References and Notes

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(2) (a) J. Berger, A. I. Rachlin, W. E. Scott, L. H. Sternbach, and M. W. Goldberg, *J. Am. Chem. Soc.* **73**, 5295 (1951). (b) Yu. A. Ovchinnikov, V. T. Ivanov, and A. M. Shkrob, "Membrane-Active Complexones", Elsevier, Amsterdam, 1974, pp 77, 78.

(3) E. C. Bissel and I. C. Paul, *Chem. Commun.*, 967 (1972).

(4) C. A. Maier and I. C. Paul, *Chem. Commun.*, 181 (1971).

(5) S. M. Johnson, J. Herrin, S. J. Lin, and I. C. Paul, *Chem. Commun.* 72 (1970): S. M. Johnson, J. Herrin, S. J. Lin, and I. C. Paul, *J. Am. Chem. Soc.*, **92**, 4228 (1970).

(6) H. Degani and H. Friedman, *Biochemistry*, **13**, 5022 (1974).

(7) J. R. Clark, *Rev. Pure Appl. Chem.*, **13**, 50 (1963); D. H. Templeton, *Acta Crystallogr.*, **13**, 684 (1960); as cited in ref 6.

(8) A. V. Stuart and G. B. B. M. Sutherland, *J. Chem. Phys.* **24**, 559 (1956).

(9) S. Krimm, C. Y. Liang, and G. B. B. M. Sutherland, *J. Chem. Phys.*, **24**, 778 (1956).

(10) W. Weltner, Jr., *J. Am. Chem. Soc.*, **77**, 3941 (1955).

(11) N. B. Colthup, L. H. Daley, and S. E. Wiberley, "Introduction to Infrared and Raman Spectroscopy", Academic Press, New York, N.Y., 1964, pp 269–277.

(12) M. Avram and G. Mateescu, "Infrared Spectroscopy", Wiley-Interscience, New York, N.Y., 1972, pp 250–289, 384–415.

Wurster's Blue as a Fluorescence Quencher for Anthracene, Perylene, and Fluoranthene

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Received October 6, 1975

Abstract: The Wurster's Blue cation radical (TMPD$^+$, where TMPD = *N,N,N′,N′*-tetramethyl-*p*-phenylenediamine) strongly quenches fluorescence from anthracene, perylene, and fluoranthene in acetonitrile. Apparent stationary second-order rate constants from fluorescence yield data are 4.9×10^{10}, 8.6×10^{10}, and 3.1×10^{10} M^{-1} s^{-1}, respectively. Such large values indicate a long-range interaction and support Förster's transfer as the mechanism. Quantitative comparisons have been made with the Yokota–Tanimoto treatment of resonance transfer in a diffusing system. For these tests, all necessary parameters, viz., fluorescence yields (Φ_f), lifetimes (τ_0), diffusion coefficients (D), and critical transfer radii (R_0), were evaluated experimentally.

Radicals and radical ions have received interest as quenchers of aromatic singlets[1-10] because they may exert important limitations on emission yields from chemiluminescent systems, liquid scintillators, or other samples subjected to radiation damage. The interaction itself is also interesting from a mechanistic standpoint because several possible quenching modes exist. These species are often easily reduced or oxidized; thus reversible charge transfer quenching of the type demonstrated first by Leonhardt and Weller[11-16] is conceivable. Alternatively, Förster's transfer according to

$$^1A^* + {}^2Q \rightarrow A + {}^2Q^* \qquad (1)$$

is allowed, so that a long-range interaction might occur.[17,19] In addition, the paramagnetism in the quenching radical may cause exchange-induced intersystem crossing to be important.[20]

Van Duyne studied the quenching of several long-lived aromatic hydrocarbon singlets by the cation radical of *N,N,N′,N′*-tetramethyl-*p*-phenylenediamine (TMPD$^+$, the Wurster's Blue cation) in acetonitrile.[9] He reported rate constants up to 3.0×10^{10} l./mol·s, which is significantly above the diffusion-controlled limit for collisional quenching (about 2.0×10^{10} l./mol·s).[9,15,16] Furthermore, there was a correlation between the quenching rate constant and the spectral overlap for singlet emission and TMPD$^+$ absorption. From this evidence he suggested that Förster's transfer was a significant element in the quenching process.

Independently, Lisovskaya et al.[10] showed that diphenylpicrylhydrazyl free radicals can quench singlets even in solid matrices. Their work has given strong support to the idea of efficient long-range singlet-doublet resonance transfer.

