Photochemistry and Spectroscopy of “Stable Organic Radicals”: Steric and Electronic Effects in Intermolecular Photoinduced Electron Transfer

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The intermolecular reactivities of amino-substituted perchlorotriphenylmethyl radicals **1**−**3** were studied, with particular emphasis on electron transfer (ET) reactions. The natural fluorescence lifetimes and the rates of the electron-transfer quenching were studied with several electron donors and acceptors. Fluorescence quenching studies demonstrate the importance of the redox potentials of the ET pair on the observed steric and electronic properties.

Introduction

The “inert carbon free radicals,” such as perchlorotriphenylmethyl (PTM) radical, are passive toward bond-formation because of steric shielding of the central carbon atom by the chlorinated phenyl rings.[1] They do not dimerize under any circumstances, they are insensitive to oxygen, and they do not react with typical radical reagents or with such highly reactive polar as concentrated mineral acids, dihalogens, etc. However, these “inert” radicals are photosensitive and are active in electron-transfer, where steric shielding is ineffective.[1]

As such, derivatives of PTM radicals are useful reaction partners in the study of steric and electronic effects on reversible electron-transfer chemistry. In bimolecular electron transfer (ET) between electron donors and acceptors in solution, the closest approach of the reactants in the transition-state defines the donor/acceptor separation and orbital overlap limits on the intrinsic rate of electron exchange. Steric hindrance has been reported[2] to be very important to a comprehensive understanding of the factors governing charge-transfer (CT). Significant steric effects were observed on the kinetics of CT to ketones and quinones from aromatic donors.[3] Electron transfer from hindered and unhindered arenes to p-chloranil also showed steric-dependent kinetics and established a clear distinction between inner and outer-sphere et in the electronic coupling of a donor and an acceptor in the transition state complex preceding the observed electron transfer.[3]

Photoinduced electron-transfer reactions are often performed in polar solvents, such as acetonitrile, in which separation of the initial geminate radical-ion pair can occur.[4] The contact radical-ion pairs are short-lived, and if physical separation does not take place, secondary chemical reactions would have to be very rapid in order to compete with back electron transfer and other rapid first-order deactivation pathways. Once separated, however, chemistry characteristics of solvent-separated radicals ions are observed.

Several chemical reactions are known to be sufficiently fast to compete with charge recombination. For example, some nucleophilic reactions can compete with single electron-transfer (SET) process. Both nucleophilic and SET processes involve a charge shift, and the principal factors that favor SET include: 1) a strong electrostatic attraction between the nucleophile and the electrophile; 2) minimal steric hindrance to close approach in the transition state; 3) substantial delocalization of the odd electron in the radical ion pairs; and 4) the bond strength of the putative chemical bond that could be formed through radical combination.

Synthesis. Radicals **1**−**3** were prepared by ammoniation and reduction of the carbenium salt **4**, which in turn was obtained by oxidation of the parent radical PTM with $SbCl_5$ in SO_2Cl_2.[5] As shown in Scheme 1, the synthesis of the amino radical **1** was performed following the method of Ballester et al.[5] Treatment of cation **4** in CH_2Cl_2 with NH_3 gave a benzimine which reacts with $SnCl_2$ in ether to give the 4-aminotetradecachlorotriphenylmethyl radical **1**. Radical **1** reacts with acetyl chloride or pivaloy lchloride to produce 4-[(acetyl)amino]tetradecachlorotriphenylmethyl radical **2**, or 4-[(pivaloyl)amido]tetradecachlorotriphenylmethyl radical **3**, Scheme 2**.** The latter species **3** was also prepared following the procedure reported by Julia et al.[6]

Spectral Characterization of 1−**3. EPR.** The EPR spectra of radicals **1**[5] and **3** in degassed THF exhibit a single resonance with two pairs of ^{13}C satellites. The spectrum of radical **2** shows two lines and computer simulation allowed calculation of the H coupling constant (Table 1, Figure 1). Coupling with N was not observed because the introduction of the acetyl group sterically inhibits spin delocalization, placing the proton further from the nodal plane of the lone-electron π orbital while increasing hyperconjugation. The electron-withdrawing character of the carbonyl group diminishes the availability of the nitrogen electron pair, thus indirectly

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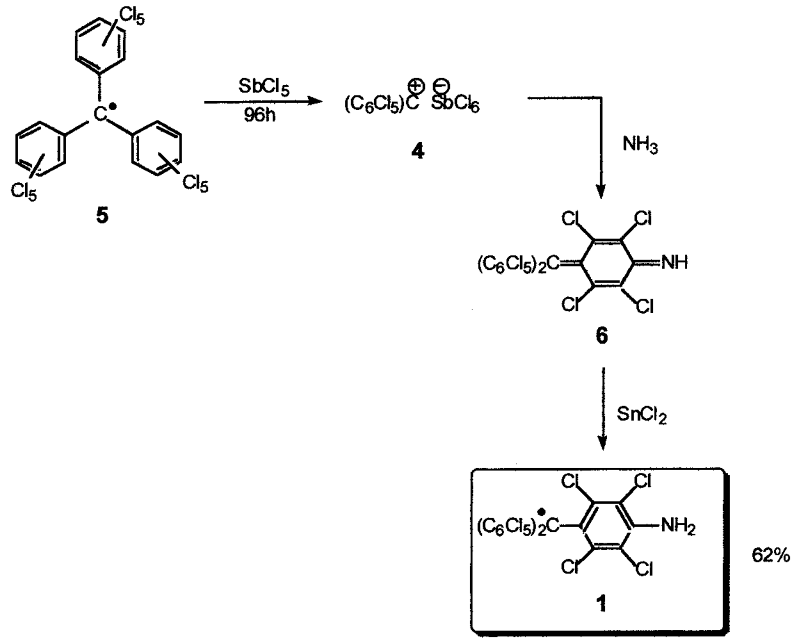
Scheme 1. Synthesis of 4-Aminotetradecachlorotriphenylmethy Radical



