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Comparative Photophysics of $C_{61}H_2$ Isomers[†]

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Photophysical properties have been measured and compared for the two known isomers ([6,6]-closed and [5,6]-open) of $C_{61}H_2$, the parent C_{60} methano adduct. Optical absorption spectra from the ground and triplet states are consistent with C_{60} π-electron systems that are significantly less perturbed by [5,6] than [6,6] derivatization. However, intrinsic nonradiative decay of triplet state [5,6]-$C_{61}H_2$ is the most rapid yet found in any C_{60} adduct, occurring with a characteristic time of 2 μs, a factor of 70 faster than in pristine C_{60}. By contrast, the triplet decay time of [6,6]-$C_{61}H_2$ is 65 μs under the same conditions. The S_1 and T_1 energies of both isomers have been deduced by various methods. It is found that the S_1-T_1 energy gap of [5,6]-$C_{61}H_2$ is larger than that of C_{60}, whereas the opposite relation holds for [6,6]-$C_{61}H_2$. Quantum yields of triplet state formation and fluorescence were found to be 0.06 and $<2 \times 10^{-5}$ for the [5,6] isomer and 0.93 and 7.8×10^{-4} for the [6,6] isomer, respectively. The anomalously low quantum yields for [5,6]-$C_{61}H_2$ indicate efficient nonradiative decay from its S_1 state with a rate constant estimated at ca. 1.5×10^{10} s^{-1}. It is concluded that isomeric forms of simple C_{60} monoadducts can show major differences in excited-state relaxation.

Introduction

The high symmetry and 60 π electrons of buckminsterfullerene (C_{60}) give it unique electronic characteristics that intrigue basic researchers and suggest the possibility of useful applications.[1] As is the case in other compounds, chemical derivatization provides an important tool for systematically modifying molecular traits to aid fundamental studies or optimize suitability for specific uses. Although all 60 carbon atoms in C_{60} are equivalent, it is found that the molecule contains two types of carbon−carbon bonds. The 60 bonds at the junction of five- and six-membered rings are weaker and longer (0.146 nm) than the 30 bonds at junctions between six-membered rings (0.140 nm).[2] The latter have more double-bond character than the former. C_{60} can form simple derivatives by addition to both types of bonds, giving either a so-called "[5,6]-open" adduct that breaks the original underlying C−C bond or a "[6,6]-closed" adduct with a weakened but intact underlying cage bond. In crude approximation, a [5,6]-open addend has inserted into a σ bond, letting the adduct retain 60 electrons in its π system, whereas a [6,6]-closed addend attacks a π bond, leaving the cage with only 58 π electrons. Although both types of derivatization break the icosahedral symmetry of C_{60}, one would expect [5,6]-open adducts to be more similar in electronic structure to pristine C_{60} than the [6,6]-closed adducts would be.

The goal of the present study is to explore electronic differences between the two isomeric forms by measuring and comparing photophysical properties for isomers of a representative C_{60} monoadduct. We require an adduct whose isomers are experimentally accessible and stable against reaction or interconversion. The sample should also model an important class of compounds and be simple enough to permit refined quantum chemical computations of its properties. We have chosen the methano adduct $C_{61}H_2$, which is the parent of a large class of cyclic adducts with a single bridging atom. Figure 1 shows structures of its [6,6]-closed (methanofullerene) and [5,6]-open (homofullerene or fulleroid) isomers.

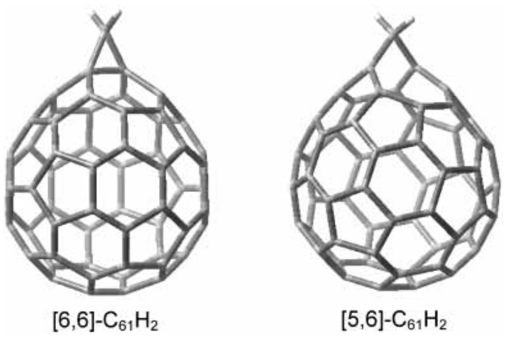

Figure 1. Structures of the [6,6]-closed (C_{2v}) and [5,6]-open (C_s) isomers of $C_{61}H_2$.