We report here some studies of the quenching of anthracene, perylene, and fluoranthene fluorescence by TMPD$^+$ in acetonitrile. The rate constants are very large, and there is a strong correlation with the product of the spectral overlap integral and the fluorescer's oscillator strength; hence the Förster mechanism appears to operate. Several theories have been advanced to describe resonance energy transfer in diffusing systems,[21-29] and we have chosen the widely cited one by Yokota and Tanimoto[27] for comparison with our data. Strictly quantitative tests are possible in these cases, because all parameters required by the theory, including diffusion coefficients, have been evaluated experimentally.

Experimental Section

Blue-violet fluorescence grade anthracene (Eastman or Aldrich) or Prinz quality material (Princeton Organics, 99.999%, zone refined) was used without further purification. There were no noticeable differences in behavior. Fluoranthene (Eastman, White Label) and perylene (Aldrich, Gold Label) were also used as received.

Wurster's Blue perchlorate (TMPD$^+$ClO$_4^-$) was synthesized by an adaptation of the procedure of Michaelis and Granick.[30] The starting material was *N,N,N′,N′*-tetramethyl-*p*-phenylenediamine dihydrochloride (Eastman), but it was half-neutralized with NaOH upon dissolution into the water-methanol reaction solvent. Oxidation to TMPD$^+$ was accomplished with a stoichiometric amount of bromine generated at reaction time by the addition of a slight excess of H_2SO_4 to an aqueous solution of NaBr and $NaBrO_3$. This solution was added dropwise with stirring to the cold TMPD solution. Good purity in the product could be obtained only when the reaction temperature was at or below −10°. The precipitated TMPD$^+$ClO$_4^-$ was filtered, washed, and recrystallized from methanol.

The purity of this product was monitored by its absorbance maximum at 566 nm as measured on a Cary Model 14 or a Coleman Model 124 spectrophotometer. Beer's law plots were linear and showed $\epsilon = (1.29 \pm 0.02) \times 10^4$ for acetonitrile solutions. This figure is comparable to the value of 1.26×10^4 for 568 nm reported by Van Duyne for coulometrically generated TMPD$^+$.[9]

Spectroquality acetonitrile from Aldrich, Eastman, Burdick and Jackson, and Matheson Coleman and Bell were used without further purification and without noticeable differences in behavior. Solutions of TMPD$^+$ in these solvents showed stable absorbances for at least

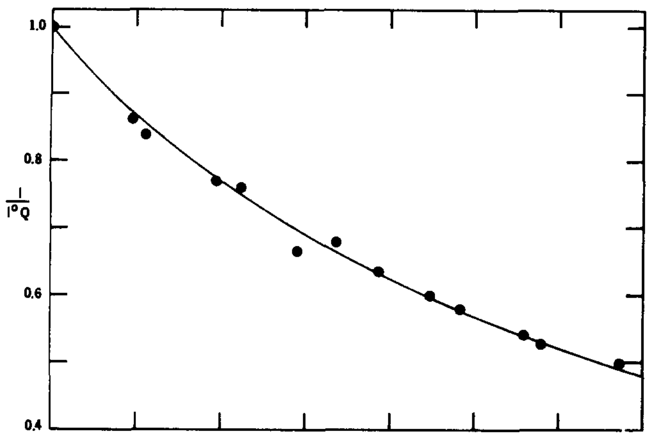

Figure 1. Quenching of anthracene fluorescence by Wurster's Blue. Solid curve is eq 4 for $\langle R_0 \rangle$ = 24.2 Å. The curve for R_0^* = 24.3 Å is indistinguishable on this scale.

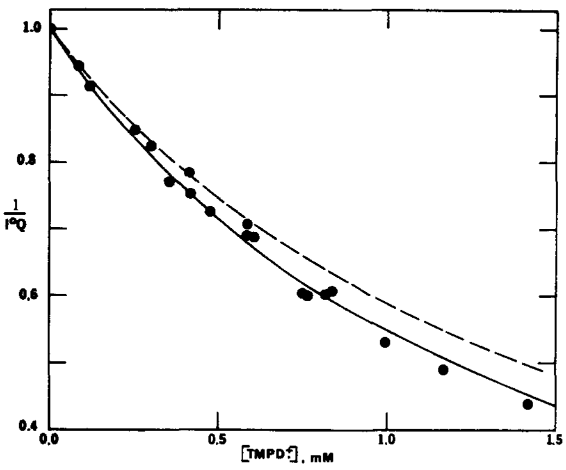

Figure 2. Quenching of perylene fluorescence by Wurster's Blue. Solid curve is eq 4 for $\langle R_0 \rangle$ = 40.1 Å. Broken curve is for R_0^* = 36.9 Å.

