for which coulombic-induced transfer has been involved,[24,26,27] most of the points, except those of anthracene, lie fairly close to the theoretical line for $k_q{}^c$ vs. $R_0{}^{1/2}D^{3/4}/\tau^{1/4}$. Using the Yokota–Tanimoto line, one estimates for fluorene–DBH ($R_0 = 25.5$ Å) in cyclohexane a $k_q{}^c$ of 2.0×10^{10} M^{-1} sec^{-1}; the experimental value is 1.83×10^{10} M^{-1} sec^{-1}. In the case of anthracene, it seems best to plot Ware's experimental values[27] of k_q vs. $R_0{}^{1/2}D^{3/4}/\tau^{1/4}$ and interpolate the value of k_q at $R_0 = 13.6$ Å. The value so obtained is $k_q{}^c = (1.9 \pm 0.6) \times 10^{10}$ M^{-1} sec^{-1}. The experimental value for anthracene–cis-AIP is 2.51×10^{10} M^{-1} sec^{-1}.

Conclusions and Problems

This study shows that the influence of coulombic and exchange interactions on the rate of singlet energy transfer can often be separated to a good degree of approximation. The data allow estimates to be made for U_e. Since U_c can be determined directly from spectral data, eq 2, 5, and 8 allow a reasonably good estimate to be made for the quenching constant (k_q) of any aromatic–azo pair.

There are, however, problems that remain. Although the diffusion-controlled quenching constants do depend upon solvent viscosity in the expected manner, the points for hexane do not differ from those for cyclohexane as much as one would expect from eq 9 (see Figure 4). Since the hexane data were taken from a different study,[6] there is always the possibility of a small

systematic error. The reason why the k_q for fluorene–trans-ATB lies below that for fluorene–trans-AIP (Table III) is also puzzling. It should not be due to a steric effect since we ran the quenching of triphenylene by azo-trans-octane, a very bulky azo compound, and obtained a k_q of 3.5×10^9 M^{-1} sec^{-1}, which is close to that of triphenylene–trans-ATB. Finally, we should mention the perylene–trans-AIP point (Figure 2). Perylene has a very high extinction coefficient (ϵ_{max} 39,500 M^{-1} cm^{-1}) but its Franck–Condon overlap integral with trans-AIP is vanishingly small. Therefore, both coulombic-induced and exchange-induced transfer should be precluded; nevertheless, the quenching constant is significant. Leonhardt and Weller[28] reported that aniline (IP = 7.7 eV) quenches perylene fluorescence with $k_q = 7.7 \times 10^9$ M^{-1} sec^{-1} in acetonitrile and with $k_q = 1.6 \times 10^7$ M^{-1} sec^{-1} in benzene. Since it seemed possible that the IP for trans-ATB could be low,[29] a charge-transfer complex could account for the high quenching constant for perylene–trans-AIP. We ran this pair in acetonitrile and also in cyclohexane, but as can be seen from Figure 2, the data afford no support for the idea of a charge-transfer complex.

(27) W. R. Ware, *J. Amer. Chem. Soc.*, **83**, 4374 (1961).

(28) H. Leonhardt and A. Weller, "Luminescence of Organic and Inorganic Materials," H. P. Kallman and G. M. Spruch, Ed., Wiley, New York, N. Y., 1962, p 74.

(29) E. Haselbach and E. Heilbronner, *Helv. Chim. Acta*, **53**, 684 (1970).

Concerning the Role of Steric Factors in the Quenching of Alkylbenzene Fluorescence by Dienes[1,2]

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Abstract: The quenching of alkylbenzenes fluorescence by cis-piperylene has been studied for benzene and 22 mono- and polyalkylated benzenes. Rate constants, k_q, have been obtained from Stern–Volmer slopes and independently measured singlet lifetimes. The k_q values seem to be relatively independent of the number and size of the alkyl substituents, changing only significantly when two or three tert-butyl groups are appended to the ring. It is proposed that in the exciplex the interplanar distance between quencher and quenchee is 4.0 to 5.5 Å.

There has been considerable recent interest in the possible role of steric factors in bimolecular "photophysical" processes involving contact or near contact between partners.[3–6] The quenching of fluorescence

(1) Organic Photochemistry. XXVI. Part XXV: F. Scully, J. Grutzner, and H. Morrison, *J. Amer. Chem. Soc.*, **95**, 5100 (1973).