$C_{61}H_2$ was first synthesized as the [5,6] isomer by Suzuki et al. in 1992[3] and as the [6,6] isomer by Smith et al. in 1993.[4] Semiempirical computations show [5,6]-$C_{61}H_2$ to be slightly more stable than the [6,6] isomer,[5] whereas ab initio methods predict [6,6]-$C_{61}H_2$ to be the more stable form.[6,7] Experimental reports indicate that neither thermal nor electrochemical treatments cause interconversion of the two isomers.[4,8] Although UV−vis and infrared absorption spectra of $C_{61}H_2$ have been available for several years,[4,9] photophysical data on this system remain incomplete. Komamine et al. have reported the triplet−triplet spectrum, fluorescence lifetime and quantum yield, triplet self-quenching constant, and triplet−triplet annihilation rate constant for the [6,6]-closed isomer of $C_{61}H_2$,[10] but no such data are available for the [5,6] isomer. In fact, to date there have been few photophysical studies of any [5,6]-open C_{60} derivatives. Guldi et al. have reported results for a [5,6]-open imino adduct and for a [5,6]-open adduct containing an aromatic-substituted methano addend.[11] In addition, Sun et al. have

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measured absorption and emission properties of a [5,6] adduct with a different aromatic methano addend.[12] The results presented here provide a direct comparison of several photophysical properties for the parent methanofullerene adduct in its two isomeric forms. Substantial differences are found.

Experimental Methods

To synthesize the two $C_{61}H_2$ isomers, we first added diazomethane to a toluene solution of C_{60} to form the [6,6]-closed pyrazoline adduct, $C_{60}CH_2N_2$, through the cycloaddition reaction and procedure described by Suzuki et al.[3] The product pyrazoline was purified on a Shimadzu HPLC system equipped with a model SPD-M10Avp photodiode array detector using a Cosmosil 5PYE column and toluene as the mobile phase. Thermolysis of the pyrazoline adduct yielded only the [5,6]-$C_{61}H_2$ isomer, whereas photolysis gave a mixture of [5,6]- and [6,6]-$C_{61}H_2$ isomers in roughly a 60:40 ratio. For this study, samples of [5,6]-$C_{61}H_2$ were obtained by dark thermolysis of the pyrazoline adduct, thereby avoiding contamination with the [6,6] isomer. To prepare [6,6]-$C_{61}H_2$ samples, we photolyzed the pyrazoline adduct and used the HPLC system described above to separate the [6,6]-$C_{61}H_2$ product from the [5,6] isomer. We found that both [5,6]- and [6,6]-$C_{61}H_2$ are thermally and photochemically stable under our experimental conditions.

Samples were studied either in toluene solution (Fisher Optima grade) or in solid films of poly(methyl methacrylate) (PMMA). Previous studies have found that fullerene photophysical properties unrelated to molecular diffusion are almost identical in these two environments.[13] To prepare a solid film sample, a toluene solution of the fullerene derivative was mixed with a viscous toluene solution of PMMA (Sigma-Aldrich, average mol wt 120 000 or 350 000) and applied to a glass substrate. Slow evaporation of the solvent gave clear films approximately 200 μm thick.

For studies from 77 K to slightly above room temperature, film samples were placed in a liquid-nitrogen cryostat (Oxford Optistat DN) temperature controlled to within 1 K. We measured steady-state absorption spectra with a Cary 400 spectrophotometer and fluorescence spectra with a Spex Fluorolog 3 spectrofluorometer. Molar absorptivities were determined using a kinetics-based method based on observing the rate of quenching of Pd-octaethylporphyrin phosphorescence by the fullerene of interest.[14]

A low-energy Nd:YAG laser system (New Wave Mini-Lase II) excited samples for studies of induced absorption or thermally activated delayed fluorescence. Our custom-built transient spectrometer used a stabilized tungsten−halogen lamp to generate a probing light beam. Light from this source passed collinearly with the excitation beam through the sample cell before entering a computer-controlled monochromator (ISA Triax 180) containing selectable gratings blazed at 1000 nm (600 gr/mm) and 500 nm (1200 gr/mm). The monochromated probe light was then detected by an amplified Si or Ge photodiode. The photodiode output was captured and averaged on a Tektronix TDS-430A digitizing oscilloscope before transfer to a laboratory computer for analysis. The Si detector gave an instrumental response time of 0.7 μs and a photometric noise level below 10^{-6} AU, low enough to obtain reliable transient absorption data from dilute, weakly excited samples. Induced absorption spectra were assembled from data at selected delays acquired with monochromator settings covering the spectral range of interest. All induced absorption measurements were made on samples that had been degassed to remove dissolved oxygen by repeated freeze−pump−thaw cycles.

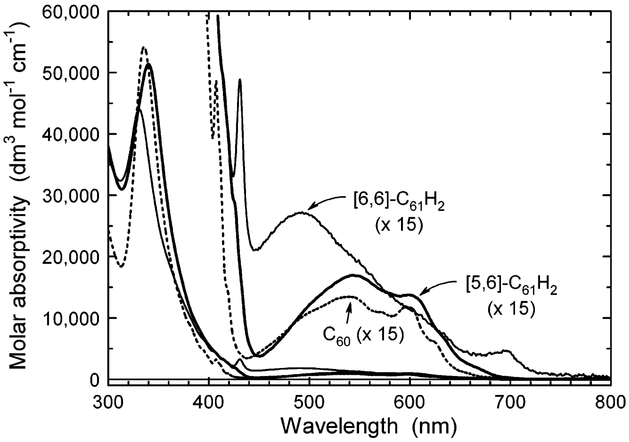

Figure 2. Ground-state molar absorptivity spectra of [6,6]-$C_{61}H_2$ (−), [5,6]-$C_{61}H_2$ (━), and C_{60} (- - -) in room-temperature toluene solution. For clarity, the spectra are also vertically expanded by a factor of 15 in the region above 400 nm.

