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Exciton Diffusion in Pyrene — A Thermally Activated Hopping Process†

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Abstract—Sensitized fluorescence and fluorescence quenching has been studied in pyrene layers, doped with small amounts of coronene, anthraquinone and acenaphthylene. Coronene exhibits strong sensitized fluorescence at room temperature, but not at 77 °K. This behaviour is due to decreased exciton mobility. The activation energy of the exciton hopping process has been determined to be $E_a = 0.055$ eV. The lifetime of pyrene excimer fluorescence is decreased by quenchers in accordance with the steady-state measurements of relative quantum efficiencies. Three possible mechanisms of excimer state hopping in pyrene are discussed.

1. Introduction

Excitons in organic molecular crystals may be described by two models, a band model(1,2) in which absorption of UV light is assumed to create a completely delocalized excited state, and a hopping model(3) which considers localized absorption at individual molecules, followed by a random hopping of the excitation energy. Whether the band or the hopping model is applicable when interpreting experimental results depends on the strength of interaction between the molecules(4) and on temperature.(5) The Davydov Splitting of the electronic levels as observed at very low temperature is explained by the band model. A further experimental evidence in favour of an exciton band is the reduction of exciton range with increasing temperature, as observed in energy transfer experiments at low temperatures.(6) This effect is due to phonon scattering shortening the mean free path or the region of coherence of the exciton. The

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hopping model becomes applicable, if the free path approaches the distance between neighbouring molecules in the lattice. It is most widely used in evaluating energy transfer experiments(3,7) in order to estimate the diffusion length, diffusion constant, and hopping time. Thermal activation of exciton hopping has not been observed in anthracene-type crystals used in most energy transfer studies.(7) In these crystals the molecules are arranged in such a way that the molecular planes do not overlap. Pyrene, on the other hand, represent rather a different lattice type in which the molecules are arranged in sandwich-like pairs (Fig. 1). Owing to this peculiar structure, the lowest excited singlet state is an excimer state,(8) due to complex formation of an excited pyrene molecule with a neighbouring ground-state molecule.(9) Excimer formation reduces the intermolecular distance and the energy is decreased considerably with respect to the first monomeric excited singlet state.(10)

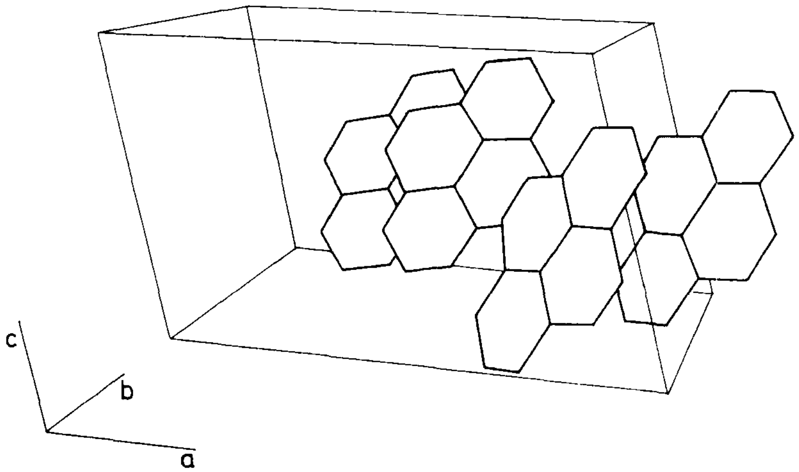

Figure 1. Molecular arrangement in the unit cell of pyrene according to Robertson and White,(23) $a = 13.6$ Å, $b = 9.2$ Å, $c = 8.4$ Å, $\beta = 100°$.

