

Photoinduced Intramolecular Electron Transfer in a Bridged C₆₀ (Acceptor)–Aniline (Donor) System. Photophysical Properties of the First “Active” Fullerene Diad

René M. Williams,* Jurriaan M. Zwier, and Jan W. Verhoeven*

Contribution from the Laboratory of Organic Chemistry, University of Amsterdam, Nieuwe Achtergracht 129, 1018 WS Amsterdam, The Netherlands

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Abstract: A covalently functionalized fullerene comprising an electron donating aniline group coupled to the fullerene unit by a saturated heterocyclic bridge is shown to undergo a photoinduced intramolecular electron transfer process that causes quenching of the fluorescence of the adduct and strong decrease of triplet population in polar solvents. VIS-absorption, fluorescence and phosphorescence at 77 K, triplet–triplet absorption, time resolved fluorescence, and redox potentials of the fullerene adduct are presented. Analysis of the solvent dependence of the energetics of the intramolecular electron transfer is given and is in good agreement with the experimental results.

Introduction

The photophysical properties¹ of C₆₀ and C₇₀ and intermolecular electron transfer interactions² in solution of these remarkable molecules have been the topic of many recent investigations. Relevant photophysical properties are summarized in Table 1.

Besides a triplet yield near unity and a very low fluorescence quantum yield, it has also been shown that, in contrast to some of the earliest reports on their photophysics,^{1g,2d} both fullerenes

Table 1. Selected Photophysical Properties of C₆₀ and C₇₀

	Φ_f^a	τ_{s1} (ps) ^b	$^1E_{00}^c$ (eV)	Φ_T^d	τ_{T1}^e	$^3E_{00}^f$ (eV)
C ₆₀	2×10^{-4}	1245 ± 120	1.99	≈ 1	325 ± 20 ns to 0.4 ms	1.57
C ₇₀	5×10^{-4}	630 ± 75	1.91	≈ 1	790 ± 20 ns to 50 ms	1.56

^a Our results regarding fluorescence quantum yields for C₇₀^{2f} and C₆₀ are in excellent agreement with those of Sun et al.^{1o,q} Other values have been reported.^{1g,p,2d} ^b Average value of the consistent data for the singlet excited state lifetime (τ_{s1}) for C₆₀ reported in refs 1d,k–m,s,t; for C₇₀ reported in refs 1h,k–m,s,t,2f. ^c The singlet state energy ($^1E_{00}$) of C₆₀^{1a,b,i,p} and C₇₀^{1a,b,p} Palewska et al.^{1r} reported 1.84 eV for C₆₀. ^d Triplet yields are reported in refs 1b–h, 2e. ^e Triplet state lifetimes (τ_{T1}) in nondegassed benzene^{1b,s,l} and in oxygen free matrices^{1c} have been reported. ^f Taken from ref 1j.

display excitation wavelength independent photophysical properties and thus obey Kasha's rule.^{1n–r,2f}

Intermolecular electron transfer quenching of the S₁ state of C₆₀ and C₇₀ in nonpolar media can be accomplished by donor molecules with an oxidation potential lower than 1.12 V (vs SCE in acetonitrile) like 1,2,4-trimethoxybenzene^{2b,f} or hexamethylbenzene.^{2a} Stronger donors like *N,N*-dimethylaniline or *N,N,N',N'*-tetramethyl-*p*-phenylenediamine also quench the T₁ state of these fullerenes.^{2c,e,g,i}

A representative first midpoint reduction potential of fullerene C₆₀ and C₇₀ is –0.4 V (vs SCE).³

From their electron acceptor properties it has been envisaged that functionalization of fullerenes with electron donating moieties can lead to the development of advanced materials with new optical and optomagnetic properties.⁴

Studies on photoinduced intramolecular electron transfer in various D(onor)–bridge–A(acceptor) systems⁵ in which a saturated hydrocarbon bridge covalently links D and A at a well defined distance have shown that photoinduced intramolecular

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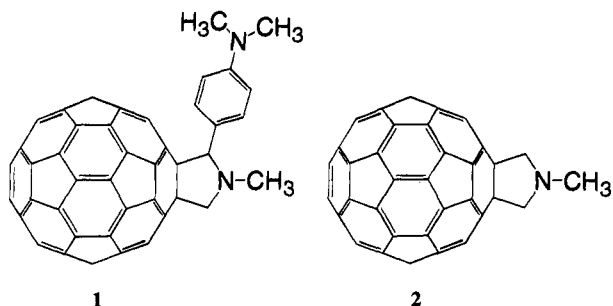


Figure 1. The compounds 1 and 2 used in this study.

charge separation can be feasible even when D and A are spaced up to 15 Å apart. Through bond interaction via the bridge contributes to the electronic coupling between donor and acceptor that is required for electron transfer.^{5,6} However, although the synthesis of several systems of the donor–bridge–fullerene (acceptor) type has been described,^{4b–d,5e} no photo-induced intramolecular electron transfer in these covalently functionalized fullerenes has been found until now.

Here we report on the synthesis, characterization, and solvent dependence of the photophysical properties of a new donor–bridge–buckyball compound (1, see Figure 1), that indeed displays photoinduced intramolecular charge separation.

