopic Instruments, Germany) interfaced to an IBM PC. At the zero delay position the probe light reaches the sample just after the end of the pump pulse. Transients surviving beyond 50 ns were studied by monitoring their absorption using a tungsten filament lamp in combination with a Bausch and Lomb monochromator (*f*/10, 350−800 nm), Hamamatsu R 928 PMT, and a 500 MHz digital oscilloscope (Tektronix, TDS-540A) connected to a PC.

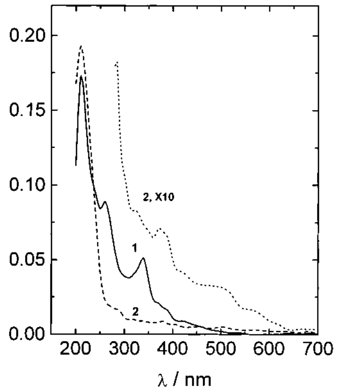

Figure 1. Ground-state absorption spectra of $C_{60}H_{18}$ (1) and $C_{60}H_{36}$ (2) in cyclohexane.

Pulse Radiolysis. High-energy (7 MeV) electron pulses of 50 ns duration generated from a linear electron accelerator were used for pulse radiolysis experiments. The details of the pulse radiolysis setup have been described elsewhere.[22] The transient species produced were detected by monitoring the optical absorption. The absorbed dose was determined by using the aerated KSCN solution with $G_\epsilon = 21\,520$ dm^3 mol^{-1} cm^{-1} for 100 eV of absorbed dose (the G value is the number of radicals or molecules produced per 100 eV of absorbed energy, and ϵ is the molar absorptivity at 500 nm for the transient $(SCN)_2^{\bullet -}$.

Results and Discussion

A. Absorption and Fluorescence Characteristics. The electronic absorption spectra of the two fullerene derivatives in cyclohexane are presented in Figure 1. Both molecules have the strongest absorption peak at ca. 210 nm. Although the other two peaks of $C_{60}H_{18}$ at 260 and 340 nm and the shoulders at 370 and 420 nm are reasonably stronger and well resolved, the other features of $C_{60}H_{36}$, except the 210 nm peak, are very weak. The dual peak feature of $C_{60}H_{18}$ in the 230−260 nm region as reported by Bensasson et al.[18] is not seen for our samples and is attributed to anthracene impurity intrinsic in their method of preparation.[17] However, owing to the very low solubilities of these molecules in cyclohexane, the molar extinction coefficient value for the ground-state absorption could not be determined accurately.

Both derivatives have been seen to be more fluorescent compared with C_{60}. Figure 2 shows the fluorescence spectra of $C_{60}H_{18}$ and $C_{60}H_{36}$ in benzene solutions. The main features of the fluorescence spectra of these two derivatives were not much different from each other. In both cases, the spectra show the dual peaks at 480 and 520 nm.[23] However, the fluorescence

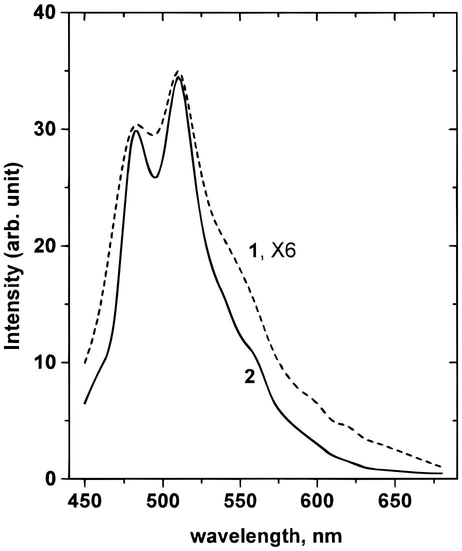

Figure 2. Fluorescence spectra of $C_{60}H_{18}$ (1) and $C_{60}H_{36}$ (2) in benzene.

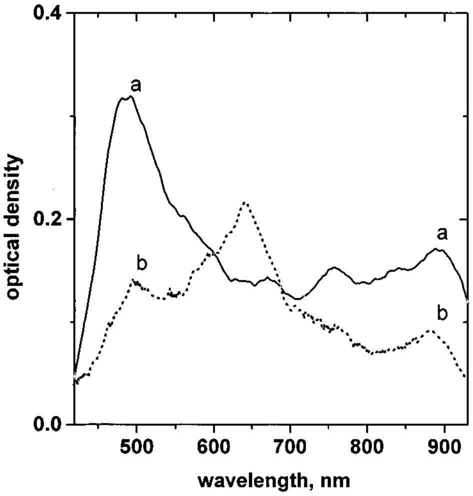

Figure 3. Singlet−singlet (a) and triplet−triplet (b) absorption spectra of $C_{60}H_{18}$ in benzene.