Table I. Extinction Coefficients for Acetonitrile Solutions

Substance	Wavelength, nm	ε, l./mol·cm × 10^{-3}
Anthracene	248	102 ± 2
	252	163 ± 2
Fluoranthene	280.4	16.5 ± 0.2
	287	41.9 ± 0.2
Perylene	436	32.4 ± 0.3
$TMPD^+ClO_4^-$	248	3.17 ± 0.04
	280.4	1.27 ± 0.03
	287	1.53 ± 0.02
	420	0.563 ± 0.006
	436	0.528 ± 0.006
	467	1.47 ± 0.03
	566 (max)	12.9 ± 0.02

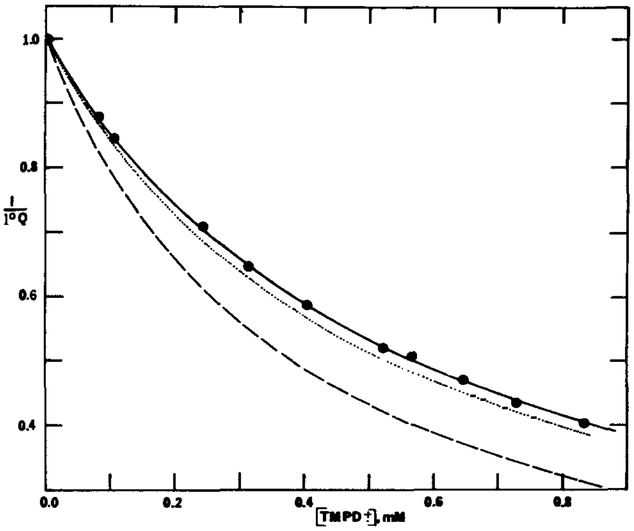

Figure 3. Quenching of fluoranthene fluorescence by Wurster's Blue. Solid curve is eq 4 for $\langle R_0 \rangle$ = 25.6 Å. Broken curve is for R_0^* = 33.3 Å. Dotted curve is eq 6 for R_0^* = 33.3 Å.

the several hours needed to perform the experiments.

Fluorescence intensity measurements were made on an Aminco-Bowman fluorescence spectrometer. Excitation was carried out frontally with light from a 200-W Xe-Hg lamp, and emission was recorded via a Hamamatsu R446S or 1P21 photomultiplier. Spectral correction factors were obtained by the quantum counter technique of Melhuish[31] and were verified by comparing corrected quinine sulfate spectra against published data.[32]

Fluorescence lifetimes were acquired from measurements on the phase and modulation apparatus of Spencer and Weber.[33] Excitation of the samples took place at a right angle by light selected through a monochromator. Perylene samples were excited at 430 nm and emission was observed through a Corning C.S. 3-73 filter. Anthracene was excited at 340 nm, and its emission was observed through Oriel G-772-3900 and G-774-4000 filters.

All fluorescence measurements were made on solutions that were deoxygenated by bubbling with acetonitrile-saturated argon or nitrogen, and an oxygen-free blanket of gas remained over the solutions during the measurements themselves.

These studies were carried out at room temperature, which was 25 ± 2 °C.

Results

Fluorescence Quenching. Because $TMPD^+$ is a strong absorber throughout nearly all the spectral range of interest and the half-quenching concentrations are in the millimolar range, one must work with solutions that are optically very dense in fluorescer in order to avoid severe inner filter effects. We employed constant anthracene, perylene, and fluoranthene concentrations of 1.00, 1.00, and 2.00 mM, respectively. Excitation was effected by mercury lines at 248 (for anthracene), 436 (for perylene), and 280.4 nm (for fluoranthene), and the extinction coefficients given in Table I show that the absorbances of these solutions due to the fluorescer alone were such that 90% of the light was absorbed in less than 0.3 mm.

Self-absorption effects were not present for fluoranthene, whose absorption and emission spectra overlap only very weakly, but both anthracene and perylene showed some distortions in their emission curves. Corrected anthracene spectra featured first and second maxima at 380 and 402 nm. The ratio of their intensities differed by less than 5% in spectra taken at 10^{-6} and 10^{-3} M, so it seems unlikely that self-absorption will noticeably influence the quenching results discussed below. For perylene, these peaks were at 442 and 470 nm, and their height ratio I_{442}/I_{470} was 1.13 at 10^{-6} M and 0.98 at 10^{-3} M. This effect probably is not entirely negligible.

The results of the quenching experiments are shown in Figures 1-3. The ordinate in each case is $I/(I^0Q)$, where I^0 is the intensity observed for the emitter at the fixed wavelength of observation in the absence of $TMPD^+ClO_4^-$ and I is the intensity observed at the indicated quencher concentration. Emission was recorded at 420 nm for anthracene and at 467 nm for perylene and fluoranthene. The factor Q is included to correct for the inner filter effect and is given by

$$Q = \frac{\epsilon_{F,1}[F]}{\epsilon_{F,1}[F] + (\epsilon_{Q,1} + \epsilon_{Q,2})[Q]}$$

where F refers to the fluorescer, Q to the quencher, subscript

Table II. Fluorescence Quantum Yields

Substance	Concentration, M[a]	Φ_f
Anthracene	1.00×10^{-4}	0.23
	1.00×10^{-3}	0.23
Fluoranthene	1.01×10^{-3}	0.25
	1.30×10^{-2}	0.25
Perylene	9.95×10^{-4}	0.89

[a] In acetonitrile.