(2) Abstracted from the doctoral dissertation of P. Froehlich, Purdue University, August 1971; presented, in part, at the 162nd National Meeting of the American Chemical Society, Washington, D. C., Sept 1971.

(3) P. J. Wagner, J. M. McGrath, and R. G. Zepp, *J. Amer. Chem. Soc.*, **94**, 6883 (1972).

(4) A. Yekta and N. J. Turro, *Chem. Phys. Lett.*, **17**, 31 (1972).

(5) J. C. Dalton, D. M. Pond, and N. J. Turro, *J. Amer. Chem. Soc.*, **92**, 2173 (1970).

(6) K. Janda and F. S. Wettack, *J. Amer. Chem. Soc.*, **94**, 305 (1972).

of aromatic hydrocarbons by dienes is believed to be such a process, occurring via a transitory complex (exciplex) of the lowest excited singlet of the aromatic hydrocarbon with the ground state of the diene.[7] The suggested fate of the exciplex is outlined in eq 1, where

$$A^* + Q \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} (AQ)^* \overset{k_2}{\longrightarrow} A_v + Q_v \qquad (1)$$
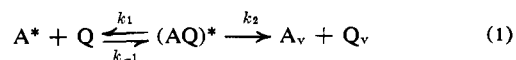
A^* is the aromatic hydrocarbon in its electronically excited singlet state, Q is the quencher, $(AQ)^*$ is the

(7) (a) L. M. Stephenson, D. G. Whitten, G. F. Vesley, and G. S. Hammond, *J. Amer. Chem. Soc.*, **88**, 3665 (1966); (b) D. A. Labianca, G. N. Taylor, and G. S. Hammond, *ibid.*, **94**, 3679 (1972), and reference therein.

exciplex, and A_v and Q_v are vibrationally excited levels of the ground electronic states.[7b] The rate constant for fluorescence quenching (k_q) is therefore a function of k_1, k_2, and k_{-1} as indicated below.[7b]

$$k_q = k_1 k_2 / (k_{-1} + k_2) \qquad (2)$$

This exciplex is thus an example of the type of process described above and, as a means of better defining our physical picture of this species, it is of interest to determine its steric requirements. Ideally, one would like to delineate the influence of structural factors on each of the components of k_q, but in practice such an approach has not proven feasible in the attempts made in this direction.[7b] Rather, one is forced to study overall changes in quenching rate as a function of various parameters, including not only steric interactions[7b,8] but (a) the ionization potential of the diene,[9] (b) the electron affinity of the aromatic hydrocarbon excited singlet state,[7b] (c) solvent polarity,[10] and (d) the vibrational modes (C–H or C–C) involved in deactivation of the exciplex.[11]

The efforts of other workers have primarily been directed at substituted polycyclic aromatics with very little information yet available for benzene and its derivatives.[12,13] We have extended our earlier studies with toluene and 1-phenyl-2-butene[12] and have determined Stern–Volmer slopes for quenching of a number of alkylbenzenes using cis-piperylene; these data, together with independently measured singlet lifetimes,[14] allow the extraction of k_q, and our results and interpretations are presented below.

Results and Discussion

Stern–Volmer plots have been obtained for the fluorescence quenching of hexane solutions of benzene and 22 alkylbenzenes using cis-piperylene. The associated slopes ($k_q\tau$) and measured lifetimes are presented in Tables I, II, and III, together with calculated k_q values.

A rapid perusal of these tables indicates (a) the quenching rate constants are quite high,[12] approaching the diffusion-controlled value[15] of 2.1×10^{10} l. mol^{-1} sec^{-1} (and some 60 times faster than comparable quenching in the naphthalene system),[8] and (b) somewhat unexpectedly in the light of early reports with naphthalene derivatives,[8] only modest changes in k_q result from increasing steric bulk about the ring. With respect to the latter point, it is only with 1,3,5-tri-tert-butylbenzene (cf. Table III) that a large (25-fold decrease relative to toluene) diminution in k_q is observed, although definite trends in this direction can be dis-

(8) L. M. Stephenson and G. S. Hammond, Pure Appl. Chem., 16, 125 (1968).

(9) T. R. Evans, J. Amer. Chem. Soc., 93, 2081 (1971).

(10) G. N. Taylor and G. S. Hammond, J. Amer. Chem. Soc., 94, 3684 (1972).

(11) G. N. Taylor and G. S. Hammond, J. Amer. Chem. Soc., 94, 3687 (1972).