band of $C_{60}H_{18}$ is broader than that of $C_{60}H_{36}$. Fluorescence yields determined by a comparative method using quinine bisulfate in 0.1 N H_2SO_4 ($\Phi = 0.55$)[24] as a standard have shown that $C_{60}H_{36}$ ($\Phi_f = 0.37$) is 6 times more fluorescent than $C_{60}H_{18}$ ($\Phi_f = 0.06$). $C_{60}H_{36}$ in benzene has been seen to have a very long lifetime of 27.0 ± 1 ns compared with 2.8 ± 0.2 ns for $C_{60}H_{18}$. The fluorescence characteristics of these two derivatives can be compared with those of the parent fullerene. C_{60} is very weakly fluorescent in solution; the fluorescence quantum yield is about 1×10^{-4} in benzene, the fluorescence spectra shows a peak at ca. 720 nm and a shoulder at 690 nm, and the fluorescence lifetime is about 1.2 ns.[25] Hence, it is seen that the radiative properties of the excited singlet state of the fullerene have been significantly affected because of hydrogenation.

B. Laser Flash Photolysis Study. Curve a in Figure 3 represents the transient absorption spectrum obtained on laser flash photolysis of an N_2-saturated solution of $C_{60}H_{18}$ in benzene recorded immediately after the 35 ps laser pulse of 355 nm. The growth of the transient monitored at 480 nm was seen to follow the rise of the excitation pulse profile, and hence, the transient absorption spectra could be due to the singlet−singlet ($S_1 \rightarrow S_n$) absorption. Also, the lifetime of the S_1 state has been determined by monitoring the decay of the transient absorption at the same wavelength and has been found to be 2.5 ± 0.3 ns, which matches well that (2.8 ns) obtained by fluorescence lifetime measurement. Singlet−singlet absorption spectrum shows very broad overlapping absorption bands extending throughout the visible wavelength region (400−950 nm), similiar to that of C_{60}.[17] However, for $C_{60}H_{18}$ the visible band with a peak at 480 nm is more intense compared with that in the near-IR with a peak at 880 nm that has been suppressed compared with that in the case of C_{60}. Curve b in Figure 3, which shows the spectrum recorded 6 ns after the laser pulse, can be provisionally assigned to the triplet state of $C_{60}H_{18}$ formed because of intersystem crossing from the singlet to the triplet. This spectrum, which has a major peak at 640 nm with shoulders or smaller peaks at 500 and 880 nm, may have some contribution from the singlet state surviving at 6 ns delay.

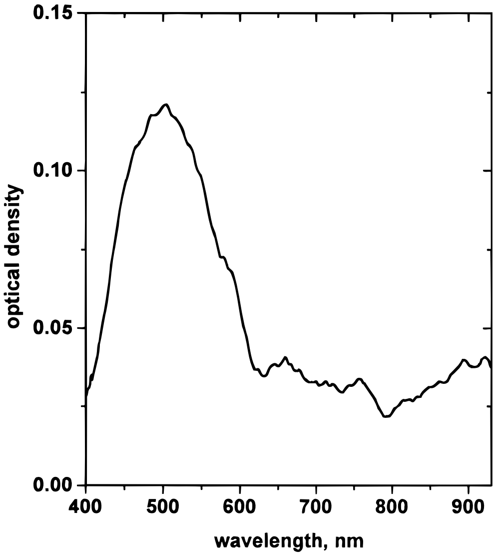

Figure 4. Singlet−singlet absorption spectra of $C_{60}H_{36}$ in benzene.

Figure 4 represents the singlet−singlet absorption spectrum of $C_{60}H_{36}$ in N_2-saturated benzene solution excited by 355 nm laser pulses of 35 ps duration. It has the only relatively narrow absorption band with a peak at 480 nm. In this case, the absorption band seen at 880 nm is very weak. The singlet−singlet absorption did not show any decay up to 6 ns, in agreement with its lifetime of 27.0 ns determined from fluorescence lifetime measurements.

The molar extinction coefficient values for the singlet−singlet absorption in benzene has been determined by comparing the absorbance values at 480 nm with that of the benzophenone triplet at 525 nm in acetonitrile ($\epsilon = 6500$ dm^3 mol^{-1} cm^{-1})[26] formed on photoexcitation of their solutions with the same ground-state absorbance at 355 nm. Under these conditions the molar extinction coefficient values of the excited singlet states of $C_{60}H_{18}$ and $C_{60}H_{36}$ were determined to be 5700 ± 1000 and 4500 ± 1000 dm^3 mol^{-1} cm^{-1}, respectively, at 480 nm. Hence, it is seen that owing to addition of more and more hydrogen atoms to the double bonds of C_{60}, both the fluorescene yield and the singlet lifetime increase; the singlet absorption spectra show considerable change, with the band in the 480 nm region being the prominent one compared to that in the 880 nm region.[21,25]

