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# A Long-Lived Triplet Exciplex of Acetone and Durene. Absorption Spectrum, Energy Transfer, and Kinetics[1]

**L. J. Johnston,[2] J. C. Scaiano,*[2] and T. Wilson*[3]**

*Contribution from the Division of Chemistry, National Research Council of Canada, Ottawa, Ontario, Canada K1A 0R6, and The Biological Laboratories, Harvard University, Cambridge, Massachusetts 02138.* *Received August 1, 1986*

**Abstract:** Acetone triplets interact with durene in acetonitrile solution with a rate constant of $5.4 \times 10^7$ M$^{-1}$ s$^{-1}$ at room temperature to form a transient species with an absorption spectrum distinctly different from the spectra of duryl or acetone ketyl radicals and from triplet acetone, which it replaces. This new species can be readily characterized as an excited state, since it can be quenched by triplet energy acceptors such as 1,3-cyclohexadiene, 2,5-dimethyl-2,4-hexadiene, and 9,10-dibromoanthracene (DBA). Energy transfer to DBA results in sensitized DBA fluorescence; its intensity decay profiles (obtained by single-photon counting) reveal the formation of the same excited transient observed by direct detection (laser photolysis). This transient species is assigned to a triplet exciplex of acetone and durene. The kinetic information obtained on this transient by the two methods is in good agreement. The combined data at several temperatures lead to $E_a = 1.5$ kcal/mol and log $(A/\text{M}^{-1}\ \text{s}^{-1}) = 8.85$ for bimolecular exciplex formation ($k_{EA} = 5 \times 10^7$ M$^{-1}$ s$^{-1}$ at 20 °C). Thus the photoassociation process is orders of magnitude slower than the diffusion-controlled limit (as previously observed in the case of the triplet exciplex of cyclohexanone and mesitylene). This remarkably stable exciplex lives ca. 7 μs at room temperature; such a long lifetime tends to limit the accuracy of the exciplex relaxation data obtained by either technique.

Triplet exciplexes have often been invoked as transient intermediates in the quenching of triplet alkanones by benzene and its methyl derivatives.[4] An indirect method for visualizing such transient complexes, and studying the kinetics of their formation and decay, relies on energy transfer to 9,10-dibromoanthracene (DBA) which acts as a fluorescent probe.[4c,5,6] Both the triplet ketone, generated by pulsed UV excitation, and its triplet exciplex with the aromatic substrate are quenched by DBA. The triplet energy of these two donors is thus passed on to the DBA, and part of it is subsequently reemitted as DBA fluorescence. The fluorescence decay curves, obtained by the time-correlated single-photon counting technique, clearly show the formation and decay of long-lived excited intermediates.

Although much kinetic information can be deduced from the analysis of such decay profiles,[5,6] thus far direct spectroscopic evidence for these exciplexes had been lacking. Now a transient absorption assigned to the triplet exciplex of acetone and durene has been observed. This paper presents the triplet–triplet absorption spectrum and its time dependence after laser flash excitation of acetonitrile solutions containing acetone and durene and compares this information to that obtained by the DBA method on the same system and under comparable experimental conditions. The results, which show the slow buildup and decay of a long-lived excited intermediate, are consistent with eq 1, where A is acetone, D is durene, and E* is the triplet exciplex. The discussion will review the supporting evidence and speculate on the nature of the complex.

$$\begin{tikzcd} {}^3A^* + D \arrow[r, shift left, "k_{EA}"] \arrow[d, "k^A_d"] & {}^3E^* \arrow[l, shift left, "k_{AE}"] \arrow[d, "k^E_d"] \\ A & A + D \end{tikzcd} \qquad (1)$$

## Experimental Section

For the laser photolysis experiments, durene was recrystallized from benzene, 2,5-dimethyl-1,3-hexadiene and 1,3-cyclohexadiene were distilled, and di-*tert*-butyl peroxide was passed through an alumina column. Acetone (Fischer, spectrograde) and acetonitrile (Baker, Photrex) were used as received. The samples were deaerated by purging with nitrogen. Either a Lumonics TE-860-2 excimer laser (XeCl mixtures, 308 nm, ca. 5-ns pulses) or a Molectron UV-24 nitrogen laser (337.1 nm, ca. 8-ns pulses) was used for sample excitation. Further details have been reported elsewhere.[7] A gated-intensified optical multichannel analyzer (OMA-III from E.G.&G) was used to monitor the time evolution of the fluorescence intensity in the laser photolysis experiments.

For the fluorescence decay measurements, the samples were degassed by 4 freeze–pump–thaw cycles. Acetone (Baker Instra-Analyzed) and acetonitrile ("Distilled in Glass" from Burdick and Jackson) were used as received. Durene (Aldrich) was vacuum sublimed. 9,10-Dibromo-

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(2) NRC, Canada.

(3) Harvard University.

(4) (a) Loufty, R. O.; Yip, R. W. *Can. J. Chem.* **1973**, *51*, 1881–1884. (b) Loufty, R. O.; Dogra, S. K.; Yip, R. W. *Can. J. Chem.* **1979**, *57*, 342–347. (c) Wilson, T.; Halpern, A. M. *J. Am. Chem. Soc.* **1980**, *102*, 7279–7283.

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(6) Wilson, T.; Halpern, A. M. *J. Am. Chem. Soc.* **1981**, *103*, 2412–2413.

(7) Scaiano, J. C. *J. Am. Chem. Soc.* **1980**, *102*, 7747–7753. Scaiano, J. C.; Tanner, M.; Weir, D. *J. Am. Chem. Soc.* **1985**, *107*, 4396–4403.

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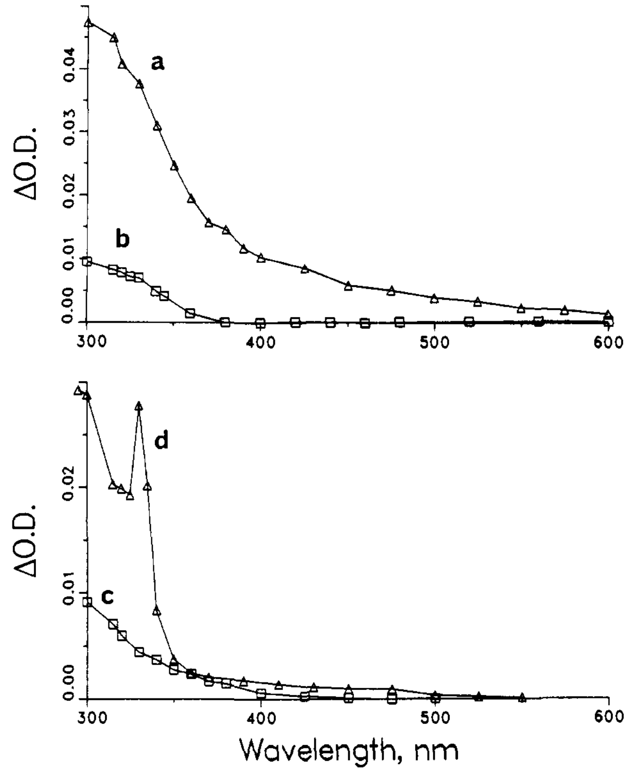