(12) H. Morrison, J. Pajak, and R. Peiffer, J. Amer. Chem. Soc., 93, 3978 (1971), and references therein.

(13) Singlet quenching of several alkylbenzenes by oxygen (see, for example, T. Brewer, J. Amer. Chem. Soc., 93, 775 (1971)) and by chlorocarbons (J. Klein, V. Pinaud-Plazanet, and G. Laustriat, J. Chim. Phys. Physicochim. Biol., 67, 303 (1970)) has been reported. For an interesting discussion of the quenching of 1,4-dimethoxybenzene fluorescence, see F. A. Carroll, M. T. McCall, and G. S. Hammond, J. Amer. Chem. Soc., 95, 315 (1973).

(14) P. M. Froehlich and H. Morrison, J. Phys. Chem., 76, 3566 (1972).

(15) J. G. Calvert and J. N. Pitts, Jr., "Photochemistry," Wiley, New York, N. Y., 1966, p 627.

Table I. Quenching of Straight Chain Aromatic Hydrocarbons by cis-Piperylene in Hexane

Alkylbenzene	n^a	$k_q\tau$, M^{-1} ^{c}	τ, nsec^c	k_q, 10^9 sec^{-1} M^{-1}
Benzene	0	223.5 ± 5.8	33.6 ± 0.5	6.65 ± 0.20
Toluene^b	1	202.1 ± 2.2	35.2 ± 0.4	5.73 ± 0.05
Ethyl-	2	150.9 ± 8.1	35.1 ± 0.5	4.30 ± 0.24
n-Propyl-	3	136.6 ± 6.3	36.0 ± 0.7	3.79 ± 0.17
n-Butyl-	4	122.9 ± 7.3	35.1 ± 0.2	3.50 ± 0.21
n-Hexyl-	6	106.3 ± 7.6	35.3 ± 0.3	3.01 ± 0.21

^{a} Number of carbon atoms in the chain. ^{b} Average of three determinations. ^{c} Errors represent standard deviations of least-squares plots of the data.

Table II. Quenching Data for Branched Chain Benzenes

Alkylbenzene	$k_q\tau$, M^{-1} ^{a}	τ, nsec^a	k_q, 10^9 sec^{-1} M^{-1}
Toluene	202.7 ± 2.2	35.2 ± 0.4	5.73 ± 0.05
Ethyl-	150.9 ± 8.1	35.1 ± 0.5	4.30 ± 0.24
Isopropyl-	100.4 ± 4.9	24.5 ± 0.7	4.10 ± 0.22
Cyclohexyl-	101.0 ± 6.3	29.2 ± 0.5	3.46 ± 0.28
sec-Butyl-	93.9 ± 5.8	29.2 ± 1.2	3.22 ± 0.24
tert-Butyl-	47.4 ± 5.4	10.0 ± 0.4	4.74 ± 0.57
Isobutyl-	131.0 ± 6.2	33.3 ± 0.03	3.93 ± 0.17

^{a} Errors represent standard deviations of least-squares plots of the data.

Table III. Quenching Data for Polysubstituted Benzenes

Alkylbenzene	$k_q\tau$, M^{-1} ^{a}	τ, nsec^a	k_q, 10^9 sec^{-1} M^{-1}
Toluene	202.7 ± 2.2	35.2 ± 0.4	5.73 ± 0.05
1,2-Dimethyl-	156.7 ± 6.8	38.2 ± 0.3	4.10 ± 0.19
1,3-Dimethyl-	138.9 ± 5.3	32.7 ± 0.4	4.25 ± 0.17
1,4-Dimethyl-	151.2 ± 6.6	33.3 ± 0.4	4.54 ± 0.20
1,3,5-Trimethyl-	128.4 ± 9.6	38.5 ± 0.4	3.35 ± 0.25
1,2,3,4-Tetramethyl-	77.8 ± 2.1	33.8 ± 1.3	2.30 ± 0.08
1,2,3,5-Tetramethyl-	103.4 ± 5.0	27.9	3.69 ± 0.18
1,2,4,5-Tetramethyl-	86.5 ± 4.8	28.6 ± 0.3	3.05 ± 0.16
Pentamethyl-	35.9 ± 3.0	15.7 ± 0.6	2.47 ± 0.20
Hexamethyl-	3.17 ± 1.08	<1.6	
Hexaethyl-	0.13 ± 0.69	<1.6	
1,4-Di-tert-butyl-	26.0 ± 1.4	14.5 ± 0.1	1.79 ± 0.09
1,3,5-Tri-tert-butyl-	3.09 ± 1.30	15.1 ± 0.4	0.20 ± 0.08

^{a} Errors represent standard deviations of least-squares plots of the data.

cerned in the smaller changes which occur upon extension of the alkyl chain (Table I) or upon increased substitution about the ring (Table III). Also, 1,4-di-tert-butylbenzene shows a sizable decrease in k_q relative to 1,4-dimethylbenzene (Table III).