Figure 5 shows the transient optical absorption spectra obtained by laser flash photolysis of N_2-saturated benzene solutions of $C_{60}H_{18}$ and $C_{60}H_{36}$ recorded 500 ns after the 35 ps laser pulse. The spectrum represented by curve a for $C_{60}H_{18}$ in the wavelength region 450−700 nm is very similiar to the one presented in Figure 3b. The transient for $C_{60}H_{36}$ (curve b)

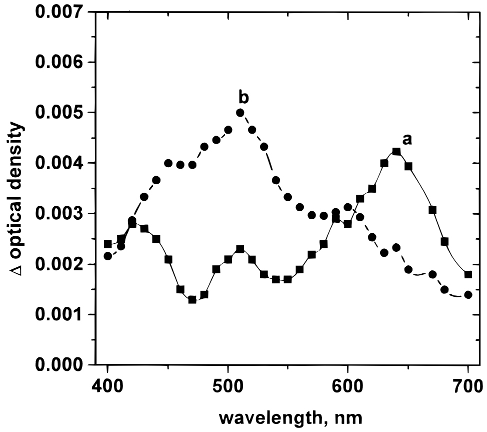

Figure 5. Triplet−triplet absorption spectra of $C_{60}H_{18}$ (a) and $C_{60}H_{36}$ (b) in benzene obtained after 1 μs of the laser excitation.

has a major peak at 510 nm and shoulders at 470 and 590 nm. In both cases, the transient absorptions in the entire spectral region were seen to follow the same decay law (see later). Confirmation that the spectra are due to the triplet states of these fullerene derivatives has been obtained from complete quenching of the transients in the presence of oxygen and also by β-carotene leading to the formation of the triplet state of the latter. However, the formation of the β-carotene triplet in the case of $C_{60}H_{36}$ could not be followed owing to overlapping absorptions of the triplet states of $C_{60}H_{36}$ and β-carotene. By comparison of the triplet-state absorption spectrum of $C_{60}H_{18}$ reported by Bensasson et al.[18] with that obtained with our samples, it is seen that both of them have quite different features. The former has the main peak at 550 nm with the two other minor peaks at 650 and 715 nm. However, the triplet absorption spectra of $C_{60}H_{18}$ recorded with our sample have the major peak at 640 nm with the two other minor peaks at 420 and 510 nm. It is important to note that Bensasson et al. have not detected the formation of the triplet state with their samples of $C_{60}H_{36}$.[18]

C. Pulse Radiolysis Study. The conclusive evidence for the formation of the triplet states has been obtained from the electron pulse radiolysis study of these compounds in N_2-saturated benzene solutions of these compounds. The radiolysis of the solvent benzene produces its triplet state of very high energy (353 kJ mol^{-1}) with high yield. The triplet state of benzene can transfer its energy to that of another solute having $E_T < 353$ kJ mol^{-1}, generating the triplet state of the latter (eqs 1 and 2):[26]

$$C_6H_6 \rightarrow TC_6H_6^* \tag{1}$$

$$^{T}C_6H_6^* + \text{solute} \rightarrow C_6H_6 + {}^{T}(\text{solute})^* \tag{2}$$

The transient absorption spectra obtained on pulse radiolysis (dose = 50 Gy/pulse) of $C_{60}H_{18}$ and $C_{60}H_{36}$ in benzene solutions have been presented in Figure 6.

The molar extinction coefficient for the triplet−triplet absorption of $C_{60}H_{18}$ has been determined by the energy-transfer method as suggested by Amouyal et al.[26,27] For this purpose the p-terphenyl triplet ($\lambda_{max} = 460$ nm, $\epsilon_T = 90\,000$ dm^3 mol^{-1} cm^{-1}, $E_T = 244$ kJ mol^{-1})[28] has been chosen as the donor to transfer the energy to the triplet of the fullerene derivative. The triplet of p-terphenyl was generated on pulse radiolysis of N_2-saturated solution in benzene. The concentration of p-terphenyl, the donor, was kept at 1×10^{-2} mol dm^{-3} and that of $C_{60}H_{18}$, the acceptor, was varied from 0 to 2×10^{-5} mol dm^{-3}. Under these conditions, only the triplet of the donor was initially produced, which in turn transferred its energy to the acceptor. The decay of the donor triplet was monitored as a function of the concentration of $C_{60}H_{18}$. The pseudo-first-order decay (k_{obs}) of p-terphenyl triplet became faster as the concentration of $C_{60}H_{18}$ was increased, suggesting energy-transfer quenching of the p-terphenyl triplet by the fullerenes. Concomitant to the decay of the p-terphenyl triplet, the absorption at 640 nm, which is characteristic of the triplet state of $C_{60}H_{18}$, was observed to grow. The rate constant for the energy-transfer reaction from the p-terphenyl triplet to the $C_{60}H_{18}$ triplet was determined to be 4.2×10^9 dm^3 mol^{-1} s^{-1}. The molar extinction coefficient of the triplet state of $C_{60}H_{18}$ at 640 nm has been calculated to be 26 000 ± 4000 dm^3 mol^{-1} cm^{-1} after applying necessary corrections for the participation of processes other than energy-tranafer processes mentioned above.[19,20] By application of the same method, the molar extinction coefficient values of the triplet of $C_{60}H_{36}$ could not be determined because of overlapping absorptions of the triplet states of p-terphenyl and $C_{60}H_{36}$. Also, an attempt was made to determine the extnction coefficient value of the $C_{60}H_{36}$ triplet by the method of energy transfer from the triplet state of biphenyl to the former. Although we observed the quenching of the biphenyl triplet by $C_{60}H_{36}$, owing to low concentration of the latter, no appreciable growth of its triplet could be obtained, and hence, the extinction coefficient value of the $C_{60}H_{36}$ triplet could not be determined with reasonable accuracy and is not being reported here.