Scheme 2. Synthesis of 4-[(acetyl)Amino]tetradecachlorotriphenylmethyl and 4-[(pivaloyl)Amido]tetradecachlorotriphenylmethyl Radicals

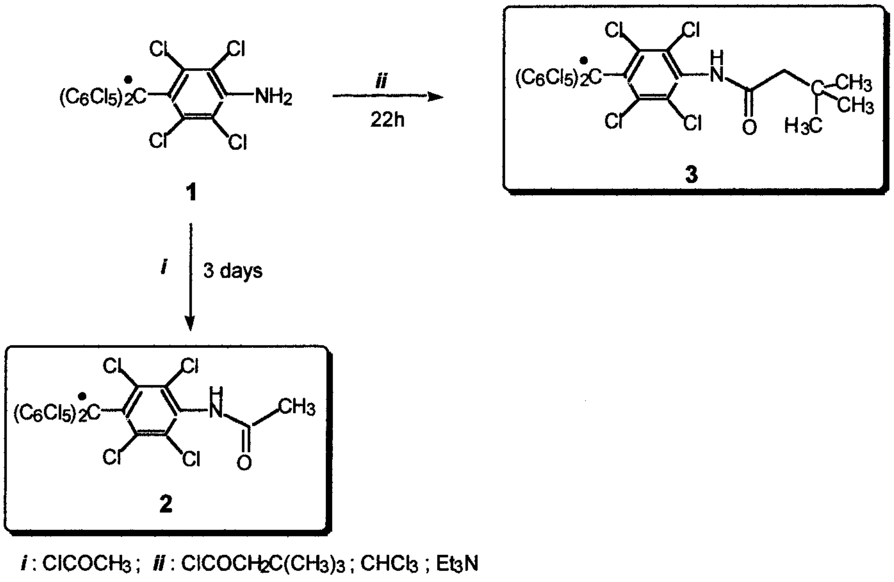


Table 1. EPR Spectral Data of Radicals 1−3

		splittings, G			
				^{13}C	
radicals	lines	N[a]	H[a]	α[a]	aromatic[a]
1	1	1.00		25.0	10.3, 12.9
2	2		1.65	29.6	10.6, 13.3
3	1			29.9	10.3, 12.6

[a] Derived by spectral simulation using a Lorentzian line shape and a line width of 1.3 G.

diminishing still further the observed spin coupling with the nitrogen.

In radical **3** the bulky pivaloyl group introduces steric twisting[7,8] of the phenyl substituents even more strongly than the acetyl group in radical **2**. Such a twisting reduces the proton splitting constants because of diminished delocalization of the unpaired electron, Figure 2. In contrast, the spectrum of radical **1** shows substantial coupling with N, since the nitrogen electron pair is delocalized by resonance with the aromatic ring, Figure 3.

Electronic Absorption Spectra. Absorption spectra of these radicals are characterized by two degenerate one-electron transitions: from the SOMO to the LUMO and from the HOMO to the SOMO. The spectra of the amino radical **1** in a nonpolar solvent shows a marked bathochromic shift with solvent polarity, indicating strong solvation of the excited state relative to the ground state.[5] The spectra of radicals **2** and **3** in cyclohexane or in DMSO show instead a hypsochromic shift with incrased solvent polarity, partly because of inhibited resonance from the amino group to the aromatic system caused by

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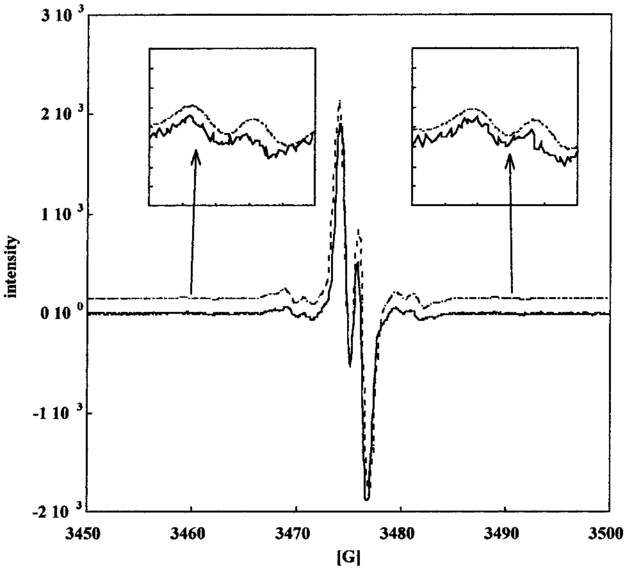

Figure 1. EPR spectrum of radical **2** (—) and its computer simulation (- - -).