Experimental Section

Syntheses. The bridged fullerene(acceptor)–aniline(donor) system 1 (see Figure 1) was obtained by a 1,3 dipolar addition to C₆₀ (MER corporation) of the decarboxylated iminium ion formed from 4-(*N,N*-dimethylamino)benzaldehyde and *N*-methylglycine following a procedure slightly modified from that described by Maggini et al.⁷

¹H NMR (400 MHz Bruker ARX 400, CS₂, C₆D₆ (3:1), 308 K) δ (ppm) = 2.63, 3H, s, NCH₃; 2.71, 6H, s, N(CH₃)₂; 4.04, 1H, d, CH (exo), *J* = 9.24 Hz; 4.71, 1H, s, CH; 4.74, 1H, d, CH (endo), *J* = 9.24 Hz; 6.55, 2H, d, CH (arom), *J* = 8.91 Hz; 7.51, 2H, d (br), CH (arom), *J* = 7.43 Hz; ¹³C NMR (400 MHz, CS₂, C₆D₆ (3:1), 300 K, APT) δ (ppm) = 40.75, NCH₃; 40.79, N(CH₃)₂; 69.90, C sp³ C₆₀; 70.85, CH₂; 78.74 (C sp³ C₆₀), 84.39, CH; 113.35, CH (arom); 125.05, C_q (arom); 131.08, CH (arom); 136.73, 136.86, 137.72, 137.75, 140.71, 141.01, 141.12, 141.20, 142.57, 142.68, 142.87, 143.02, 143.03, 143.05, 143.12, 143.16, 143.18, 143.30, 143.34, 143.56, 143.58, 143.61, 143.69, 144.03, 144.17, 145.40, 145.44, 145.71, 146.21, 146.22, 146.24, 146.27, 146.39, 146.48, 146.49, 146.55, 146.61, 146.81, 146.91, 147.08, 147.12, 147.15, 147.22, 147.22, 147.32, 147.58, 147.72, 147.99, 148.23, 148.28, 151.06, 155.07, 155.14, 155.18, 157.64, C_q C₆₀ and C_qN (arom); IR (KBr, Perkin-Elmer 1310) ν (cm⁻¹) = 2940 (w), 2905 (w), 2830 (w), 2760 (m), 1605 (s), 1515 (s), 1458 (m), 1438 (m), 1422 (m), 1352 (m), 1328 (m), 1180 (s), 815 (m); Mass spectra were obtained with a JEOL SX/SX 102A mass spectrometer using field desorption, positive ion: calcd for 1, C₇₁H₁₆N₂ 896.13134, found 896.1 (and 720 and 176.1). Extinction coefficients of 1 in toluene (in M⁻¹ cm⁻¹) are 704 nm (320), 640 sh (377), 430 (3566), 327 (37370).

The acceptor model 2 (see Figure 1) was obtained with the procedure described in ref 7 and gave correct spectroscopic data.

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Photophysical and Electrochemical Measurements. Fluorescence and excitation spectra were recorded on a SPEX Fluorolog 2 instrument equipped with a red sensitive GaAs photomultiplier (RCA C31034, Peltier cooled) of which the spectral response extends to 900 nm and is known to be quite flat from the UV to about 860 nm.

Fluorescence spectra were measured on dilute solutions (10⁻⁵ M) using a 570 nm (emission-path) cutoff filter. Excitation and emission bandwidths of 4.5 nm were employed, and no corrections were applied to the fluorescence spectra. Long integration times (10 s) and low increments (0.2 nm) were used.

For determination of the fluorescence quantum yields C₆₀ in nondegassed methylcyclohexane ($\Phi_{fl} = 2 \times 10^{-4}$, see Table 1) was used as a standard. Excitation wavelength was 470 nm, and the absorbance of both the reference and the sample was adjusted to 0.1 (1 cm) at this wavelength.

Cryogenic measurements were performed with an Oxford Instruments liquid nitrogen DN 1740 cryostat, equipped with a ITC4 control unit. Samples were degassed with three freeze–pump–thaw cycles at ca. 10⁻⁵ mbar. Bandwidths of 28 (excitation) and 2.5 nm (emission) were used. Absorption spectra were recorded on a CARY 3 spectrophotometer, using 0.5 nm bandwidth.

Transient absorption spectra were obtained with a gated Optical Multichannel Analyzer of EG&G instruments described earlier.⁸ As excitation and white probe sources the third harmonic of a Nd-YAG laser (355 nm, nanosecond pulses) and a 450 W high pressure Xe arc (white light 300–880 nm) coupled to a Müller Elektronik MSP05 pulser were used, respectively. The excitation beam is at a right angle to the probing beam. The probing path length is 1 cm. Samples were adjusted to an absorption of 1.5 (1 cm) at the excitation wavelength. Laser-power was 10 mJ per pulse (0.2 cm²).

Fluorescence lifetimes were measured with time correlated single photon counting using a Hamamatsu microchannel plate (R 3809) detector in a setup slightly modified from that previously described,⁹ employing a frequency doubled DCM dye laser which is synchronously pumped with a mode locked Argon ion laser resulting in 317 nm 20 ps FWHM pulses. Decays were analyzed with a home written deconvolution program.

Cyclic voltammetry was performed with a Bank Electronic POS 73 Wenking Potentiostat, glassy carbon or Pt working electrodes, Pt gauze auxiliary electrode and a saturated calomel reference electrode with tetraethylammoniumtetrafluoroborate (0.1 M) in acetonitrile or acetonitrile/toluene mixtures as electrolyte.

Spectroscopy grade solvents were used in all determinations (dried with alumina for electrochemistry). Benzonitrile was distilled over P₂O₅ before use.

Results and Discussion

Figure 2 shows the fluorescence and the VIS absorption of 1 in methylcyclohexane.

A beautiful symmetry of vibrational progressions is observed, a very minor Stokes shift (51 cm⁻¹) and an ¹E₀₀ of 14 207 cm⁻¹ (704 nm, 1.76 eV). Absorption maxima are observed at (cm⁻¹) 14 225, 14 468, 14 671, 14 952, 15 175, 15 708, 18 416 (sh), 20 886 (sh), 23 256, and 24 765. Fluorescence maxima are observed at (cm⁻¹) 12 715, 13 504, 13 966, and 14 174. Furthermore a shoulder shows up at 14 440 cm⁻¹ (see Figure 2A) that probably is a “hot band” (it is absent in low temperature emission, see later), and a similar feature can be seen at 13 970 cm⁻¹ in the absorption spectrum.