**Figure 1.** Transient absorption spectra obtained by 308-nm excitation of (a) 0.13 M acetone and 0.11 M durene in acetonitrile (exciplex), (b) 0.13 M acetone in acetonitrile (triplet), (c) 0.13 M acetone in 2-propanol (ketyl radical), and (d) 0.1 M durene and 5% di-*tert*-butyl peroxide in acetonitrile (duryl radical).

anthracene (Aldrich) was recrystallized from xylene and vacuum sublimed. The experimental techniques and instrumentation for time-resolved single-photon counting[5] have been described previously.

## Results

**A. Laser Photolysis Experiments.** Excitation (308 nm) of 0.13 M acetone in acetonitrile produces a weak transient which is readily characterized as triplet acetone.[8] Addition of durene (0.02–0.2 M) results in the appearance of a new transient with $\lambda_{max} \leq 300$ nm (Figure 1). It is obvious from the comparison of the spectra shown in Figure 1 for triplet acetone and the new transient that the latter is substantially different from and more strongly absorbing than the triplet. Both the duryl radical and the acetone ketyl radical were possible candidates for the new transient. The duryl radical was generated independently by hydrogen abstraction from durene by *tert*-butoxyl radicals produced by excitation of di-*tert*-butyl peroxide.[9] This spectrum is also shown in Figure 1, along with that of the acetone ketyl radical produced via hydrogen abstraction by triplet acetone from 2-propanol. These results indicate that the new transient formed by excitation of acetone in the presence of durene cannot be attributed to either of these species or to a combination of the two. However, on the basis of the spectra in Figure 1 we cannot rule out the possibility that the spectrum of the new transient has a small contribution from duryl and ketyl radicals.[10]

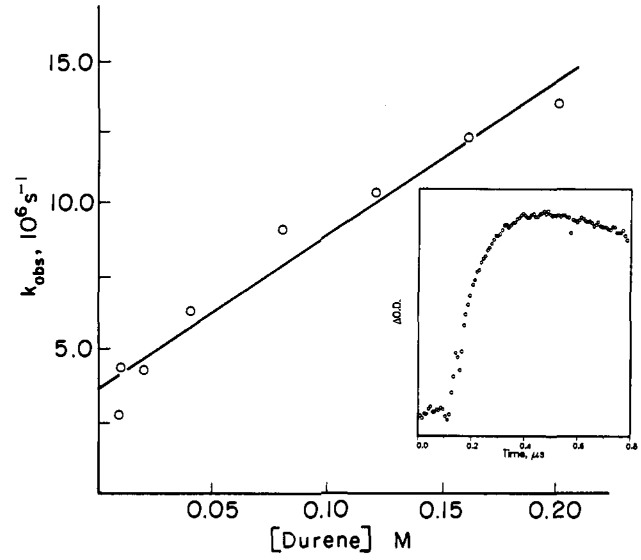

**Figure 2.** Plot of the pseudo-first-order rate constants for transient growth as a function of durene concentration. Inset: Growth of the transient monitored at 325 nm following 308-nm excitation of an acetonitrile solution of 0.13 M acetone and 0.2 M durene, at 28.4 °C.

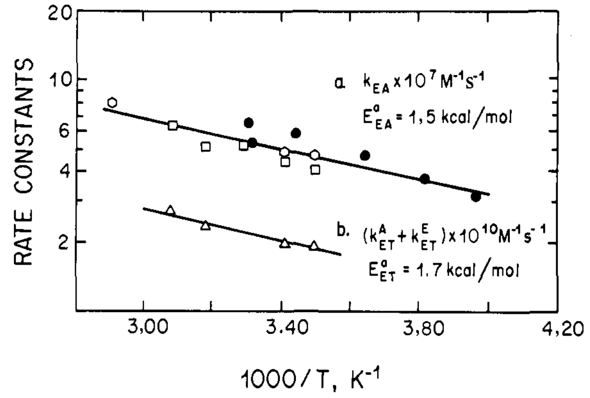

**Figure 3.** Arrhenius plots for (a) the rate of exciplex formation, $k_{EA}$ (●, transient absorption experiments; □, DBA energy transfer experiments with 0.056 M acetone and $1.2 \times 10^{-4}$ M DBA; ○, same, with $1.2 \times 10^{-5}$ M DBA) and (b) △, the sum of the rate constants for DBA quenching of triplet acetone and triplet exciplex ($k_{ET}^A + k_{ET}^E$) with 0.056 M acetone, 0.09 M durene, and $0.65–3.0 \times 10^{-4}$ M DBA.

On short time scales the buildup of the transient follows reasonable first-order kinetics (Figure 2, inset) with the pseudo-first-order growth rate constants depending linearly on the durene concentration (Figure 2). The rate of growth of the signal was unaffected by using durene-$d_{14}$ instead of durene, indicating that radical formation is of minor importance.[11] Analysis of the transient growth as a function of durene concentration gave a value of $5.4 \times 10^7$ $M^{-1}$ $s^{-1}$ for the rate constant for formation of the transient at room temperature.

The transient decayed with mixed kinetics which varied with the laser intensity. Clean first-order decays were observed at low laser intensity (beam attenuated with a neutral density filter to ~15% of its original intensity), when the transient was monitored at longer wavelengths (370–400 nm), which tends to minimize interference from other species (see Figure 1).

The transient formed in the acetone triplet–durene reaction was readily quenched by typical triplet quenchers such as 1,3-cyclohexadiene and 2,5-dimethyl-1,3-hexadiene. For the former, a quenching rate constant of ca. $4.3 \times 10^9$ $M^{-1}$ $s^{-1}$ was obtained from a plot of the rate of transient decay as a function of diene concentration.

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(8) Porter, G.; Dogra, S. K.; Loutfy, R. O.; Sugamori, S. E.; Yip, R. W. *J. Chem. Soc., Faraday Trans. 1* **1973**, *69*, 1462–1474.

(9) Johnson, P. M.; Albrecht, A. C. *J. Chem. Phys.* **1968**, *48*, 851–865.