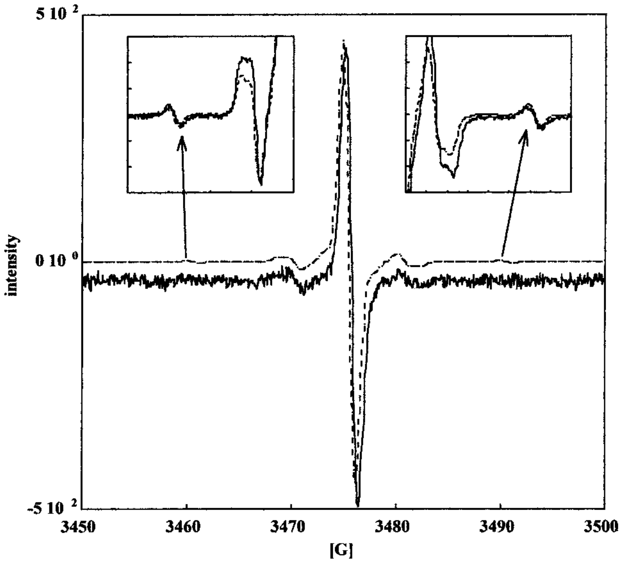

Figure 2. EPR spectrum of radical **3** (—) and its computer simulation (- - -).

the steric blockage of the preferred conformation by the acetyl group by the two ortho-chlorines and partly because of electron-withdrawal by the carbonyl groups, Figure 4. The steric bulk near the carbonyl group in radical **3** suppresses this solvent effect, Figure 5. The spectra of radicals **2** and **3** in cyclohexane are unshifted from the maximum observed for **1**.

Electrochemistry. The redox potentials of radicals **1**−**3** were determined by cyclic voltammetry (CV) of 1 mM radical solutions in degassed acetonitrile at room temperature, Table 2. Tetrabutylammonium tetrafluoroborate (0.01 M) was used as supporting electrolyte.

The cyclic voltammogram of the amino radical **1** exhibits a reversible single-electron reduction wave at −510 mV and one reversible single-electron oxidation wave at + 500 mV, Figure 6. Therefore, this radical can, in principle, act as an electron donor or as an electron acceptor, and its absorption spectrum would indicate enhanced redox reactivity in the excited state. In **2** and **3**, only a single reversible reduction wave was observed, Figures 7 and 8. The introduction of the amido group shifts the half-redox potential ($E_{1/2}$) by 260 mV and 335 mV negative, respectively, for **2** and **3**. Thus, in the ground state, both **2** and **3** are expected to be good electron acceptors but poor donors. The insertion of the additional methylene makes **3** even a better electron acceptor than **2**. The ease of reduction of **3** might be attributed partly to the weaker hyperconjugation by the pivaloyl group than with a simple methyl group. A methyl group produces stronger electron release by hyperconjugation[9] and the formation of the anion derived from **2** is less favorable than from **3**. There is already evidence that hypeconjugation plays an important role in the chemical reactivity of free radicals[9] and in **2** and **3** this effect seems to be considerable. These shifts are particularly evident with the parent perchlorotriphenylmethyl radical (PTM).[10]

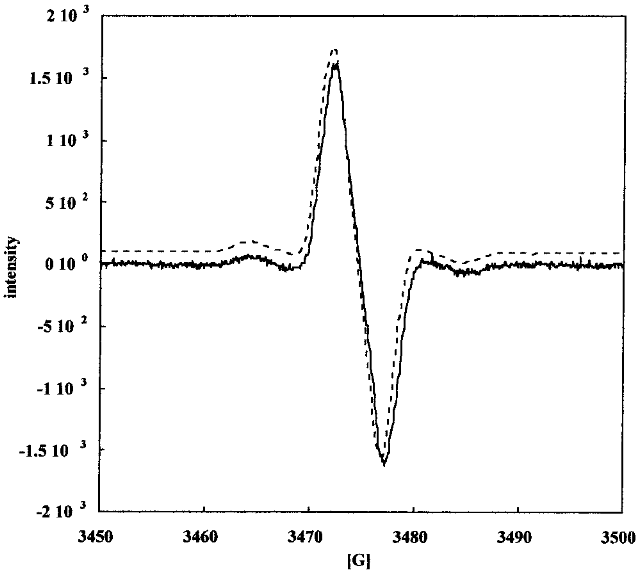

Figure 3. EPR spectrum of radical **1** (—) and its computer simulation (- - -).

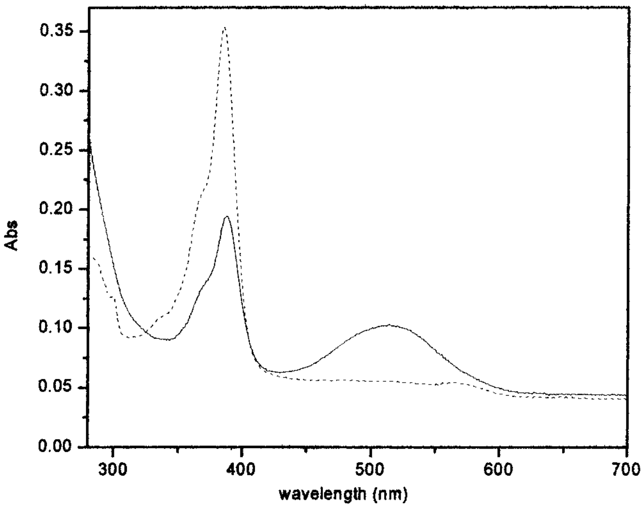

Figure 4. UV−vis spectra of **2** in DMSO (—) and in cyclohexane (- - -).