Therefore, one might expect that the electronic excitation is trapped in these states. On the other hand, host-to-guest energy transfer has been observed in pyrene (see Table 1) by Northrop and Simpson,(11) Hochstrasser,(12) Kearns and Kawaoka,(13) and Y. Tomkiewicz and Loewenthal.(14)

TABLE I Fluorescent Guest Substances in Pyrene

Substance(a)	S_1(b) (cm^{-1})	Sensitized Fluorescence	Lit.
Anthracene	26,700	0	(c)
Picene	26,600	0	(c)
Tetraphenylethylene	26,600	0	(c)
1,2-benzanthracene	26,050	0	(c)
9,10-diphenylanthracene	25,450	0	(c)
1,2,5,6-dibenzanthracene	25,400	0	(c)
Coronene	23,350	+	(c)(11((18)
Perylene	23,100	+	(c)(12)(14)
Anthanthrene	23,100	+	(11)
Ovalene	21,550	+	(11)
Tetracene	21,100	+ (d)	(13)
Violanthrene	20,350	+	(11)
Dinaphthopyrene	19,400	+	(11)
Isoviolanthrene	19,100	+	(11)

(a) the concentrations used for screening were 10^{-3} m/m,
(b) from absorption in solution,
(c) this paper,
(d) weak because of poor solubility.(13)

Energy transfer in pyrene may be due to exciton diffusion (monomer or excimer), long-range transfer by dipole–dipole resonance from either the monomer or the excimer level and reabsorption of fluorescent light. In order to distinguish experimentally between these different possibilities, it is important to use substances with very weak absorption in the host fluorescence region and samples consisting of thin layers or crystals. Energy transfer by dipole–dipole resonance or by reabsorption will then be negligible.

If under these conditions effective energy transfer does occur, it is due to excitons. It should be possible to distinguish between monomer and excimer excitons by studying the temperature dependence of energy transfer: excimer state diffusion should freeze in at low temperature, whereas monomer exciton diffusion should not. Furthermore, the lifetime of the excimer state, if mobile, should be reduced by quenching substances.

In recent publications, excimer state diffusion has been postulated in order to explain several experimental observations. Birks(15) found the excimer lifetime of pyrene crystals to be dependent on the purity of the material. Kearns and Kawaoka⁽¹⁶⁾ postulated the existence of both monomer and excimer excitons and observed a partial freezing-in of energy transfer at liquid nitrogen temperature. Goldschmidt, Y. Tomkiewicz and Berlman⁽¹⁷⁾ measured the lifetime of the excimer state at excitation with high intensity laser radiation. They found the lifetime to be shortened with increasing intensity and attributed this to the mutual annihilation of mobile excimer states.

We performed experiments on sensitized fluorescence, excimer lifetime, and the temperature dependence of fluorescence quenching by guest molecules. According to our results, a clear-cut distinction between monomer and excimer diffusion can be made. The activation energy of the excimer-hopping process has been determined.

Preliminary results of this work have been published elsewhere.⁽¹⁸⁾

2. Experimental

2.1. Purification of Pyrene

Pyrene, puriss. (Fluka), was recrystallized from ethanol and zone-refinded in 50 zone passes using an apparatus by Desaga (Heidelberg). Zone-refining has been performed vertically at a rate of 2 mm/h and a ratio zone length/total length of 1.5/30 cm. We exclusively used material from the first third of the ingot. M.p. = 152.5 °C (TDA); melting enthalpy $\Delta H = 3.95$ kcal/mole; fluorescence lifetime at room temperature $\tau_0 \approx 120$ ns.

2.2. Sample Preparation

The samples have been prepared by melting a small amount of an intimate pyrene/guest mixture between two quartz plates to yield layers about 1 μm thick.

The guest substances coronene (purum, Fluka), anthraquinone (p.a., Schuchardt), and acenaphthylene (pure, Rütgerswerke) were used without further purification.

2.3. Fluorescence Spectra

All spectra have been recorded with a Hitachi-Perkin Elmer MPF-2A spectrofluorimeter, equipped with a 150-W Xenon lamp and a photomultiplier R 136 (Hitachi). The apparatus has been calibrated by means of a tungsten lamp (Wi 21, Osram) of known spectral distribution. All spectra were corrected to equal quantum intensity. Spectra at 77 °K have been obtained with the Hitachi low temperature ancillary equipment. The temperature dependence between −30 and 70 °C has been measured with the variable temperature cell in which the sample was mounted on a brass sample holder. Absorption spectra have been recorded in a Beckman DK-2 A spectrophotometer.

2.4. DECAY TIMES

Fluorescence decay times of the pyrene samples were measured upon exposure to a Fischer Nanolite lamp supplying flashes of 20 nsec halfwidth through a filter combination with a narrow passband centred on 325 nm.