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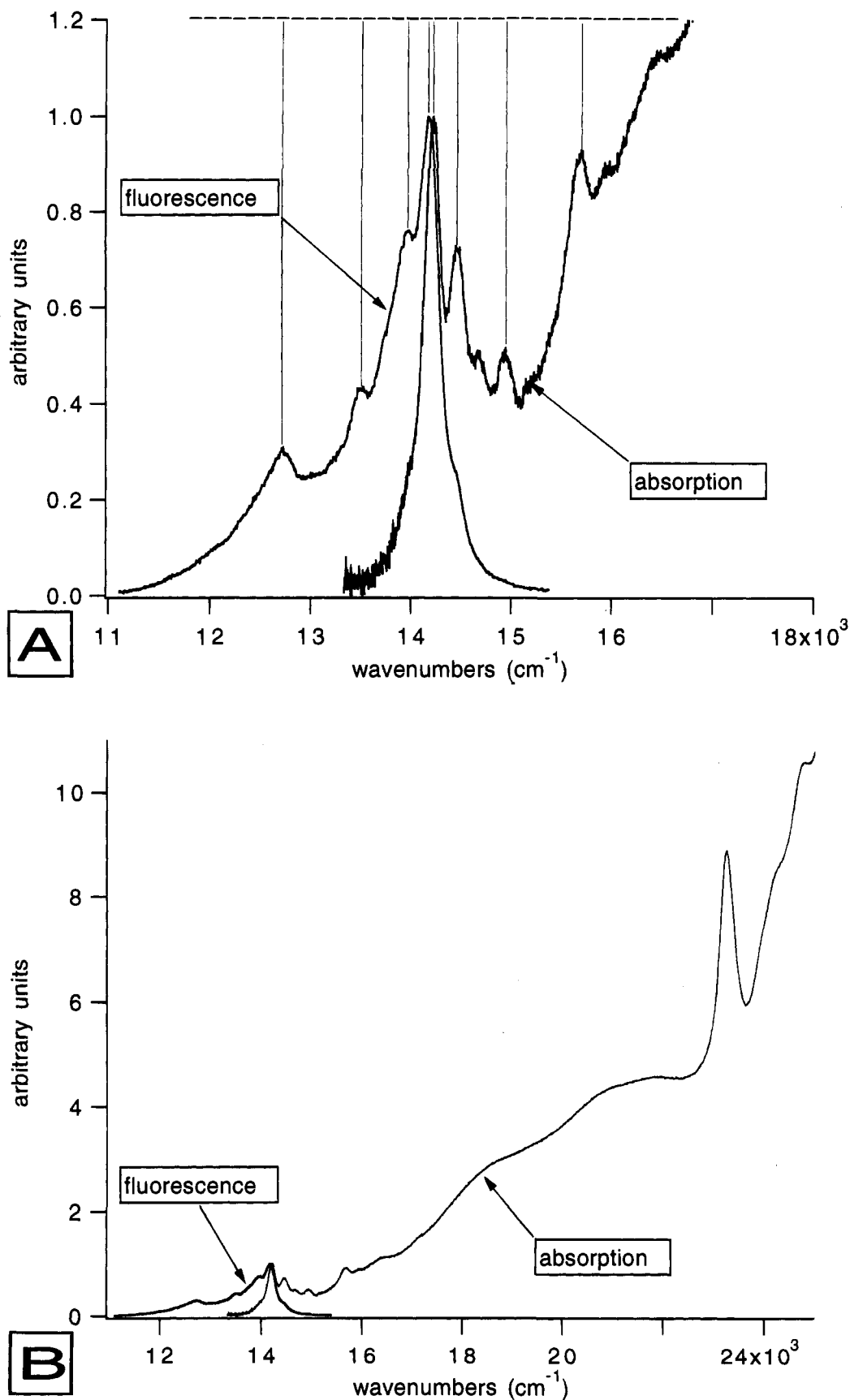


Figure 2. VIS-absorption and fluorescence of compound 1 in methycyclohexane at room temperature. The symmetry relation of the emission and absorption is emphasized by the lines in part A.

Vibrational spacings are in reasonable agreement with theoretical and experimental values for native C₆₀.¹¹ Fluorescence excitation spectra are in excellent agreement with the UV-vis absorption spectra, indicating "normal" photophysical behavior

(like C₆₀ and C₇₀, see refs 1n-r and 2f), and the absence of interfering impurities.

Fluorescence quantum yields of 1 in different solvents are given in Table 2. Interestingly the adduct shows a sharp