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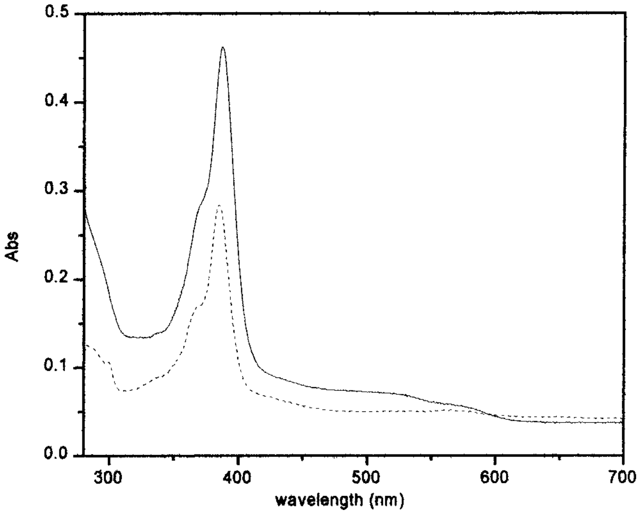

Figure 5. UV–vis spectra of **3** in DMSO (—) and in cyclohexane (- - -).

Table 2. Redox Potentials[a] (vs Ag/Ag$^+$) for Radicals 1–3 and PTM

radicals	$E_{1/2}$ (mV)
1	500; −510
2	−250
3	−175
PTM	−430

[a] Measured as 1 mM radical solutions containing tetrabutylammonium tetrafluoroborate (0.01 M) in degassed acetonitrile; Pt cathode, 100 mV/sec.

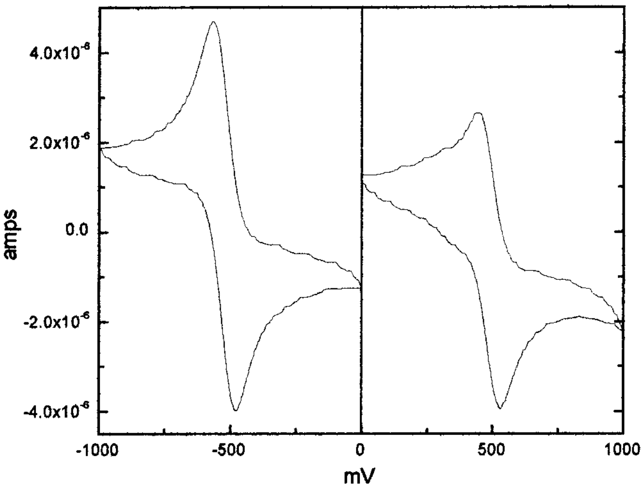

Figure 6. Cyclic voltammogram of radical **1** (10^{-3} M in acetonitrile containing 0.01M tetrabutylammonium tetrafluoroborate). Potentials are reported against a Ag/AgNO$_3$ reference and were measured in the dark.

Time-Resolved Measurements. The fluorescence lifetimes of radicals **1**–**3** are reported in Table 3. The amino-substituted radicals **1** and **3** exhibit very similar lifetimes in the presence of O$_2$, but under the same conditions the lifetime of the acetylaminoradical **2** is significantly shorter. This is surprising in that the excited doublet state[10] of the PTM radical was not quenched by oxygen or by electron acceptors such as duroquinone ($E_{1/2}$ = −0.235 mV), even though its ground-state reduction potential (−430 mV) was less negative than required.

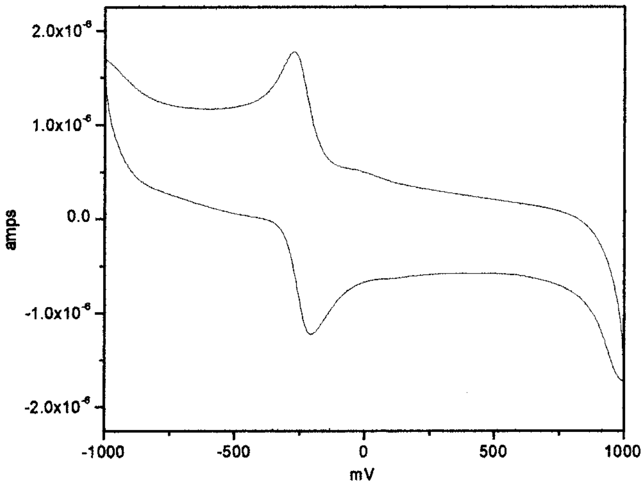

Figure 7. Cyclic voltammogram of radical **2** (10^{-3} M in acetonitrile containing 0.01 M tetrabutylammonium tetrafluoroborate). Potentials are reported against a Ag/AgNO$_3$ reference and were measured in the dark.