A cut-off filter (50% transmission at 490 nm) surpressed the excitation light between sample and photomultiplier. Therefore, only the excimer-fluorescence light was detected by a RCA 1P28 photomultiplier tube working into a fast cathode follower circuit. The decay curves were displayed on a tektronix Type 545 oscilloscope and then analyzed on a multiple exposure photograph yielding decay times with an accuracy of 20%. For decay times below 50 nsec the finite duration of the excitation flash was taken into account. This was achieved by comparing the recorded decay curve to a family of curves calculated from the time function of the excitation and a set of decay times.

3. Sensitized Fluorescence

The first excited singlet level of the guest must of course lie below the exciton level of the host material in order to show sensitized fluorescence upon excitation of the host. The first (monomer) singlet level of pyrene is found in the solid state absorption spectrum at 26,700 cm^{-1}, whereas from experimental results by Birks(10) the excimer level was inferred to be at 23,860 cm^{-1}. Several guest substances with appropriate energy levels have been screened. The results are compiled in Table 1 together with data reported in the literature. As can be seen, only those guest substances whose S_1 levels are below 23,500 cm^{-1} act as fluorescent traps for the excitation energy, whereas guests with $S_1 > 25{,}000$ do not.

Several guest substances showing sensitized fluorescence in pyrene exhibit very strong absorption bands in the region of pyrene fluorescence so that Förster's transfer and reabsorption may be important. Only coronene absorbs weakly in this region ($\epsilon < 400$ for $\nu' < 27{,}000\ \mathrm{cm}^{-1}$).[19] It was therefore chosen for a more detailed study. Experimentally, coronene has the disadvantage of its fluorescence overlapping with the host excimer emission. Nevertheless, the fluorescence guest-to-host intensity ratio can be determined since the shapes of the two spectra are known and can thus be separated into the two components.

Figure 2 shows a fluorescence spectrum of coronene doped pyrene. The structured coronene emission dominates at room temperature. The host has been excited at 30,000 cm^{-1} where its optical density exceeds that of the guest at least by a factor of 1,000.

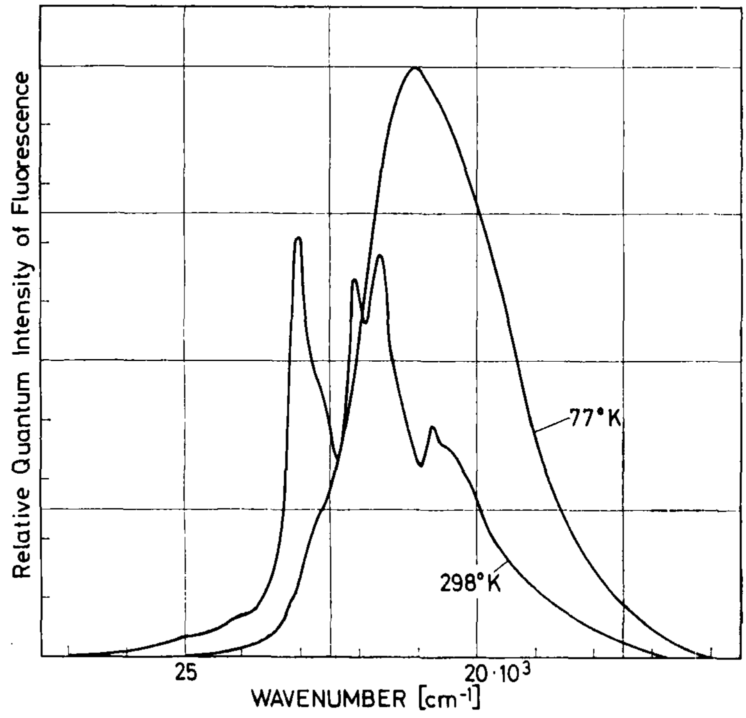

Figure 2. Fluorescence spectra of pyrene, doped with coronene (2×10^{-3} mole/mole dimer) at excitation via the host.

The fluorescence intensity ratio I_G/I_H depends on guest concentration ($c_G \leqslant 4 \times 10^{-3}$) according to

$$I_G/I_H = 1{,}100\, c_G \tag{1}$$

where c_G is given in mole guest/mole dimer. This dimension of guest concentration should be preferred to mole guest/mole host as previously used by us(18) because the exciton is dimeric in nature (as will be shown later) and because substitution of only one pyrene molecule in a pair already transforms the pair into a trapping centre.