1 to the wavelength of excitation, and subscript 2 to the wavelength of observation. This expression is easily derived from the law of optical absorption under the assumptions that excitation is carried out and emission is observed at normal incidence. These conditions are essentially true for the experimental configuration employed. It should be noted, however, that the expression for Q does not take into account secondary fluorescence arising from self-absorption. If that factor is not important, then $I/(I^0Q)$ is proportional to the quantum yield ratio Φ_f/Φ_f^0. The excitation coefficients needed for the evaluation of Q were determined from Beer's law plots and are given in Table I. Values of Q ranged only from 1.00 to 0.89.

An additional study showed that anthracene emission is not quenched by tetra-n-butylammonium perchlorate at concentrations up to 8 mM. The perchlorate ion, therefore, has no role in the fluorescence quenching by $TMPD^+ClO_4^-$.

Likewise, ground-state complexation can be ruled out as a contributor to the quenching effect. Over the 450-1000-nm range, the absorption spectra of solutions containing 5.10×10^{-5} M $TMPD^+ClO_4^-$ and 1.00 mM anthracene, perylene, or fluoranthene were indistinguishable from that of a solution containing only the Wurster's Blue perchlorate.

Fluorescence Quantum Yields. The emission yields for fluoranthene, anthracene, and perylene in acetonitrile were determined via the method for high optical densities reviewed by Demas and Crosby,[34] and the results are summarized in Table II. Excitation in each case was carried out with the 248-nm Hg line, and the absorbance of each solution was 10 cm^{-1} or greater. The areas of corrected spectra were computed, and quantum yields were calculated under the assumption that anthracene in ethanol at 10^{-4} M has $\Phi_f = 0.27$.[34] The refractive index correction for normal viewing and the Melhuish correction for reabsorbed emission were both applied.[35] The latter was calculated according to Melhuish's limiting case for emission isolated to the first millimeter of solution depth. It lowered the apparent yield (ratio of areas and refractive indices only) by 13% for perylene and 1% for anthracene at 10^{-3} M. It had no effect on any result for fluoranthene or on the anthracene yield for 10^{-4} M.

Not surprisingly, the yields are comparable to those reported for these compounds in other media.[19,34-37] Anthracene appears to have a slightly lower yield in acetonitrile than in many other solvents. This effect is not an artifact due to self-quenching. Careful intensity measurements at 420 nm under conditions of high optical density to 252-nm excitation showed that anthracene's quantum yield declines only at concentrations greater than 5×10^{-4} M, and the decrease from the level value at lower concentrations is only about 5% in going to 10^{-3} M. Similar results were reported by Melhuish for other media.[35] The perylene yield in acetonitrile is essentially the same as that reported for solutions in ethanol (0.87) and benzene (0.89) by Melhuish,[35] but it is slightly lower than the Dawson and Windsor value for ethanol (0.94).[37] From the data of Melhuish, it appears that the yield in Table II is depressed by about 5% from the dilute solution value as a consequence of self-quenching.[35] The fluoranthene yield in acetonitrile is the same as that reported by Birks[19] after renormalizing the data of Berlman et al. for cyclohexane.[38] Parker, Hatchard, and Joyce found a value of 0.21 in ethanol.[39] Self-quenching is not a factor for fluoranthene, as the comparison of values for 10^{-3} and 1.3×10^{-2} M shows.

Fluorescence Lifetimes. A deoxygenated 10^{-5} M anthracene solution showed a fluorescence decay time of 4.8 ns. The studies of concentration quenching mentioned above indicate that at 10^{-3} M the decay time is reduced to 4.6 ns, so this figure has been used in the discussion below.

Perylene at 10^{-5} M in deaerated solution has a lifetime of 5.8 ns. This, too, would be slightly reduced at 10^{-3} M by self-quenching, but a precise correction could not be obtained.

Van Duyne has already reported a value of 52.6 ns for fluoranthene in acetonitrile.[9] This figure should be independent of concentration at least to 10^{-2} M.

Diffusion Coefficients. Adams et al.[40-42] have determined diffusion coefficients for several aromatic substances in acetonitrile solution. Each of their values was determined in at least two ways. From their data, we have taken values for anthracene and perylene at 25° to be 2.9×10^{-5} and 2.3×10^{-5} cm^2/s, respectively.