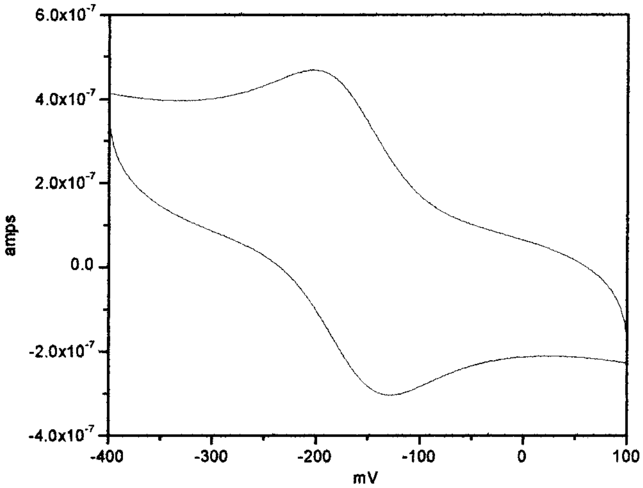

Figure 8. Cyclic voltammogram of radical **3** (10^{-3} M in acetonitrile containing 0.01 M tetrabutylammonium tetrafluoroborate). Potentials are reported against a Ag/AgNO$_3$ reference and were measured in the dark.

Quenching Experiments. Fluorescence quenching of radicals **1**–**3** by a redox partner follows a Stern–Volmer relationship[11]

$$I_0/I = 1 + K_{SV} = 1 + k\tau_0[Q]$$

where I_0 and I are the relative fluorescence intensities in absence and presence of the quencher Q, K_{SV} is the Stern–Volmer quenching rate constant, τ_0 is the fluorescence lifetime of the fluorophore in absence of the quencher, and k is the bimolecular rate constant of quenching. Although electron transfer is assumed to be the dominant nonradiative decay pathway, solvent polarity is believed to alter the quenching mechanism.[12–14] In polar solvents, quenching is governed by solvation of the

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Table 3. Fluorescence Lifetimes[b] (λ_{exc} = 337 nm) in Cyclohexane at the λ_{max} Observed in the Emission Spectrum of Each Compound (608 < λ_{em} < 634 nm)

radicals	λ_{em} (nm)	τ (ns)
1	634	8.9
2	613	4.6
3	608	8.2
PTM	605	7.0[a]

[a] Reference 10. [b] Typical errors in observed fluorescence lifetime are 10%.

Table 4. Kinetic Constants[a] for Fluorescence Quenching of 1−3 Calculated from the Stern−Volmer Plots

radical	solvent	quencher	$k_{*10}{}^{13}$ [M^{-1} sec^{-1}]
1	cyclohexane	Ph_{3N}	2.69
2	cyclohexane	Ph_{3N}	1.97
3	cyclohexane	Ph_{3N}	1.88
1	acetonitrile	Ph_{3N}	2.95
2	acetonitrile	Ph_{3N}	0.64
3	acetonitrile	Ph_{3N}	0.84
2	acetonitrile	p-chloranil	3.97
3	acetonitrile	p-chloranil	0.81

[a] Typical errors in calculated rate constants are 10%.

resulting ions and only a minor steric effect could be observed. In nonpolar solvents, exciplex formation is likely to be dominant in the observed quenching. Steric hindrance should therefore be very significant, since the transition-state geometry limits the intrinsic rate of the electron exchange.

The samples of radical **1** in cyclohexane were freshly prepared before each measurement because they showed appreciable decomposition under irradiation, with fluorescence intensity rapidly decreasing. In contrast, solutions of **1** in acetonitrile were very stable. Both an oxidative and reductive quencher were used in these experiments. Triphenylamine and p-chloranil are known to be excellent electron-transfer reagents ($E^0{}_{ox}$ = 0.70 V vs SCE[2,15−17] and $E^0{}_{red}$ = 0.02 V vs SCE, respectively). In addition, p-chloranil is reported[3] to have a long-lived (μs) excited (triplet) state that exhibits a high reduction potential ($E^*{}_{red}$ = 2.15 V vs SCE).

To calculate the rate constant for quenching in accord with the Stern−Volmer relationship, we collected the fluorescence intensities of each radical in solution in the absence of the quencher (I_0) and monitored fluorescence intensities (I) after each addition of the quencher. The reaction of radical **1** in acetonitrile with triphenylamine allowed us to calculate the quenching rate constant (Table 4) within the range of applicability of the Stern−Volmer relationship, Figure 9. The experiments were performed both in aerated and in deoxygenated solvent. Consistent results were obtained under either condition.

Analogous quenching of radical **1** in degassed acetonitrile by chloranil showed anomalous behavior. Each addition of the quencher caused the fluorescence intensity (I) to significantly increase, Figure 9. Neither emission from the solvent nor from the quencher produce this effect when examined separately.

In cyclohexane (whether deoxygenated and not), quenching of **1** by triphenylamine gave the expected decrease of intensity, and we could calculate the derived rate constant, Table 4.

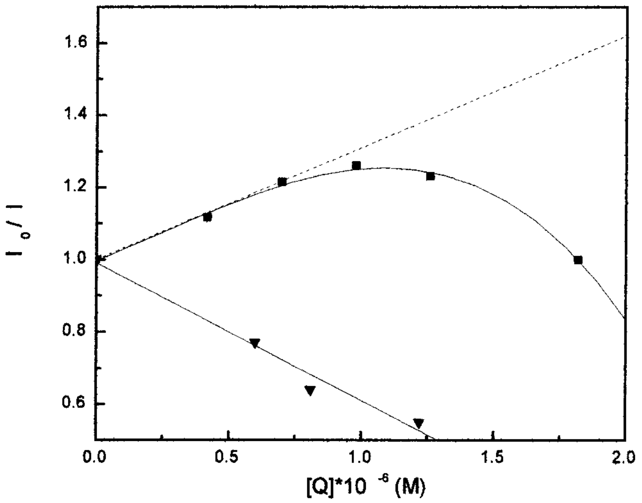

Figure 9. Stern−Volmer plot of fluorescence quenching of radical **1** by triphenylamine (ν) and by p-chloranil (τ) in acetonitrile.