Results and Discussion

Ground-State Spectra. In Figure 2, we plot ground-state absorption spectra of [5,6]- and [6,6]-$C_{61}H_2$ in room-temperature toluene solution, plus that of C_{60} for comparison, on an absolute molar absorptivity scale. Our spectra are very similar in shape to those reported by other researchers.[4,10] The UV spectrum of [5,6]-$C_{61}H_2$ shows a peak at 340 nm (ϵ = 51 400 dm^3 mol^{-1} cm^{-1}), lower in frequency by ca. 350 cm^{-1} compared to the corresponding peak in C_{60}. By contrast, [6,6]-$C_{61}H_2$ has a maximum at 331 nm (ϵ = 44 000 dm^3 mol^{-1} cm^{-1}), ca. 450 cm^{-1} higher in frequency than the 336-nm C_{60} peak. The absorption spectrum of [5,6]-$C_{61}H_2$ can be viewed as a slightly broadened and red-shifted variant of the C_{60} spectrum, except for the absence of a feature corresponding to the sharp 407-nm peak of C_{60}. Such similarity has been noted previously for [5,6]-open adducts and presumably reflects the limited perturbation of C_{60}'s π-electron system when a π-electron-deficient [5,6] bond is attacked. The visible spectrum of [6,6]-$C_{61}H_2$ differs from that of the [5,6] isomer in several ways. First, it shows a sharp and distinctive peak at 432 nm, within the wavelength range characteristic of other [6,6]-closed C_{60} derivatives.[15] In addition, there is a broader peak at 491 nm with an absorptivity 65% higher than the 543-nm peak of [5,6]-$C_{61}H_2$. The final distinctive feature of the [6,6]-$C_{61}H_2$ visible spectrum is the peak near 698 nm attributable to the molecule's $S_1 \leftarrow S_0$ transition, which is symmetry-allowed in the adduct's C_{2v} point group.

Fluorescence Spectra and Quantum Yields. We show in Figure 3 the fluorescence intensity measured as a function of wavelength for [6,6]-$C_{61}H_2$ dissolved in toluene at 297 K, in a polymer film at 297 K, and in a polymer film at 77 K. Komamine et al. have previously reported a 705-nm fluorescence band for this compound in toluene.[10] We find that the principal maximum, assigned as the $S_1 \rightarrow S_0$ origin band, shifts to 702 nm at 77 K from its 711-nm room-temperature value. The sharpened low-temperature spectrum reveals a major vibronic band at 781 nm and shoulders at 715 and 736 nm representing shifts from the origin of 1440, 260, and 660 cm^{-1}, respectively. We assign these frequency intervals to distinct ground-state vibrational modes that are coupled to the $S_1 \leftrightarrow S_0$ electronic transition of [6,6]-$C_{61}H_2$ and can be excited in fluorescence. In addition, a weak shoulder near 825 nm seems likely to represent a 660-cm^{-1} red shift relative to the 0−1 member of the 1440-cm^{-1} progression (which appears at 781 nm). As illustrated in Figure 4, the fluorescence and absorption spectra of [6,6]-$C_{61}H_2$ show a strong mirror-image relation,

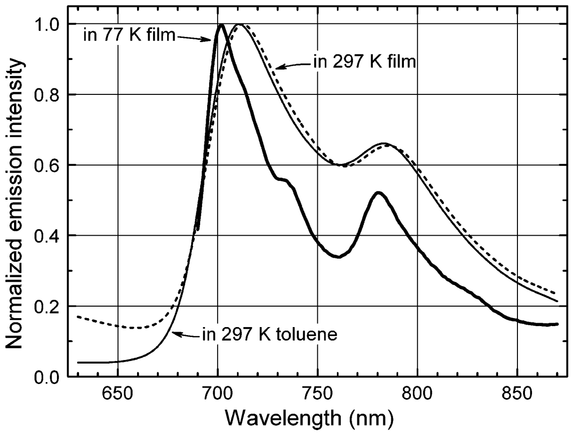

Figure 3. Fluorescence emission intensity vs emission wavelength for [6,6]-$C_{61}H_2$, measured in toluene at 297 K with 500-nm excitation (−), in a PMMA film at 297 K with 340-nm excitation (- - -), and in a PMMA film at 77 K with 330-nm excitation (—).

