

- (20) $\text{Eu}(\text{fod})_3$ is tris(6,6,7,7,8,8,8-heptafluoro-2,2-dimethyl-3,5-octanedione)europium.
- (21) This synthesis of **25** has already been reported: S. Wolff, A. B. Smith, III, and W. C. Agosta, *J. Org. Chem.*, **39**, 1607 (1974).
- (22) The lower homologue of **2**, 4-methoxymethyl-4-methylcyclopentenone, rearranges photochemically to an oxabicyclooctanone analogous to **24** and also yields a second bicyclic product which has lost the methoxy carbon atom.² No similar second process was observed with **2**.
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Indirect Detection of a Reversibly Formed Nonfluorescing Exciplex between Benz[*a*]anthracene and *cis*-1,3-Pentadiene. A General Method for Treating Photochemical Kinetic Data^{1a}

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Abstract: Oxygen enhancement of Stern–Volmer plot slopes for the quenching of benz[*a*]anthracene fluorescence by *cis*-1,3-pentadiene in benzene is shown to reveal the presence of a reversibly formed exciplex in this system. In establishing a relationship between experimental lifetime and quantum yield data and the rather complicated rate laws, an iterative least-squares analysis method has been applied which should find general applicability to problems of fitting photochemical kinetic data. The method is also applied to the system benz[*a*]anthracene-7-*d*/*cis*-1,3-pentadiene.

Exciplexes are thought to arise generally from the interaction of electronically excited aromatic hydrocarbon singlets and 1,3-dienes.² When exciplex fluorescence can be detected readily, measurement of quantum yields and lifetimes of this emission as well as that of the parent hydrocarbon can establish the pertinent rate parameters for the system.^{3,4} In the more usual case of weakly fluorescent⁵ or nonfluorescent² exciplexes, establishment of the presence of the exciplex and derivation of rate parameters associated with its formation and decay can be considerably more difficult.⁶ Recent experience with the effect of oxygen on aromatic hydrocarbon/exciplex decay has suggested that fluorescence lifetimes and quantum yields of the parent hydrocarbon alone can yield definitive proof of the existence of an exciplex provided that its formation is reversible.^{3,5,7,8}

The oxygen quenching method for inferring the presence of a nonfluorescing exciplex is applied to the benz[*a*]anthracene (BA)/ and benz[*a*]anthracene-7-*d* (DBA)/*cis*-1,3-pentadiene (P) systems. A method has been developed for correlating the data to the proposed kinetic scheme.

Results

Relative BA and DBA fluorescence quantum yields were determined as a function of [P] in degassed and air-saturated benzene solutions by measuring the reduction of emission intensity at 388 nm (Table I). Data for air-saturated solutions are reported in Table I relative to I_0 for degassed solutions. No

change in the shape of the fluorescence spectra could be detected with addition of P.

Decay rate constants of BA and DBA fluorescence were obtained by monitoring the emission at 430 nm from degassed and air-saturated benzene solutions with and without added P. First-order rate constants and estimated uncertainties are shown in Table II. These rate constants were obtained from semilogarithmic plots of the decaying side of the emission profiles. Visual inspection of these plots showed excellent adherence to single exponential decay.

Discussion

The mechanism

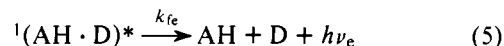
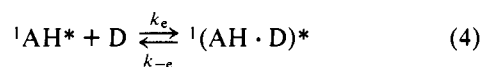
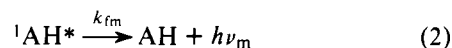


Table I. Quenching of BA and DBA Fluorescence by P^a

[P], M	Degassed		Air-saturated	
	I_0/I^b	I_0/I^c	I_0/I_{ox}^b	I_0/I_{ox}^c
	BA			
0	1.00	1.00	2.71	2.69
0.5	1.06	1.04	2.99	2.84
0.5	1.07	1.04	3.01	2.84
1.0	1.01	1.08	2.99	3.00
1.0	1.07	1.08	3.09	3.00
2.0	1.13	1.17	3.42	3.33
2.0	1.16	1.17	3.52	3.33
2.5	1.16	1.21	3.61	3.50
2.5	1.15	1.21	3.63	3.50
	DBA			
0	1.00	1.00	2.80	2.70
0.5	1.03	1.04	2.91	2.84
1.0	1.07	1.08	3.06	2.98
1.5	1.09	1.12	3.18	3.12
2.0	1.13	1.16	3.27	3.26
2.5	1.18	1.20	3.50	3.41

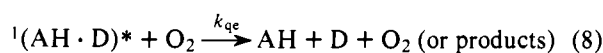
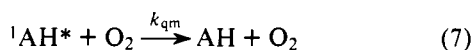
^a [BA] = [DBA] = 1.0×10^{-5} M; BA and DBA measurements carried out at 22.8 and 22.3 °C, respectively. ^b Measured. ^c Calculated; see text.