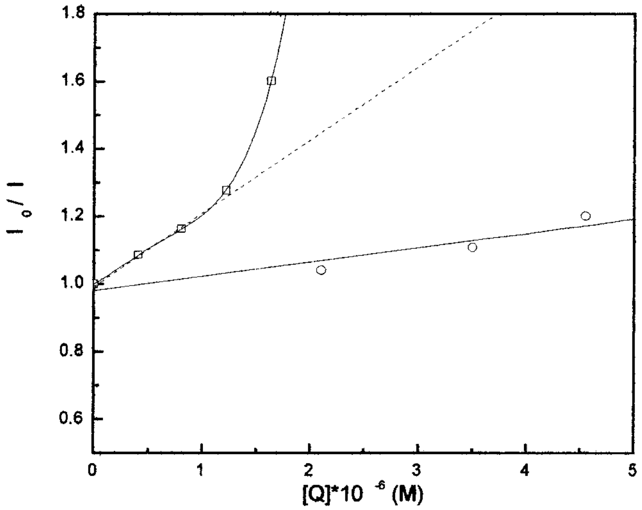

Figure 10. Stern−Volmer plot of fluorescence quenching of radical **2** by p-chloranil (□) and by triphenylamine (○) in acetonitrile.

Fluorescence of solutions of **2** and **3** both in cyclohexane and acetonitrile were monitored by adding the same quenchers as with **1**, and the corresponding Stern−Volmer plots were obtained, Figures 10 and 11. (The raw data, establishing the range over which the Stern−Volmer law remains linear, are available in the Supporting Information.)

Discussion

The above data can be interpreted by the general Scheme 3 illustrating electronic and solvent effects on the quenching rate.

The rate constant for fluorescence quenching (k) is therefore a function of k_1, k_{-1}, k_2, and k_3.

$$k = k_1\left(\frac{k_2 + k_3}{k_{-1} + k_2 + k_3}\right)$$

In cyclohexane (a nonpolar solvent), k_3 is negligible but it is very significant in polar solvents as acetonitrile.

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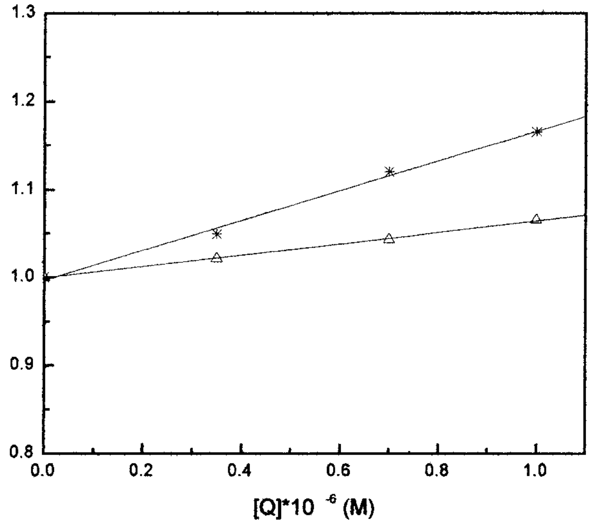
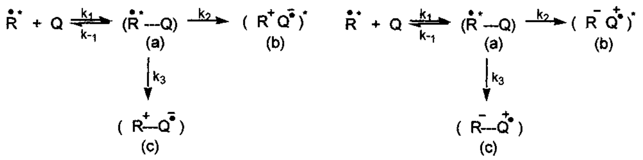


Figure 11. Stern−Volmer plot of fluorescence quenching of radical **3** by triphenylamine in cyclohexane (T) and in acetonitrile (Δ).

Scheme 3[a]



[a] $R^{\bullet *}$ is the radical in the excited state. Q is the quencher, (a) is an encounter complex, (b) is an exciplex, and (c) is an ion pair. Oxidative quenching by an electron acceptor is shown on the left; reductive quenching by an electron donor is shown on the right.

Therefore, in a less polar solvent, k_2 determines the quenching rate. This process involves geometric and solvent relaxation of the encounter complex to an equilibrium exciplex and an increase in steric hindrance plays an important role on the observed quenching rate.

In cyclohexane, the rate constants for **2** ($k = 1.97{*}10^{13}$ [M^{-1} sec^{-1}]) are lower than those for **1** ($k = 2.69{*}10^{13}$ [M^{-1} sec^{-1}]) under the same conditions. This behavior has been attributed to the increased steric bulk of the substituent rather than to an electronic effect, since a specific geometry is required between the radical and the quencher in order to generate an emissive exciplex. In accord with our hypothesis, we found the lowest rate constant for radical **3** ($k = 1.88{*}10^{13}$ [M^{-1} sec^{-1}]).

