ELSEVIER

Journal of Photochemistry and Photobiology
A: Chemistry 86 (1995) 103–108

Journal of
PHOTOCHEMISTRY
AND
PHOTOBIOLOGY
A:CHEMISTRY

Photophysical and fluorescence quenching properties of 1,7-diazaperylene in solution

T. Sander [a], H.-G. Löhmannsröben [a,*], H. Langhals [b]

[a] *Institut für Physikalische und Theoretische Chemie, TU Braunschweig, Hans-Sommer-Strasse 10, D-38106 Braunschweig, Germany*
[b] *Institut für Organische Chemie, Universität München, Karlstrasse 23, D-80333 München, Germany*

Received 20 June 1994; accepted 6 September 1994

Abstract

The photophysical and fluorescence quenching properties of 1,7-diazaperylene (DAP) were determined in acetonitrile and benzene solutions. The absorption spectra of the triplet molecules ($^3DAP^*$) and of the radical anions and cations were recorded. The quantum yield of intersystem crossing from the S_1 state was determined to be $\Phi_{ISC}=0.015$ (in methylcyclohexane at room temperature). In acetonitrile, radical anions $^2DAP^-$ were detected as primary products of the reductive fluorescence quenching of singlet excited DAP ($^1DAP^*$) with anthracene as quencher molecule. The DAP radical cation $^2DAP^+$ was generated by the method of secondary electron transfer with photoexcited 9,10-dicyanoanthracene ($^1DCA^*$) as energy donor.

Keywords: Fluorescence quenching; 1,7-diazaperylene

---

1. Introduction

In current photophysical research, the electron transfer reactions of aromatic hydrocarbon molecules and the spectroscopic properties of their radical ions are of prime importance. Due to their outstanding fluorescence capabilities and photochemical stabilities, perylene and its derivatives have been applied as fluorescence probes in many photophysical investigations. The structure, spectral and photophysical properties and excited state dynamics of newly synthesized 1,7-diazaperylene (DAP) [1] are therefore of considerable interest, and the fundamental absorption and fluorescence properties and X-ray structures of DAP and two of its derivatives have recently been determined [1,2].

In this paper, we report the intermolecular deactivation of singlet excited DAP ($^1DAP^*$) and the photophysical properties of the triplet state molecules ($^3DAP^*$), radical cations ($^2DAP^+$) and radical anions ($^2DAP^-$) which are formed as primary products in the fluorescence quenching process. The properties of these transient species were studied by stationary and time-resolved absorption and fluorescence spectroscopy. The initial motivations of this work were twofold. (1) Earlier studies have shown that perylene and perylene dyes are suitable molecular probes for the determination of intermolecular energy and electron transfer [3–5] and electrogenerated chemiluminescence (ECL) [6] processes, and it was therefore of interest to include DAP in our investigations. (2) Polarity effects on electron transfer reactions, e.g. the determination of standard free energy changes in low-polarity solvents and the possible influence of different charge distributions, are not well understood at present [7–14]. Many photophysical properties of DAP and perylene are quite similar but, due to the presence of the nitrogen atoms, the DAP redox potentials are distinctly different from those of perylene (see below). Therefore perylene and DAP represent a pair of molecules particularly suited for the distinction between photophysical and electrochemical effects in electron transfer reactions.

2. Experimental details

The synthesis of DAP has been outlined previously [1]. All other substances employed as quencher molecules or reference compounds were commercially available and were purified by vacuum sublimation, recrystallization or distillation if necessary. Spectroscopic grade solvents were used.

Absorption and fluorescence spectra were recorded with a Shimadzu UV-240 photometer and a Per-

---

* Corresponding author.

1010-6030/95/$09.50
SSDI 1010-6030(94)03954-2

kin–Elmer MPF 44E fluorometer (attached to a PC for numerical quantum correction of the fluorescence spectra) respectively. Fluorescence quantum yields were determined relative to literature values (in cyclohexane at room temperature) of perylene ($\Phi_F = 0.98$ [15]) and tetracene ($\Phi_F = 0.17$ [16]). The experimental apparatus for the measurement of the fluorescence lifetimes by time-correlated single-photon counting and the transient absorption spectra by laser flash excitation have been described previously [17,18]. The DAP triplet state properties were determined by triplet energy transfer and reference excitation methods [18,19]. The following triplet extinction coefficients (ϵ_T) and intersystem crossing quantum yields (Φ_{ISC}) of the reference compounds were used (room temperature) [16,19]: chrysene: $\epsilon_T = 21\,600$ M^{-1} cm^{-1} (at $\lambda_{max} = 565$ nm in cyclohexane); anthracene: $\epsilon_T = 64\,700$ M^{-1} cm^{-1} (423 nm, cyclohexane); tetracene: $\epsilon_T = 31\,200$ M^{-1} cm^{-1} (465 nm, benzene), $\Phi_{ISC} = 0.63$; perylene (see Table 1, Section 3): $\epsilon_T = 14\,000$ M^{-1} cm^{-1} (482 nm, acetonitrile).