Table II. Effective First-Order Decay Constants of Emission from BA/P and DBA/P Solutions^a

[P], M	BA		DBA	
	k_{obsd}^b , $s^{-1} \times 10^{-7}$	k_{calcd}^b , $s^{-1} \times 10^{-7}$	k_{obsd}^b , $s^{-1} \times 10^{-7}$	k_{calcd}^b , $s^{-1} \times 10^{-7}$
0	2.46 ± 0.06	2.46	2.50 ± 0.06	2.50
0.992	2.51 ± 0.06	2.49	2.51 ± 0.06	2.52
2.98	2.57 ± 0.06	2.54	2.58 ± 0.06	2.55
3.97	2.62 ± 0.06	2.56	2.60 ± 0.06	2.57
0 ^b	6.43 ± 0.04	6.62	6.45 ± 0.04	6.75
0.992 ^b	6.72 ± 0.04	6.91	6.90 ± 0.04	6.95
2.98 ^b	7.31 ± 0.04	7.48	7.35 ± 0.04	7.37
3.97 ^b	7.68 ± 0.04	7.76	7.46 ± 0.04	7.57

^a Measurement at 25 ± 1 °C in degassed solutions, unless otherwise noted. ^b Air-saturated solutions.

can be applied to the aromatic hydrocarbon (AH)/1,3-diene (D) systems under investigation, where k_{de} includes all unimolecular decay processes of the exciplex except fluorescence and dissociation. In the presence of molecular oxygen it is necessary to add the quenching steps



The nature of the interactions with oxygen,⁹ which probably involve formation of ${}^3\text{AH}^*$ and possibly ${}^3(\text{AH} \cdot \text{D})^*$, is not addressed by, nor is relevant to, what follows.

The fluorescence time dependences of ${}^1\text{AH}^*$ and ${}^1(\text{AH} \cdot \text{D})^*$, $I_{fm}(t)$ and $I_{fe}(t)$, respectively,^{6,10} have been described elsewhere and are given by eq 9 and 10, where the parameters λ_1 , λ_2 , C_1 , and C_2 are defined by eq 11–14.

$$I_{fm}(t) = k_{fm}(C_1 e^{-\lambda_1 t} + C_2 e^{-\lambda_2 t}) \quad (9)$$

$$I_{fe}(t) = \frac{k_{fe} k_e [D]}{(\lambda_2 - \lambda_1)} (e^{-\lambda_1 t} - e^{-\lambda_2 t}) \quad (10)$$

$$\lambda_{1,2} = \frac{1}{2} [(k_{fm} + k_{is} + k_{qm}[\text{O}_2] + k_e[\text{D}] + k_{-e} + k_{fe} + k_{de} + k_{qe}[\text{O}_2]) \mp \{(k_{-e} + k_{fe} + k_{de} + k_{qe}[\text{O}_2] - k_{fm} - k_{is} - k_{qm}[\text{O}_2] - k_e[\text{D}])^2 + 4k_{-e}k_e[\text{D}]\}^{1/2}] \quad (11)$$

$$C_1 = (\lambda_2 - X)/(\lambda_2 - \lambda_1) \quad (12)$$

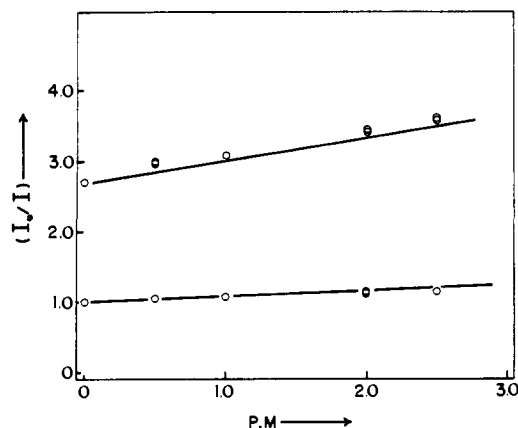


Figure 1. Quenching of BA fluorescence by P: lower, degassed; upper, air saturated. Lines are calculated; see text.