In acetonitrile, steric effects are less relevant. Here, the quenching process is governed by electron transfer which requires only a loose encounter complex. Therefore, it is possible to isolate electronic effects on the quenching. The fluorescence quenching with triphenylamine as electron donor is favored in radical **1** ($k = 2.95{*}10^{13}$ [M^{-1} sec^{-1}]) over radical **2** ($k = 0.64{*}10^{13}$ [M^{-1} sec^{-1}]), but a higher value for the rate constant is found for **2** with p-chloranil ($k = 3.97{*}10^{13}$ [M^{-1} sec^{-1}]). In this polar solvent, electron-withdrawal by the substituent plays an important role in the resonance stabilization of the ground state of **2**. Thus, the rate constant for SET to **2** in acetonitrile from Ph_3N is lower than with the amino radical **1**. Electron-transfer between radical **2** and p-chloranil in acetonitrile is faster, since the formation of the carbocation is favored by hyperconiugation by the methyl group which produces the most powerful electron releasing effect in this series.

Further evidence for the importance of the substitutent group in fluorescence quenching is found by studying radical **3**. The pivaloyl group in the radical **3** does not release electrons effect as powerfully as does the methyl group in radical **2**. The rate constant for SET from **3** in acetonitrile to p-chloranil ($k = 0.81{*}10^{13}$ [M^{-1} sec^{-1}]) is much lower than for **2** ($k = 3.97{*}10^{13}$ [M^{-1} sec^{-1}]) where the carbocation was strongly stabilized by hyperconjugation by the methyl group. Therefore, in this solvent, fluorescence quenching by triphenylamine as electron donor is favored in radical **3** ($k = 0.84{*}10^{13}$ [M^{-1} sec^{-1}]) over radical **2** ($k = 0.64{*}10^{13}$ [M^{-1} sec^{-1}]).

Deviations from the Stern−Volmer Law. At low concentrations, the quenching of the fluorescence by a quencher molecule in solution follows the classic Stern−Volmer relationship. Since the fluorescence lifetime is independent of the quencher concentration, Stern−Volmer plots will be linear as long as the rate constant k is independent of quencher. It has been known for many years that associative quenching reactions can lead to curved Stern−Volmer plots.[18,19] Both positive and negative deviations have been observed, and several plausible explanations have been proposed.[20−26] Negative curvature involves a decrease in K_{SV} and is associated with a change in the absorption and fluorescence spectrum of the fluorophore.[20] Deviations from the Stern−Volmer equation in such reactions have been explained by the existence of multiple fluorescing states[27] or by compound formation.[20] In our experiments we observed appreciable Stern−Volmer deviations upon adding large quantities of quencher. Reactions with radicals **2** and **3** exhibited positive deviations (Figure 10), which has been explained in the literature as either "static" quenching[19] at high quencher concentration, or as deviations from free diffusion in solution.[28,29] The latter effect is based on the assumption that the quenching reaction is very rapid and, hence, diffusion contolled.[30−32] On the other hand, radical **1** possesses an amino group not protected as an amide as in radicals **2** and **3.** If photoexcited, radical **1** can undergo reactions with a range of quenchers.[33] Thus, the plots show negative deviations in the experiments with triphenylamine both in cyclohexane and in acetonitrile. In particular in acetonitrile, the classical polar solvent, the reaction between the photoactivated radical **1** and p-chloranil is so fast that it was not possible for us to observe the net quenching, Figure 9.

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Conclusions

The reactivity of a new series of amino-substituted perchlorotriphenylmethyl radicals with electron acceptors and donors has been described. In general, fluorescence quenching follows a normal Stern−Volmer relationship, and clear evidence for steric and electronic effects on the rate of electron transfer were obtained. Significant mechanistic diversion observed in polar and nonpolar solvents allowed us to distinguish between steric and electronic effects in these single electron-transfer reactions.

Experimental Section

Apparati. NMR spectra were recorded with a Varian Gemini 200 MHz instrument. IR spectra were recorded with a Bio-Rad FT-500 with a UMH-600 microscope using a germanium crystal ATR objective. Absorption spectra were recorded on a Shimadzu PC-3101PC instrument and ESR spectra were recorded on an IBM-Bruker E200SRC spectrometer.

Fluorescence spectra of solutions were measured on a PTI QuantaMaster Model C-60/2000 spectrofluorometer. Lifetime measurement were made on a PTI StrobeMaster fluorescence spectrometer with a photon counting stroboscopic detector.

Cyclic voltammetry (CV) was performed with a BAS-100 electrochemical analyzer on a platinum electrode in a standard three electrode cell. Measurements were reported against a $Ag/AgNO_3$ reference electrode and were done in the dark. Solutions were approximately 1 mM radical in acetonitrile containing 0.1 M tetra-*n*-butylammonium tetrafluoroborate.

Materials. Solvents. SO_2Cl_2 was freshly distilled before each reaction and was allowed to react under Ar. Chloroform (anhydrous 99.9% Aldrich) was used without further purification. Ethyl ether and THF were distilled under Ar from metallic Na, with benzophenone being used as the indicator. Methylene chloride was distilled over P_2O_5 under Ar. Cyclohexane (HPLC grade, 99.9% Aldrich) was used without further purification, as was DMSO spectroscopic grade (99.9%, Aldrich) and anhydrous carbon tetrachloride (99%, Aldrich). Acetonitrile HPLC grade (Fisher) for the CV measurements and quenching experiments was purified by refluxing over P_2O_5, followed by distillation from P_2O_5 first and then from CaH_2. The purified solvent was stored under Ar over molecular sieves activated in an oven.