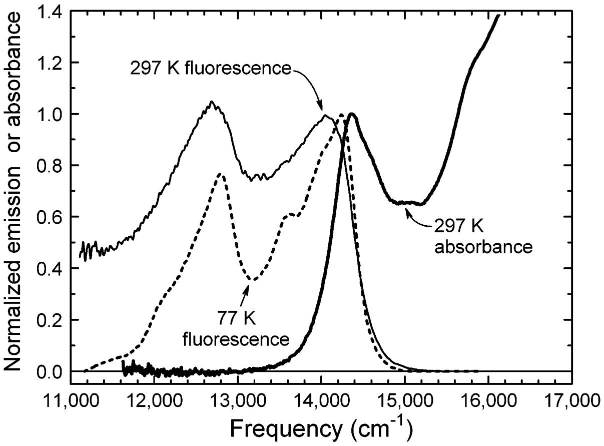

Figure 4. Normalized spectra of [6,6]-$C_{61}H_2$ showing fluorescence in 297 K toluene solution with 500-nm excitation (−), fluorescence in a PMMA film at 77 K with 330-nm excitation (- - -), and absorbance in a 297 K toluene solution (—).

allowing us to estimate the S_1-S_0 energy gap in toluene solution as 14 260 ± 30 cm^{-1}. An absorption shoulder can be seen near 15 800 cm^{-1}, or approximately 1440 cm^{-1} above the room-temperature absorption origin. This is a vibronic feature involving the same vibrational mode that is most active in the fluorescence spectrum.

Fluorescence measurements of [5,6]-open $C_{61}H_2$, the homofullerene or fulleroid isomer, revealed only a weak featureless spectrum approximately 3000 cm^{-1} in width, peaking near 750 nm (13 300 cm^{-1}). Also, as can be seen from Figure 2, this isomer shows no clear S_1 origin band in absorption. These spectral characteristics make it very difficult to estimate the singlet origin energy by a mirror-relation approach. However, the long-wavelength portion of the [5,6]-$C_{61}H_2$ absorption spectrum strongly resembles that of C_{60} with a red shift of approximately 230 cm^{-1}, suggesting that its singlet origin is lowered from that of C_{60} by this amount. By subtracting this shift from a value of 15 300 cm^{-1} for the S_1 origin of C_{60} in toluene,[13] we estimate that [5,6]-$C_{61}H_2$ has an S_1 origin energy of 15 070 ± 100 cm^{-1}. The higher S_1 energy of [5,6]-$C_{61}H_2$ compared to that of [6,6]-$C_{61}H_2$ is qualitatively similar to the findings of Guldi et al. for an unmatched pair of [5,6] and [6,6] methano adducts.[11]

Quantum yields of fluorescence also differ markedly between the two isomers of $C_{61}H_2$. Published fluorescence quantum yields of several [6,6] monoadducts are in the range of (1.0 to 1.2) × 10^{-3},[16,17] and those of [5,6] derivatives have been reported to be similar or only slightly greater than the 3.2 × 10^{-4} yield of C_{60}.[11,12,18] We find the fluorescence quantum yield of [6,6]-$C_{61}H_2$ to be 7.8 × 10^{-4}, intermediate between the 5.6 × 10^{-4} value reported by Komamine et al.[10] and the values mentioned above for other [6,6] derivatives. By contrast, our measurements on [5,6]-$C_{61}H_2$ found a much lower fluorescence quantum yield. We estimate an upper limit of 2 × 10^{-5} for this yield, but the true value may lie still lower if the sample contains even small amounts of an efficiently fluorescing impurity. Our quantum yield limit is a factor of 10 to 20 below the values previously reported for two different [5,6]-open methanofullerenes containing aromatic-derivatized addends.[11,12] In assessing the cause of this difference, one should note that impurities can substantially increase the apparent quantum yields of weakly fluorescing samples above the true values. In view of the reported photoinstability of one of the previously studied samples,[11] it seems plausible that unintended photoreactions may have caused sample contamination during measurement and introduced impurity errors into the prior results. The relatively mild excitation conditions of our experiment caused no sample composition changes detectable by HPLC analysis. Assuming a typical radiative rate constant of ca. 3 × 10^5 s^{-1} for a C_{60} monoadduct, we deduce that the S_1 state of [5,6]-$C_{61}H_2$ has a lifetime below ca. 60 ps. This value is much shorter than the 1.4-ns lifetime typical of methano-C_{60} adducts (including [6,6]-$C_{61}H_2$),[10,12,16] thereby indicating the presence of an unusual and efficient excited-state decay channel in [5,6]-$C_{61}H_2$.