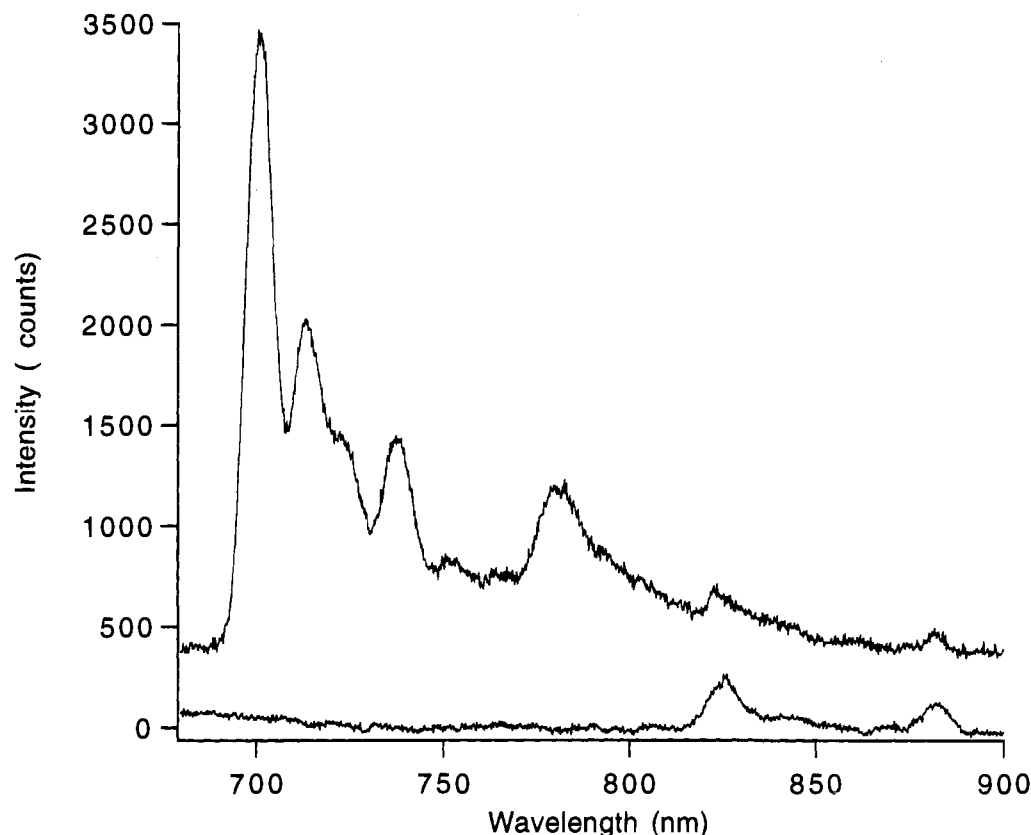


Figure 3. Emission spectra of compound **2** at 77 K, in methylcyclohexane (upper spectrum) and in a methylcyclohexane, methyltetrahydrofuran, ethyl iodide (2:1:1) mixture (lower spectrum). The upper spectrum is vertically shifted. Bandwidth is 2.5 nm.

Table 2. Fluorescence Quantum Yields (Absolute and Relative) and Relative Triplet Quantum Yields of Compound **1** in Various Solvents of Increasing Dielectric Constant^a

solvent	ϵ	Φ_f (relative)	Φ_T
methylcyclohexane	2.07	6×10^{-4} (100)	1
toluene	2.38	5×10^{-4} (83)	
chloroform	4.70	2.8×10^{-4} (46)	0.85*
dichloromethane	8.93	0.2×10^{-4} (3)	0.80*
1,2-dichlorobenzene	9.93	0.6×10^{-4} (10)	
benzonitrile	25.20	0.2×10^{-4} (3)	0.03
dichloromethane/TFA		6×10^{-4} (100)	

^a Fluorescence quantum yields in dichloromethane and benzonitrile are near detection limit. Triplet yields in chloroform and dichloromethane (denoted with an asterisk) are estimates due to sample decomposition under laser irradiation.

decrease of fluorescence intensity upon going to more polar solvents. A strong indication that the quenching process responsible for this involves the electron donating substituent dimethylaniline is the fact that addition of 10 μ L of trifluoroacetic acid (TFA) to a solution of **1** in dichloromethane (dcm) results in a sharp increase in the fluorescence intensity restoring it to the level in nonpolar solvents (fluorescence yield of 6×10^{-4} , see Table 2).

Protonation of the nitrogens results in a slight hypsochromic shift of both the emission (713 nm (in for example toluene) to 696 nm (dcm + TFA)) and absorption maxima (704 nm (dcm) to 686 nm (dcm + TFA)). These shifts and the increase in luminescence can be reversed by addition of a few drops of pyridine. The observation that compound **2** does show fluorescence in benzonitrile, dichloromethane, benzene, and methylcyclohexane with a quantum yield of ca. 6×10^{-4} indicates that the pyrrolidine "bridge" moiety is not involved in the quenching process in compound **1**.

Emission spectra of **2** at 77 K in methylcyclohexane and in a mixture of methylcyclohexane, methyltetrahydrofuran, and ethyl iodide (2:1:1) are shown in Figure 3. Whereas in the

former matrix fluorescence peaks are sharpened and two new emission maxima are observed at 825 and 880 nm, in the latter all fluorescence is absent, and only the maxima at 825 (1.50 eV) and 880 nm are observed. This is a clear indication that the external heavy atom effect caused by ethyl iodide induces enhanced spin-orbit coupling and only phosphorescence is observed in the mixed matrix.^{1j}

The triplet energy (${}^3E_{00}$) of **1** and **2** is thus determined to be 1.50 eV. Interestingly the singlet-triplet splitting of the C₆₀ adducts (i.e., $\Delta(S_1-T_1) = 0.26$ eV) is smaller than for "native" C₆₀ ($\Delta(S_1-T_1) = 0.42$ eV, see Table 1).

Representative triplet-triplet absorption spectra of **1** and of C₆₀ are depicted in Figure 4. Compared to C₆₀ the adduct shows a slightly broader transient absorption spectrum with the strongest absorption maximum at a little higher energy and a pronounced T₁-T_n absorption at 800 nm (shoulder) indicating a smaller T₁-T₂ energy gap for **1**. Interestingly the relative triplet yields of **1** also show a solvent dependence (see Table 2). Whereas the fluorescence of **1** is fully quenched in dichloromethane, the triplet is still populated for ca. 80% in this solvent. In benzonitrile however also the triplet is strongly quenched.

The solvent dependence of the fluorescence and triplet-triplet absorption of **1** indicates that in polar solvents an extra deactivation path of the excited states (S₁ or T₁) of **1** becomes available. As the population of a charge transfer state is energetically possible in polar solvents (according to the Weller equation, see below) we attribute this quenching path to an intramolecular electron transfer that deactivates the excited state.