The quenching factor Q of host fluorescence, as defined by Northrop and Simpson(11) $Q = (I_{H,0} - I_H)/I_H(I_{H,0}$ and I_H intensity without guest and with guest of concentration c_G) is related to the intensity ratio according to(20)

$$Q = \frac{I_G}{I_H} \cdot \frac{\eta_H}{\eta_G} \tag{2}$$

where η_H = quantum efficiency of the pure host and η_G the quantum efficiency of the guest molecules at direct excitation. Several values of Q have been determined. Taking the value $\eta_H = 0.64$ proposed by Birks(15) for pyrene crystals at room temperature, we find $\eta_G = 0.3$.

According to the simple hopping model(3,11,20)

$$Q = nc_G \tag{3}$$

where n = number of steps of the exciton in the pure host. From (1) to (3) we find $n = 2.4 \times 10^3$.

The room temperature experiments alone do not allow a distinction to be made between monomer and excimer diffusion because competitive trapping of monomer excitons by guest molecules and host molecular pairs may lead to the same linear dependence of the intensity ratio on guest concentration as has been demonstrated in the case of polyvinyl carbazole.(21) Evidence for excimer-state diffusion is derived from two kinds of experiments: lifetime measurements (Sec. 5) and study of energy transfer at low temperature.

From the potential energy diagram of the pyrene excimer(10) one would expect that the excimer state is immobile at low temperature, whereas monomer excitons should be able to move. The 77 °K pyrene/coronene spectrum (Fig. 2) shows clearly the disappearance of sensitized fluorescence. Apart from a weak shoulder, the curve is identical with the 77 °K spectrum of pure pyrene. Direct excitation of the guest on the other hand gives rise to the coronene spectrum. This proves that the drastic decrease in guest intensity is not due to a decrease of η_G which, in another experiment, was found to be temperature-independent between −30 and +70 °C. The critical radius for dipole–dipole resonance (pyrene excimer → coronene) at 77 °K is still about equal to a pyrene pair–pair distance. Therefore, coronene should be able to act as a trap at the low temperature, too, so that the observed effect would indeed be due to decreased mobility of the migrating excited state.

4. Activation Energy of Exciton Hopping

A first attempt at measuring the exact temperature dependence of energy transfer from the fluorescence guest-to-host ratio failed, since not only the shape of the pyrene fluorescence spectrum depends on temperature (Fig. 3) but also the shape of the vibrational structure of the coronene emission. It was not possible therefore to separate the two components accurately. An alternative method consists in

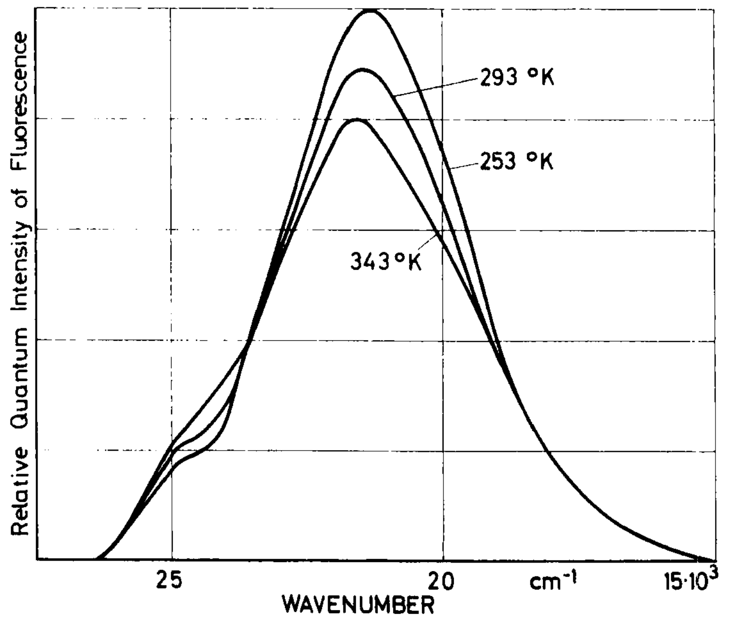

Figure 3. Fluorescence of layers of pure pyrene at different temperatures.