Reagents. The handling of radicals in solution was performed in the dark.

αH-quasi-Perchlorotriphenylmethane (PTM-H) and perchlorotriphenylmethyl radical (PTM) were prepared by the method of Ballester et al.[1]

Sample for the Quenching Experiments. Triphenylamine was purified by recrystallization from petroleum ether. Chloranil was recrystallized from toluene.

The radicals were purified by column flash-chromatography under Ar and stored under vacuum in the dark. The solutions were prepared for each radical both in cyclohexane and in acetonitrile with a concentration on the order of 10^{-6} M.

Perchlorotriphenylcarbenium Hexachloroantimonate (4). $SbCl_5$ (2.8 mL) was added slowly at room temperature to a solution of PTM radical (0.61 g) in SO_2Cl_2 (78.5 mL) and the resulting mixture was left undisturbed under Ar in the dark (96 h). The small dark green cubes which formed were separated, washed with anhydrous CCl_4, and dried under vacuum to give the salt. Precipitation from the mother liquors by the addition of CCl_4 afforded more pure salt (0.75 g, 86.5%). IR (polypropylene) 340 cm^{-1}.

Ammonolysis of Carbenium Salt 4. Dry NH_3(g) was passed slowly (4 min) through a suspension of salt **4** (0.100 g) in CH_2Cl_2 anhydrous (10 mL). The reaction was performed under extremely dry conditions: the glassware was dried under vacuum and then washed with argon many times; a CaO trap was used to dehydrate the NH_3(g) after the CaO was preheated at 800 °C overnight. The resulting mixture was filtered and the filtrate was evaporated to dryness giving NH-tetradecachlorofuchsonimine which was used in the next reaction without further purification.

4-Aminotetradecachlorotriphenylmethyl Radical (1). Anhydrous $SnCl_2$ (0.040 g) was added to a solution of crude fuchsonimine (0.080 g) in ethyl ether anhydrous (18 mL) and the mixture was stirred in the dark under Ar overnight. The green solution was then filtered, washed with aqueous HCl and with water, dried and evaporated. The residue was purified by column flash-chromatography (silica gel hexane−CCl_4) giving amino radical: 0.050 g (62%), dark green needles. The structure was confirmed by using IR spectroscopy (germanium crystal): 3500, 3395, 1600, 1530, 1440, 1375, 1360, 1340, 1330, 1325, 1295, 1260, 820, 775, 760, 735, 710, 650 cm^{-1}.

4-[(acetyl)Amino]tetradecachlorotriphenylmethyl Radical (2). A solution of amino radical **2** (0.050 g) in acetyl chloride (5 mL) was left (3 days) under argon in the dark. On elimination of the solvent a red residue corresponding to the radical **4** was obtained: 90%.

UV−vis (C_6H_{12}) 385, 565 nm; (Me_2SO) 388, 514 nm. IR (germanium crystal): 2950, 1800, 1675, 1530, 1360, 1330, 1260, 1225, 815, 730, 710, 650 cm^{-1}. Anal. Calcd. for $C_{21}H_4Cl_{14}NO$: C, 32.2; H, 0.5; Cl, 63.4; N, 1.8; O, 2.0. Found: C, 35.1; H, 1.8; Cl, 52.8; N, 1.7; O, 3.4.

4-[(*tert*-Butylacetyl)amino]tetradecachlorotriphenylmethyl Radical (3). A solution of *tert*-butylacetyl chloride (0.027 g, 0.198 mmol) in $CHCl_3$ (1 mL) was added dropwise to a cold stirred (0 °C) solution of radical **2** (0.100 g, 0.135 mmol) and triethylamine (0.024 g, 0.235 mmol) in $CHCl_3$ (1.5 mL) under argon. The resulting mixture was stirred further at 0 °C for 1 h and then at room temperature for 22 h. Evaporation of the solvent gave a residue that was placed in $CHCl_3$, washed with diluted aqueous HCl and water, and dried with anhydrous Na_2SO_4. The solution was filtered and evaporated to give a residue which was purified by flash-chromatography (silica gel hexane−CCl_4) to afford radical **5** (0.010 g, 10%).

IR (germanium crystal): 2950, 2850, 1725, 1660, 1520, 1460, 1390, 1330, 1260, 1220, 1150, 1120, 1100, 820, 740, 720, 700, 660 cm^{-1}. UV−vis (C_6H_{12}): 385, 580 nm; (Me_2SO) 385, 580 nm. Anal. Calcd. for $C_{25}H_{12}Cl_{14}NO$: C, 35.8; H, 1.4; Cl, 59.2; N, 1.7; O, 1.9. Found: C, 40.4; H, 3.5; Cl, 44.6; N, 1.15; O, 2.0.

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Supporting Information Available: Tables 1−3, quenching experiments of radical 1 in acetonitrile and cyclohexane; Tables 4−6, quenching experiments of radical 2; Tables 7−9, quenching experiments of radical 3; Figures 12 and 13, Stern−Volmer plots of fluorescence quenching for radical **1** and **2** in cyclohexane with Ph_3N; Figure 14, Stern−Volmer plot for radical **3** in acetonitrile with quencher p-chloranil. This material is available free of charge via the Internet at http://pubs.acs.org.

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