This relatively small sensitivity to steric factors, in a quenching act which has been viewed as involving intimate contact between partners, seems contradictory and it is made even more interesting in the light of similar observations for short-range exothermic singlet–singlet[4] and triplet–triplet[3] energy transfer.[16] With respect

(16) Steric inhibition has been reported for singlet interactions between substituted cyclohexanones and electron deficient olefins[5] (a process which appears to have a very specific directional stereoelectronic requirement) and singlet–singlet energy transfer between benzene and aliphatic ketones.[6] The fact that the latter study was made in the gas phase may be of some significance.[4]

to the latter report we have done a preliminary study of phosphorescence quenching of several alkylbenzenes using an isopentane medium at 77°K;[17] the data are presented in Table IV. Though changes in k_q seem

Table IV. Quenching of Alkylbenzene Phosphorescence by cis-Piperylene in Isopentane at 77°K

Compd	$k_q\tau$, M^{-1a}	τ, sec^a	k_q, sec^{-1} M^{-1}
Toluene	942 ± 106	3.50 ± 0.07	269 ± 30
n-Propylbenzene	737 ± 77	3.72 ± 0.03	198 ± 21
Isopropylbenzene	407 ± 53	2.17 ± 0.03	185 ± 24
1,4-Dimethylbenzene	740 ± 196	4.60 ± 0.06	161 ± 42
1,4-Di-tert-butyl-benzene	480 ± 49	3.94 ± 0.03	122 ± 12

^{a} Errors represent standard deviations of least-squares plots of the data.

modest, they may be more significant than is immediately apparent, since the high viscosity of the medium can be expected to inhibit diffusion apart of the partners and thus mask larger steric effects.[3,4]

The relative insensitivity of singlet quenching to methyl substitution, by contrast with the more pronounced response to tert-butyl groups, can be used to estimate the optimum interplanar distance of quencher and quenchee in the exciplex. If one assumes the van der Waals radius of a methyl group to be 2.0 Å,[18] then twice this value or 4.0 Å should represent the minimum interplanar distance between piperylene and the polymethylbenzenes. The exciplex appears to be unaffected by this restriction. On the other hand, the tert-butyl group extends some 3.5 Å above the plane of the benzene ring (see below)[19] and this, together with the 2.0-Å radius for piperylene, makes the interplanar distance some 5.5 Å; this value now seems to lead to significantly less efficient complexation. We thus conclude that the optimum interplanar separation in the exciplex is 4.0 to 5.5 Å.[19] Sasse and coworkers[20] have

$x = \sin 71°$ (1.54 Å); $y = 2.0$ Å; $z = 3.45$ Å
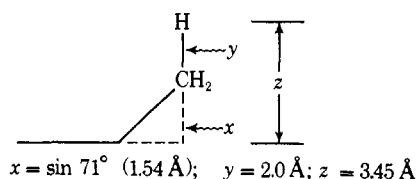
observed a similar variation in sensitivity toward methyl vis-a-vis tert-butyl, in the singlet quenching of alkylnaphthalenes by diphenylacetylene; they concluded, using models, that the interplanar distance in the exciplex is 3–4 Å. Our approach, applied to their system, gives a separation of 3.7 to 5.2 Å (using a van der Waals radius for the π cloud as 1.7 Å[19]), and these numbers compare favorably to our own. It is interesting that similar distances between donor and acceptor have

been suggested[3] for triplet energy transfer in solution.[21]

Finally, there is evidence that singlet exciplexes can serve as precursors to cycloadducts of aromatic hydrocarbons and olefins,[22,23] and it is reasonable to inquire as to the extent that covalent bonding may be intrinsic to the "exciplex" itself. The interplanar distances cited above would suggest that the formation of such covalent bonds plays no role at the exciplex stage.[24]