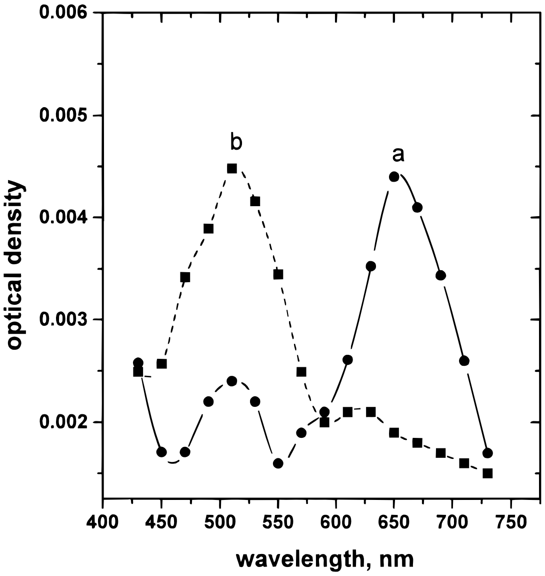

Figure 6. Triplet−triplet absorption spectra of $C_{60}H_{18}$ (a) and $C_{60}H_{36}$ (b) in benzene obtained by pulse radiolysis.

D. Quantum Yield of Triplet Formation. By use of the values of the extinction coefficients for the singlet and triplet absorptions of $C_{60}H_{18}$ at 480 and 640 nm, respectively, the quantum yield of triplet formation can be easily calculated by comparing their absorbance values at these two wavelengths as shown in Figure 3. The quantum yield value was determined to be 0.15 ± 0.2, which is much smaller than unity as determined for C_{60}.[21,23] This quantum yield value agrees well with that ($\phi = 0.12$) reported by Bensasson et al.[18] Since we could not determine the molar extinction coefficient value of the $C_{60}H_{36}$ triplet, it is truly not possible to estimate the value of Φ_T. However, the extinction coefficient value for the triplet absorption of $C_{60}H_{36}$ at 510 nm may be assumed to be about 18 000 ± 4000 dm^3 mol^{-1} cm^{-1}, which should not be a too bad an estimation because the extinction coefficient values of the triplet absorptions at their corresponding absorption maxima

TABLE 1: Photophysical Properties of the Fullerene and the Hydrogenated Fullerenes

parameters	C_{60}	$C_{60}H_{18}$	$C_{60}H_{36}$
$\lambda_{max}(S_0 \rightarrow S_n)$, nm	231, 257, 329, 440−670 (ref 31)	210, 260, 340, 370(sh), 420(sh)	210, 329
λ_{max}(emission), nm	690 (sh), 720	480, 520	480, 520
Φ_f	~1 × 10^{-4} (ref 25b)	0.06 ± 0.01	0.37 ± 0.1
τ_f, ns	1.3 ± 0.1 (refs 23b, 21b)	2.6 ± 0.2	27 ± 1
$\lambda_{max}(S_1 \rightarrow S_n)$, nm ($\epsilon$, dm^3 mol^{-1} cm^{-1})[a]	480 (3000), 880 (6300) (refs 21a, 23b)	480 (5700), 880 (3000)	480 (4500), 880 (1300)
$\lambda_{max}(T_1 \rightarrow T_n)$, nm ($\epsilon$, dm^3 mol^{-1} cm^{-1})[a]	510 (3000), 740 (14000) (ref 21b)	510 (15000), 640 (26000)	510, 600[b]
Φ_T	0.95 ± 0.05 (refs 21b, 23b, 30)	0.15 ± 0.2	0.1 ± 0.02[c]
τ_T, ns	130 μs (refs 30, 33)	42 ± 2 μs	25 ± 2 μs

[a] Error limit in determination of the ϵ values is about 10%. [b] ϵ_T values could not be determined (see text). [c] Φ_T value is determined assuming the value of ϵ_T is about 18 000 dm^3 mol^{-1} cm^{-1} (see text).

for the fullerene itself and its different derivatives fall in the same range.[23,29,30] By use of this value, the Φ_T value could be estimated to be about 0.1 ± 0.02, which is comparable to that of $C_{60}H_{18}$.