Polarographic halfwave reduction potentials ($E_{1/2}^{red}$) of the quencher molecules were measured in acetonitrile vs. a saturated calomel electrode (SCE) using a Metrohm Polarecord E 506 polarograph. The halfwave oxidation potentials ($E_{1/2}^{ox}$) were determined in acetonitrile vs. SCE with a PC-connected cyclovoltammetry apparatus. The supporting electrolyte was 0.1 M tetrabutylammonium hexafluorophosphate (Fluka). Ferrocene was used as internal reference and the potentials were converted to SCE with the value of + 0.395 V determined for the redox couple ferrocene/ferrocenium. For some quencher molecules, improvements in the electrochemical measurements have led to redox potentials slightly different from those reported previously [3] (deviations of less than 0.1 V). Details of the electrochemical measurements will be published separately [20].

3. Results and discussion

In Fig. 1, the singlet (extinction coefficient ϵ_S) and triplet (extinction coefficient ϵ_T) absorption and fluorescence emission spectra of DAP in methylcyclohexane are shown. The triplet absorption spectrum was obtained after sensitization with anthracene or chrysene as triplet energy donors and has been corrected for ground state depletion in the range of spectral overlap with the singlet absorption spectrum. A summary of the photophysical properties of DAP determined in this study is given in Table 1. A comparison with the corresponding data for perylene (see Table 1) shows that the spectral and photophysical properties of singlet and triplet DAP and perylene are very similar. In particular, both molecules are highly fluorescent with fluorescence quantum yields Φ_F close to unity. (Previously, for DAP, values of $\Phi_F = 0.84$ in CHCl$_3$ [1] and $\Phi_F = 0.81$ in MeOH [2] were determined in air-saturated solvents.)

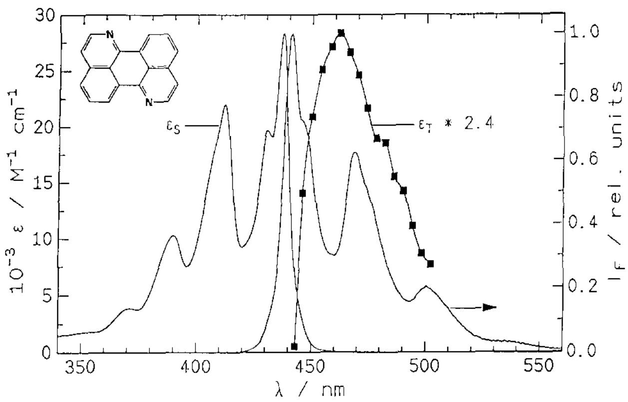

Fig. 1. Singlet and triplet absorption and fluorescence emission spectra of DAP in methylcyclohexane at room temperature.

Table 1
Photophysical properties of singlet and triplet DAP (in methylcyclohexane) and of the radical ions DAP$^+$ and DAP$^-$ (in acetonitrile) at room temperature. Also given are the measured halfwave oxidation ($E_{1/2}^{ox}$) and reduction ($E_{1/2}^{red}$) potentials, the vertical ionization potential (IP$_v$) and, for comparison, the corresponding data for perylene (Per)

Parameter	DAP	Per [a]
10^{-3} ϵ_S (M^{-1} cm^{-1}) (λ_{max})	27 (437 nm)	40 (433 nm)
E(S$_1$) (eV)	2.80	2.85
Φ_F	0.97 ± 0.03	0.98 [b]
τ_F (ns) [c]	6.2 ± 0.2	5.5
10^{-3} ϵ_T (M^{-1} cm^{-1})	12.5 ± 1.5 (462 nm)	14 ± 1 (482 nm)
E(T$_1$) (eV)	(1.5) [d]	1.55 [e]
Φ_{ISC}	0.015 ± 0.004	0.01
τ_T (μs) [f]	570 ± 60	300
10^{-3} ϵ_K (M^{-1} cm^{-1})	20 ± 3 (562 nm)	35 [g] (535 nm)
10^{-3} ϵ_A (M^{-1} cm^{-1})	29 ± 3 (520 nm)	59 [h] (577 nm)
$E_{1/2}^{red}$ (V) [i]	−1.28	−1.73
$E_{1/2}^{ox}$ (V) [i]	(1.55) [j]	1.00
IP$_v$ (eV) [k]	7.5 [b]	6.9 [l], 7.0 [m]

[a] Results from Refs. [3,4,21,22] in acetonitrile, if not denoted otherwise.