Dvorak et al. showed that the limiting current for TMPD oxidation to $TMPD^+$ at a rotating platinum electrode in acetonitrile was only 1% larger than that for oxidation of p-phenylenediamine.[43] These results imply that the diffusion coefficients for the two substances are essentially equal. Miller et al.[40,41] have given $D = 2.0 \times 10^{-5}$ cm^2/s for p-phenylenediamine at 25° in acetonitrile, and we have taken this figure also for $TMPD^+$.

The diffusion coefficient for fluoranthene under the same conditions appears to be $(2.6 \pm 0.2) \times 10^{-5}$ cm^2/s. This figure was obtained in two ways. First, cyclic voltammetric data[44] for an acetonitrile solution of thianthrene and fluoranthene showed a ratio of peaks indicating $D = 2.4 \times 10^{-5}$ cm^2/s for fluoranthene, given $D = 2.9 \times 10^{-5}$ cm^2/s for thianthrene.[45] These figures apply to solutions containing supporting electrolyte. Extrapolation by the viscosity factor to zero electrolyte gives $D = 2.7 \times 10^{-5}$ cm^2/s for fluoranthene. Secondly, the chronocoulometric data of Bezman and Faulkner for N,N-dimethylformamide solutions of 9,10-diphenylanthracene (DPA)[46] and fluoranthene[47] indicate that fluoranthene's diffusion coefficient is 1.15 times larger than that for DPA. If Walden's rule holds, the data of Bacon and Adams for DPA in electrolyte-free acetonitrile imply that $D = 2.4 \times 10^{-5}$ cm^2/s for fluoranthene.

Discussion

Apparent stationary second-order rate constants k_q can be calculated from the data of Figures 1-3 by the technique of Rehm and Weller.[15,16] That is,

$$\frac{\Phi_f}{\Phi_f^0} = \frac{I}{I^0Q} = \frac{\exp(-\lambda k_q \tau_0 [Q])}{1 + k_q \tau_0 [Q]} \tag{2}$$

with

$$\lambda = \frac{k_q}{4\pi N'}\left[\frac{(\Phi_f/\Phi_f^0)}{D^3\tau_0}\right]^{1/2} \tag{3}$$

where D is the relative diffusion coefficient (sum of quencher and fluorescer coefficients), N' is Avogadro's number per millimole, and τ_0 is the fluorescer lifetime for $[Q] = 0$. Given k_q, τ_0, D, and [Q], the theoretical ratio Φ_f/Φ_f^0 is found by successive approximation. For the data sets at hand, k_q values were found such that the least-squares condition was satisfied when each point was given equal weight. These rate constants are reported as (k_q) in Table III; the corresponding theoretical functions are indistinguishable from the solid curves in Figures 1-3.

Weller's theory of diffusion-controlled reactions, on which this procedure is based, takes into account transient quenching

Table III. Parameters for Quenching by TMPD$^+$

	Experimental^a			Theoretical				
Fluorescer	(k_q), M^{-1} s^{-1}	R_c, Å	(R_0), Å	$R_0{}^*$,^{b} Å	10^{33} $(R_0{}^*)^6/\tau_0$, cm^6/s	$\bar{r}$, Å	$\bar{r}/R_0{}^*$	$k_q{}^*$,^{c} M^{-1} s^{-1}
Perylene	8.6×10^{10}	26	40.1	36.9^d	390	71	1.9	7.7×10^{10}
Anthracene	4.9×10^{10}	13	24.2	24.3	45	67	2.8	4.9×10^{10}
Fluoranthene	3.1×10^{10}	8.9	25.6	33.3	26	220	6.6	4.5×10^{10}

^{a} Calculated by fitting to experimental data. ^{b} Calculated from overlap integral and $\Phi_f{}^0$. ^{c} Calculated by fitting the Yokota–Tanimoto relation (4) for $R_0{}^*$ to the Weller equation (2). ^{d} $\Phi_f{}^0$ taken as 0.94. See text.

effects via the numerator in (2).[48] This treatment involves the conditions of collisional quenching, viz., unit reaction probability for approach of reaction centers to radius R_c and no forces between centers at distances larger than R_c. Then k_q is the Smoluchowski value $4\pi N'DR_c$.

Values of R_c corresponding to k_q are also included in Table III. The effective quenching radii for anthracene and perylene are plainly much larger than the values (~6 Å) normally seen for collisional quenching;[15,16] hence a long range interaction such as dipole-dipole coupling is indicated. For fluoranthene, the situation is less clear. However, k_q is significantly larger than the rate constants previously reported for the quenching of fluorescence from fluoranthene itself[9] or several other species of similar size[16] by TMPD (1.5-2.0×10^{10} l/mol s).