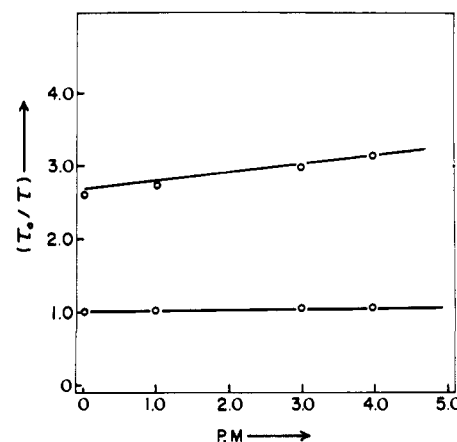


Figure 2. The effect of P on the fluorescence lifetime of BA: lower, degassed; upper, air saturated. Lines are calculated, λ_1/λ_1^0 ; see text.

$$C_2 = (X - \lambda_1)/(\lambda_2 - \lambda_1) \quad (13)$$

$$X = k_{fm} + k_{is} + k_{qm}[\text{O}_2] + k_e[\text{D}] \quad (14)$$

Integration of eq 9 and 10 from zero to infinite time gives the quantum yield expressions

$$\phi_{fe} = \frac{k_{fe} k_e [D]}{\lambda_1 \lambda_2} \quad (15)$$

$$\phi_{fm} = k_{fm} \left(\frac{C_1}{\lambda_1} + \frac{C_2}{\lambda_2} \right) \quad (16)$$

The necessity of proposing a reversibly formed exciplex at all in systems in which exciplex emission has not yet been observed might well be questioned. It is clear, however, that if diene quenching of ${}^1\text{AH}^*$ were irreversible, oxygen quenching of the same fluorescence would be strictly competitive. In such cases

$$\phi_{fm}^0/\phi_{fm} = \tau_m^0/\tau_m = 1 + k_{qm}\tau_m^0[\text{O}_2] + k_e\tau_m^0[\text{D}] \quad (17)$$

where $\phi_{fm}^0 = k_{fm}/(k_{fm} + k_{is}) = k_{fm}\tau_m^0$, would describe both fluorescence quantum yield and lifetime dependence on diene concentration. Slopes $k_e\tau_m^0$ would then be identical for ϕ_{fm}^0/ϕ_{fm} and τ_m^0/τ_m Stern–Volmer plots with and without oxygen. The data for BA/P, plotted in Figures 1 and 2, give four different slopes (Figure 1, 0.060 and 0.35 M⁻¹; Figure 2, 0.016 and 0.13 M⁻¹) obviously ruling out this simple mechanism. The same conclusion can be reached by considering the DBA/P data.

In order to show that the mechanism outlined in eq 1–8 is satisfactory it is necessary to find sets of reasonable rate con-

Table III. Rate Parameters for AH/D Systems^a

Parameter, units	BA/P	DBA/P
$k_x,^b \text{ s}^{-1}$	2.47×10^7	2.50×10^7
$k_e, \text{ M}^{-1} \text{ s}^{-1}$	$(2.25 \pm 0.2) \times 10^9$	$(2.21 \pm 0.2) \times 10^9$
$k_{-e}, \text{ s}^{-1}$	$3.16 \times 10^{10} f$	$3.16 \times 10^{10} f$
$k_y,^c \text{ s}^{-1}$	$(2.89 \pm 0.2) \times 10^7$	$(2.81 \pm 0.2) \times 10^7$
$k_q[\text{O}_2],^d \text{ s}^{-1}$	$(4.15 \pm 0.07) \times 10^7$	$(4.25 \pm 0.06) \times 10^7$
VC ^e	$(6.34 \pm 0.9) \times 10^{-2}$	$(4.49 \pm 0.7) \times 10^{-2}$

^a Three significant figures may be needed to generate lifetimes and quantum yields in Tables I and II; for comments concerning the significance of the given deviations see text. ^b $k_x = k_{\text{fm}} + k_{\text{is}}$. ^c $k_y = k_{\text{fe}} + k_{\text{de}}$. ^d $k_q = k_{\text{qm}} = k_{\text{qe}}$. ^e See text. ^f An assumed value; see text.