We can so far not attribute any transient to the radical cation and anion of the charge separated state, due to the time resolution of our flash photolysis apparatus. This indicates that the charge separated state has a very short (subnanosecond) lifetime. Picosecond resolved transient absorption spectroscopy will be undertaken in the future.

In contrast to adduct **1**, the adduct **2** shows strong triplet-

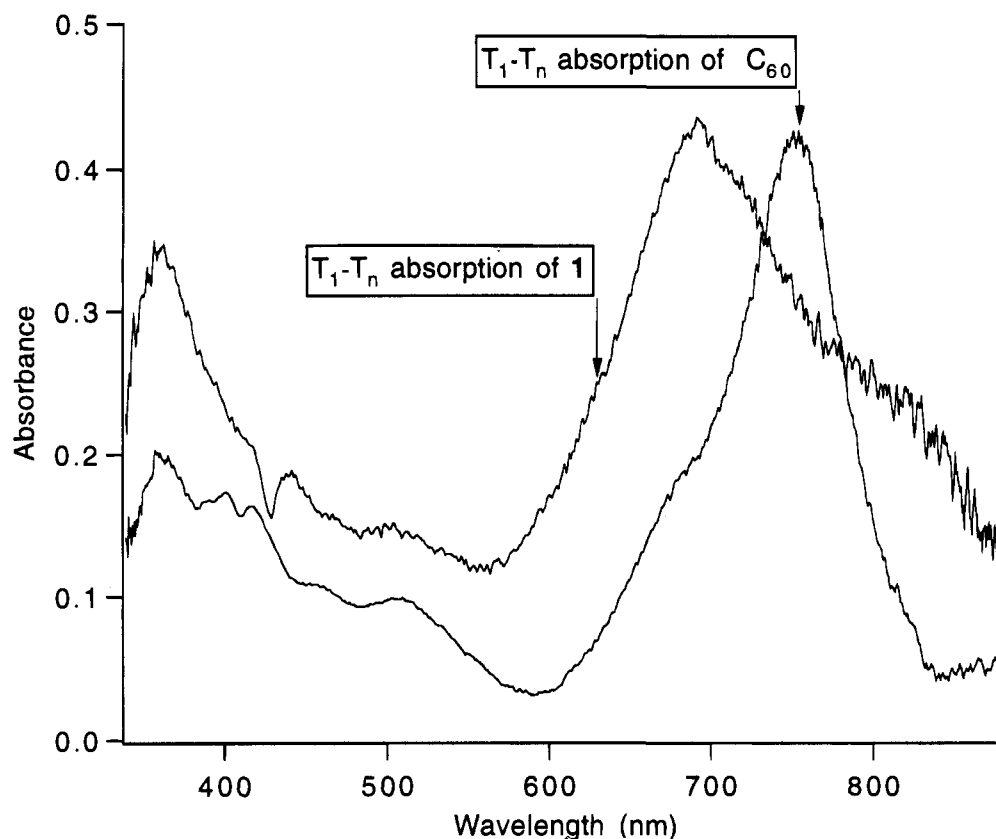


Figure 4. Comparison of scaled triplet-triplet absorption of compound 1 and C_{60} in methylcyclohexane.

triplet absorption ($\Phi_T \approx 1$) not only in low polarity but also in high polarity solvents (benzonitrile).

The extinction coefficient of the triplet-triplet absorption ($\epsilon^{(T_1-T_n)}$) of 1 at 692 nm is estimated to be $16\,700\text{ M}^{-1}\text{cm}^{-1}$, on the assumption that 1 has a triplet yield near unity in methylcyclohexane. This is obtained by comparison of 1 and C_{60} under identical experimental conditions and application of

$$(P_1/A_1(\lambda_{ex}))/\epsilon_1^{(T_1-T_n)} \cdot C_1 \cdot l = (P_2/A_2(\lambda_{ex}))/\epsilon_2^{(T_1-T_n)} \cdot C_2 \cdot l$$

P = peak intensity, A = absorbance, C = concentration, l = pathlength, subscript 1 refers to adduct 1, and subscript 2 refers to C_{60} . For C_{60} a $\epsilon^{(T_1-T_n)}$ of $14\,500\text{ M}^{-1}\text{cm}^{-1}$, at 750 nm was used.^{1d,m}

Fluorescence decays obtained with single photon counting in methylcyclohexane and benzonitrile are represented in Figure 5. Monoexponential deconvolution of the decay in the nonpolar methylcyclohexane (in which electron transfer quenching is not exergonic, see below) gives a fluorescence lifetime of 1280 ± 40 ps (i.e., comparable to native C_{60}). In the polar solvent benzonitrile, in which both luminescence and population of the triplet state are strongly quenched, the fluorescence decay is not monoexponential but displays three components: a long living component with a lifetime of 1750 ps and a very low amplitude (0.008) and two fast components of 481 ps and 78 ps with an equal amplitude of 0.032.^{10a} Single photon counting thus indicates that the quenching process in benzonitrile takes place with a rate between 1.3×10^9 and $1.2 \times 10^{10}\text{ s}^{-1}$ by applying one of the fast components as τ and the lifetime of 1 in methylcyclohexane as τ_{ref}

$$k_{et} = 1/\tau - 1/\tau_{ref}$$

The decay in benzonitrile is clearly not monoexponential, which can be attributed to the presence of more conforma-

tions^{10b-e} of the compound due to ring inversion of the pyrrolidine ring. However, multiexponential behavior seems to be a problem often encountered in the determination of the time resolved quenching of local fluorescence by intramolecular electron transfer.