(10) A two-laser experiment[7] was performed in which the 308-nm laser was followed 0.5–1 μs later by 337 nm laser excitation. It resulted in a weak fluorescence which was spectrally identical with that obtained by 337-nm excitation of the duryl radical generated by *tert*-butoxyl abstraction from durene. It was not possible to demonstrate whether the duryl radical fluorescence results from excitation of the exciplex followed by cleavage or of a small amount of duryl radical produced by the first laser. Comparison of the fluorescence intensities in the exciplex and the duryl radical experiments indicated that, if the latter was used as a reference, then only ca. 10% of the transient at 337 nm in the exciplex experiment could be due to duryl radical.

(11) Hydrogen abstraction by ketone triplets generally shows relatively large isotope effects: for example, triplet benzophenone has a lifetime of 125 ns in cyclohexane and 500 ns in cyclohexane-$d_{12}$ (23 °C).

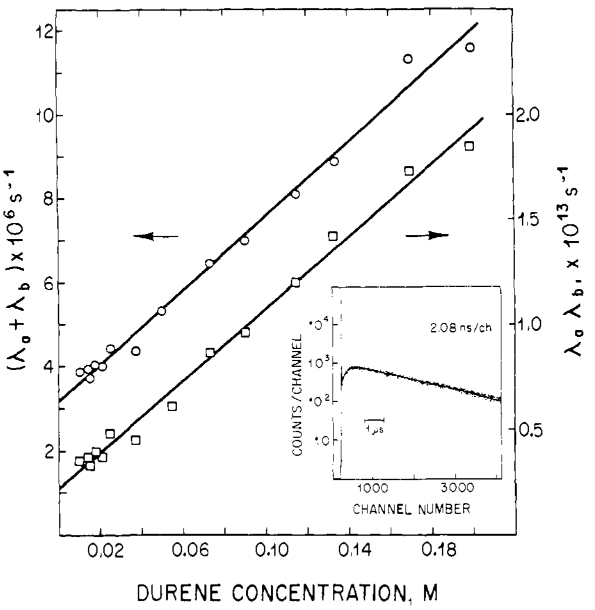


**Figure 4.** Plots of $(\lambda_a + \lambda_b)$ and $\lambda_a\lambda_b$ as a function of durene concentration for a series of acetonitrile solutions of 0.056 M acetone and 1.2 × $10^{-4}$ M DBA at 20 °C. Inset: Fluorescence decay curve of an acetonitrile solution of 0.056 M acetone, 0.081 M durene, and 1.2 × $10^{-5}$ M DBA at 12 °C. Excitation was at 305 nm and fluorescence was monitored at 433 ± 20 nm. The full line is the convoluted "best-fit" triple exponential function which gives a $\chi^2$ of 1.41 for channels 200–4096.

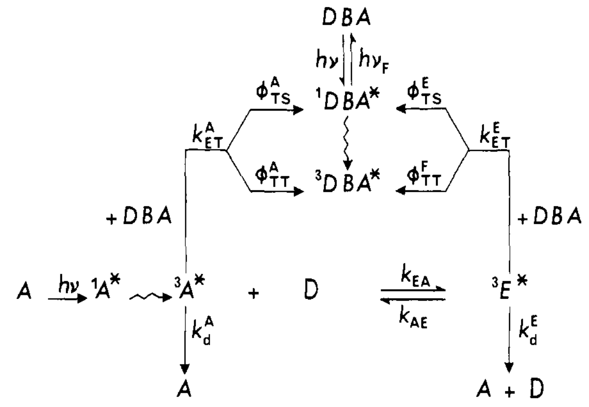
The rate of transient formation was measured in acetonitrile at five temperatures over a 50 °C range. The Arrhenius plot of the data (Figure 3) gives the following activation parameters: $E_a$ = 2.2 ± 0.2 kcal/mol and log $(A/M^{-1}\ s^{-1})$ = 9.4 ± 0.2 (errors as $\pm 2\sigma$).

The data obtained from these laser flash photolysis experiments are consistent with the assignment of the new transient to an acetone–durene triplet exciplex, which has also been observed indirectly by the DBA method (vide infra).

Finally, it is important to note that under the conditions of the laser experiments it is difficult to eliminate completely contributions from T–T annihilation. The use of sets of neutral density filters covering the 100–15% range suggests that with the latter the decay has only minor contributions from T–T annihilation. Typical transient concentrations generated in our experiments were in the 0.5–10 μM range. In addition, at wavelengths near the maximum for duryl the decays never become completely free from second-order components, presumably reflecting self-reaction of the duryl radicals which are responsible for a small fraction of the absorption at that wavelength.

**B. Energy-Transfer Experiments with DBA, by Single-Photon Counting. 1. Intensity Decay Profiles of DBA Fluorescence in Solutions Containing Acetone and Durene.** Upon nanosecond pulsed excitation at any wavelength within its absorption spectrum, the fluorescence of DBA decays as a single exponential ($\tau$ = 2.1 ± 0.1 ns, at room temperature in degassed acetonitrile solution). In the presence of ca. 0.06 M acetone and upon excitation at ca. 305 nm, where both acetone and DBA absorb, the fluorescence of DBA decays as the sum of two exponentials of very different rate parameters: ~2 ns for the short component and of the order of several microseconds for the long decay component, a value which depends on the concentration of DBA.[4c] But if durene, which has a negligibly small absorbance at the excitation wavelength and at concentrations ≤0.2 M, is added to degassed solutions of acetone and DBA, the fluorescence curves show a third component which reflects the buildup of a transient energy donor to DBA. The inset in Figure 4 shows a typical example. Similar results have been previously reported for cyclohexane solutions of DBA and cyclohexanone with either o-xylene[6] or mesitylene.[5] The presence of a growth component in the trace is indicative of the formation of a species that is a better energy donor than acetone toward DBA.[12]

**Scheme I**



Previous results for the cyclohexanone–mesitylene system[5] have shown that the DBA fluorescence decay curves, convoluted with lamp pulse profiles, could be fitted to triple exponential functions of the form

$$I_t \propto \alpha e^{-k_F t} + \beta e^{-\lambda_a t} + e^{-\lambda_b t} \tag{2}$$

as predicted by Scheme I, where A is acetone and D is durene.