Experimental Section

Aromatic hydrocarbons and hexane were purified as described earlier.[14] cis-Piperylene was supplied by Chemical Samples Co. and was analyzed for purity by vpc using an Aerograph Autoprep A-700 P instrument equipped with a 20 ft by $^1/_4$ in. 30% oxidipropionitrile column; the purity of the diene was found to be higher than 99%. It was molecularly distilled at room temperature before use. Fluorescence spectra and molar absorption coefficients at 253.7 nm were obtained as discussed elsewhere.[14]

Stern–Volmer Quenching Constants. A stock solution of the aromatic hydrocarbon in hexane ($\sim 10^{-3}$ M) was prepared and varying amounts of the diene were added to aliquots of the stock. The solutions were deoxygenated with argon for 15 min and the fluorescence spectra recorded. The peak height of the stock solution was taken as I_0 and the height of the solution containing both quencher and aromatic hydrocarbon taken as I. A correction was made for background emission. Eight to ten solutions were used for a typical experiment. Correction was made for the difference in absorbance of each solution. A plot of I_0/I vs. quenching concentration, via a least-squares computer program, yielded $k_q\tau$, the Stern–Volmer quenching constant.

Singlet Lifetimes. Singlet lifetimes were obtained with a TRW nanosecond spectral source (TRW Corp., Model 31 A) and associated electronics as described earlier.[14] Samples were prepared in the same way as for the quenching experiments.

Phosphorescence Quenching. The aromatic hydrocarbons and isopentane were purified as described elsewhere.[14] Phosphorescence spectra were recorded on a homemade spectrophotofluorometer[14] using 3-mm Suprasil optical quartz tubes. Samples were deoxygenated by eight freeze–pump–thaw cycles at less than 1 μ. Stern–Volmer data were collected by measuring the emission of a series of solutions containing $\sim 1.5 \times 10^{-3}$ M aromatic hydrocarbon and varying amounts of diene ~ 1–5×10^{-3} M. Correction was made in each intensity for background emission. Phosphorescence peak areas were calculated by a computer program which corrected the spectra and integrated the area.

Triplet lifetimes were obtained by setting the emission monochromator at a wavelength of maximum phosphorescence intensity. A piece of sheet metal $^1/_8$ in. thick was placed between the sample and the light source and the decay curve was displayed on the recorder. The decay curve was analyzed by the first-order kinetic rate expression to determine k_d, the decay constant.

(17) P. Froehlich and H. Morrison, Chem. Commun., 184 (1972); there is no fluorescence quenching under these conditions.

(18) J. M. Robertson in "Determination of Organic Structures by Physical Methods," E. A. Braude and F. C. Nachod, Ed., Academic Press, New York, N. Y., 1955, p 494.

(19) This diagram is comparable to that given by Wagner.[3] We obtain his value of 2.8 Å for the effective "height" of the tert-butyl groups by using the staggered methyls closer to the ring. The exciplex interplanar distance would then be narrowed to 4.0 to 4.8 Å.

(20) W. H. F. Sasse, P. J. Collin, D. B. Roberts, and G. Sugowdz, Aust. J. Chem., 24, 2151 (1971).

(21) It has been noted[7b] that there is no way, at present, to sort out electron affinity and steric effects. However, it is reasonable to presume that the electron affinity of the excited singlet alkylbenzene would decrease as alkyl groups are added to the ring, and k_q would therefore also diminish.[7b] Thus, the effect on k_q would be in the same direction as with steric inhibition, and the surprisingly small effect of alkyl substitution becomes all the more significant.

(22) W. Ferree, Jr., J. Grutzner, and H. Morrison, J. Amer. Chem. Soc., 93, 5502 (1971).

(23) N. C. Yang and J. Libman, J. Amer. Chem. Soc., 94, 1405 (1972).

(24) There is one interesting anomaly in Table I which deserves brief comment; i.e., k_q for tert-butylbenzene is high, higher in fact than for any other monoalkylbenzene. Though the differences under discussion are small, it is tempting to speculate that this observation is related to our earlier report[14] that tert-butylbenzene has an unusually high nonradiative decay rate constant. We attributed this to the number of β hydrogens, and thus C–H stretching vibrations, available for dissipation of electronic energy.[14,25] Though other work[7b] would seem to preclude the involvement of such stretching modes in exciplex decay, a final judgement on this point must await a study of a suitably deuterated derivative.

(25) J. W. Rabalais, H. J. Maria, and S. P. McGlynn, J. Chem. Phys., 51, 2259 (1969).