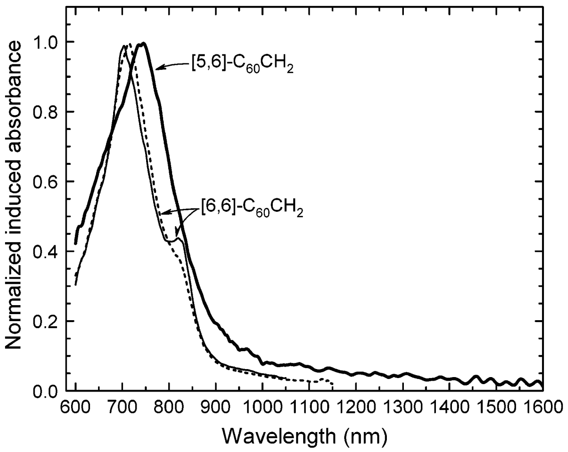

Figure 5. Normalized induced absorbance spectra following 532-nm excitation for [6,6]-$C_{61}H_2$ in toluene at 297 K (- - -), [6,6]-$C_{61}H_2$ in a PMMA film at 77 K (−), and [5,6]-$C_{61}H_2$ in toluene at 297 K (—).

Triplet−Triplet Absorption Spectra. We measured long-wavelength induced absorption spectra following 532-nm excitation for both isomers of $C_{61}H_2$ in room-temperature toluene solution and for the [6,6]-closed isomer in a polymer film at 77 K. These results are plotted in Figure 5. The [6,6]-closed isomer shows a peak, assigned to $T_n \leftarrow T_1$ absorption, that shifts from 715 nm at room temperature to 705 nm in the cryogenic film. There is also a weaker transition visible near 820 nm. Both of these features are typical of C_{60} [6,6] monoadducts.[19] The triplet−triplet spectrum of the [5,6] isomer has a peak at 740 nm, substantially to the red of the [6,6]-closed adduct but only ca. 5 nm shifted from the 745-nm maximum of pristine C_{60}. Comparison among the triplet−triplet spectral data again suggests that the π-electron system of C_{60} is much less perturbed by formation of the [5,6]-open CH_2 adduct than the [6, 6]-closed isomer.

Triplet Decays. To find the intrinsic (unimolecular) decay constants for the T_1 states of [5,6]- and [6,6]-$C_{61}H_2$, we prepared

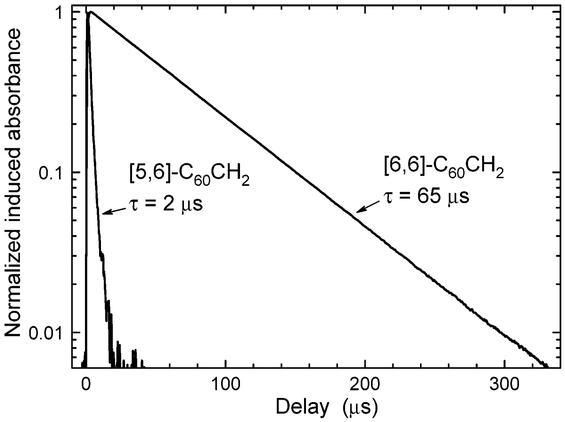

Figure 6. Normalized induced absorbance kinetics for both isomers of $C_{61}H_2$ in toluene at 297 K following 532-nm excitation.

dilute sample solutions in toluene and measured the time-dependent induced absorbance near 700 nm following mild excitation with 532-nm light pulses. The results are plotted in semilogarithmic form in Figure 6. As can be seen from the highly linear data for [6,6]-$C_{61}H_2$, the measured decay was accurately first order, with an exponential decay time of 65 μs. A comparable experiment on [6,6]-$C_{61}H_2$ dissolved in a thin PMMA film gave a very similar triplet lifetime of 64 μs. Although this value is substantially shorter than the 142-μs lifetime of pristine C_{60} under the same conditions, it is typical of intrinsic triplet lifetimes measured for C_{60} monoadducts.[20]

In sharp contrast, we find the triplet lifetime of [5,6]-$C_{61}H_2$ to be anomalously short. Although our sample of the [5,6] isomer was chromatographically pure before and after optical measurements, the observed triplet decay was not accurately first order. The data, plotted in Figure 6, could be fit using models either for sequential or biexponential decay. Using the latter, the main (0.95 amplitude) component had a 2-μs lifetime, and the minor (0.05 amplitude) component had a 15-μs lifetime. We conclude that [5,6]-$C_{61}H_2$ has a T_1 decay mechanism that is different from and much more efficient than that of the [6,6] isomer and other conventional C_{60} monoadducts.