**2. Estimate of the Rate of Exciplex Formation and the Rates of Quenching of the Triplet Donors by DBA.** Scheme I further predicts[16] that, at a given concentration of DBA, the sum as well as the product of $\lambda_a$ and $\lambda_b$ should be linear functions of the durene concentration. The corresponding plots are shown in Figure 4. If [D] is kept constant, $(\lambda_a + \lambda_b)$ is expected and was confirmed to be a linear function of [DBA]. Analysis of these plots immediately provides the following information regarding the rate constants of Scheme I: (a) the slope of $(\lambda_a + \lambda_b)$ vs. [D] is $k_{EA}$, the rate constant for formation of the exciplex, and (b) the slope of $(\lambda_a + \lambda_b)$ vs. [DBA] is $(k_{ET}^A + k_{ET}^E)$, i.e., the sum of the rate constants for overall quenching of triplet acetone and of triplet exciplex by DBA, via energy transfer resulting in the formation of $^1DBA^*$ as well as of $^3DBA^*$.

The effect of durene concentrations was investigated at 20 °C for two concentrations of DBA: 1.2 × $10^{-4}$ M (9 points at [D] from 0.02 to 0.2 M) and 1.2 × $10^{-5}$ (5 points between 0.02 and 0.18 M). However, at the lower DBA concentration the $(\lambda_a\lambda_b)$ plot (Figure 4) deviates from linearity, showing upward curvature. The average value of $k_{EA}$ so obtained is 4.8 × $10^7\ M^{-1}\ s^{-1}$, and at [D] = 0.09 M, the value of $(k_{ET}^A + k_{ET}^E)$ is 1.93 × $10^{10}\ M^{-1}\ s^{-1}$.

**3. Estimation of Approximate Values for the Triplet Exciplex Lifetime and Its Rate Constant for Dissociation, $k_{AE}$.** It is unfortunately not easy to obtain the values of either $k_d^E$ or $k_{AE}$ from the computer fit of the decay curves according to eq 1. If $k_1$ and $k_2$ are defined as the rates of decay of the uncomplexed triplet ketone and of the exciplex, respectively (eq 3 and 4), and if the

$$k_1 = k_{EA}[D] + k_{ET}^A[DBA] + k_d^A \tag{3}$$

$$k_2 = k_{AE} + k_{ET}^E[DBA] + k_d^E \tag{4}$$

assumptions of Scheme I are correct and sufficient, then, at any

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[12] It should be noted that such results are not obtained from a mixture of duryl and acetone ketyl radicals in the presence of DBA. This was demonstrated by exciting a solution of 3% di-*tert*-butyl peroxide, 0.04 M 2-propanol, 0.08 M durene, and 1.3 × $10^{-5}$ M DBA in acetonitrile. Under these conditions *tert*-butoxyl abstraction from propanol and durene should yield approximately equal concentrations of the two radicals.[13,14] However, no delayed DBA fluorescence was observed.

[13] The rate constant for reaction of *tert*-butoxy radicals with durene was assumed to be similar to that for mesitylene (8.3 × $10^5\ M^{-1}\ s^{-1}$).[15]

[14] The rate constant for reaction of *tert*-butoxyl radicals with 2-propanol is 1.8 × $10^6\ M^{-1}\ s^{-1}$.[15]

[15] Paul, H.; Small, R. D., Jr.; Scaiano, J. C. *J. Am. Chem. Soc.* **1978**, *100*, 4520–4526.

[16] For a full derivation of the equations in this and the following sections see ref 5.

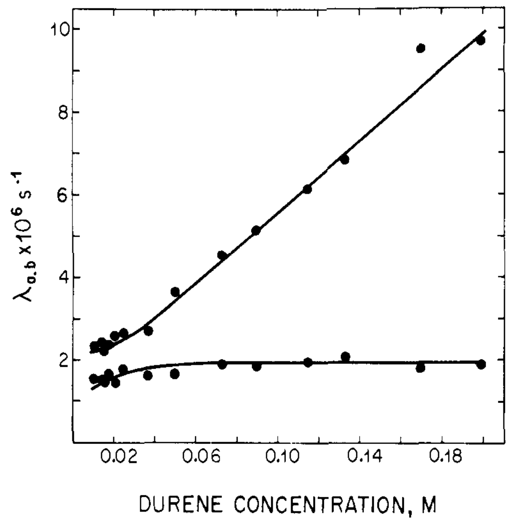

**Figure 5.** Plot of the experimental values of $\lambda_a$ and $\lambda_b$ as a function of the durene concentration in degassed acetonitrile at 20 °C for 0.056 M acetone and $1.2 \times 10^{-4}$ M DBA, as determined from the convoluted "best fit" triple exponential functions ($\chi^2$ range 1.06–1.50 for channels 150–4096). The solid lines through these points are the calculated functions of $\lambda_a$ and $\lambda_b$ vs. D according to eq 5, with $k_{EA} = 4.43 \times 10^7$ M$^{-1}$ s$^{-1}$, $k_{AE} = 1.52 \times 10^5$ s$^{-1}$, and $k_2 = 2.14 \times 10^6$ s$^{-1}$.

given temperature $k_1$ should depend linearly on [D] whereas $k_2$ should remain constant. An expression was derived (eq 5) which

$$\lambda_{a,b} = \tfrac{1}{2}(k_1+k_2) \pm \tfrac{1}{2}\sqrt{(k_1 - k_2)^2 + 4k_{EA}k_{AE}[D]} \qquad (5)$$

relates $k_1$ and $k_2$ to the experimental values of $\lambda_a$ and $\lambda_b$ and to the product $k_{EA}k_{AE}$ of the rate constants for exciplex formation and dissociation.[5] Equation 5 rearranges to give $k_1$ and $k_2$:

$$k_{1,2} = \tfrac{1}{2}(\lambda_a + \lambda_b) \pm \tfrac{1}{2}\sqrt{(\lambda_a - \lambda_b)^2 - 4k_{EA}k_{AE}[D]} \qquad (6)$$

An approximate and roundabout way of estimating $k_1$, $k_2$, and $k_{AE}$ is based on the postulate that the correct value of $k_{AE}$ should, when introduced in eq 6, yield values of $k_1$ and $k_2$ which display the expected dependence and independence on [D], respectively. Thus, a series of experiments at constant [DBA] and temperature, and varying concentrations of durene, were analyzed as follows. *Arbitrary* values were assigned to the product $k_{EA}k_{AE}$ (with $k_{EA}k_{AE} < (\lambda_a - \lambda_b)^2/4[D]$) in eq 6 until a value of this product was found which rendered one of $k_{1,2}$ independent of the concentration of durene, i.e., $k_2$, while the other, i.e., $k_1$, became linearly dependent on [D]. This method involves an element of subjectivity in the choice of the correct $k_{AE}$. Figure 5 shows the experimental data points and the theoretical line calculated according to eq 5, with the "best" values of $k_2$ and $k_{AE}$ determined by the procedure outlined above and the value of $k_{EA}$ obtained from the slope of $(\lambda_a + \lambda_b)$ vs. [DBA]. The data indicate that the equilibrium constant for the exciplex $K_E = k_{EA}/k_{AE} \simeq 5 \times 10^7$ M$^{-1}$ s$^{-1}$/$1.5 \times 10^5$ s$^{-1}$ $\simeq$ 333 M$^{-1}$. An upper limit for $k_{AE}$, such that the term under the square root bracket in eq 6 is 0, is $1.9 \times 10^5$ s$^{-1}$ at 20 °C. The lower limit of $k_{AE}$ is estimated to be $1.2 \times 10^5$ s$^{-1}$; values of $k_1$ and $k_2$ calculated with $k_{AE} < 1.2 \times 10^5$ s$^{-1}$ do not satisfy the criteria for $k_1$ and $k_2$.