Cyclic voltammetry of the adduct 1 in a toluene-acetonitrile mixture (3:1) using glassy carbon (0 to -2 V vs SCE,) shows three reduction waves at -0.76, -1.24, and -1.79 V and reoxidation waves at -1.30, -0.83, and -0.38 V vs SCE. The first midpoint reduction potential of the fullerene adduct is thus estimated to be ca. -0.57 V vs SCE, i.e., in good agreement with literature reports for other fullerene adducts.¹¹ A model of the donor (4-(dimethylamino)benzylamine from Aldrich) shows an irreversible oxidation wave of +0.74 V vs SCE in acetonitrile leading to an estimated midpoint potential +0.71 V vs SCE (i.e., comparable to *N,N*-dimethylparatoluidine¹²).

The structure of the adduct 1, obtained by minimization with semiempirical AM-1 calculations is shown in Figure 6. The aromatic ring of the donor is in an orthogonal relation to the

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(10) (a) Reasonable triexponential fits ($\chi^2 < 1.3$) of the decay in benzonitrile can also be obtained by keeping t_1 fixed at 1280 ps (a probable lifetime for an impurity, see ref 10 (d)). (b) Hoffman, B. M.; Ratner, M. A. *J. Am. Chem. Soc.* **1987**, *109*, 6237. (c) Harrison, R. J.; Pearce, B.; Beddard, G. S.; Cowan, J. A.; Sanders, J. K. M. *Chem. Phys.* **1987**, *116*, 429. (d) Other explanations are possible, such as the presence of impurities or decomposition of the solute. The substance may contain less than 1% monoepoxide of 1. The existence of a nonexponential electron transfer rate, recently proposed in a theoretical paper, see ref 10e is another possibility. It has to be noted that the fluorescence quantum yield of 1 in benzonitrile is extremely low: ca. 2×10^{-5} , which introduces experimental difficulties. (e) Zahrikov, A. A.; Scherer, P. O. J.; Fischer, S. F. *J. Phys. Chem.* **1994**, *98*, 3424.

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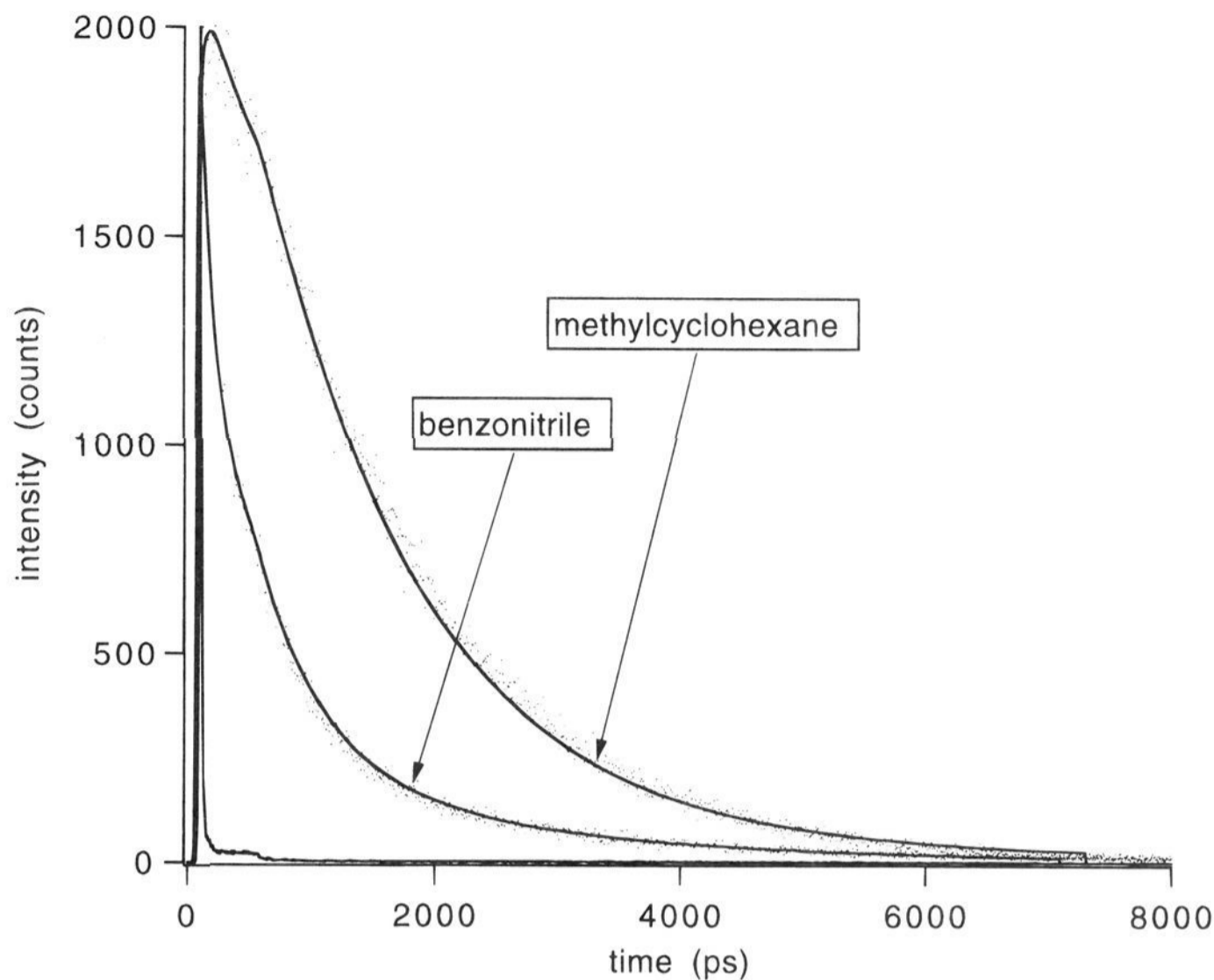


Figure 5. Fluorescence decays of compound **1** in methylcyclohexane and in benzonitrile. Laserpulse is also shown.