Fullerene triplet states are often subject to significant self-quenching: triplet deactivation through encounters with ground-state molecules of the same type. This bimolecular but pseudo-first-order decay channel can interfere with attempts to measure intrinsic triplet lifetimes by artificially shortening observed lifetimes in experiments that are not designed to account for the effect.[20] To find the rate constant for triplet state self-quenching in [6,6]-$C_{61}H_2$, we measured T_1 transient absorption decay kinetics for well-degassed samples spanning a concentration range from 1.4 to 84 μM in room-temperature toluene solution. The resulting first-order decay constants are plotted in Figure 7a as a function of ground-state concentration. The data fit reasonably well to a linear relation with a slope, equal to the self-quenching constant, of $3.4 \pm 0.2 \times 10^7$ M^{-1} s^{-1}. This value is approximately twice that found earlier for the self-quenching constant of C_{60} under comparable conditions,[21] but it is far lower than the value of 1.2×10^9 M^{-1} s^{-1} reported earlier for [6,6]-$C_{61}H_2$ by Komamine et al.[10] We were unable to perform self-quenching studies on the [5,6]-open isomer because of its rapid intrinsic decay.

The temperature variation of intrinsic triplet decay can sometimes provide insights into nonradiative decay mechanisms. We therefore measured the triplet lifetime of [6,6]-$C_{61}H_2$ at temperatures between 77 and 320 K in a PMMA film, a medium rigid enough to suppress bimolecular decay processes. Figure 7b shows our kinetic results. The main finding here is a remarkably mild variation with temperature: intrinsic triplet decay is faster at 300 K than at 77 K, but only by a factor of 1.36. Arrhenius analysis indicates activation energies no larger than ca. 100 cm^{-1}, thus giving no evidence within this temperature range of strong vibrational induction of the $T_1 \rightarrow S_0$ nonradiative decay. By contrast, the T_1 decay of [6,6]-closed $C_{60}O$ (an isoelectronic compound) was previously found to show significantly stronger temperature variations over the same range.[22] In the case of the [5,6]-open isomer of $C_{61}H_2$, a chemical incompatibility of the sample with the film material prevented us from making cryogenic measurements. However, we found no evidence for thermal activation of [5,6]-$C_{61}H_2$ triplet decay between 288 and 342 K in dilute toluene solution.

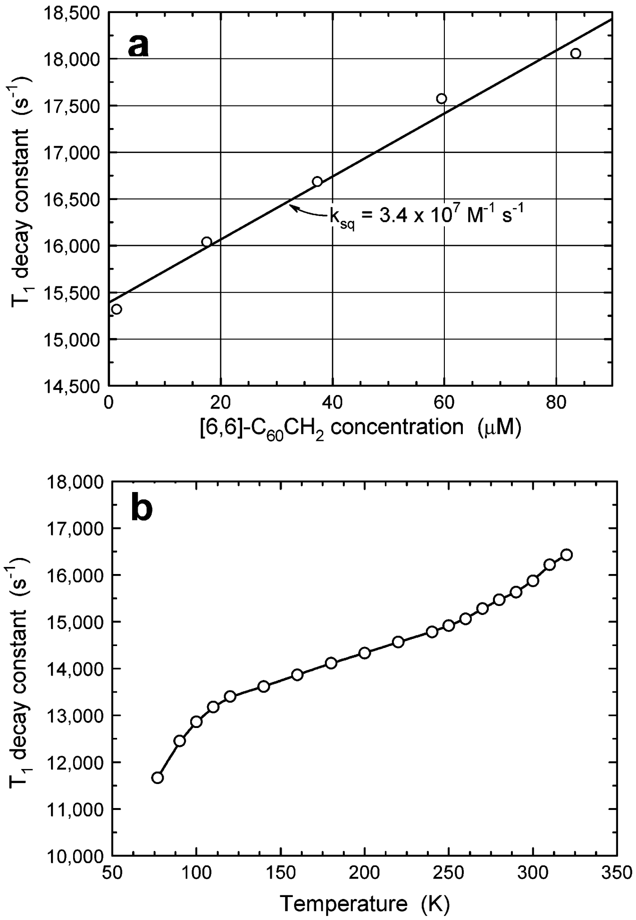

Figure 7. (a) First-order triplet decay constants for [6,6]-$C_{61}H_2$ in toluene at 297 K vs ground-state sample concentration. The points show measured data, and the solid line is a linear best fit. (b) First-order triplet decay constants for [6,6]-$C_{61}H_2$ in a PMMA film vs sample temperature.