measuring the temperature dependence of fluorescence quenching with nonfluorescent guests. A search for effective quenching substances with weak absorption in the region of pyrene fluorescence proved anthraquinone ($S_1 = 23{,}600\ \mathrm{cm}^{-1}$, $\epsilon < 10^2$ for $\nu' < 27{,}000\ \mathrm{cm}^{-1}$)[22a] and acenaphthylene ($S_1 = 21{,}400\ \mathrm{cm}^{-1}$, $\epsilon < 300$ for $\nu' < 27{,}000\ \mathrm{cm}^{-1}$)[22b] to be very suitable quenchers. Both substances do not fluoresce in pyrene at temperatures between -30 and $+70$ °C. Anthraquinone shows weak phosphorescence at the long wavelength tail of the excimer fluorescence.

We measured the quenching factor as a function of temperature in the above-indicated range and deduced from the results the temperature dependence of the hopping time. The quenching factor at room temperature has been determined to be $Q = 5$ (anthraquinone) and $Q = 3.5$ (acenaphthylene) with $c_G = 2 \cdot 10^{-3}$ mole/mole dimer in both cases (Fig. 4). These values are in excellent agreement with the value of $Q = 4.8$ expected for coronene according to (3), and show that both quenching substances are as effective traps as coronene.

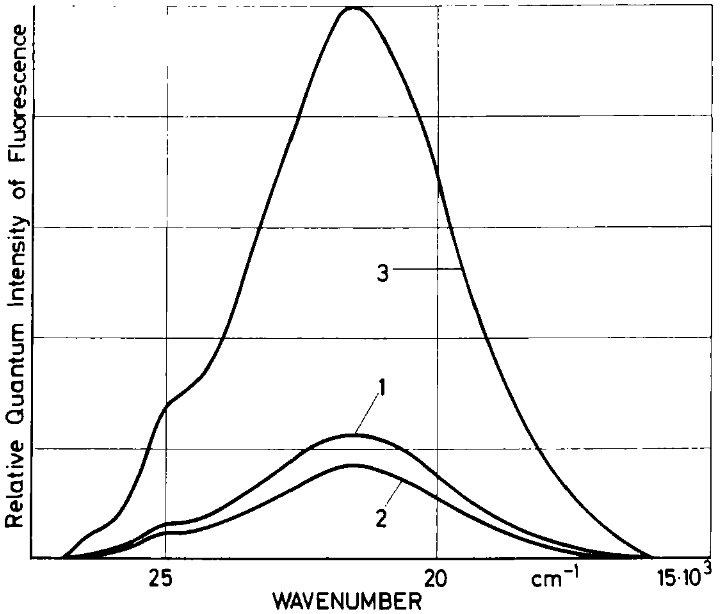

Figure 4. Fluorescence spectra at room temperature of pure pyrene (3) and pyrene doped with acenaphthylene (1) and anthraquinone (2) (2×10^{-3} mole/mole dimer each).