stants which when substituted into eq 9–16 reproduce the observed data for each AH/D system. The classical approach is to reduce the quantum yield expression 16 to a linear form such that the slope and intercept will assist in determining the rate parameters (the Stern–Volmer approach)

$$\phi_{\text{fm}}^0/\phi_{\text{fm}} = 1 + k_{\text{qm}}\tau_{\text{m}}^0[\text{O}_2] + k_e p \tau_{\text{m}}^0[\text{D}] \quad (18)$$

$$p = (k_{\text{fe}} + k_{\text{de}} + k_{\text{qe}}[\text{O}_2]) / (k_{-e} + k_{\text{fe}} + k_{\text{de}} + k_{\text{qe}}[\text{O}_2]) \quad (19)$$

where p represents the fraction of exciplexes which do not regenerate monomer, eq 19, and increases in the presence of oxygen. Indeed, it was due to the expected increase in p that the Stern–Volmer plot slope enhancement had been anticipated and proposed as a criterion for reversible exciplex formation; cf. eq 19, ref 3.⁷ In the present system such an analysis is also possible but very tedious owing to the complexity of the expression describing the time dependence of monomer fluorescence. If certain parameters are not uniquely defined by the data (i.e., the data may be sensitive only to the ratio k_e/k_{-e} and satisfied for a large range of absolute values of k_e and k_{-e}) the problem can become too complex to solve completely by the classical method. Clearly a more direct approach is needed.

In determining the suitability of any one set of rate constants one could substitute them into eq 9–16 and then compare theoretically predicted values with the observed data in a point by point fashion. If the rate parameters could now be adjusted in order to minimize the difference between predicted and observed values, the objective of finding a satisfactory set of rate constants could be reached. Computer assistance in adjusting the parameters and carrying out the point by point difference analysis is essential in this technique. Fortunately a standard iterative least-squares fitting program is applicable and DeTar's GENLSS program¹¹ was used in this case. Since the sets of parameters which comprise the solutions must fit both the fluorescence lifetimes and quantum yields, a method was devised whereby the computer fits *both* types of data *simultaneously* as it adjusts the values of the rate parameters.

The Method. Since the fluorescence decay profiles in the system under discussion show excellent adherence to essentially single exponentials, the observed rate constants from the slopes of the $\ln I_{\text{fm}}(t)$ vs. t plots were assigned to λ_1 , eq 9, 11. This requires that either λ_2 be relatively large and/or that C_2 be near zero. These conditions will later be shown to obtain. Values of $\phi_{\text{fm}}^0/\phi_{\text{fm}}$ can be computed directly from eq 16. The equations for λ_1 (from eq 11) and $\phi_{\text{fm}}^0/\phi_{\text{fm}}$ (from eq 16) were entered into the GENLSS subroutine FUNCT as illustrated in the Appendix. The data from Tables I and II were entered in the input data file. The values of τ were entered in triplicate in order to ensure that the program equally weight the quantum yield and lifetime data. Note that the independent variables $X(1, \text{NN})$, $X(2, \text{NN})$, and $X(3, \text{NN})$ define the diene

Table IV. Medium Viscosities and Indexes of Refraction

[P], M	η , mP	n^a	$n_{\text{B}}^2/n_{\text{mix}}^{2b}$
0	6.09	1.4926	1.000
0.50	5.70	1.4895	1.004
1.00	5.38	1.4863	1.008
2.00	4.80	1.4799	1.017
3.00	4.33	1.4734	1.026
4.00	3.91	1.4667	1.036
Neat	2.23	1.4229	1.100

^a Calculated from the molar fractions and the indexes of refraction of the pure liquids at 25 °C, $n_{\text{B}} = 1.4926$ and $n_{\text{P}} = 1.4229$, ref 13. ^b n_{mix} = index of refraction of the mixed solvent.

concentration, key for the presence of oxygen, and key the FUNCT subroutine to calculate either τ_1 or $\phi_{\text{fm}}^0/\phi_{\text{fm}}$, respectively. The relative fit option was used, as scalar and/or variable weight options are inappropriate when using two equations in FUNCT.

GENLSS can simultaneously adjust all rate parameters to obtain a fit but caution needs to be exercised if convergence is to be obtained. To avoid divergence it is advantageous to adjust each parameter independently before proceeding to adjust two or more at a time. A good first estimate of the parameters is essential. If parameters are correlated (an adjustment in one is compensated by an adjustment in another) divergence will occur. In such cases sequential adjustment or use of the search option is necessary.