[b] From Ref. [15].

[c] Fluorescence lifetimes.

[d] Estimated value (by comparison with perylene).

[e] From Ref. [23].

[f] These triplet lifetimes may be affected by oxygen and impurity quenching.

[g] From Ref. [24].

[i] Halfwave potentials vs. SCE measured in acetonitrile. From Ref. [25].

[j] Irreversible oxidation peak (see text).

[k] Vertical ionization potentials.

[l] From Ref. [26].

[m] From Ref. [27].

Cyclic voltammetry of DAP in acetonitrile reveals an irreversible oxidation peak at approximately 1.55 V vs. SCE. Reversible DAP oxidation is not observed which indicates that the lifetime of the electrochemically produced radical cation (^{2}DAP$^+$) is small (see below).

The vertical ionization potentials (IP_v) of perylene and DAP have been measured using photoelectron spectroscopy by Rademacher [26] (see Table 1). A comparison of the two molecules shows the expected trend: due to the electron-accepting nature of the nitrogen atoms, DAP has a higher (π electron) ionization potential (and is more readily reduced than perylene). Often, linear relationships between ionization and oxidation potentials are invoked for the calculation of the latter ($E_{1/2}^{ox} = a + b \times IP_v$). However, after a review of several correlations in use for aromatic hydrocarbons (e.g. from Pysh and Yang [28]) or azaaromatics (e.g. from Miller et al. [29]), we came to the conclusion that a reliable estimation of $E_{1/2}^{ox}$ of DAP cannot be achieved. (Probably the best estimation can be obtained by combination of the experimental results available for perylene and DAP, i.e. $E_{1/2}^{ox}$(perylene) $- E_{1/2}^{ox}$(DAP) $= b \times \{IP_v(\text{perylene}) - IP_v(\text{DAP})\} = b \times \{0.55 \pm 0.05\}$. With $b = 0.8 \pm 0.15$ [28,29], $E_{1/2}^{ox}$(DAP) $= 1.44 \pm 0.15$ V vs. SCE is then calculated.) Therefore due to the lack of better information, we have taken the irreversible oxidation peak as the half-wave oxidation potential of DAP: $E_{1/2}^{ox} = 1.55$ V vs. SCE.

The quenching of $^1DAP^*$ fluorescence by eight organic quencher molecules in their singlet ground states was investigated using stationary fluorescence measurements in acetonitrile and benzene solutions (Table 2). The standard free energy change (ΔG_{CS}) for the intermolecular electron transfer leading to a charge separation (CS) process and oxidative or reductive DAP fluorescence quenching was calculated using the Weller equation. Experimental fluorescence quenching rate constants k_q^F (Table 2) were obtained using the modified Stern–Volmer equation introduced by Weller [31]. Diffusion coefficients were estimated from the empirical relationship of Othmer and Thakar [32]. For DAP in acetonitrile, $D = 1.5 \times 10^{-5}$ cm^2 s^{-1} at 298 K was obtained. A more detailed discussion of the influence of diffusion coefficients on fluorescence quenching is presented in Ref. [33].

The log k_q^F values are presented, together with the results from the fluorescence quenching of perylene [3], as a function of ΔG_{CS} in Figs. 2 and 3 (Rehm–Weller plots). The curve in Fig. 2 was calculated using the usual kinetic scheme for electron transfer quenching processes in solution and the original parameters reported by Rehm and Weller for the quenching of several aromatic molecules by electron donors in acetonitrile [34]. In Fig. 3, the ΔG_{CS} values obtained for acetonitrile are also taken for benzene as solvent and the full curve in Fig. 3 was calculated as for Fig. 2, except that the lower rate constant of diffusion in benzene was taken into account. Details of the data evaluation and of the calculation of the Rehm–Weller curves are given in Ref. [3]. The results presented in Figs. 2 and 3 support the following observations.

(1) In both solvents, the k_q^F values measured for perylene and DAP tend to be larger than predicted by the original Rehm–Weller parameters; this is particularly evident in the endergonic regime ($\Delta G_{CS} > 0$), e.g. for 9-bromophenanthrene (9) or 1-bromonaphthalene (4) as quenchers.

