*J. Am. Chem. Soc.* **1994,** *116,* 9763–9764

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Photophysical Characterization and Singlet Oxygen Yield of a Dihydrofullerene

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Many C_{60} adducts, ("dihydrofullerenes") have been described.[1-12] We wished to study how the photophysical properties of the fullerene core are perturbed by functionalization,[13] since the enhanced solubility in polar solvents of these derivatives suggests potential uses in biological systems where such properties such as singlet oxygen generation can be exploited. We now report the photophysical properties of a model dihydrofullerene, the C_{60} adduct 1,9-(4-hydroxycyclohexano)buckminsterfullerene[1] (**1**), summarized in Table 1.
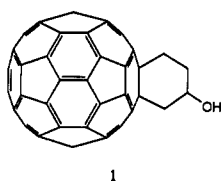
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Unlike C_{60}, which has its longest wavelength absorption at 620 nm,[18] the dihydrofullerenes have a weak absorption maximum in benzene at 708 nm ($\epsilon \approx 400$ M^{-1} cm^{-1}).[1] Although weak, this absorption could be important for photobiological activity, since near-IR light penetrates tissue more efficiently than shorter wavelength light. Compound **1** gives very weak fluorescence emission ($\lambda_{max} = 715$ nm) with a quantum yield of <0.001; the excitation spectrum is similar to the absorption spectrum.[1] Using the intersection of the absorption and emission maxima, the singlet energy is estimated to be 40.2 kcal/mol, almost 6 kcal/mol lower

Table 1. Photophysical Properties of Dihydrofullerene (**1**) and C_{60}

property	dihydrofullerene (**1**)	$C_{60}{}^a$
E_S	40.2 kcal/mol	46.1 kcal/mol
E_T	33.5 ± 0.6 kcal/mol^b	36.3 kcal/mol^i
ϵ_T (λ_{max})	(4.2 ± 0.2) × 10^3 M^{-1} cm^{-1} (700 nm)^c	2.0 × 10^4 M^{-1} cm^{-1} (750 nm)^i
τ_T	23 ± 4 μs^d	40 μs
$k_q(O_2)$	(1.8 ± 0.2) × 10^9 M^{-1} s^{-1}	2 × 10^9 M^{-1} s^{-1}
Φ_{fl}	(6 ± 4) × 10^{-4} ^{e}	10^{-5}–10^{-4} ^{i}
Φ_Δ (355 nm)	0.72 ± 0.05^f	0.76
Φ_Δ (532 nm)	0.84 ± 0.05^g	0.96
$k_q({}^1O_2)$	(9.7 ± 0.5) × 10^5 M^{-1} s^{-1} ^{h}	(5 ± 2) × 10^5 M^{-1} s^{-1}

^{a} Adapted from ref 14, unless otherwise noted. ^{b} Average of triplet energies of TPP, a lower limit, and E_T(TPP) + E_a, an upper limit (see discussion); energy transfer measurements done in C_6H_6 or THF. ^{c} At 700 nm, assuming $\Phi_T(1) = 1$. ^{d} In argon-saturated solutions, [**1**] ≈ 5 × 10^{-5} M. ^{e} In benzene, using TPP ($\Phi_\Delta = 0.11$)[14] as standard. ^{f} Average of eight determinations in air-saturated C_6D_6, using C_{60} ($\Phi_\Delta = 0.76$)[15] and acridine ($\Phi_\Delta = 0.84$)[16] as standards. ^{g} Average of eight determinations in air-saturated C_6D_6, using C_{60} ($\Phi_\Delta = 0.96$)[15] and TPP ($\Phi_\Delta = 0.55$)[17] as standards. ^{h} Combined physical and chemical quenching of $^1O_2$ by **1** in air-saturated C_6D_6 with C_{70} ($\lambda_{ex} = 532$ nm) as sensitizer. ^{i} See discussion in ref 34.

than that for C_{60}. Phosphorescence was not observed, despite the high triplet yields discussed below.