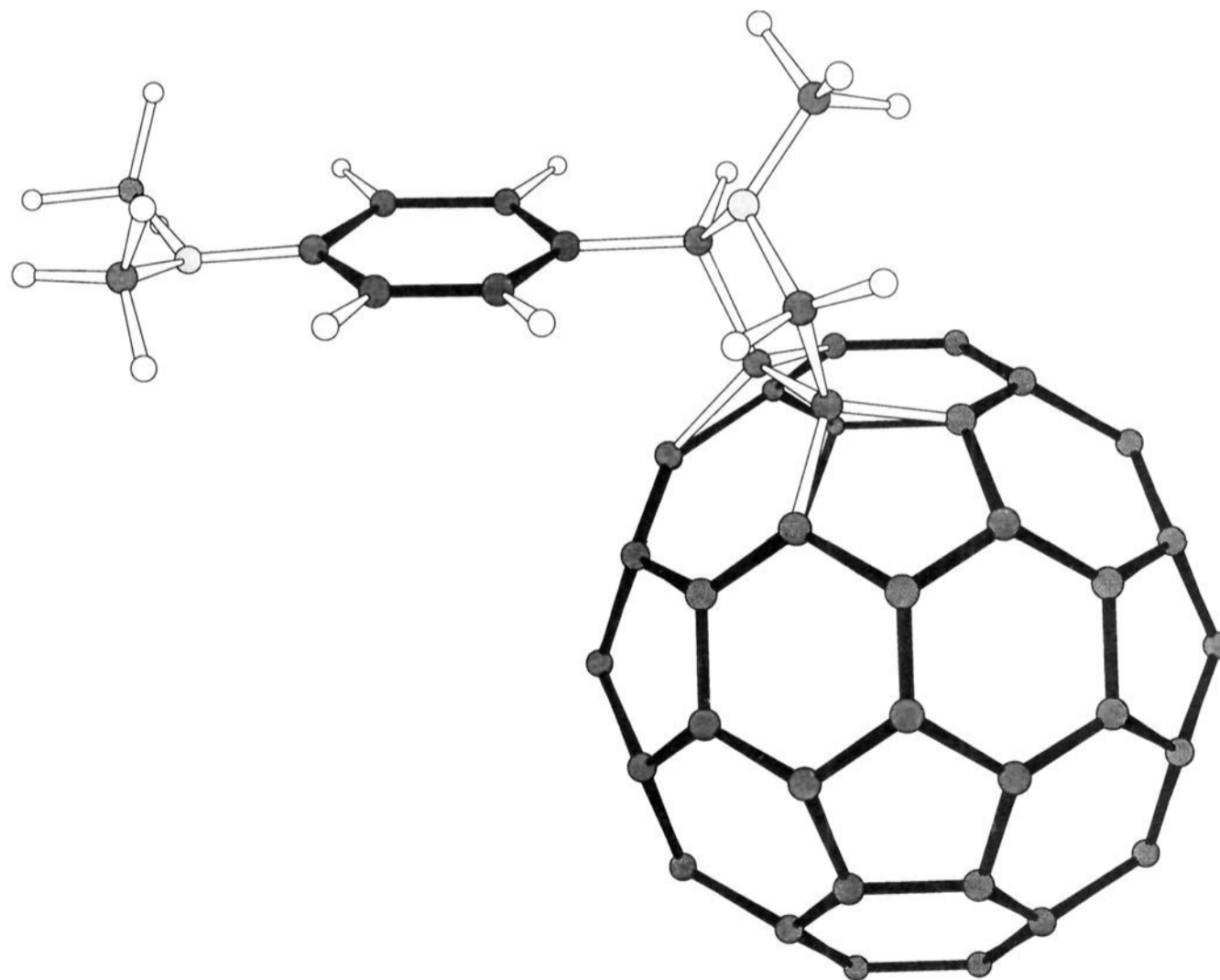


Figure 6. Structure of compound **1** obtained with AM-1.

plane that bisects the two sp^3 carbons of the fullerene. Although the center to center distance of the two chromophores is estimated to be ca. 9 Å, the edge to edge distance is only ca. 5 Å.

Energetic Considerations. An estimate of the driving force for photoinduced charge separation ($-\Delta G_{cs}$) in compound **1** was made using the standard Weller-type approach.¹³ This requires, in addition to the donor and acceptor redox potentials (+ 0.71

V and -0.57 V vs SCE, see above) and the singlet or triplet state energy ($^1E_{00} = 1.76$ eV and $^3E_{00} = 1.50$ eV, see above), substitution of the center to center distance (R_c) and of the effective ionic radii of the donor and acceptor radical cation and anion (r^+ resp. r^-). For R_c a value of 9 Å was estimated

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Table 3. Gibbs Free Energy Change for Charge Separation (ΔG_{cs}), Barrier to Charge Separation (ΔG^*), and Gibbs Free Energy Change for Charge Recombination (ΔG_{cr}) and the Reorganization Energy (λ) in Different Solvents (Given with Dielectric Constants (ϵ) and Refractive Indices (n)) for Both the Singlet and Triplet (T) state, Obtained for Compound **1** with $R_c = 9 \text{ \AA}$, $r^+ = 3.7 \text{ \AA}$, and $r^- = 5.6 \text{ \AA}$

solvent	ϵ	n	ΔG_{cs} (eV)	λ (eV)	ΔG^* (eV)	ΔG_{cr} (eV)	ΔG_{cs} (T) (eV)	$\Delta G^*(T)$ (eV)
methylcyclohexane	2.07	1.423	0.22	0.63	0.29	-1.98	0.48	0.49
toluene	2.38	1.497	0.12	0.67	0.23	-1.88	0.38	0.41
chloroform	4.70	1.446	-0.22	1.02	0.16	-1.54	0.04	0.28
dichloromethane	8.93	1.424	-0.38	1.18	0.14	-1.38	-0.12	0.24
1,2-dichlorobenzene	9.93	1.552	-0.40	1.11	0.11	-1.36	-0.14	0.21
benzonitrile	25.20	1.528	-0.50	1.22	0.11	-1.26	-0.24	0.20