Triplet-Formation Quantum Yield. To measure the triplet quantum yield of [6,6]-$C_{61}H_2$, we used a recently developed self-calibrating method based on fluorescence intensity analysis.[23] In this method, one assesses the relative populations of the singlet and triplet excited states from the intensity ratio of prompt fluorescence to delayed fluorescence arising from triplet−triplet annihilation. We found a triplet-formation quantum yield of 0.93 in room-temperature toluene solution. Similarly high yields have been reported for triplet formation in other [6,6] monoadducts.[24,25] Because the triplet state of the $C_{61}H_2$ [5,6]-open isomer has a very short lifetime, we used a different method for measuring its formation yield. We compared the [5,6]-$C_{61}H_2$ triplet−triplet absorption signals from one sample containing only [5,6]-$C_{61}H_2$ with another in which Pd-

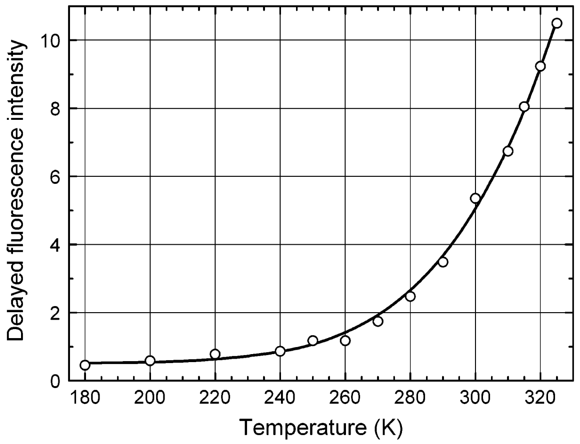

Figure 8. Intensity of delayed fluorescence (in arbitrary units) from [6,6]-$C_{61}H_2$ in a PMMA film vs sample temperature. The points show measured data, and the solid curve is a best fit computed using the function described in the text.

octaethylporphyrin had been added as a triplet sensitizer. Using sample conditions in which complete energy transfer to the fullerene was expected, we deduced a triplet-formation quantum yield of 0.06 for [5,6]-$C_{61}H_2$.

The unusually low quantum yields of triplet formation and fluorescence in [5,6]-$C_{61}H_2$ both indicate the presence of a rapid competing S_1 decay channel that is not evident in most other C_{60} adducts. Comparing our S_1 lifetime estimate of 60 ps (from fluorescence yield data) to the typical value of 1.4 ns, one deduces a rate constant for this new channel of ca. 1.6×10^{10} s^{-1}. Alternatively, one can divide a presumed rate constant for $S_1 \rightarrow T_1$ intersystem crossing, 7×10^8 s^{-1}, by the 0.06 triplet-formation yield to estimate the constant for the competing S_1 decay channel. This gives 1.2×10^{10} s^{-1}, in general agreement with the first estimate. Because no permanent photochemistry was observed in [5,6]-$C_{61}H_2$, we presume the rapid decay channel to be $S_1 \rightarrow S_0$ internal conversion. The [5,6] isomer also shows unusually rapid decay from its T_1 state. Quantum chemical explorations of the excited potential surfaces of this adduct may help to identify the structural distortions or mechanisms that accelerate its nonradiative decays.

Triplet-State Energies. A less common but very useful method for deducing excited-state energies involves monitoring thermally activated delayed fluorescence (TADF) as a function of temperature. This emission arises when optically excited sample molecules that have relaxed to the T_1 state become thermally promoted to S_1 and then emit $S_1 \rightarrow S_0$ fluorescence. As shown in earlier reports,[26−30] the intensity of this emission is proportional to a Boltzmann factor in ΔE_{ST}, the thermodynamic (nonvertical) energy gap between S_1 and T_1 states:

$$I_{\mathrm{fl}}^{\mathrm{delayed}} = C \exp\left(\frac{-\Delta E_{\mathrm{ST}}}{k_{\mathrm{B}}T}\right) \qquad (1)$$

This relation is especially reliable when the delayed fluorescence emission is time-resolved and measured before there is any significant decay of the triplet-state population.[30] The TADF method is suitable for samples that have a high quantum yield for triplet-state formation, a reasonably long-lived triplet state, and a relatively small value of ΔE_{ST}.

We performed time-resolved TADF experiments on [6,6]-$C_{61}H_2$ dissolved in a PMMA film. Data points in Figure 8 show the measured intensity of initial delayed fluorescence as a function of sample temperature. These data are well fit using eq 1 (with a small added constant term) and a ΔE_{ST} value of 2215 ± 90 cm^{-1}, giving the solid curve shown in the Figure. By combining this value with the spectroscopically determined S_1 origin energy, we deduce that the T_1 state of [6,6]-$C_{61}H_2$ lies 12 040 ± 100 cm^{-1} above S_0.