Critical transfer radii $R_0{}^*$ for the alternative of Förster's quenching have been computed from spectral overlap integrals and Φ_f values and are included in Table III.[17,19] According to the Förster theory, the energy transfer rate at any distance between reactants is proportional to $(R_0{}^*)^6/\tau_0$.[17,19] If the resonance mechanism applies, this ratio should correlate with (k_q), and Table III shows that it actually does for the cases at hand. Direct proportionality is not expected because each of these systems involves diffusion by distances comparable to or greater than $R_0{}^*$.[19,21] This is seen in the table entries for $\bar{r} = (2D\tau_0)^{1/2}$, which is the root mean square diffusion distance for time τ_0. The diffusion process tends to increase the effective quenching rate for weakly interacting systems to a greater extent than for strongly coupled ones. Any comparison between theory and experiment must therefore be related to a treatment expressly accounting for the influence of diffusion. Of the several available approaches,[19,21-29] that by Yokota and Tanimoto[27] is among the most useful because it involves few approximations and, in one form, is expressed analytically:

$$\frac{\Phi_f}{\Phi_f{}^0} = \frac{1}{\tau_0} \int_0^\infty \exp(-t/\tau_0) \exp\{-2B\gamma(t/\tau_0)^{1/2}\} \, dt \qquad (4)$$

where $B = [(1 + 10.87x + 15.5x^2)/(1 + 8.743x)]^{3/4}$ with $x = D\alpha^{-1/3}t^{2/3}$, $\alpha = R_0{}^6/\tau_0$, and $\gamma = 2\pi^{3/2}N'R_0{}^3[Q]/3$. Given D, R_0, τ_0, and [Q], one calculates the theoretical value of $\Phi_f/\Phi_f{}^0$ by numeric integration. Birks and his co-workers, who have supplied the only extensive tests of this theory, found approximate agreement with measured data.[49,50] Their comparisons retained some ambiguity, because the diffusion coefficients were usually calculated from the Stokes–Einstein relation. In the present case, all the necessary parameters are available from experimental information; hence one can make a rigorous comparison between the actual and predicted quenching curves.

We have fitted each data set to (4) by finding R_0 such that the least-squares condition is satisfied for equally weighted points. These values are listed in Table III; their corresponding functions are displayed as the solid curves in Figures 1-3. The strictly theoretical curves (i.e., those calculated from spectroscopic $R_0{}^*$ and experimental D and τ_0 values) are given as dashed traces in the figures.

For anthracene, the agreement between theory and experiment is obviously excellent, but significant deviations are noted for the other systems. In the case of perylene, the actual quenching rate seems larger than that predicted by (4). Several effects might account for this observation: (1) self-absorption could lengthen the effective lifetime; (2) secondary fluorescence is emitted mainly at points deeper in solution than the primary emission,[35] so that the effective value of Q could be smaller than that applied; (3) the effects of excitation migration (either by radiative or nonradiative means) may not be wholly negligible;[51,52] (4) higher multipole interactions possibly contribute.[18] Points 1 and 2 definitely apply, and an approximate calculation suggests that they could account for the entire discrepancy. Points 3 and 4 are difficult to evaluate, but cannot be wholly discounted. Under the circumstances, the agreement between the Yokota–Tanimoto treatment and the experimental data for anthracene and perylene seems good, and it supports both the quantitative validity of the theory (in this range of $\bar{r}/R_0{}^*$) and the Förster mechanism for the quenching of these compounds by TMPD$^+$.

The discrepancy for fluoranthene cannot be understood in similar terms, because negative deviations from the predicted quenching rate do not usually arise from artifacts and secondary effects like those enumerated above. Instead, it appears that either fluoranthene is a less effective donor than one would anticipate from $R_0{}^*$ or (4) is inaccurate for $\bar{r} \gg R_0{}^*$.

The latter is more likely. In deriving (4), Yokota and Tanimoto obtained B as a Padé approximant to a power series in x.[27] Its range of validity is unknown. The value of the series is extremely sensitive to $\bar{r}/R_0$, and at larger ratios the approximation may become less reliable (note that $x(\tau_0) = \frac{1}{2}(\bar{r}/R_0{}^*)^2$). It is easily seen that in the limit of large x, B approaches $[15.50x/8.743]^{3/4}$ and the argument of the second exponential in (4) becomes linear in both time and [Q]. The constant of proportionality is therefore equivalent to the second-order rate constant k_q, where

$$k_q = (0.91)4\pi N'D^{3/4}\tau_0{}^{-1/4}R_0{}^{3/2} \qquad (5)$$

Yokota and Tanimoto approached this limiting condition in a more direct way via a scattering length method, and they found

$$k_q = (0.676)4\pi N'D^{3/4}\tau_0{}^{-1/4}R_0{}^{3/2} \qquad (6)$$

Thus the Padé approximant may overestimate B substantially in the limit of large x. A tendency for (4) to predict too high a quenching rate as $(\bar{r}/R_0{}^*)$ increases is also noticeable in the figures reported by Birks and Leite for the quenching of naphthalene fluorescence by DPA in several solvents with successively smaller viscosities.[50]

For fluoranthene, $x(\tau_0) = 21.8$ and the asymptotic case for (4) is approached quite closely; thus one could expect (6) to be a better approximation to the data. As Figure 3 shows, this expectation is borne out. The dotted curve there is the quenching function predicted by (6) from the fluoranthene parameters τ_0, D, and $R_0{}^*$.