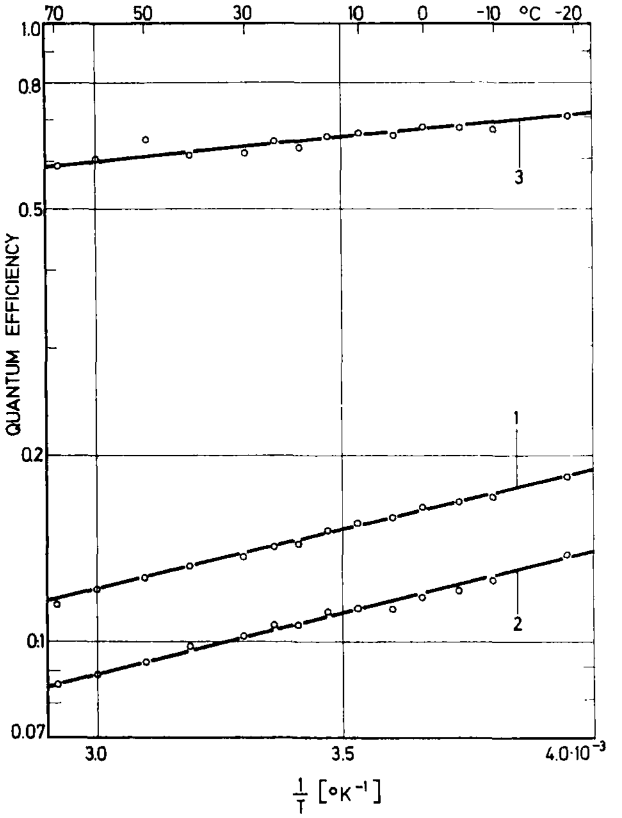

Figure 5. Quantum efficiency of pure pyrene (3), and pyrene doped with acenaphthylene (1) and anthraquinone (2) (2×10^{-3} mole/mole dimer each).

Figure 5 shows the temperature dependence of the quantum efficiencies for pure pyrene (3) and pyrene doped with anthraquinone (2) and acenaphthylene (1) . The values have been obtained from the areas under the corrected emission curves recorded at the temperatures indicated. They have been normalized to $\eta_H = 0.64$ (293 °K).(15)

The quenching factor, which yields the number of steps n (3), has been determined from the values in Fig. 4 as a function of temperature. Knowing n, the hopping time τ_h is easily determined from

$$\tau_h = \frac{\tau_0}{n} \tag{4}$$

The excimer lifetime of pure pyrene, τ_0, has been measured by Birks, Kazzaz and King;(15) it varies from 121 ns (−20 °C) to 95 ns (+70 °C).

In Fig. 6, the hopping time is shown in a semilogarithmic plot as a function of $1/T$ for the two quenchers. The two lines are exactly parallel; the activation energy deduced from the plot is

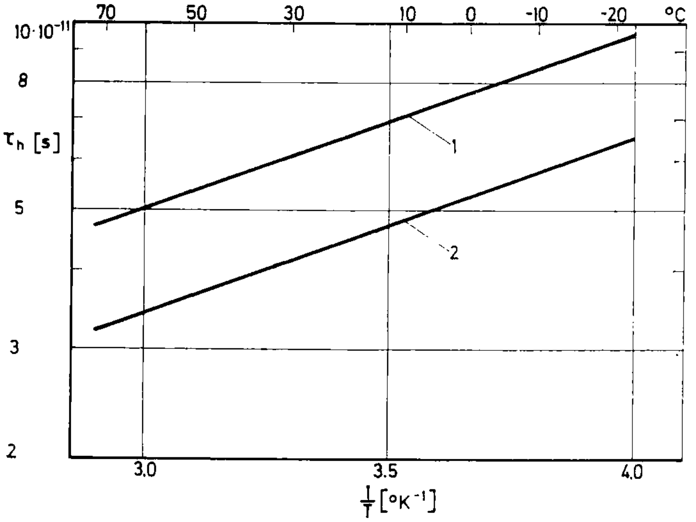

Figure 6. Hopping time τ_h as a function of temperature; acenaphthylene (1), anthraquinone (2).

$$E_a = 0.055\ \text{eV}.$$

This value corresponds to about $2\,kT$ at room temperature and is large enough to account for the freezing-in of energy transfer observed at liquid nitrogen temperature.

The fact that both quenching substances give the same activation energy clearly demonstrates that we are measuring exciton mobility rather than the temperature dependence of exciton-capture cross section.

5. Fluorescence Quenching and Lifetime Reduction by Guest Molecules

The lifetime of the mobile excited state is reduced in the presence of quenchers as a consequence of energy transfer. If the mobile state is identical with the fluorescent state, the fluorescence intensity quenching is due to this reduction of lifetime. In this case the quenching factor Q can be determined either from intensity measurements

$$Q_1 = \frac{I_0 - I}{I}$$

or from fluorescence-decay time measurements

$$Q_2 = \frac{\tau_0 - \tau}{\tau}$$

The influence of the dopants anthraquinone and acenaphthylene on the intensity and the decay time of pyrene host fluorescence was determined for a wide range of guest concentrations. Coronene proved to be unsuitable as guest molecule for the lifetime studies because its fluorescence lies within the wavelength and decay-time range of the pyrene fluorescence.