When the energy-transfer experiments are performed at low DBA concentration (here $1.2 \times 10^{-5}$ M), the plots of $\lambda_a\lambda_b$ vs. durene concentration begin to show an upward curvature. This indicates that another pathway for exciplex deactivation, not included in Scheme I, begins to play a role. The simplest explanation, which would account for the observed trend but has not been tested quantitatively, is that the exciplex is deactivated via collisions with a ground-state molecule of durene.

$$E^* + D \xrightarrow{k_q^E} A + 2D$$

The predictions of Scheme I are in agreement with the experimental results for [DBA] = $1.2 \times 10^{-4}$ M throughout the range of durene concentrations (0.02–0.2 M), indicating that at this concentration of DBA, $k_{ET}^E[DBA] > k_q^E[D]$, and thus $k_q^E < 2 \times 10^7$ M$^{-1}$ s$^{-1}$. Interestingly, a very similar effect was observed previously in the case of the less stable exciplex of acetone and benzene. One of the advantages of the energy-transfer method is that the very presence of DBA in appropriate concentration eliminates unwanted complications and therefore "simplifies" the system. Another, evidently, is the very low intensity of the excitation pulses used in the single-photon counting method, which suppresses all danger of triplet–triplet annihilation processes playing an unwanted role.

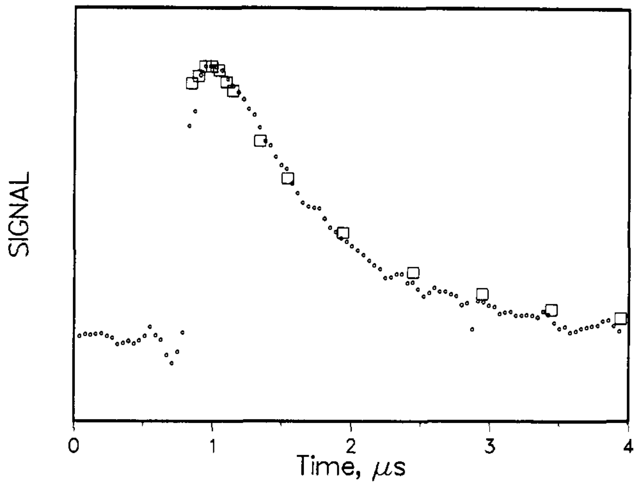

**Figure 6.** DBA fluorescence intensity as a function of time after 308-nm excitation of an acetonitrile solution of 0.054 M acetone, 0.1 M durene, and $2.6 \times 10^{-5}$ M DBA (□), and exciplex growth and decay monitored by laser flash photolysis at 370 nm for the same sample (o).

**4. Effect of Temperature.** The fluorescence decay curves of each degassed solution of acetone, durene, and DBA in acetonitrile were acquired at five temperatures from 12 to 51 °C at [DBA] = $1.2 \times 10^{-4}$ M and at three temperatures between 12 and 71 °C at [DBA] = $1.2 \times 10^{-5}$ M. The rate parameters $\lambda_a$ and $\lambda_b$ derived from the computer fit of these decay curves were treated as above to obtain the values of $k_{EA}$ and $(k_{ET}^A + k_{ET}^E)$ as a function of temperature. The corresponding Arrhenius plots are given in Figure 3. The activation energy of $k_{EA}$ so determined is 1.9 kcal/mol. The sum $(k_{EA}^A + k_{ET}^E)$ has an activation energy of 1.7 kcal/mol over the same 40 deg temperature range.

As discussed earlier, fully reliable values of $k_{AE}$ are difficult to determine. Figure 5, which shows the results obtained at 20 °C, is representative of the quality of the data at other temperatures. An evaluation of Arrhenius parameters associated with $k_{AE}$ is not warranted at this time, because the contribution of this process to the exciplex decay is too small. However, the data suggest an upper limit for the activation energy for the dissociation of the exciplex, $E_{AE}^a \leqslant 7$ kcal/mol.

**C. DBA Experiments in the Laser System.** The laser photolysis and energy-transfer experiments, described in the preceding sections, were carried out at very different intensities of exciting light. The following experiment was therefore carried out to ensure that the DBA results could be reproduced in the laser system. A solution of 0.054 M acetone, 0.1 M durene, and $2.6 \times 10^{-5}$ M DBA in acetonitrile was excited with the 308-nm laser, and the DBA fluorescence intensity was measured with a gated Optical Multichannel Analyzer (OMA) at various delay times after the laser excitation and with a 20-ns gate. The results are shown in Figure 6 along with a kinetic trace of the transient absorbance observed by flash photolysis for the same sample. The agreement between these two measurements shows beyond doubt that the flash photolysis and single photon counting methods are probing the same processes. The sharp spike (due to direct DBA fluorescence) observed in the single photon counting experiments was also detected with the OMA but could not be measured accurately because of timing jitter in the laser.

## Discussion

**Analysis of the Kinetic Results.** The absorption spectrum of a new transient species, of microsecond lifetime, has been observed following 308 nm laser flash excitation of mixed solutions of acetone and durene in degassed acetonitrile. The absorption spectrum of Figure 1 is distinctly different from that of triplet acetone, which it replaces. The transient spectrum is considerably broader, extending past 500 nm. A comparison of the traces shown in Figure 1 rules out the assignment of the transient to either the duryl or the ketyl radical or a superposition of these. Benzene shows triplet–triplet absorption at $\lambda < 320$ nm;[17a] much weaker absorption bands in the visible region have been reported earlier for benzene and its methyl derivatives ($\lambda_{max}$ at 480 nm for durene).[17b] Further, the lifetime of triplet durene is not expected to be significantly different from that of xylene triplets in solution, i.e., <1 $\mu$s at concentration >0.01 M and, thus, too short to be the long-lived transient seen here.[18] Another argument for ruling out triplet durene as the species detected will be presented later in this discussion.