The rate parameters obtained for the BA/P and DBA/P systems are shown in Table III. Since k_x is $1/\tau_{\text{fm}}^0$, the monomer decay rate constant in the absence of P and O₂, this parameter was not adjusted. The ratios of $k_e/k_{-e} = K_e$ are $0.070 \pm 0.010 \text{ M}^{-1}$ for both systems, but the fits are largely insensitive to values of k_{-e} between 10^9 and 10^{12} s^{-1} . The value of $k_{-e} = 10^{10.5} \text{ s}^{-1}$ was chosen as an upper limit, since it is near that expected for a diffusion-controlled separation of an encounter pair.^{6,12} It was also assumed that oxygen quenches ¹AH* and ¹(AH·D)* at the same diffusion-controlled rate, i.e., $k_q = k_{\text{qm}} = k_{\text{qe}} = k_{\text{dif}}$. This has been verified experimentally for the anthracene/*N,N*-dimethylaniline system where strong exciplex emission is observed.⁸ The parameter VC was introduced in order to account for viscosity change effects on k_q and/or changes in [O₂] as the diene concentration is increased. It was treated as an adjustable parameter such that $(k_q[\text{O}_2])_{\text{effective}} = (k_q[\text{O}_2])_0(1 + \text{VC}[\text{D}])$. The average value of VC corresponds to a 5.4% increase in $(k_q[\text{O}_2])_{\text{effective}}$ per mol of diene in benzene. If each encounter with molecular oxygen led to quenching, the actual change in medium viscosity with diene concentration in benzene at 24 °C (Table IV) predicts a $(13.6 \pm 0.1)\%$ increase in k_q per mol of diene. The smaller increase in $(k_q[\text{O}_2])_{\text{effective}}$ indicated by the data suggests either that the concentration of oxygen decreases with diene concentration, or that ~60% of the solution encounters between oxygen and singlet electronically excited species do not lead to quenching. It should be noted that in the absence of reversibly formed exciplexes the diene concentration dependent oxygen interactions predict two slopes for the I_0/I and τ_0/τ plots, one for degassed and one for air-saturated solutions, instead of four different slopes. An attempt to fit the data by also assigning a VC_e parameter to k_e gave VC_e = 0.0 ± 0.1 , suggesting that exciplex formation is not diffusion controlled for the BA/P and DBA/P systems. The radiative rate constants k_{fm} and k_{fe} were assumed to be medium independent since the relative change in the square of the index of refraction was $\leq 3.6\%$ for the [P] range employed (Table IV).¹⁴

For a discussion of the deviations given in Table III the reader is referred to DeTar's GENLSS paper and the Appendix.¹¹ They may be considered to represent a relative indication

of how precisely the data define specific parameters, but are also affected by parameter correlation as is the case for k_e and k_{-e} in the systems under consideration.

It is now possible to examine whether it was proper to assign the observed decay rate constants entirely to λ_1 . Table V gives values of λ_2 , f_{λ_1} , ϕ_m^{\max} , and ϕ_e^{\max} calculated for the BA/P system using eq 11 and 20–22

$$f_{\lambda_1} = \frac{(C_1/\lambda_1)}{(C_1/\lambda_1) + (C_2/\lambda_2)} \quad (20)$$

$$\phi_m^{\max} = k_x \left(\frac{C_1}{\lambda_1} + \frac{C_2}{\lambda_2} \right) \quad (21)$$

$$\phi_e^{\max} = k_y k_e [D] / \lambda_1 \lambda_2 \quad (22)$$

In eq 20 f_{λ_1} represents that fraction of $^1\text{AH}^*$ fluorescence being emitted with exponential constant λ_1 . In eq 21 and 22 ϕ_m^{\max} and ϕ_e^{\max} represent the total unimolecular decay quantum yields for $^1\text{AH}^*$ and $^1(\text{AH}\cdot\text{D})^*$, respectively. In the absence of information concerning the relative values of k_{fe} and k_{de} , ϕ_e^{\max} sets the upper limit for the quantum yield of product formation from the singlet exciplex. The quantities in Table V are calculated for $k_{-e} = 10^9 \text{ s}^{-1}$, the lowest k_{-e} for which a satisfactory fit to I_0/I and τ values was obtained, and for $k_{-e} = 10^{10.5} \text{ s}^{-1}$ which should be close to the maximum possible value for exciplex dissociation. It can be seen that f_{λ_1} , ϕ_m^{\max} , and ϕ_e^{\max} are relatively insensitive to this change in k_{-e} . In agreement with the assignment of the experimental decay rate constants to λ_1 , more than 98% of $^1\text{BA}^*$ emission is predicted to correspond to this component for all diene concentrations. The minor λ_2 components are predicted to be too fast for resolution with the equipment used to measure the fluorescence lifetimes. Thus, the observation of single exponential decay in the two AH/D systems under consideration can be attributed to rapid equilibration in exciplex formation relative to decay from either $^1\text{AH}^*$ or $^1(\text{AH}\cdot\text{D})^*$. When this condition obtains, the equilibrium constant for exciplex formation is given by eq 23.¹⁵