In summary, we have corroborated Van Duyne's suggestion that TMPD$^+$ quenches aromatic singlets by a long range interaction,[9] and the evidence is persuasive that Förster's transfer applies. If this point is accepted, our results also serve as a strict test of the Yokota–Tanimoto treatment for transfer in diffusing systems. On the basis of these limited data, their result from the Padé approximant method seems accurate for $\bar{r}/R_0^*$ values near 2 or 3 and probably for lower values as well. For ratios above 7, the limiting result for $\bar{r} \gg R_0^*$, as obtained from the scattering length method, is a much better choice. However, more data in the region of $\bar{r}/R_0^* \geq 5$ are needed to clarify the validity of (6) in view of Swenberg and Stacy's criticism of it.[53]

Acknowledgment. We are grateful to Professor G. Weber for the use of his phase and modulation apparatus and to the National Science Foundation for supporting this work with Grants GP-37335X and MPS-75-05361.

References and Notes

(1) B. Stevens, *Trans. Faraday Soc.*, **51**, 610 (1955).
(2) J. T. Dubois, *J. Chem. Phys.*, **25**, 178 (1956).
(3) G. Porter and M. W. Windsor, *Proc. R. Soc. London, Ser. A*, **245**, 238 (1958).
(4) A. L. Buchachenko, M. S. Khlopyankina, and S. N. Dobryakow, *Opt. Spektrosk.*, **22**, 304 (1967).
(5) S. Siegel and H. S. Judeikis, *J. Chem. Phys.*, **48**, 1613 (1968).
(6) J. T. Bowman, Ph.D. Dissertation, University of Texas at Austin, 1970.
(7) J. B. Birks, *J. Lumin.*, 1, 154 (1970).
(8) J. A. Green, II, L. A. Singer, and J. H. Parks, *J. Chem. Phys.*, **58**, 2690 (1973).
(9) R. P. Van Duyne, *J. Am. Chem. Soc.*, **95**, 7164 (1973).
(10) I. A. Lisovskaya, V. G. Plotnikov, and M. V. Alfinov, *Opt. Spektrosk.*, **35**, 1091 (1973).
(11) H. Leonhardt and A. Weller, *Ber. Bunsenges. Phys. Chem.*, **67**, 791 (1963).
(12) A. Weller, *Pure Appl. Chem.*, **16**, 115 (1968).
(13) A. Weller, Proceedings of the International Exciplex Conference, London, Ontario, May 1974, in press.
(14) N. Mataga in ref 13.
(15) D. Rehm and A. Weller, *Ber. Bunsenges. Phys. Chem.*, **73**, 834 (1969).
(16) D. Rehm and A. Weller, *Isr. J. Chem.*, **8**, 259 (1970).
(17) Th. Förster, *Discuss. Faraday Soc.*, **No. 27**, 7 (1959); and references contained therein.
(18) D. L. Dexter, *J. Chem. Phys.*, **21**, 836 (1953).
(19) J. B. Birks, "Photophysics of Aromatic Molecules", Wiley, New York, N.Y., 1970, and references contained therein.
(20) G. J. Hoytink, *Acc. Chem. Res.*, **2**, 114 (1969).
(21) I. M. Rozman, *Izv. Akad. Nauk SSSR, Ser. Fiz.*, **36**, 922 (1972), and references contained therein.
(22) Yu. A. Kurskii and A. S. Selivanenko, *Opt. Spektrosk.*, **8**, 643 (1960).
(23) M. D. Galanin and I. M. Franck, *JETP*, **21**, 114 (1961).
(24) K. S. Bagdasaryan and A. L. Muler, *Opt. Spektrosk.*, **18**, 990 (1965).
(25) R. Voltz, G. Laustriat, and A. Coche, *J. Chim. Phys., Phys.-Chim. Biol.*, **63**, 1253 (1966).
(26) J. Feitelson, *J. Chem. Phys.*, **44**, 1497 (1966).
(27) M. Yokota and O. Tanimoto, *J. Phys. Soc. Jpn.*, **22**, 279 (1967).
(28) I. Z. Steinberg and E. Katchalski, *J. Chem. Phys.*, **48**, 2404 (1968).
(29) M. M. Agrest, S. F. Kilin, M. M. Rikenglaz, and I. M. Rozman, *Opt. Spektrosk.*, **27**, 946 (1969).
(30) L. Michaelis and J. Granick, *J. Am. Chem. Soc.*, **65**, 1747 (1943).
(31) W. H. Melhuish, *J. Opt. Soc. Am.*, **52**, 1256 (1962).
(32) W. H. Melhuish, *J. Res. Natl. Bur. Stand., Sect. A*, **76**, 547 (1972).
(33) R. D. Spencer and G. Weber, *Ann. N. Y. Acad. Sci.*, **158**, 361 (1969).
(34) J. N. Demas and G. A. Crosby, *J. Phys. Chem.*, **75**, 991 (1971).
(35) W. H. Melhuish, *J. Phys. Chem.*, **65**, 229 (1961).
(36) C. A. Parker, "Photoluminescence of Solutions", Elsevier, Amsterdam, 1968, and references contained therein.
(37) W. R. Dawson and M. W. Windsor, *J. Phys. Chem.*, **72**, 3251 (1968).
(38) I. B. Berlman, H. O. Wirth, and O. J. Steingraber, *J. Am. Chem. Soc.*, **90**, 566 (1968).
(39) C. A. Parker, C. G. Hatchard, and T. A. Joyce, *J. Mol. Spectrosc.*, **14**, 311 (1964).
(40) T. A. Miller, B. Lamb, K. Prater, J. K. Lee, and R. N. Adams, *Anal. Chem.*, **36**, 418 (1964).
(41) T. A. Miller, B. Prater, J. K. Lee, and R. N. Adams, *J. Am. Chem. Soc.*, **87**, 121 (1965).
(42) J. Bacon and R. N. Adams, *Anal. Chem.*, **42**, 524 (1970).
(43) V. Dvorak, I. Nemec, and J. Zyka, *Microchem. J.*, **12**, 324 (1967).
(44) H. Tachikawa, unpublished results.
(45) C. P. Keszthelyi, H. Tachikawa, and A. J. Bard, *J. Am. Chem. Soc.*, **94**, 1522 (1972).
(46) R. Bezman and L. R. Faulkner, *J. Am. Chem. Soc.*, **94**, 6317 (1972).
(47) R. Bezman and L. R. Faulkner, *J. Am. Chem. Soc.*, **94**, 6331 (1972).
(48) A. Weller, *Z. Phys. Chem.* (*Frankfurt am Main*), **13**, 335 (1957).
(49) J. B. Birks and S. Georghiou, *J. Phys. B*, 1, 958 (1968).
(50) J. B. Birks and M. S. S. C. P. Leite, *J. Phys. B*, **3**, 513 (1970).
(51) A. I. Burshtein, *JETP*, **62**, 1695 (1972).
(52) S. I. Golubov and Y. V. Konobeev, *Phys. Status Solidi B*, **56**, 69 (1973).
(53) C. E. Swenberg and W. T. Stacy, *Phys. Status Solidi B*, **36**, 717 (1969).