Compound **1** produces singlet oxygen efficiently, with a quantum yield (Φ_Δ) in benzene-d_6 of 0.72 ± 0.05 (355 nm) and 0.86 ± 0.05 (532 nm), 5–10% lower than those for C_{60}.[19] The wavelength dependence of the quantum yield resembles that of C_{60};[15] the yields are lower limits for triplet production, Φ_T. Singlet oxygen is quenched by **1** with a rate constant of (9.7 ± 0.5) × 10^5 M^{-1} s^{-1}, almost twice that of C_{60}.

The triplet–triplet absorption spectrum is remarkably similar to that of C_{60} (Figure 1) with maxima near 400 and 700 nm. The differential extinction coefficient at 700 nm ($\epsilon_T - \epsilon_0$) is (3.8 ± 0.2) × 10^3 M^{-1} cm^{-1}, estimated by the relative actinometry method,[20] which compares the optical density of a standard (triplet benzophenone (BP)) with that of triplet **1** in solutions optically matched at the excitation wavelength (355 nm), according to eq 1, where OD$_T$ is the triplet optical density at 700 nm for **1** and

$$(\epsilon_T - \epsilon_0) = \frac{OD_T \epsilon_T{}^{BP}(1 - 10^{-OD^{BP}})\phi_T{}^{BP}}{OD_T{}^{BP}(1 - 10^{-OD})\phi_T} \tag{1}$$

532 nm for BP; OD is the ground state optical density of each solution at the excitation wavelength; $\epsilon_T{}^{BP}$ is the triplet extinction coefficient of benzophenone at 532 nm (7630 M^{-1} cm^{-1});[21] and ϕ_T is the triplet quantum yield, 1.0 for benzophenone.[22] This extinction coefficient is a lower limit: since ϕ_T must be $\geq \Phi_\Delta$, it cannot be less than 85%; given the low fluorescence quantum yield, it could well be unity.[23] When the ground state extinction coefficient at 700 nm (ϵ_0) is added, the triplet extinction coefficient is found to be (4.2 ± 0.2) × 10^3 M^{-1} cm^{-1}. The ground state and triplet extinction coefficients found for **1** are considerably lower than those for C_{60}.[24] The triplet lifetime in Ar-purged 5 × 10^{-5} M solutions of **1** at low laser power is 23 ± 4 μs. This value may be limited by T–T annihilation or T–S$_0$ quenching, which were

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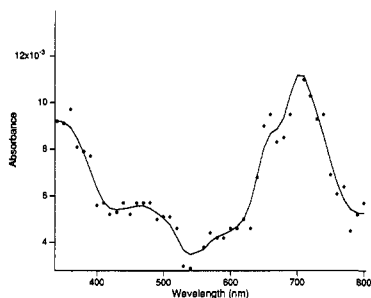
9764 *J. Am. Chem. Soc., Vol. 116, No. 21, 1994*

Communications to the Editor

Figure 1. Triplet–triplet absorption spectrum of **1** in toluene (3.0×10^{-5} M), obtained by 355 nm excitation (5.0 mJ/pulse).
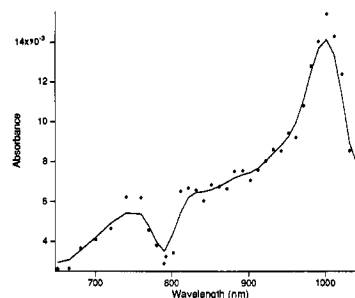

Figure 2. Transient absorption spectrum of the radical anion of **1**, obtained by 430 nm irradiation (5.0 mJ/pulse) of argon-saturated solutions of **1** (2×10^{-4} M) and DMA (0.012 M) in benzonitrile.

not investigated. The triplet was efficiently quenched by oxygen with a rate constant, $k_q(O_2)$, of $(1.8 \pm 0.2) \times 10^9$ M^{-1} s^{-1}, similar to the value observed for C$_{60}$.[15]