$$K_e = \{(I_0/I)(\tau/\tau_0) - 1\}[D]^{-1} \quad (23)$$

Application of eq 23 to the BA/D experimental data gives K_e values of 0.06 ± 0.04 and $0.14 \pm 0.06 \text{ M}^{-1}$ for measurements in degassed and air-saturated solutions, respectively, in satisfactory agreement with the best fit value of $0.070 \pm 0.010 \text{ M}^{-1}$ obtained above. Substitution of calculated I_0/I and τ/τ_0 (interpolated) values from Tables I and II into eq 23 gives excellent agreement with the 0.070 M^{-1} value. For comparison, $K_e \approx 20 \text{ M}^{-1}$ for the DCA/DMH system.^{3,18}

Conclusions

The agreement of the calculated lines with the experimental data for BA/P in Figures 1 and 2 is gratifying. Although not shown in the figures, examination of the entries in Tables I and II shows that deuteration of the seven position of BA causes no significant changes either in the calculated parameters, or in the goodness of fit obtained. It should be noted that for air-saturated samples calculated I_0/I and τ_0/τ values are systematically slightly lower and slightly higher than the observed values, respectively. Possible causes for these small deviations could be the slight temperature difference between the two sets of measurements, and/or failure to allow for complete resaturation of the degassed samples with air prior to measuring the lifetimes.

The present paper demonstrates the usefulness of oxygen quenching observations in determining the degree of involvement of reversibly formed exciplexes. Also, the kinetic analysis method employed should be readily applicable to many other similar photochemical problems. Specific examples which are entirely analogous to the systems discussed above are those

Table V. Values of λ_2 , f_{λ_1} , ϕ_m^{\max} , and ϕ_e^{\max} for BA/P^a

[P], M	$k_{-e} = 10^9 \text{ s}^{-1}$				$k_{-e} = 10^{10.5} \text{ s}^{-1}$			
	λ_2^d	f_{λ_1}	ϕ_m^{\max}	ϕ_e^{\max}	λ_2^d	f_{λ_1}	ϕ_m^{\max}	ϕ_e^{\max}
0	1.03 ^c	1.000	1.000	0	31.7 ^c	1.0000	1.000	0
0.992	1.11	0.998	0.927	0.073	34.0	1.0000	0.924	0.076
2.98	1.25	0.996	0.809	0.191	38.5	0.9999	0.801	0.199
3.97	1.33	0.994	0.761	0.239	40.7	0.9998	0.751	0.249
0 ^b	1.07 ^c	1.000	0.372	0	31.8 ^c	1.0000	0.372	0
0.992 ^b	1.15	0.996	0.334	0.025	34.1	0.9999	0.333	0.028
2.98 ^b	1.30	0.988	0.274	0.062	38.5	0.9996	0.272	0.067
3.97 ^b	1.38	0.984	0.251	0.075	40.8	0.9995	0.248	0.081

^a Degassed benzene solutions, unless otherwise indicated. ^b Air-saturated solutions. ^c An extrapolated value corresponding to $k_y + k_{-e} + k_{qe}[\text{O}_2]$. ^d Units, ns⁻¹.

involving the quenching of exciplex emission by a second quencher molecule possibly via the formation of a triplex³ (or exterplex).¹⁹