Reactions of π-Allylnickel Bromide Complexes with Quinones. Synthesis of Isoprenoid Quinones

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Abstract: The reaction of π-allylnickel bromide complexes with quinones under a standard set of conditions results in a 1:1 mixture of allylhydroquinone and hydroquinone (eq 1). By varying reaction conditions, production of allylhydroquinones can be favored in some cases. This method was used to synthesize coenzyme Q_1 (**6**) and plastoquinone-1 (**9**). With various dimethylbenzoquinones, the allyl group is introduced exclusively at the noncarbonyl ring site of highest spin density in the corresponding radical anion, leading either to allylhydroquinones or enediones. Electron transfer processes are thought to be involved.

Introduction

Isoprenoid quinones play a pivotal role in the electron transport chain in both photosynthetic and respiratory processes.[2] The usual method of synthesis of these compounds involves a Lewis acid-catalyzed reaction between the appropriate allylic alcohol and hydroquinone, followed by oxidation to the quinone.[3] This method suffers from side reactions such as cyclization of the unsaturated side chain, cyclization of the isoprenoid hydroquinone to the chromanol, and polyalkylation of the aromatic ring. Recently vitamin K,[4] coenzyme Q_1,[5] and vitamin E[6] analogues have been synthesized in moderate yields by a multistep procedure involving as a key step the well-known[7] reaction of π-allylnickel halide complexes with the appropriate aryl halide of the protected hydroquinone. A preliminary communication from this laboratory reported a direct reaction of π-allylnickel bromide complexes with quinones to produce allylhydroquinones (eq 1). We report herein the full details of this study.

Results and Discussion

Synthetic Studies. The course of the reaction between π-allylnickel bromides and quinones was quite sensitive to reaction conditions, small changes in conditions often resulting in significantly altered yields and product distributions. The results of a series of reactions between a variety of nickel complexes and quinones under similar conditions (1 mol of