E. Decay Kinetics of Triplet States. Like the parent C_{60} molecule, the decay kinetics of $C_{60}H_{18}$ and $C_{60}H_{36}$ were seen to be dependent on the concentration of the fullerene derivatives used and also on the laser intensity used for excitation, i.e., the concentration of the triplets produced. Hence, it is expected that in addition to the normal first-order decay of the triplet to the ground state (eq 3), other possible processes contributing to the decay of it might be the triplet−triplet annihilation (eq 4) and quenching of the triplet by the ground state (eq 5).[29,30]

$$T_1 \rightarrow S_0 \qquad (3)$$

$$T_1 + T_1 \rightarrow 2S_0 \qquad (4)$$

$$T_1 + S_0 \rightarrow 2S_0 \qquad (5)$$

The self-quenching rate constant (k_{TS}) for the $C_{60}H_{18}$ triplet has been determined by monitoring its decay at 640 nm for various concentrations of $C_{60}H_{18}$ (0.5−8.6) × 10^{-5} mol dm^{-3} using the same laser energy for excitation. The pseudo-first-order rate constants of the triplet decay were seen to decrease with a decrease in concentration of $C_{60}H_{18}$. The rate constants thus obtained were plotted against the concentration of $C_{60}H_{18}$ used. The quenching rate constant (k_{TS}) thus determined, from the slope of the least-squares fit line, is 2.1 × 10^7 dm^3 mol^{-1} s^{-1}. The value of the rate constant obtained by extrapolation of the least-squares fit line to the zero concentration of $C_{60}H_{18}$ has been found to be 2.56 × 10^4 s^{-1}, which can be taken as the value of k_T, the triplet decay rate constant. The inverse of k_T should be the actual lifetime (τ = 39 ± 2 μs) of the $C_{60}H_{18}$ triplet in the absence of reactions 2 and 3. This value is much lower than the one (τ = 210 μs) reported by Bensasson et al.[13] However, owing to very low solubility of $C_{60}H_{36}$ in benzene and, hence, the very low optical density of the sample at the excitation wavelength, no meaningful variation of the triplet decay rate constants could be obtained. The lifetime of the triplet state of $C_{60}H_{36}$ in benzene was determined to be 27 ± 2 μs. The intrinsic lifetimes determined by the pulse radiolysis study of $C_{60}H_{18}$ and $C_{60}H_{36}$ in benzene solvents were found to be 42 ± 2 and 25 ± 2 μs, respectively. Both these values are in good agreement with those obtained by the flash photolysis study.

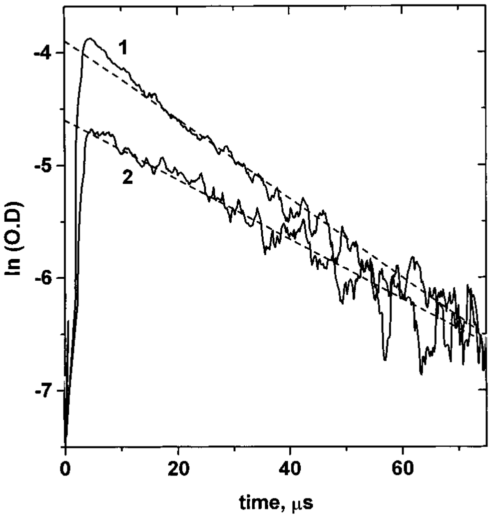

Figure 7. Decay profiles for the $C_{60}H_{18}$ triplet monitored at 650 nm with higher (curve 1, about 6 mJ at 355 nm) and lower (curve 2, about 1.5 mJ at 355 nm) laser excitation energy. Dashed lines represents the single-exponential fit to the decay. Deviation of the fitted function from linearity at early time in the case of curve 1 indicates the presence of the second-order component due to T−T annihilation reaction.