Experimental Section

Materials. Benz[*a*]anthracene, J. T. Baker reagent grade or Sigma grade II, was chromatographed on alumina with benzene as eluent, mp 161.8–162.3 °C. Benz[*a*]anthracene-7-*d* was prepared from 1,2-benzanthracene using the method of Badger and Cook.²⁰ To a solution of 1,2-benzanthracene (2.02 g) in CS₂ (30 mL, Fisher reagent) was added 0.48 mL of bromine (Mallinckrodt reagent). The resulting solution was stirred at room temperature for 12 h and the solvent was evaporated leaving a light brownish crystalline residue. Chromatography on alumina with *n*-hexane as eluent resulted in 1.90 g (70%) of light yellow crystals: mp 146.8–148.1 °C; NMR (60 MHz, CS₂) 7.30–8.00 (m, 7 H), 8.10–8.70 (m, 3 H), and 8.89 ppm (s, 1 H); mass spectrum (low resolution, 70 eV) *m/e* 305 (100), 307 (98). A solution of 7-bromobenz[*a*]anthracene (1.85 g) in freshly distilled benzene (120 mL) was placed in a thoroughly dried round-bottom flask equipped with a N₂ inlet, a reflux condenser, and a distillation head. The system was flushed with dry N₂ and approximately 10 mL of benzene was distilled to remove the last traces of water. After the solution was cooled to room temperature, *n*-butyllithium (7.5 mL of 1.22 M in *n*-hexane, Foote Mineral Co.) was added dropwise and the resulting solution heated to reflux for 45 min. The solution was cooled to 0 °C and D₂O (5.0 mL, 99.8%, Mallinckrodt Deuter AR) was added dropwise. The benzene layer was washed four times with distilled water and dried over Na₂SO₄, and the benzene was evaporated to leave light-orange crystals. Chromatography on alumina with *n*-hexane as eluent resulted in 0.97 g (70%) of white crystals which were recrystallized from 95% ethanol: mp 162.0–162.5 °C; NMR (60 MHz, CS₂) 7.10–8.10 (m, 9 H), 8.17 (s, 0.18 H), 8.50–8.70 (m, 1 H), 8.99 ppm (s, 1 H); mass spectrum (low resolution, 30 eV) *m/e* 228 (17.4), 229 (100), 230 (25.2); isotopic composition 84.6% benz[*a*]anthracene-7-*d*, 15.4% benz[*a*]anthracene.

cis-1,3-Pentadiene, Columbia Organic Chemicals, was bulb-to-bulb distilled under vacuum immediately prior to use. The isomeric impurity level varied among separate purchases and in general was about 0.07–0.10% trans as determined by GLC. An impurity with GLC retention time identical with that of cyclopentene was present at a level of ~0.5%. Benzene, Mallinckrodt spectral grade, was used without purification.

Analytical Procedures. Melting points were determined using a Kofler hot stage apparatus and are not corrected. NMR spectra were obtained using a Varian HA-60 spectrometer. Mass spectra were obtained using an AEI MS-902 double focusing mass spectrometer. Steady state fluorescence measurements were made using a Perkin-Elmer Hitachi MPF-2A spectrophotometer. Measurements with degassed samples were made in 1-cm Pyrex cells (five to six freeze-pump-thaw cycles as previously described).³ Standard 1-cm quartz cells were used for air-saturated solutions. The equipment and procedure used for the measurement of fluorescence lifetimes have been described.³ Following measurements with degassed solutions, air was admitted into the samples and the measurements were repeated.

Efflux times were measured at 24 °C using a Canon-Manning semimicro viscometer No. 25-A225, viscometer constant 2.58×10^{-2} , courtesy of Professor G. Levy. Viscosities, η , in mP were calculated