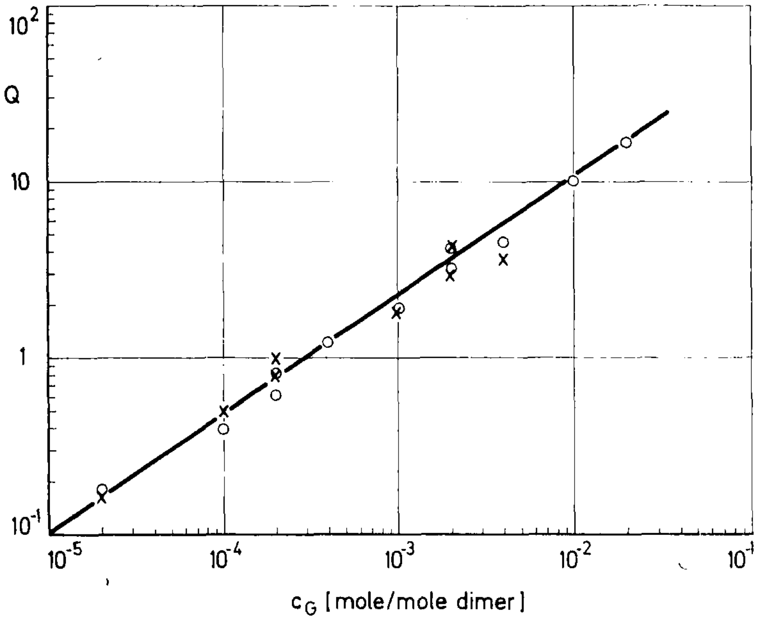

Figure 7. Pyrene/acenaphthylene: quenching factors Q_1 and Q_2 obtained from relative quantum efficiencies (O) and from decay measurements (×), respectively.

The decay time of the pyrene fluorescence was significantly reduced by the addition of the guest molecules. The fluorescence intensity, compared to that of pure pyrene, has been measured for each sample.

The results are presented in Fig. 7 for pyrene plus acenaphthylene and in Table 2 for pyrene plus anthraquinone. In both cases the two sets of values agree reasonably well, and this shows that steady state quenching is wholly due to lifetime reduction.

TABLE 2 Comparison of Q-values in Pyrene/Anthraquinone

c_G (mole/mole dimer)	Q_1	Q_2
10^{-4}	0.50	0.30
2×10^{-4}	0.87	0.85
4×10^{-4}	1.2	1.4
10^{-3}	2.4	2.5
2×10^{-3}	3.5	5.7
4×10^{-3}	9.8	7.0
10^{-2}	10	
2×10^{-2}	22	

Contrary to the behaviour expected from the simple quenching formula (3), the curve shown in Fig. 7 and the data of Table 2 indicate a sublinear dependence of $Q(c_G)$ as has frequently been observed by other authors.(7) The slope of the straight line best fitting the data in a bilogarithmic plot is about 0.8 for anthraquinone and 0.7 for acenaphthylene.

6. Discussion

In the preceding sections we have presented experimental evidence in favour of a thermally activated exciton hopping process in pyrene. The essential points are:

Sensitized fluorescence is observed, if $S_1(G) \lesssim 23{,}500$ cm^{-1} and is not observed, if $S_1(G) \gtrsim 25{,}000$ cm^{-1}.

Coronene shows intense sensitized fluorescence at room temperature but none at 77 °K.

The freezing-in of sensitized coronene fluorescence at low temperature is due to decreased exciton mobility.

Anthraquinone and acenaphthylene are effective non-fluorescent quenching substances for an investigation of the temperature dependence of exciton mobility.

The hopping time at room temperature has been found to be about $\tau_h = 5 \times 10^{-11}$ s.

The activation energy of exciton hopping has been determined to be $E_a = 0.055$ eV.

In accordance with steady-state measurements, the lifetime of pyrene excimer fluorescence is decreased by quenchers.

These results show clearly that it is the excimer state that moves around in the lattice by a hopping process.

In principle, the excimer state could be transferred from one pyrene pair to a neighbouring one via three mechanisms:

(a) The excimer state dissociates to give an excited monomer and a ground state pyrene molecule, the S_1 (monomer) is transferred to an adjacent pyrene molecule and is trapped again as excimer.

(b) There is still excimer interaction at the ground-state equilibrium position of the molecules in the pairs (vertical distance $d = 3.53$ Å);(23) this position is reached by thermal activation of the excimer, followed by excimer-energy transfer to a neighbouring pair in its equilibrium position.