It was observed that although the decay kinetics of the $C_{60}H_{18}$ triplet followed good first-order kinetics when the initial concentration of the triplet produced was very low (e.g., ~10^{-6} mol dm^{-3} obtained using lower excitation energy), the decay of the triplet was not purely single exponential when higher concentrations of the triplet was initially produced (e.g., ~10^{-5} mol dm^{-3} obtained using higher excitation energy) (for example, see Figure 7). In the latter case the triplet decay was seen to follow mixed-order (one component followed first-order and another one followed second-order) kinetics. The component following second-order kinetics arises because of the T−T annihilation reaction at relatively higher concentrations of the triplet. However, owing to the very low quantum yield of the $C_{60}H_{18}$ triplet, the T−T annihilation reaction was not appreciable, and from the mixed-order fit of the kinetic data, not very reliable rate constant values could be recovered and, hence, are not being reported here. In the case of $C_{60}H_{36}$, no indication of T−T annhiliation reaction could be obtained beacuse of the very low concentration of its triplet that could be generated in solution.

In conclusion, we have investigated the spectroscopic and photophysical properties of the singlet and triplet states of the two hydrogenated derivatives of C_{60}, namely, $C_{60}H_{18}$ and $C_{60}H_{36}$. The important photophysical parameters determined here have been collected in Table 1, which also shows a comparison with those of their parent molecule. Table 1 shows that owing to hydrogenation, both the fluorescence yield and the singlet-state lifetime increase compared with those of their parent. The excited singlet-state absorption spectra also are quite different. On the other hand, the quantum yield and the lifetime of the triplet decrease compared with that of C_{60}. Although the properties of the singlet state of these two derivatives are being reported for the first time, the spectroscopic and photophysical properties of the triplet state have been seen to be quite different from those already reported by Benssason et al.[18] It is believed that the different hydrogenation methods should produce different isomers of the hydrogenated derivatives, and their spectroscopic properties are also expected to be different. However, to prove this belief, further studies with samples prepared by different methods and properly characterized for their structures are requird.

Acknowledgment. We thank Drs. A D. Darwish and A. K. Abdul Sada of the University of Sussex, U.K., for providing us with samples of $C_{60}H_{18}$ and $C_{60}H_{36}$. We also thank Dr. A. V. Sapre of the Chemistry Division, B.A.R.C., for his critical comments on the manuscript.

References and Notes

(1) (a) Olah, G. A.; Bucsi, I.; Lambert, C.; Aniszfeld, R.; Trivedi, R. J.; Sensharma, D. K.; Prakash, G. K. *J. Am. Chem. Soc.* **1991**, *113*, 9385. (b) Tebbe, F. N.; Becker, J. Y.; Chase, D. B.; Firment, L. E.; Holler, E. R.; Malone, B. S.; Krusic, P. J.; Wasserman, E. J. *J. Am. Soc*. **1991**, *119*, 9900. (c) Selig, H.; Lifshitz, C.; Peres, T.; Fischer, J. E.; McGhie, A. R.; Romanow, W. J.; McCauley, J. P., Jr.; Smith, A. B., III. *J. Am. Chem. Soc.* **1991**, *113*, 5475. (d) Birkett, P. R.; Hitchcock, P. B.; Kroto, H. W.; Taylor, R.; Walton, D. R. M. *Nature* **1992**, *357*, 479. (e) Holloway, J. H.; Hope, E. G.; Taylor, R.; Langley, R.; Avent, A. G.; Dennis, T. J.; Hare, J. P.; Kroto, H. W.; Walton, D. R. M. *J. Chem. Soc., Chem. Commun*. **1991**, 966. (f) Bausch, J. W.; Prakash, G. K. S.; Olah, G. A. *J. Am. Chem. Soc.* **1991**, *113*, 3205. (g) Seshadri, R.; Govindaraj, A.; Nagarajan, R.; Pradeep, T.; Rao, C. N. R. *Tetrahedron Lett*. **1992**, *33*, 2069.

(2) Haufler, R. E.; Conceicao, J.; Chibante, P. F.; Chai, Y.; Byrne, N. E.; Flanagan, S.; Haley, M. M.; O'Brien, S. C.; Pan, C.; Xiao, Z.; Billups, W. E.; Cinufolini, M. A.; Hauge, R. H.; Margrave, J. L.; Wilson, L. J.; Curl, R. F.; Smalley, R. E. *J. Phys. Chem.* **1990**, *94*, 8634.

(3) (a) Taylor, R. *J. Chem. Soc., Perkin Trans. 2* **1992**, 1667. (b) Taylor, R. *Philos. Trans. R. Soc. London A* **1993**, *343*, 87. (c) Austin, S. J.; Batten, R. C.; Fowler, P. W.; Redmond, D. B.; Taylor, R. *J. Chem. Soc., Perkin Trans*. **1993**, 1383. (d) Rathna, A.; Chandrasekhar, J. *Chem. Phys. Lett*. **1993**, *206*, 217. (e) Dunlop, B. I.; Brenner, D. W.; Schriver, G. W. *J. Phys. Chem.* **1994**, *98*, 4283. (f) Book, L. D.; Scunseria, G. E. *J. Phys. Chem.* **1994**, *98*, 4283.