Three lines of evidence suggest that the new transient absorptions are dominated by those from the triplet exciplex of acetone and durene: (1) The transient is an electronically excited species, since it is quenched by dienes at a near-diffusion-controlled rate and can transfer energy to DBA in agreement with the single photon counting experiments. (2) The kinetics of its growth and decay are compatible with the exciplex assignment, since the kinetics of transient growth (Figure 2) shows a pseudo-first-order dependence on durene concentration and its decay approaches first order at low laser fluences. Note that eq 1 dictates that the growth and decay of an exciplex follow a double exponential function (eq 7) as derived by Birks.[19] The rate parameters are functions of

$$[E^*] \propto e^{-\lambda_1 t} - e^{-\lambda_2 t} \tag{7}$$

the durene concentration and of all the rate constants of eq 1 (see below). It is the long lifetime of this exciplex ($k_d^E + k_{AE}$) compared to its much faster rate of formation which makes its kinetics of growth approximate first order for as long as 200–300 ns. This is the same characteristic that makes the accurate determination of exciplex decay parameters virtually impossible. However, the slopes of such near-first-order plots (Figure 2, inset) can yield values of $k_{EA}$ slightly larger than the true value of $k_{EA}$ which would be obtained from the fit of the growth and decay of the transient to a double exponential function, eq 7. (A semiquantitative allowance for decay has been introduced by assuming the plateau region as the signal level obtained by extrapolating the decay part of the traces to the time of laser excitation.) (3) Importantly, there is good agreement between the rates of formation and decay of this transient and those of the excited intermediate observed via energy transfer to DBA, as confirmed by the data shown in Figure 6. The basis for the exciplex interpretation of those experiments will now be reviewed.

The typical fluorescence decay curves of DBA, when excited at 305 nm in solutions containing both acetone and durene (Figure 4, inset), are entirely similar to those previously reported for cyclohexane solutions of DBA with cyclohexanone and mesitylene.[5] In both cases, the decay curves revealed the formation of an excited transient capable of transferring its energy to DBA. The appearance of this transient requires the presence of both the alkanone and the aromatic in the solution, and pulse-excitation must be at a wavelength absorbed by the ketone. On the other hand, the nature of the solvent is not critical (acetonitrile or cyclohexane, for example). The assignment of the excited transient was supported in the case of cyclohexanone/mesitylene, and is supported in the case of acetone/durene, by the internal consistency between the predictions based on the exciplex assumption (Scheme I) and the experimental results: for example, the excellent fit of the fluorescence decay curves to a triple exponential function, as the mechanism requires, and the dependence of $\lambda_a$ and $\lambda_b$ on durene concentrations. Scheme I, which postulates a bimolecular exciplex, is the simplest hypothesis compatible with the DBA data; there is no indication of a "triple" exciplex. The presence of DBA simplifies the reaction system; at a concentration of $\sim 10^{-4}$ M, as in most of the experiments reported here, quenching of the exciplex by DBA is its dominant mode of decay. It follows that at low DBA concentration modes of deactivation not included in the scheme may play a role: for example, triplet–triplet annihilation in the laser flash experiments, or quenching of the exciplex by durene.

Figures 3 and 6 establish convincingly that the transients seen directly in absorption and indirectly in emission are the same species. Although at 20 °C the rate constant $k_{EA}$ for association of triplet acetone with durene is only $5 \times 10^7$ M$^{-1}$ s$^{-1}$, i.e., over two orders of magnitude smaller than the diffusion-controlled limit, it is important to note that this is not the consequence of a large activation energy. The two sets of data agree well on that, and this accord is the more meaningful given that $k_{EA}$ is much smaller than $k_{dif}$. The activation energy calculated from all the data points in the Arrhenius plot (Figure 3) is 1.5 kcal/mol and log ($A$/M$^{-1}$ s$^{-1}$) is 8.85.

Unfortunately, measurements of exciplex relaxation parameters are far more difficult than those for its formation. Thus, the rate constants for the dissociation of the exciplex to give triplet acetone and ground-state durene ($k_{AE}$) and its decay to ground-state products ($k_d^E$) are poorly determined. Nevertheless, it is clear that this exciplex lives several microseconds. Analysis of the DBA results leads to good order of magnitude estimates of $k_{AE}$, $k_2$ (eq 4), and consequently also of $k_d^E$. For example, at 31 °C, $k_{AE} \simeq 1.5 \times 10^5$ s$^{-1}$, $k_2 \simeq 2.3 \times 10^6$ M$^{-1}$ s$^{-1}$, and $k_d^E \simeq 5 \times 10^5$ s$^{-1}$. Unfortunately, the values of these rate constants are extremely difficult to obtain as a function of temperature by the flash photolysis method, because of the weakness of the signal associated with the transient at the low laser intensity which is necessary to avoid second-order effects such as T–T annihilation, and because of the very slow rate of decay of the transient. The kinetics of growth and decay of the transient observed in the laser experiments obey reasonably well eq 7, as expected,[19] where $\lambda_1$ and $\lambda_2$ are given by

$$\lambda_{1,2} = \tfrac{1}{2}\{X + Y \mp \sqrt{(Y - X)^2 + 4k_{EA}k_{AE}[D]}\} \tag{8}$$

with

$$X = k_d^A + k_{EA}[D] \tag{9}$$

$$Y = k_d^E + k_{AE} \tag{10}$$

Theoretical curves calculated from these equations with the rate parameters taken from the DBA fluorescence data fit well the growth curves obtained in the laser experiments. The decay part of these traces, although entirely consistent with the DBA data obtained under the same conditions of laser excitation (Figure 6), is not directly comparable with the DBA results acquired by single-photon counting, mainly because of the contribution from T–T annihilation in the laser system, as already noted.

**Exciplex Binding Energy and Entropy of Association. A Comparison with Literature Data.** In spite of the uncertainty attached to the values of $k_{AE}$ and the activation energy $E_{AE}^a$, it is interesting to speculate on the binding energy of this quite stable exciplex, which forms so remarkably slowly.

As Figure 3 shows, the absorption and the DBA fluorescence methods are in reasonable agreement regarding the activation energy associated with the formation of the exciplex, $E_{EA}^a = 1.5$ kcal/mol. As pointed out before, the Arrhenius parameters for exciplex dissociation cannot be determined accurately, largely because this mode of decay usually accounts for less than 20% of the global exciplex decay. However, examination of the data at the various temperatures suggests that $E_{AE}^a \leqslant 7$ kcal/mol. If

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[18] (a) Cundall, R. B.; Voss, A. J. R. *J. Chem. Soc., Chem. Commun.* **1969**, 116. (b) Note that the triplet lifetime of *o*-xylene appears to be limited by excimer formation.