Table VI

```

SUBROUTINE DEFINE (NPARM,NIDVAR,KCONST,KFF,NFNAME,CNAME,FNAME,
1 PNAME,VNAME)
C
C USER SUPPLIED SUBROUTINE
CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
DIMENSION CNAME(2,10),FNAME(20),PNAME(2,30),VNAME(2,4),CC(2,10),
1 PP(2,30),VV(2,4)
DATA VV / 6H Y(X), 2H , 6H DIENE, 4H CON/
DATA PP / 6HKX ,6H ,6HKKQ(02),6H
+6HKE ,6H ,6HK-E ,6H
+6HKY ,6H ,6HCV ,6H
DATA CC/6H ,6H ,6H
NFNAME = 9
NPARM = 6
NIDVAR = 3
KCONST = 0
KFF = 0
CALL FNSET(NFNAME,FNAME,
1 84HSUBROUTINE BY J CHARLTON
2
3,84H
4
)
CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
DO 10 I=1,NPARM
PNAME(1,I) = PP(1,I)
10 PNAME(2,I) = PP(2,I)
NV = NIDVAR + 1
DO 20 I=1,NV
VNAME(1,I) = VV(1,I)
20 VNAME(2,I) = VV(2,I)
DO 30 I=1,KCONST
CNAME(1,I) = CC(1,I)
30 CNAME(2,I) = CC(2,I)
RETURN
END
SUBROUTINE FUNCT
COMMON/FUNC/NPARM,NIDVAR,PARM(30),YCALC(1000),X(3,1000),F(31),
1 IT(4),NH,IN,IP,IPP,IVV
COMMON/CONSTS/CONST(10,30),CNAME(2,10),KPOINT(30),SETID(12,30),
1KSET,KST,KCONST,MXCON,MXSET
GO TO 20
10 WRITE(6,9001)
9001 FORMAT(32H PARAMETER ADJUSTMENT HAS FAILED)
STOP
20 PLIMIT1 = 1.0E20
DO 30 I=1,NPARM
IT(ABS(PARM(I)).GT.PLIMIT1) GO TO 10
30 CONTINUE
ABOVE ESCAPE PROVIDED FOR UNREASONABLE PARM VALUES
C
C USER SUPPLIED SUBROUTINE BELOW
CCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCCC
AK1 = PARM(1)
ADD = (1+PARM(6))*X(1,NN)
AK2 = PARM(2)*X(2,NN)*ADD
AK3 = PARM(3)
AK4 = PARM(4)
AK5 = PARM(5)
AK6 = PARM(2)*X(2,NN)*ADD
ALAM1 = 0.5*(AK1+AK2+AK3*X(1,NN)+AK4+AK5+AK6)
+SQRT((AK4+AK5+AK6-AK1-AK2-AK3*X(1,NN))*
*(AK4+AK5+AK6-AK1-AK2-AK3*X(1,NN))+4*AK4*AK3*X(1,NN))
ALAM2 = 0.5*(AK1+AK2+AK3*X(1,NN)+AK4+AK5+AK6)
+SQRT((AK4+AK5+AK6-AK1-AK2-AK3*X(1,NN))*
*(AK4+AK5+AK6-AK1-AK2-AK3*X(1,NN))+4*AK4*AK3*X(1,NN))
CONE = (ALAM2-AK1-AK2-AK3*X(1,NN))/(ALAM2-ALAM1)
CTWO = (AK1+AK2+AK3*X(1,NN)-ALAM1)/(ALAM2-ALAM1)
IT(X(3,NN)) 41,42,42
41 YCALC(NN) = 1/((CONE/ALAM1+CTWO/ALAM2)*(AK1))
GO TO 50
42 YCALC(NN) = ALAM1
50 RETURN
END

```

from the expression $\eta = (2.582)(10^{-2})(\text{density})(\text{efflux time})$.²¹ Aliquots (1 mL), 24 °C, of each solution were weighed in order to determine densities. These were found to be within 0.3% of values calculated from the densities of the pure components and the mole fractions.

Appendix

In order to use GENLSS¹¹ the user must supply information in subroutines DEFINE and FUNCT as well as the data input file. Listed in Table VI are the Fortran listings for DEFINE and FUNCT used in this work. For information on the format of the data input the reader is referred to the original article by DeTar.¹¹

In Figure 3 are plotted values of the parameters vs. the total variance. This figure illustrates the change in the variance as an individual parameter is stepped away from the convergence minimum. At each step the remaining parameters are adjusted for lowest variance. The variance V is the total relative variance in both I_0/I and τ

$$V = \left\{ \sum_{i=1}^n [(Y_{\text{obsd}} - Y_{\text{calcd}})/Y_{\text{calcd}}]^2 \right\} / (n - p) \quad (24)$$

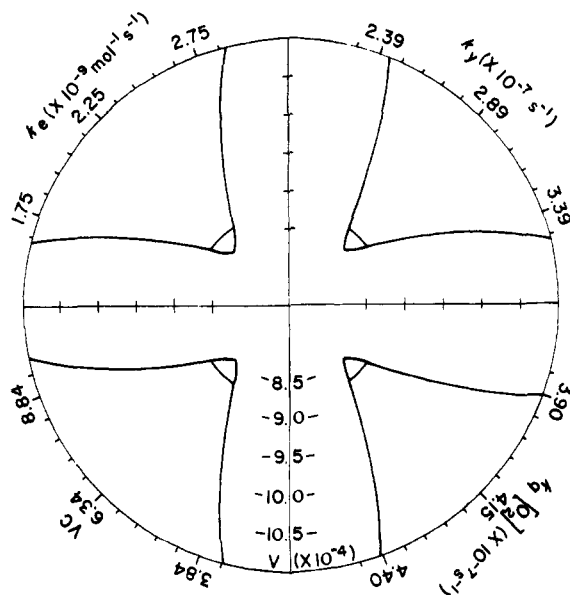


Figure 3. Polar plots of variance vs. parameter values for the BA/P system.

where Y is the observed and calculated data point (I_0/I or τ), n is the number of data points, and p is the number of parameters being adjusted.

References and Notes

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