(4) (a) Tutt, L.; Kost, K. *Nature* **1992**, *356*, 225. (b) Maggini, M.; Scarrano, G.; Prato, M.; Brusatin, G.; Innocenzi, P.; Guglielmi, M.; Renier, A.; Signorini, R.; Meneghettt, M.; Bozio, R. *Adv. Mater*. **1995**, *7*, 404.

(5) (a) Richmond, R. C.; Gibbson, U. J. In *Recent Advances in the Chemistry and Physics of Fullerenes and Related Materials*; Kadish, K. M., Ruoff, R. S., Eds.; The Electrochemical Society: Pennigton, NJ 1995; p 684. (b) Boutorine, A. S.; Tokuyama, H.; Takasugi, M.; Isobe, H.; Nakamura, E.; Helene, C. *Angew. Chem*. **1994**, *23*, 2526. (c) Hirsch, A. *The Chemistry of the Fullerenes*; Thieme Medical Publishers Inc.: New York, 1994.

(6) Guldi, D. M.; Asmus, K. D. *J. Phys. Chem. A*. **1997**, *101*, 1472.

(7) (a) Vesella, A.; Uhlmann, P.; Waldraff, C. A. A.; Diedrich, F.; Thilgen, C. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1388. (b) Hawker, C.; Saville, P. M.; White, J. W. *J. Org. Chem.* **1994**, *59*, 3503. (c) Zhang, X.; Foote, C. S. *J. Org. Chem.* **1994**, *59*, 5235. (d) Lamparth, I.; Hirsch, A. *J. Chem. Soc., Chem. Commun*. **1994**, 1727. (e) Maggini, M.; Scorrano, G.; Prato, M. *J. Am. Chem. Soc.* **1993**, *115*, 9798. (f) Wilson, S. R.; Kaprindis, N.; Wu, Y.; Schuster, D. I. *J. Am. Chem. Soc.* **1993**, *115*, 8495. (g) Birgel, C. *Chem. Ber*. **1957**, 126. (h) Hirsch, A.; Lamparth, I.; Karfunkal, H. R. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 437. (i) Anderson, J. L.; An, Y.-Z.; Rubin, Y.; Foote, C. S. *J. Am. Chem. Soc.* **1994**, *116*, 9763.

(8) (a) Mohan, H.; Palit, D. K.; Mittal, J. P.; Chiang, L. Y.; Smus, K. D.; Guldi, D. M. *J. Chem. Soc., Faraday Trans*., in press. (b) Guldi, D. M.; Hungerbuhler, H.; Asmus. K. D. *J. Phys. Chem. A*. **1997**, *101*, 1783. (c) Guldi, D. M. *J. Phys. Chem. A* **1997**, *101*, 3895. (d) Guldi, D. M. *Res. Chem. Intermed*., in press. (e) Guldi, D. M.; Hungerbuhler, H.; Asmus, K. D. *J. Phys. Chem. A*. **1995**, *99*, 13487. (f) Guldi, D. M.; Liu, D.; Kamat, P. V. *J. Phys. Chem. A* **1997**, *101*, 6195. (g) Kamat, P. V.; Sauve, G.; Guldi, D. M.; Asmus, K. D. *Res. Chem. Intermed.* **1997**, *23*, 575. (h) Kamat, P. V.; Sauve, G.; Ruoff, R. S. *J. Phys. Chem.* **1995**, *99*, 2162.

(9) Deleted in proof.

(10) (a) Bendale, R. D.; Zenner, M. C. *J. Phys. Chem.* **1995**, *99*, 13830. (b) Benz, M.; Fauti, M.; Fowler, P. W.; Fuchs, D.; Kappes, M. M.; Lehner, C.; Michel, R. H.; Orlandi, G.; Zerbetto, F. *J. Phys. Chem.* **1996**, *100*, 13399. (c) Orlandi, G.; Zerbetto, F.; Fowler, P. W.; Manolopoulos, D. E. *Chem. Phys. Lett*. **1993**, *208*, 441. (d) Kikuchi, K.; Nakahara, N.; Wakbayashi, T.; Suzuki, S.; Shiromaru, H.; Miyake, Y.; Sato, Y.; Kemoto, I.; Kainosho, M.; Achiba, Y. *Nature* **1992**, *357*, 142.

(11) (a) Dunlap, B.; Brenner, D. W.; Mintmire, J. W.; Mowery, R. C.; White, C. T. *J. Am. Chem. Soc.* **1991**, *95*, 5763. (b) Guo, T.; Scuseria, G. E. *Chem. Phys. Lett*. **1992**, *191*, 527.

(12) Walton, D. R. M. Private communication.