(2) No systematic difference is discernible in the dependence of k_q^F on ΔG_{CS} for the fluorescence quenching of perylene and DAP; it is remarkable that, for 1-bromonaphthalene (4), which leads to oxidative fluorescence quenching of perylene and

Table 2

Standard free energy changes of charge separation (ΔG_{CS}) and bimolecular rate constants of DAP fluorescence quenching (k_q^F) in acetonitrile and benzene (estimated accuracy of k_q^F is ±10% if $k_q^F \geq 10^8$ M^{-1} cm^{-1}). Also given are the measured halfwave oxidation and reduction potentials of the quencher molecules

Number	Quencher	Acetonitrile				Benzene
		$E_{1/2}^{ox}$ (V) [a]	$E_{1/2}^{red}$ (V) [a]	ΔG_{CS} (eV) [b]	k_q^F (M^{-1} s^{-1})	k_q^F (M^{-1} s^{-1})
1	1,3-Dinitrobenzene	>2.3 [c]	-0.89	-0.36 [d]	1.7×10^{10}	2.0×10^{10}
2	Nitrobenzene	>2.3 [c]	-1.14	-0.11 [d]	2.0×10^{10}	3.1×10^9
3	9-Cyanoanthracene	1.52	-1.43	0.0 [e]	1.3×10^{10}	3.8×10^9
4	1-Bromonaphthalene	1.85	-2.17	0.33 [e]	9.3×10^8	1.8×10^8
5	Bromobenzene	2.54	-2.32 [f]	1.02 [e]	$<10^6$	$<10^6$
6	1-Bromopyrene	1.38	-1.75	-0.14 [e]	–	6.3×10^9
7	9-Bromophenanthrene	1.81	-2.03	0.29 [e]	–	1.1×10^9
8	Anthracene	1.09 [f]	-1.96 [f]	-0.43 [e]	1.4×10^{10}	–

[a] Halfwave potentials vs. SCE measured in acetonitrile [20].

[b] Calculated from the Weller equation (without a work term correction): $\Delta G_{CS} = E_{1/2}^{ox}(D) - E_{1/2}^{red}(A) - E(^1DAP^*)$.

[c] Estimated from $E_{1/2}^{ox}$ (benzene) $= 2.30$ V vs. SCE [30].

[d] For oxidative fluorescence quenching of $^1DAP^*$.

[e] For reductive fluorescence quenching of $^1DAP^*$.

[f] From Ref. [30].

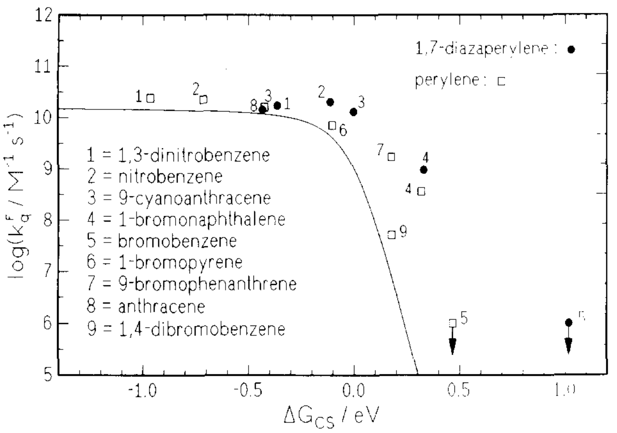

Fig. 2. Logarithmic rate constants of DAP fluorescence quenching (k_q^F) as a function of the standard free energy change for charge separation (ΔG_{CS}) in acetonitrile. The quencher molecules 1 and 2 lead to oxidative fluorescence quenching and 3–8 to reductive fluorescence quenching of $^1DAP^*$ (see Table 2). The curve was calculated with the original parameters given by Rehm and Weller [34]. The results for perylene (oxidative fluorescence quenching) are from Ref. [3].