(c) A pair adjacent to the excimer is compressed by a lattice vibration to about the excimer equilibrium distance ($d < 3.53$ Å), followed by excimer-energy transfer to this pair.

Mechanism (a), a trap-controlled monomer-exciton diffusion, has been proposed by Birks.(24) It will only be applicable if the energy of the excimer state is very close to the monomer S_1 level (26,700 cm^{-1}). According to Birks,(10) the excimer level plus zero point vibrations is at 23,860 cm^{-1}. It is therefore too low in order to explain the small activation energy of 0.055 eV (=450 cm^{-1}) if mechanism (a) applies.

Mechanism (b) requires that the excimer potential at a distance of about 3.5 Å is still below the monomer level. This is indicated in Birks's(10) energy level diagram. If the excimer potential was still more shallow, the activation energy of 450 cm^{-1} could be sufficient

Table 3 Comparison between Excimer and Monomer Exciton Diffusion

	T (°K)	$n^{(a)}$	D (cm^2 s^{-1})	$L^{(b)}$ (Å)	$\tau_h{}^{(c)}$ (s)	τ_0 (s)	Lit.
Pyrene	293	$2.5 \times 10^{3(d)}$	5×10^{-5}	240	5×10^{-11}	$1.13 \times 10^{-7(e)}$	
	77	9	10^{-7}	14	$2 \times 10^{-8(f)}$	$1.8 \times 10^{-7(e)}$	
Naphthalene	293	2.5×10^{4}	5×10^{-4}	500	4×10^{-12}	10^{-7}	25
	170		3×10^{-4}	500 ± 100	$\geqslant 2 \times 10^{-13(g)}$		26
	90	3×10^{4}					25
Anthracene	60	6×10^{4}	5×10^{-3}	1000	3×10^{-13}	2×10^{-8}	7

(a) number of jumps during lifetime τ_0 in the pure crystal,

(b) diffusion length L and mean radial displacement $\bar{r}$ are connected by $\bar{r} = L \cdot \sqrt{3}$(7); $\bar{r} = a\sqrt{n}$ (a = mean distance between adjacent lattice sites),

(c) according to formula (4),

(d) mean value from experiments with coronene, anthraquinone, and acenaphthylene,

(e) according to (15),

(f) extrapolated from τ_h values obtained between 273 and 343 °K with $E_a = 0.055$ eV,

(g) calculated from Davydov splitting.

to bring the pyrene molecules from their excimer equilibrium distance to the ground-state equilibrium distance without dissociation of the excimer.

Mechanism (c) requires a rather flat repulsive ground state potential in order to be in accord with the small activation energy. It cannot yet be decided whether mechanism (b) or (c) prevails.

The hopping time at room temperature is longer by a factor of 10 to 100 as compared with that encountered in anthracene-type crystals. Table 3 compares some characteristic values with corresponding values of anthracene and naphthalene. As a consequence of the long hopping time, the diffusion coefficient and the diffusion length are much smaller in pyrene than in the other crystals. The difference diminishes at higher temperatures. The hopping time for $T = \infty$ is calculated to be $\tau_h = 5.5 \times 10^{-12}$ s and this corresponds to the value for naphthalene. The extrapolated hopping time at 77 °K differs by 4 or 5 orders of magnitude from that in anthracene and naphthalene. It shows that the exciton performs, on the average, less than ten jumps and explains very well the lack of sensitized fluorescence at this temperature.

The extrapolation down to liquid nitrogen temperature might not be accurate because, as has been pointed out by Hochstrasser and Malliaris,(27) a phase transition occurs in pyrene at about 120 °K. These authors found a small discontinuous change in pyrene fluorescence intensity at this temperature. A transition at 115 °K with an enthalpy of about 20 cal/mole was first reported by Jacobs and Parks.(28) In the thermo-differential analysis diagram of pure pyrene we observed a peak at about 120 °K. The crystal lattice should not be drastically altered by this phase transition, since there is still excimer fluorescence below the transition temperature. This suggests that the pair-wise arrangement of molecules is not changed. We therefore believe that the mechanism of exciton diffusion is basically the same in both phases.

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