The TADF method was not feasible for [5,6]-$C_{61}H_2$ because of its triplet state's low formation yield and short lifetime. However, we were able to estimate the T_1 energy by measuring transient absorption kinetics in a mixed solution containing [5,6]-$C_{61}H_2$ and a reference compound (tetraphenylporphyrin). Because this reference compound has a reasonably long intrinsic triplet lifetime and a (known) triplet energy near that of the methanofullerenes, the triplet kinetics revealed the pooling and decay of triplet energy in the mixed sample.[21] Analysis indicated a free-energy difference of 265 cm^{-1} between the two triplet species, letting us deduce a T_1 energy for [5,6]-$C_{61}H_2$ near 11 970 cm^{-1}, which is within ca. 100 cm^{-1} of that found for the [6,6]-open isomer. This result contrasts with a prior study of unmatched methano adducts in which the T_1 state was reported to lie 400 cm^{-1} higher in the [5,6]-open species than in the [6,6]-closed adduct.[11]

Comparison with $C_{60}O$. It is of interest to compare the photophysical properties found for $C_{61}H_2$ with those of the isoelectronic adduct $C_{60}O$, which has also been studied in its [6,6]-closed (epoxide) and [5,6]-open (oxidoannulene) isomeric forms.[22,31] In ground-state absorption spectra, both [5,6] adducts show near-UV peaks that are 8 or 9 nm red-shifted from those of the corresponding [6,6] isomers and within 4 nm of the peak of pristine C_{60}. This spectral similarity between C_{60} and the [5,6] adducts also extends to their visible bands. In the triplet−triplet absorption spectra, we find peaks at 715 nm for [6,6]-$C_{61}H_2$ and 710 nm for [6,6]-$C_{60}O$, whereas the corresponding [5,6] isomer peaks appear at 740 and 730 nm, significantly closer to the 745-nm peak of pristine C_{60}. Both ground and triplet−triplet absorption spectra therefore suggest a pattern of greater π-electronic perturbation in these [6,6]-closed adducts than in the [5,6]-open isomers. Triplet-state intrinsic decay kinetics, however, differ markedly between $C_{61}H_2$ and $C_{60}O$. For $C_{61}H_2$, it is the [5,6]-open isomer that shows anomalously rapid (2 μs) triplet decay. However, for $C_{60}O$ the [5,6]-open isomer has a relatively normal triplet lifetime of 31 μs,and that of the [6,6]-closed isomer is shortened to ca. 4 μs.[22,31] It was proposed earlier that the rapid triplet decay of [6,6]-closed $C_{60}O$ involves the reversible cleavage of one C−O bond. The present results suggest that major structural distortions may also be important features of the S_1 and T_1 excited states of [5,6]-open $C_{61}H_2$. It is hoped that quantum chemical computational methods may be able to explore this possibility.

TABLE 1: Photophysical Property Comparison for the [5,6]-Open and [6,6]-Closed Isomers of $C_{61}H_2$

compound	$\lambda_{\max}$ (S_0)[a] (nm)	$\lambda_{\max}$ (T_1) (nm)	ϕ_T	ϕ_{fl}	τ_T[b] (μs)	k_{sq}[c] (M^{-1} s^{-1})	E (S_1) (cm^{-1})	E (T_1) (cm^{-1})	ΔE_{ST} (cm^{-1})
[6,6]-$C_{61}H_2$	331	715	0.93	7.8×10^{-4}	65	3.4×10^7	14 260	12 040	2220
[5,6]-$C_{61}H_2$	340	740	0.06	$<2 \times 10^{-5}$	2		15 070	11 970	3100

[a] For the near-UV absorption band in toluene solution. [b] Intrinsic exponential lifetime for unimolecular T_1 decay. [c] Bimolecular rate constant for triplet state self-quenching in 297 K toluene solution.

Conclusions

We have performed a variety of photophysical measurements on [5,6]-open and [6,6]-closed $C_{61}H_2$ to uncover systematic differences in electronic properties between isomeric forms of this prototypical fullerene monoadduct. Table 1 summarizes some of our quantitative findings. We find that the energy gap between S_1 and T_1 states is smaller in [6,6]-$C_{61}H_2$ than in the [5,6] isomer, with the 2700-cm^{-1} value for pristine C_{60} falling in between. Although ground-state and triplet−triplet absorption spectra show the [5,6]-open isomer to resemble pristine C_{60} in its π-electron structure, its has anomalously low quantum yields of triplet formation and fluorescence. These reveal the presence of a rapid $S_1 \rightarrow S_0$ nonradiative decay channel for [5,6]-$C_{61}H_2$. In addition, the lowest triplet state of [5,6]-$C_{61}H_2$ shows the fastest intrinsic decay found to date for a C_{60} adduct, suggesting an unusually efficient deactivation pathway. Although the mechanisms for these processes are not yet clear, our findings clearly demonstrate the presence of strong photophysical differences between isomers of simple fullerene adducts.

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