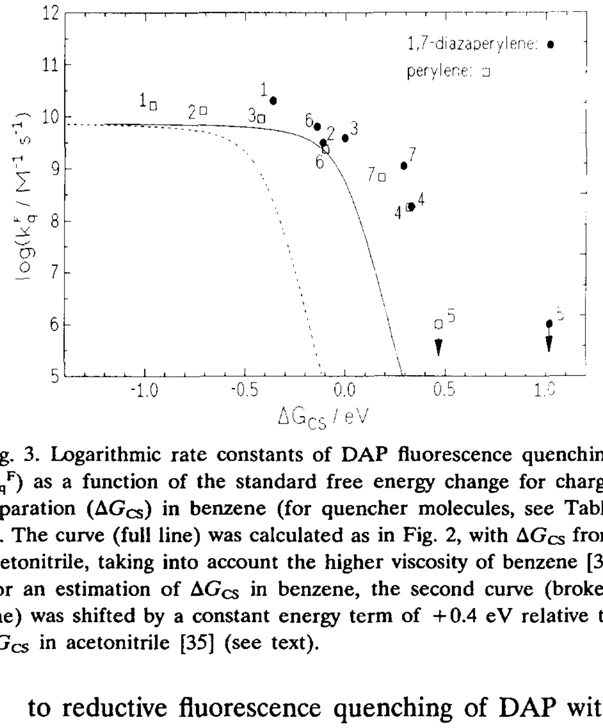

Fig. 3. Logarithmic rate constants of DAP fluorescence quenching (k_q^F) as a function of the standard free energy change for charge separation (ΔG_{CS}) in benzene (for quencher molecules, see Table 2). The curve (full line) was calculated as in Fig. 2, with ΔG_{CS} from acetonitrile, taking into account the higher viscosity of benzene [3]. For an estimation of ΔG_{CS} in benzene, the second curve (broken line) was shifted by a constant energy term of +0.4 eV relative to ΔG_{CS} in acetonitrile [35] (see text).

to reductive fluorescence quenching of DAP with coincidentally almost identical ΔG_{CS} values, the k_q^F values are very similar in both solvents.

(3) No evidence has been found to indicate that the presence of N atoms in DAP, and hence the different charge distribution in comparison with perylene, leads to different electron transfer behaviour in the fluorescence quenching processes, e.g. as expressed in so-called "multiple Rehm–Weller plots" proposed by Jacques and coworkers [13,14]. This may be due to the fact that the lowest DAP ionization potential corresponds to "π ionization" [26].

(4) To account approximately for the energy difference between free ion pairs in strongly polar solvents and contact ion pairs in non-polar solvents, we have attempted to estimate ΔG_{CS} for the non-polar solvents by adding a constant energy of +0.4 eV to ΔG_{CS} in acetonitrile [35]. During an investigation of the quenching of the fluorescence of phenanthrene and substituted phenanthrenes by amines, Chen et al. [11] found a constant energy difference of +0.7 eV between ΔG_{CS} in cyclohexane and acetonitrile. It is obvious from Fig. 3 that calculated Rehm–Weller curves obtained in this way (broken line) do not describe the experimental k_q^F values adequately. Thus it can be concluded that, for the fluorescence quenching of both perylene and DAP, the difference between the Coulomb and solvation energies is significantly smaller in acetonitrile and benzene solvents than predicted by the dielectric continuum model of electrostatics [7–10].

(5) In previous work, we have observed deviations from the Rehm–Weller curve in the endergonic fluorescence quenching of perylene for heavy-atom-substituted quencher molecules and have taken this as indirect evidence for the participation of intermolecular singlet–triplet energy transfer in the fluorescence quenching process [3]. However, our time-resolved laser flash spectroscopic investigation of the quenching of DAP fluorescence did not provide evidence for the intermediate formation of quencher molecules in the triplet state. As before [3], we therefore have no conclusive proof for the occurrence of intermolecular singlet–triplet energy transfer.

In an attempt to improve our understanding of the intermolecular deactivation of $^1DAP^*$, we have investigated the spectral properties of the DAP radical ions formed as primary products during fluorescence quenching in polar solvents. The absorption spectra of $^2DAP^+$ (extinction coefficient ϵ_K) and $^2DAP^-$ (extinction coefficient ϵ_A), as generated by laser flash photolysis in acetonitrile, are shown in Fig. 4. After dye laser excitation of DAP (λ_{exc} = 440 nm), the reductive fluorescence quenching of $^1DAP^*$ by anthracene (^{1}Ant) in nitrogen-saturated acetonitrile leads to the formation of $^2DAP^-$

$$^1DAP^* + {}^1Ant \longrightarrow {}^2DAP^- + {}^2Ant^+ \qquad (\Delta G_{CS} = -0.43\ eV) \quad (1)$$

The anthracene radical cation $^2Ant^+$ was identified by the appearance of its characteristic absorption band in the near-IR region (650–800 nm) [36]. (A recent comprehensive experimental and theoretical investigation of the anthracene radical cation can be found in Ref. [37].) With the known $^2Ant^+$ absorption spectrum, the simultaneous time-resolved detection of the $^2DAP^-$