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one accepts this limit, then one calculates that the exciplex binding energy is

$$\Delta H = E_{EA}{}^{a} - E_{AE}{}^{a} > -5.5 \text{ kcal mol}^{-1}$$

This upper limit for the exciplex binding energy ($\Delta H = -5.5$ kcal/mol) combined with an estimated $\Delta G \sim -3.4$ kcal/mol at 320 K leads to an entropy of association of −7 eu, much smaller than the −20 eu typically expected for a molecular association process.[20] Lower values of $E_{AE}{}^{a}$ would naturally lead to less negative (or positive) values of the entropy of association. This is an intriguing result which awaits confirmation in the present acetone/durene system, as well as in other examples of triplet alkanone/aromatic exciplexes.

Similarly surprising thermodynamic parameters—high $K_E$, small $\Delta H$, and positive or very small negative values of $\Delta S$—were recently reported by Kapinus et al.[21] for triplet exciplexes of porphyrins with nitro compounds, first observed by Whitten and co-workers.[22] Unfortunately, Kapinus's data on the temperature dependence of the exciplex dissociation rate show extensive scatter, and the activation energy for this particular process is poorly determined. Nevertheless, there is the suggestion in their work of a situation which seems to parallel that observed here where exciplexes are held together to some extent by entropy factors.[21b] In spite of the vast literature dealing with excimers and exciplexes, our knowledge of their thermodynamic properties in fluid solutions is almost entirely restricted to singlet excited complexes. In the majority of cases the rate of photoassociation is found to be close to the diffusion limit, as observed, for example, for the *N*,*N*-dimethylaniline/perylene singlet exciplex[23] and excimers of saturated cage amines.[24] This is certainly in contrast with the value of $k_{EA}$ reported here as well as those for the cyclohexanone/mesitylene triplet exciplex in either cyclohexane or acetonitrile.[5] Similarly, the rates of formation of two of the triplet exciplexes between porphyrins and nitro compounds studied by Kapinus are more than two orders of magnitude less than diffusion controlled,[21] and Takemura et al.[25] have measured rates of photoassociation of 2.0 and 6.0 × $10^7$ $M^{-1}$ $s^{-1}$ for triplet excimers of naphthalene and 1-chloronaphthalene, respectively. From both triplet–triplet absorption and phosphorescence measurements in isooctane, Lim and co-workers concluded that intramolecular triplet excimers are formed in $\alpha,\alpha$-dinaphthylmethane, -ethane, -propane, and -butane.[26] This contrasts with fluorescence studies of these compounds,[27] which show typical intramolecular singlet excimer fluorescence only for dinaphthylpropane, as predicted by the $n = 3$ rule. These authors concluded that the structure of the triplet intramolecular excimers was a highly skewed one, thus very different from the sandwich configuration favored by the singlet excimers. The rise time of these triplet intramolecular excimers indicated an unusually low rate of formation; Lim et al. suggest that this may be due to a potential energy barrier to achieving the skewed excimer structure.[26] Our results, inasmuch as they may bear on theirs, do not seem to support a high-energy barrier on the path to excimer formation.

When comparing the rate of formation of singlet excimers or exciplexes to that of triplet complexes, it should be kept in mind that the short lifetimes of most singlet species bias the observation of their photoassociation reactions toward fast processes; i.e., only fast processes can compete with fluorescence or with radiationless processes deactivating the excited state on the nanosecond time scale. Slow-forming singlet excimers and exciplexes may simply go unnoticed. Conversely, ideal candidates for triplet complexes should be molecules which undergo intersystem crossing rapidly and efficiently to yield fairly long lived triplets. Acetone is a case in point.

In addition to their fast rate of excimer or exciplex formation, the singlet complexes mentioned above conform to expectation regarding their thermodynamic parameters. The values of $\Delta H$ and $\Delta S$ associated with the perylene–dimethylaniline exciplex[23] are −6.6 kcal/mol and −15.6 eu, whereas the corresponding values for the ABCO excimer[24] are −11.6 kcal/mol and −19 eu, respectively. Negative $\Delta S$ values are the rule for all the singlet excimers listed in Stevens' review.[20]

Neither of the two types of interaction usually considered to be responsible for singlet excimer/exciplex binding,[28] namely dipole–dipole resonance and charge-transfer interaction, seem likely to play a major role in the binding of the present triplet exciplex. On the basis of the known oxidation and reduction potentials of durene and acetone and on the triplet energy (78 kcal/mol) of acetone, one calculates[29] that full electron transfer from the aromatic to the alkanone would be endothermic by about 13 kcal/mol and, thus, the CT state is too high to significantly stabilize the exciplex. The situation is very different for the quenching of triplet benzophenone by amines, for example, where exothermic electron transfer results in the formation of an ion pair on the picosecond time scale.[30] Dipole–dipole interactions are not expected to play a role in triplet-state association, since the electronic transitions in both acetone and durene would be spin-forbidden. A remaining possibility is some stabilization of the encounter complex of triplet acetone and durene by electron-exchange interactions, of the type responsible for collisional triplet-energy transfer. Thus it is useful to consider the conditions which influence such interactions.[31]

The rate of exchange energy transfer between triplet acetone and durene would be slow, not only because of the 2 kcal/mol endothermicity but also because of an expected entropy loss due to the different geometries of triplet- and ground-state acetone; indeed, ground-state acetone is planar whereas triplet acetone is likely to be bent, like triplet formaldehyde.[32] The importance of such entropy changes in reducing the rate of triplet energy transfer has recently been pointed out.[33] A straightforward triplet energy transfer mechanism could account neither for the quenching of triplet acetone by benzene (benzene triplet is ~7 kcal above acetone triplet, yet $k_q = 2 \times 10^6\ M^{-1}\ s^{-1}$)[4a] nor for the quenching of triplet cyclohexanone by *o*-xylene ($\Delta H \sim 5$ kcal), where a transient exciplex is observed.[6] Indeed, even if no entropy change was associated with energy transfer between triplet acetone and

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(29) Calculated according to Loufty et al.[4b] as follows: $\Delta G^{\circ} = E_{EC}{}^{\circ} - E_T{}^*$ with $E_{CT}{}^{\circ} = E_D{}^{ox} - E_A{}^{red} - e^2/\epsilon r$. Since $E_T{}^*$(acetone) = 1.8 V, $E_{1/2}{}^{ox}$(durene) = 1.8 V, and $e^2/\epsilon r = 0.1$ eV in acetonitrile, one estimates $\Delta G = +0.6$ eV or 13.8 kcal. The value of the oxidation potential of durene is taken from the following: Mann, C. K.; Barnes, K. K. *Electrochemical Reactions in nonaqueous systems*; Marcel Dekker: New York, 1970.