(13) Balasubramanian, K. *Chem. Phys. Lett*. **1991**, *182*, 257.

(14) Dunlap, B. I.; Brenner, D. W.; Schriver, G. W. *J. Phys. Chem.* **1994**, *98*, 1756.

(15) Taylor, R. *Tetrahedron Lett.* **1991**, 3731.

(16) (a) Attalla, M. I.; Vassalo, A. M.; Tattan, B. N.; Hanna, J. V. *J. Phys. Chem.* **1993**, *97*, 6329. (b) Hall, L. E.; Mckenzie, D. R.; Attalla, M. I.; Vassalo, A. M.; Davis, R. L.; Dunlop, J. B.; Cockayne, D. J. H. *J. Phys. Chem.* **1993**, *97*, 57416.

(17) (a) Ruchardt, R.; Gerst, M.; Ebenhoch, J.; Beckhaus, H. D.; Campbell, E. E. B.; Tellgmann, R.; Schwarz, H.; Weiske, T.; Pitter, S. *Angew. Chem., Int. Ed. Engl*. **1993**, *32*, 584. (b) Gest, M.; Beckhaus, H. D.; Ruchardt, C.; Campbell, E. E. B.; Tellgmann, R. *Tetrahedron Lett*. **1993,** *34*, 7729.

(18) Bensasson, R. V.; Hill, T. J.; Land, J.; Leach, S.; McGarvey, D. J.; Truscott, T. G.; Ebbenhoch, J.; Gerst, M.; Ruchardt, C. *Chem. Phys*. **1997**, *215*, 111.

(19) Darwish, A. D.; Abdul-Sada, A. K.; Langley, G. J.; Kroto, H. W.; Taylor, R. G.; Walton, D. M. *J. Chem. Soc., Perkin Trans. 2* **1995**, 2359.

(20) Clare, B. W.; Kepert, D. L. *J. Mol. Struct.:* THEOCHEM. **1994**, *303*, 1.

(21) (a) Palit, D. K.; Sapre, A. V.; Mittal, J. P. *Indian J. Chem*. **1992**, *31*, F46. (b) Palit, D. K.; Sapre, A. V.; Mittal, J. P.; Rao, C. N. R. *Chem. Phys. Lett.* **1992**, *195*, 1.

(22) (a) Priyadarsini, K. I.; Naik, D. B.; Moorthy, P. N.; Mittal, J. P. *Proc. Tihany Symp. Radiat. Chem., 7th* **1991**, 105. (b) Guha, S. N.; Moorthy, P. N.; Kishore, K.; Naik, D. B.; Rao, K. N. *Proc. Indian Acad. Sci.* (*Chem. Sci*.) **1989**, *99*, 261.

(23) (a) Sension, R. J.; Phillips, C. M.; Szarka, A. Z.; Romanow, W. J.; McGhie, A. R.; McCauley, J. R., Jr.; Smith, A. B., III; Hochstrasser, R. M. *J. Phys. Chem.* **1991**, *95*, 6075. (b) Ebbesen, T. W.; Tanigaki, K.; Kuroshima, S. *Chem. Phys. Lett*. **1991**, *181*, 501. (c) Palit, D. K.; Mittal, J. P. *Fullerene Sci. Technol*. **1995**, *3*, 643.

(24) Melhuish, W. H. *J. Phys. Chem.* **1961**, *65*, 229.

(25) (a) Seshadri, R.; Rao, C. N. R.; Pal, H.; Mukherjee, T.; Mittal, J. P. *Chem. Phys. Lett*. **1993**, *205*, 395. (b) Salzar, F. A.; Fedorov, A.; Berberan-Santos, M. N. *Chem. Phys. Lett*. **1997**, *271*, 361.

(26) Land, E. J.; Bensasson, R. V.; Truscott, T. G. In *Flash Photolysis and Pulse Radiolysis Contribution to the Chemistry, Biology and Medicine*; Pergamon Press: Oxford, 1983.

(27) Amouyal, E.; Bensasson, R.; Land, E. J. *Photochem. Photobiol*. **1974**, *20*, 415.

(28) Carmichael, I.; Hug, G. L. *J. Phys. Chem. Ref. Data* **1986**, *15*, 1.

(29) Palit, D. K.; Mohan, H.; Birkett, P. R.; Mittal J. P. *J. Phys. Chem.* **1997**, *101*, 5418.

(30) Dimitrijevic, N. M.; Kamat, P. V. *J. Phys. Chem.* **1992**, *96*, 4811.

(31) Hare, J. P.; Kroto, H. W.; Taylor, R. *Chem. Phys. Lett*. **1997**, *177*, 374.

(32) Fraelich, M. R.; Weisman, R. B. *J. Phys. Chem.* **1993**, *97*, 11145.