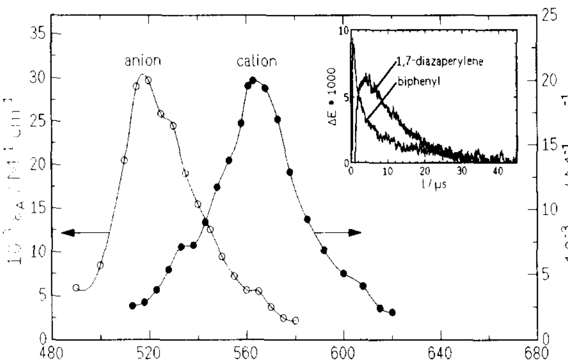

Fig. 4. Absorption spectra of $^2DAP^+$ and $^2DAP^-$ generated by flash photolysis in acetonitrile. The inset shows the absorbance signals (ΔE) due to secondary electron transfer reactions: $^2BP^+$ (monitored at 670 nm) and $^2DAP^+$ (monitored at 562 nm).

and $^2Ant^+$ absorbance signals allows a quantitative determination to be made of the $^2DAP^-$ extinction coefficient. Taking $\epsilon_K = 11\,600$ M^{-1} cm^{-1} at $\lambda_{max} = 724$ nm, previously determined for $^2Ant^+$ (in 1,2-dichloroethane) [38], and assuming that $^2DAP^-$ and $^2Ant^+$ are formed in a 1 : 1 ratio, we calculate for $^2DAP^-$ a value of $\epsilon_A = 31\,200$ M^{-1} cm^{-1} at $\lambda_{max} = 520$ nm (Table 1, Fig. 4). In air-saturated acetonitrile, the formation of $^2DAP^-$ was not detected, which is presumably due to the rapid quenching of the radical anion by electron transfer to oxygen resulting in the formation of the superoxide anion (O_2^-).

Surprisingly, we have not been able to detect $^2DAP^+$ by simple oxidative fluorescence quenching of $^1DAP^*$. The employment of several quencher molecules with suitable electron- accepting properties, for example 1,3-dinitrobenzene (^1DNB), led to diffusion-controlled quenching of $^1DAP^*$ fluorescence in acetonitrile (see Fig. 2) but not to a detectable absorbance due to $^2DAP^+$

$$^1DAP^* + {}^1DNB \not\longrightarrow {}^2DAP^+ + {}^2DNB^- \qquad (\Delta G_{CS} = -0.36 \text{ eV}) \quad (2)$$

This failure to detect $^2DAP^+$ during the oxidative fluorescence quenching of $^1DAP^*$ is discussed below.

The DAP radical cation $^2DAP^+$ can conveniently be generated by the method of secondary electron transfer elaborated by Gould et al. [39]. In our measurements, photoexcited 9,10-dicyanoanthracene ($^1DCA^*$) was used as energy donor to produce, in an intermolecular CS reaction, biphenyl cations $^2BP^+$ (Eq. (3)), which can undergo a secondary charge shift (CSh) reaction with ^1DAP (Eq. (4))

$$^1DCA^* + {}^1BP \longrightarrow {}^2DCA^- + {}^2BP^+ \qquad (\Delta G_{CS} = -0.03 \text{ eV}) \quad (3)$$

$$^2BP^+ + {}^1DAP \longrightarrow {}^1BP + {}^2DAP^+ \qquad (\Delta G_{CSh} = -0.41 \text{ eV}) \quad (4)$$

Our experiments were performed by dye laser excitation of DCA at 377 nm in air-equilibrated acetonitrile. From the simultaneously detected time-resolved absorbance signals (see inset in Fig. 4) of $^2BP^+$ (with $\epsilon_K = 14\,500$ M^{-1} cm^{-1} at $\lambda_{max} = 670$ nm [39]) and $^2DAP^+$, we obtained for $^2DAP^+$ a value of $\epsilon_K = 20\,000$ M^{-1} cm^{-1} at $\lambda_{max} = 562$ nm (Table 1, Fig. 4). The experimental lifetime of $^2DAP^+$ was $\tau_K = 13$ μs. These results indicate that the failure to detect the radical cation in DAP fluorescence quenching experiments cannot be explained by extraordinary low values of ϵ_K or τ_K for $^2DAP^+$.