The triplet energy of **1** was estimated by triplet–triplet energy transfer. Addition of **1** efficiently quenches the triplets of acridine (E_T = 45.3 kcal/mol)[25] and hypericin (E_T = 37.7 kcal/mol)[26] with rate constants of $(3.5 \pm 0.2) \times 10^9$ M^{-1} s^{-1} and $(3.8 \pm 0.3) \times 10^9$ M^{-1} s^{-1}, respectively. The quenching rate constant of tetraphenylporphine (TPP) triplet (E_T = 33.0 kcal/mol)[17] by **1** was $(1.5 \pm 0.1) \times 10^8$ M^{-1} s^{-1}, suggesting that energy transfer is nearly isothermal. The activation energy for this energy transfer, estimated by plotting ln k_q vs $1/T$, is 1.1 kcal/mol. Energy transfer from triplet **1** to β-carotene (E_T = 20.3 kcal/mol),[27] zinc phthalocyanine (E_T = 26.1 kcal/mol),[28] and tetracene (E_T = 29.3 kcal/mol)[29] was very fast, with quenching rate constants of $(4.5 \pm 0.3) \times 10^9$, $(4.9 \pm 0.4) \times 10^9$, and $(5.6 \pm 0.4) \times 10^9$ M^{-1} s^{-1}, respectively, indicating substantial exothermicity. Energy transfer was confirmed in each case by observation of the triplet–triplet absorption of the triplet acceptor.

The triplet energy of **1** must therefore be near or slightly above that of TPP. Since k_q for energy transfer from triplet TPP to C$_{60}$ is $(3.5 \pm 0.3) \times 10^7$ M^{-1} s^{-1},[15] an order of magnitude slower than that with **1**, we conclude that the triplet energy level of **1** must be lower than that of C$_{60}$ (E_T = 36.3 kcal/mol).[30] A reasonable estimate, considering the upper limit defined by the E_a, is 33–34 kcal/mol. Application of the Sandros equation,[31] which requires a comparison of several endothermic energy transfer rates,[32] would give a better estimate of the triplet energy and is currently being explored.[33] The S_1–T_0 splitting of **1** is therefore $\approx$6 kcal/mol, smaller than the ~10 kcal/mol splitting observed with C$_{60}$.[34]

As with C$_{60}$,[35] aromatic amine donors reduce triplet **1** in benzonitrile. *N,N*-Dimethylaniline (DMA) quenched triplet **1** with a rate constant of $(2.5 \pm 0.5) \times 10^8$ M^{-1} s^{-1}, an order of magnitude slower than that for triplet C$_{60}$.[35] The electron transfer mechanism was confirmed by observation of the amine radical cation at 450 nm.[36] The radical anion of **1** has absorption in the

near-IR region, with maxima at 740 and 1000 nm (Figure 2), similar to that of C$_{60}$. The lower energy of triplet dihydrofullerene (~0.1 V below C$_{60}$) as well as its smaller ground state reduction potential (–1.09 V for **1**, –0.85 V for C$_{60}$ vs ferrocene/ferrocenium in THF)[37] results in a triplet reduction potential for **1** near 0.38 V vs ferrocene/ferrocenium in benzonitrile.[38] This is approximately 0.3 V smaller than that for ^{3}C$_{60}$ and explains the decreased electron transfer rate between DMA ($E_{1/2}$ ~ 0.25 V vs ferrocene/ferrocenium in benzonitrile)[39] and triplet **1**.

Significant absorption spectral changes of **1** (loss of structure at 710 and 450 nm and across the visible region) were observed during both energy transfer and electron transfer triplet quenching studies. The most significant changes occurred with electron-rich triplet quenchers, such as anthracene, tetracene, and rubrene, which could undergo a [4 + 2] cycloaddition with **1**; this reaction has been observed frequently with dienes or polycyclic aromatics,[4,40–43] but photochemical addition has not been discussed. *N,N*-Dimethylaniline also reacts with **1**, as shown by absorption changes similar to those described above.

Conclusions. Dihydrofullerene **1** undergoes photoprocesses very similar to those of C$_{60}$;[15,35] however, there are slightly lower singlet and triplet energies, triplet–triplet extinction coefficients, singlet oxygen quantum yields, and triplet reduction potentials. Other carbon-substituted dihydrofullerenes have properties similar to those of **1**, including efficient singlet oxygen generation, near-IR absorption, and reduction potentials.[3,10,44,45] The solubility in polar solvents and the photophysical properties of some of these dihydrofullerenes make them good candidates for photodynamic agents[46–48] in cancer or viral therapy.

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