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(34) In the present case, assuming $\Delta S = -4$ eu and $\Delta H = 2$ kcal/mol for the forward process in eq 11, one can estimate $k_{ET} = k_{dif} e^{\Delta S/R} e^{-\Delta H/RT} \simeq 1 \times$

$$3_A{}^* + D \underset{k_{-ET}}{\overset{k_{ET}}{\rightleftharpoons}} A + 3_D{}^* \qquad (11)$$

$10^8\ M^{-1}\ s^{-1}$ and the equilibrium constant $K \simeq 4.5 \times 10^{-3}$ (diffusion-controlled back transfer). Hence, even though the kinetics of energy transfer (eq 11) would be the same[35] as that of exciplex formation (eq 1), the concentration of triplet durene once equilibrium is attained would be only $4 \times 10^{-3}$ that of triplet acetone, thus much too low to be the species seen growing in the DBA experiments.

(35) Nordin, S.; Strong, R. L. *Chem. Phys. Lett.* **1968**, *2*, 429–432.

durene, on the basis of the ~2-kcal/mol endothermicity one estimates that at equilibrium the concentration of triplet durene would only be 3% of that of triplet acetone (at equal concentrations of ground-state acetone and durene). Even if subsequent energy transfer from triplet durene to DBA took place with unit efficiency, the typical second peak of the decay curves (see Figures 4 and 6) would not be observed.[34] A similar argument is even stronger in the case of triplet cyclohexanone and *o*-xylene[6] where the equilibrium concentration of triplet *o*-xylene would be only 0.1% of that of triplet ketone. Thus, energetic as well as spectral considerations rule out the aromatic triplet as the excited donor species detected in these experiments.

While the analysis presented above clearly rules out the excited aromatic as the species detected in the experiments, one can still ask whether the small concentration present could affect the observable decay of the exciplex through a leakage mechanism, fed through the excited-state equilibria. Quite clearly, the equilibrium concentration of triplet durene *must* be present in the system, in equilibrium with triplet acetone, and therefore with the exciplex as well. When in addition to the ~2 kcal/mol energy difference with acetone (vide supra) we take into account $k_{AE}$ and $k_{EA}$, the concentration of triplet durene would be four orders of magnitude lower than that of the exciplex, far too low to play any role in determining the exciplex decay kinetics. Finally, we envision the mechanism proposed as applicable not only to alkanones but also to the quenching of triplet benzophenone by benzene, which has been proposed to proceed via an exciplex intermediate[36] and where energy transfer can clearly be ruled out on energetic grounds.[37]

Exciplex formation may nevertheless be coupled with endothermic energy transfer. For the sake of discussion, a possible rationalization of the results goes as follows. Triplet acetone and durene first form an encounter complex. Although the solvent cage is usually considered to allow sufficient time for the collision partners to explore all possible mutual orientations, here the preconditions for exciplex formation must be very restrictive, since most encounter complexes simply come apart ($k_{EA} \simeq 5 \times 10^7$ M$^{-1}$ s$^{-1}$). Conceivably, the solvent cage may actually reduce the probability of reaching the desired orientation. In any case, sometimes proper orbital overlap and nuclear distance are achieved, through repeated collisions within the complex, and a stabilized exciplex is formed. The possibility of a stabilized complex along the path of an electron-exchange energy-transfer process has been discussed by Turro.[31] Studies of other ketone–aromatic pairs, in solvents of different viscosities, may lead to an understanding of the factors apparently at play here.

**Registry No.** DBA, 523-27-3; acetone, 67-64-1; durene, 95-93-2.

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(37) $E_T$(benzophenone) = 69 kcal, hence $\Delta E_T$ = 15 kcal.

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# Davydov Splitting in 7-(2-Anthryl)-1-heptanoic Acid Langmuir–Blodgett Films

**William S. Durfee,[†] Winfried Storck,[†] Frank Willig,*[†] and Matthias von Frieling[‡]**

*Contribution from the Fritz-Haber-Institut der Max-Planck-Gesellschaft, D-1000 Berlin 33, West Germany, and the Institut für Kristallographie, Freie Universität Berlin, D-1000 Berlin 33, West Germany. Received August 6, 1986*

**Abstract:** 7-(2-Anthryl)-1-heptanoic acid (I) forms a monolayer at pH 4.9 and 6.0 ([Cd$^{2+}$] = 5.5 × 10$^{-4}$ M) with a zero-pressure area of 26 Å$^2$/molecule. Monolayers of I transfer at 21 mN/m to hydrophobic surfaces to form Y-type Langmuir–Blodgett multilayers. Low-angle X-ray diffraction of multilayers of I reveals a periodic distance normal to the film plane of 36.0 (pH 4.9) and 37.1 Å (pH 6.0). The absorption spectrum in the 420–250-nm range shows a polarization effect for the first and second singlet vibronic transitions of the anthracene moiety that is analogous to that seen for the *ab* face of single-crystal anthracene. For multilayers prepared at pH 6.0 the first singlet vibronic transition is split by ~360 cm$^{-1}$ (measured at the 0–0 transition) into two orthogonally polarized components with a polarization ratio of ~2.5. This polarization effect is attributed to multilayer polycrystallinity and a transfer-induced preferred orientation for the unit cell.

The last 10 years have seen a tremendous increase in the number of basic[1a] and applied[1b] studies of Langmuir–Blodgett (L–B) films. In order to understand such diverse phenomena as, for example, conductivity[2] or the electronic spectroscopy of dye molecule aggregates[3] in L–B multilayers, structural information, especially in-plane structure, is essential. Polarized IR spectroscopy and electron diffraction, in particular, have been used extensively to determine in-plane structure. Recent studies by Swalen and co-workers[4] and Allara and Swalen,[5] for instance, made use of grazing incidence and transmission Fourier transform IR to determine the orientation and crystalline packing arrangement of cadmium arachidate monolayers. Several of the earliest applications of electron diffraction[6,7] showed that some fatty acid L–B films deposited anisotropically on metal surfaces. More recent electron diffraction studies,[8-11] in some cases complemented by polarized IR spectroscopy,[8,12] have determined unit cell parameters and orientation for a number of fatty acids on various metal

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[†] Fritz-Haber-Institut der Max-Planck-Gesellschaft.

[‡] Freie Universität Berlin.

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