The reason why the radical cation $^2DAP^+$ was not observed in our experiments can be understood if the kinetics of the charge recombination (CR) reactions are considered. Taking, as in Eq. (2), the example of ^1DNB as quencher molecule, we expect the diffusion-controlled formation of the radical ion pair $^1(^2DAP^+ \cdots {}^2DNB^-)$ and its subsequent CR deactivation

$$^1(^2DAP^+ \cdots {}^2DNB^-) \longrightarrow {}^1DAP + {}^1DNB \qquad (\Delta G_{CR} = -2.44 \text{ eV}) \quad (5)$$

The $^2DAP^+$ formation efficiency as a function of the quencher concentration [^1DNB] is then calculated according to

$$\Phi_K = \Phi_{sep}\Phi_{IP} = \Phi_{sep}[1 - (k_q{}^F\tau_F[^1DNB] + 1)^{-1}] \quad (6)$$

where Φ_{IP} is the efficiency of ion pair formation, $\Phi_{sep} = k_{sep}/(k_{CR} + k_{sep})$ is the efficiency of separation into free ions, $k_{sep} = 5 \times 10^8$ s^{-1} is the rate constant of separation into free ions [4], k_{CR} is the rate constant of the CR process (Eq. (5)) and $\tau_F = 6.0$ ns is the fluorescence lifetime in acetonitrile. Even with the highest quencher concentration employed ([^1DNB] = 0.0064 M), no $^2DAP^+$ absorbance signal was observed. Given the detection limit of our apparatus, this indicates a cation formation efficiency of $\Phi_K \leqslant 0.01$ and an estimated rate constant of $k_{CR} \geqslant 10^{10}$ s^{-1} (Eq. (6)).

A quantitative interpretation of the dependence of k_{CR} on ΔG_{CR} in the theoretical framework of non-adiabatic electron transfer reactions has been performed by Gould et al. [39] and ourselves [4,5]. As predicted by Marcus theory, plots of log k_{CR} vs. ΔG_{CR} exhibit a characteristic bell-shaped behaviour. The ΔG_{CR} regime of maximum k_{CR} values is essentially determined by the reorganization energy λ, and the absolute magnitude of k_{CR} is directly proportional to the square of the electronic matrix coupling element V. The rate constant estimated here for the CR deactivation of the radical ion pair according to Eq. (5) ($k_{CR} \geqslant 10^{10}$ s^{-1} for

$\Delta G_{CR} = -2.44$ eV) is in general accordance with corresponding results from CR reactions with perylene [4,5]. Hence, if we tentatively assume that the reorganization energies involved in CR reactions with perylene and DAP in acetonitrile are similar ($\lambda \approx 1.5$ eV), it can be estimated that the matrix element for the spin-allowed CR reaction in Eq. (6) is $V \geqslant 10^{-3}$ eV.

4. Conclusions

In this work, a comparison of the quenching of DAP and perylene fluorescence in acetonitrile and benzene solutions was made. It was found that, in both solvents, the bimolecular rate constants of fluorescence quenching can approximately be described by Rehm–Weller plots with the standard free energy changes of charge separation ΔG_{CS} as determined in acetonitrile solutions. Our results indicate that the difference between the Coulomb and solvation energies in both solvents is significantly smaller than predicted by the dielectric continuum model of electrostatics. Further investigations are necessary to clarify the influence of polarity on electron transfer reactions particularly in low-polarity solvents.

Acknowledgements

It is a pleasure to thank the following colleagues for making available results of their measurements and for fruitful discussions: Professor Dr. P. Rademacher (Universität Essen), photoelectron spectroscopy of DAP; Dr. J. Salbeck (Hoechst AG, Frankfurt am Main), spectroelectrochemical measurements of DAP; Dr. T. Kircher (TU Braunschweig), measurements of redox properties; J. Küster (TU Braunschweig), measurements of fluorescence lifetimes. Financial support by the Deutsche Forschungsgemeinschaft (DFG) and the Fond der Chemischen Industrie is also gratefully acknowledged.