^a Internal reorganization energy (λ_i) is 0.3 eV.

from our modeling results (Figure 6). The r^+ and r^- values were calculated from the apparent molar volumes of *N,N*-dimethylaniline (density 0.956) and of C_{60} (density 1.65)¹⁴ using a spherical approach.^{5c} This gives $r^+ = 3.7 \text{ \AA}$ and $r^- = 5.6 \text{ \AA}$. Resulting ΔG_{cs} values in various solvents are listed in Table 3, where furthermore values are given for the barrier to charge separation (ΔG^*) as estimated via the classical Marcus equation. For this estimation the solvent reorganization term (λ_s) was calculated using the Born-Hush approach,^{5c} and the internal reorganization energy (λ_i) was set at 0.3 eV. The latter value was estimated using the charge transfer absorption maximum of C_{60} in pure diethylaniline (550 nm)¹⁵ and the charge transfer emission maximum of C_{60} in methylcyclohexane containing 0.1 M diethylaniline (740 nm).^{2d,h} The energy difference between these two maxima equals $2\lambda_i$, resulting in $\lambda_i \approx 0.3 \text{ eV}$. An estimate of the Gibbs free energy change for charge recombination ($\Delta G_{cr} = -\Delta G_{cs} - {}^1E_{00}$) in compound **1** is also given in Table 3. For the triplet state, only the Gibbs free energy change ($\Delta G_{cs}(T)$) and the barrier for electron transfer ($\Delta G^*(T)$) differ from the values for the singlet state.

Important conclusions from the data collected in Table 3 are as follows: (i) The driving force for charge separation ($-\Delta G_{cs}$) from the fullerene S_1 state becomes positive in solvents more polar than toluene, in good agreement with the fluorescence data, and from the T_1 state it requires solvents more polar than chloroform. The relatively high triplet yield and the absence of fluorescence of **1** in dichloromethane indicates that in this solvent of medium polarity charge recombination to the local triplet is a major decay path of the charge transfer state. (ii) Charge separation is in the normal region ($-\Delta G_{cs} < \lambda$) for every solvent, but charge recombination in benzonitrile is almost in the optimal region ($-\Delta G_{cr} \approx \lambda$), in agreement with the short lifetime of the charge transfer state. (iii) The barrier for electron transfer from S_1 is always at least 0.09 eV lower than from T_1 (the difference in the barrier is 0.20 eV (4.7 kcal/mol) in methylcyclohexane and 0.09 eV (2.1 kcal/mol) in benzonitrile). This indicates that electron transfer rates from the triplet should always be slower than from the singlet state, and this effect should be strongest in nonpolar solvents, in agreement with the results of Caspar and Wang.²ⁱ

Conclusions

The solvent dependence of the fluorescence and triplet-triplet absorption of **1** indicates that in polar solvents an extra deactivation path of the excited states (S_1 or T_1) of **1** becomes available. As the population of a charge transfer state is exergonic in polar solvents (according to the Weller equation) we attribute this quenching path to an intramolecular electron transfer that deactivates the locally excited states.

Fluorescence decay data indicate that the singlet state electron transfer quenching process in benzonitrile takes place with a rate between 1.3×10^9 and $1.2 \times 10^{10} \text{ s}^{-1}$.

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Because, even at the relatively small edge-to-edge donor-acceptor distance present in **1**, the charge transfer state can only be populated in rather polar solvents, our results also imply that fullerenes are not very well suited for use as electron accepting chromophores for long range electron transfer in bichromophoric donor-bridge-acceptor systems, unless a significantly stronger donor than *N,N*-dimethylaniline (e.g. *N,N,N',N'*-tetramethyl-*p*-phenylenediamine) is used. One of our previous studies on the solvent dependence of intramolecular charge separation has already shown that optimal (in a Marcus sense) electron transfer interactions (at a given distance) can only be accomplished if already in a nonpolar solvent electron transfer is energetically favorable:^{5d} i.e., by applying polar solvents one can gain driving force (and make electron transfer energetically possible) but one will never obtain the highest electron transfer rates. Our results thus suggest that high rate photoinduced intramolecular electron transfer in the systems described in ref 4b, c and 5e will not be possible due to the large separation distance or the small driving force, although the different spatial orientation of the donor and acceptor in these systems may be of influence.

Furthermore our results indicate that functionalization of C_{60} is accompanied by a decrease of the ${}^1E_{00}$ with ca. 0.23 eV and a shift to a more negative first reduction potential of ca. 0.17 V. Thus, under the same conditions (i.e. donor, distance and solvent), the driving force for charge separation for an adduct of C_{60} , compared to "native" C_{60} , would be ca. 0.40 eV less exergonic. This would mean that C_{60} adducts are less suited for photoinduced electron transfer systems than "native" C_{60} . It thus would seem preferable to incorporate a C_{60} unit into an electron transfer system by a supramolecular method, such as complexation by calix[8]arenes¹⁶ or γ -cyclodextrins,¹⁷ leaving the C_{60} unit intact.

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Supplementary Material Available: ¹H NMR, ¹³C NMR, and mass spectrum of compound **1** and Cartesian coordinates of the AM-1 optimized structure of **1** (8 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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