References

[1] C. Naumann and H. Langhals, *Chem. Ber., 123* (1990) 1881.
[2] L.B.-Å. Johansson, J. Karolin, H. Langhals, S. Reichherzer, N. v. Füner and K. Polborn, *J. Chem. Soc., Faraday Trans., 89* (1993) 49.
[3] F. Lewitzka and H.-G. Löhmannsröben, *Z. Phys. Chem. NF, 169* (1990) 181.
[4] F. Lewitzka and H.-G. Löhmannsröben, *Z. Phys. Chem. NF, 169* (1990) 203.
[5] T. Kircher and H.-G. Löhmannsröben, *GIT Fachz. Lab., 9* (1992) 914.
[6] J. Salbeck, H. Kunkely, H. Langhals, R.W. Saalfrank and J. Daub, *Chimia, 43* (1989) 6.
[7] J.A. Schmidt, J.-Y. Liu, J.R. Bolton, M.D. Archer and V.P.Y. Gadzekpo, *J. Chem. Soc., Faraday Trans. 1, 85* (1989) 1027.
[8] H. Heitele, P. Finckh, S. Weeren, F. Pöllinger and M.E. Michel-Beyerle, *J. Phys. Chem., 93* (1989) 5173.
[9] P. Suppan, *J. Chem. Soc., Faraday Trans. 1, 82* (1986) 509.
[10] P. Suppan, *Chimia, 42* (1988) 320.
[11] J.-M. Chen, T.-I. Ho and C.-Y. Mou, *J. Phys. Chem., 94* (1990) 2889.
[12] T. Niwa, K. Kikuchi, N. Matsusita, M. Hayashi, T. Katagiri, Y. Takahashi and T. Miyashi, *J. Phys. Chem., 97* (1993) 11 960.
[13] N. Ghoneim, C. Hammer, E. Haselbach, D. Pilloud, P. Suppan and P. Jacques, *J. Chem. Soc., Faraday Trans., 89* (1993) 4271.
[14] P. Jacques and X. Allonas, *J. Photochem. Photobiol. A: Chem., 78* (1994) 1.
[15] J.B. Birks (ed.), *Organic Molecular Photophysics*, Vol. 2, Wiley, New York, 1975.
[16] J.B. Birks, *Photophysics of Aromatic Molecules*, Wiley, New York, 1970.
[17] H. Dreeskamp, T. Salthammer and A.G.E. Läufer, *J. Lumin., 44* (1989) 161.
[18] C. Burgdorff, S. Ehrhardt and H.-G. Löhmannsröben, *J. Phys. Chem., 95* (1991) 4246.
[19] I. Carmichael and G.L. Hug, *J. Phys. Chem. Ref. Data, 15* (1986) 1.
[20] T. Kircher and H.-G. Löhmannsröben, to be published; T. Kircher, *PhD Thesis*, Braunschweig, 1993.
[21] F. Lewitzka, H.-G. Löhmannsröben, M. Strauch and W. Lüttke, *J. Photochem. Photobiol. A: Chem., 61* (1991) 191.
[22] M. Komfort, H.-G. Löhmannsröben and T. Salthammer, *J. Photochem. Photobiol. A: Chem., 51* (1990) 215.
[23] R.H. Clarke and R.M. Hochstrasser, *J. Mol. Spectrosc., 32* (1969) 309.
[24] N. Mataga, T. Asahi, Y. Kanda, T. Okada and T. Kakitani, *Chem. Phys., 127* (1988) 249.
[25] J. Jagur-Grodzinski, M. Feld, S.L. Yang and M. Szwarc, *J. Phys. Chem., 69* (1965) 628.
[26] P. Rademacher, personal communication, May 1994.
[27] R. Boschi, E. Clar and W. Schmidt, *J. Chem. Phys., 60* (1974) 4406.
[28] E.S. Pysh and N.C. Yang, *J. Am. Chem. Soc., 85* (1963) 2124.
[29] L.L. Miller, G.D. Nordblom and E.A. Mayeda, *J. Org. Chem., 37* (1972) 916.
[30] C.K. Mann and K.K. Barnes, *Electrochemical Reactions in Nonaqueous Systems*, Marcel Dekker, New York, 1970.
[31] A. Weller, *Z. Phys. Chem. NF, 13* (1957) 335.
[32] D.F. Othmer and M.S. Thakar, *Ind. Eng. Chem., 45* (1953) 589.
[33] F. Schael and H.-G. Löhmannsröben, *J. Photochem. Photobiol. A: Chem.*, to be submitted.
[34] D. Rehm and A. Weller, *Ber. Bunsenges. Phys. Chem., 73* (1969) 834.
[35] A. Weller, *Z. Phys. Chem. NF, 133* (1982) 93.
[36] A. Kira, S. Arai and M. Imamura, *J. Phys. Chem., 76* (1972) 1119.
[37] J. Szczepanski, M. Vala, D. Talbi, O. Parisel and Y. Ellinger, *J. Chem. Phys., 98* (1993) 4494.
[38] Y. Wang, J.J. Tria and L.M. Dorfman, *J. Phys. Chem., 83* (1979) 1946.
[39] I.R. Gould, D. Ege, J.E. Moser and S. Farid, *J. Am. Chem. Soc., 112* (1990) 4290.