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Martin Pope [a], Nicholas E. Geacintov [a] & Frank Vogel [a]
[a] Chemistry Department and Radiation and Solid State laboratory, New York University, New York, New York, 10003
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Singlet Exciton Fission and Triplet-Triplet Exciton Fusion in Crystalline Tetracene‡

MARTIN POPE, NICHOLAS E. GEACINTOV and FRANK VOGEL

Chemistry Department and Radiation and Solid State Laboratory
New York University, New York
New York 10003

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Abstract—The dominant radiationless decay channel in crystalline tetracene at 300 °K is a fission of an excited singlet into two triplet excitons with a rate constant $\gamma_S = 1.5 \times 10^{-12} \pm 5\%$ cm³-sec⁻¹. The efficiency of this process at room temperature is estimated as 95% and constitutes an efficient intersystem crossing mechanism. At light intensities $I \gtrsim 10^{15}$ quanta-cm⁻²-sec⁻¹ (366 mμ excitation), the triplet densities at 300 °K are sufficiently high to produce radiative triplet-triplet annihilation or fusion. As the light intensity is increased the quantum efficiency of fluorescence Φ increases, and eventually reaches a constant value (about twice its value in the low intensity region, where fusion is not important). It is assumed that triplet-triplet fusion gives rise to either an excited singlet (rate constant $\gamma_{TS} = (4.8 \pm 1.2) \times 10^{-10}$ cm³-sec⁻¹), or excited triplet (rate constant $\gamma_{TT} = (11 \pm 5) \times 10^{-10}$ cm³-sec⁻¹). The effect of a magnetic field $\mathbf{H} = 4000$ gauss on the rate constants is determined. The radiative triplet-triplet fusion constant and γ_S both decrease in approximately the same manner when a magnetic field is applied. γ_{TT} is shown to be at most slightly dependent on $\mathbf{H}$.

Introduction

It has been shown that the fission[1,2] of a singlet exciton into two triplet excitons is the dominant radiationless decay channel in crystalline tetracene at room temperature. This mechanism accounts for the low fluorescence quantum efficiency Φ ($\sim$0.002[3])

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at 293 °K. Furthermore, the fission process is magnetic field sensitive. The fluorescence efficiency may be increased[4] by as much as a factor of 1.4[1] in a magnetic field above 2000 gauss. The fission mechanism is operative in tetracene because the double-triplet energy level is only about 0.2 eV above that of the fluorescence emitting singlet;[5] Φ therefore increases substantially as the temperature is lowered because the fission channel is closed thereby.[1]

In this paper we show that the triplet excitons formed from the fission process recombine (exciton fusion) to form singlets when the excitation intensity is sufficiently high. When the exciton fusion process is operative, there is therefore an increase in the overall quantum efficiency of fluorescence. We also calculate the kinetic rate constants involved in the fission and fusion processes. The increase in quantum efficiency of fluorescence with increasing light intensity in crystalline tetracene is in sharp contrast to the behavior of anthracene crystals where the fluorescence efficiency decreases at high light intensities.[6] In anthracene this effect is due to the annihilation of two singlet excitons to produce one vibrationally excited singlet, with a resultant loss in fluorescence efficiency.

Experimental

Tetracene powder was subjected to four successive vapor-gradient zone purifications and single flakes 10–20 μ in thickness were grown in an argon atmosphere. The light source was a 1000 watt Hg–Xe lamp. The 366 mμ line was isolated by means of a monochromator, interference filter and a combination of suitable Corning glass filters to eliminate stray light. A fraction of the filtered light was deflected by a beam-splitter onto a light intensity monitoring photodiode. Absolute light intensity measurements were carried out by placing a calibrated photodiode in the place of the crystals. This photodiode was calibrated with a National Bureau of Standards lamp. The fluorescence of the crystal was viewed by means of a fiber optic and magnetically shielded photomultiplier tube.

Results

The fluorescence quantum efficiency in the absence of a magnetic field **H**, $\Phi(0)$, in relative units at 300 °K is plotted as a function of incident light intensity in part (b) of Fig. 1. The fluorescence is enhanced in a magnetic field **H** and the ratio $\Phi(\mathbf{H})/\Phi(0)$ is shown in part (a) of Fig. 1. $\Phi(0)$ is independent of the light intensity I up to values of $I \sim 5-8\times10^{14}$ quanta-cm^{-2}-sec^{-1}.

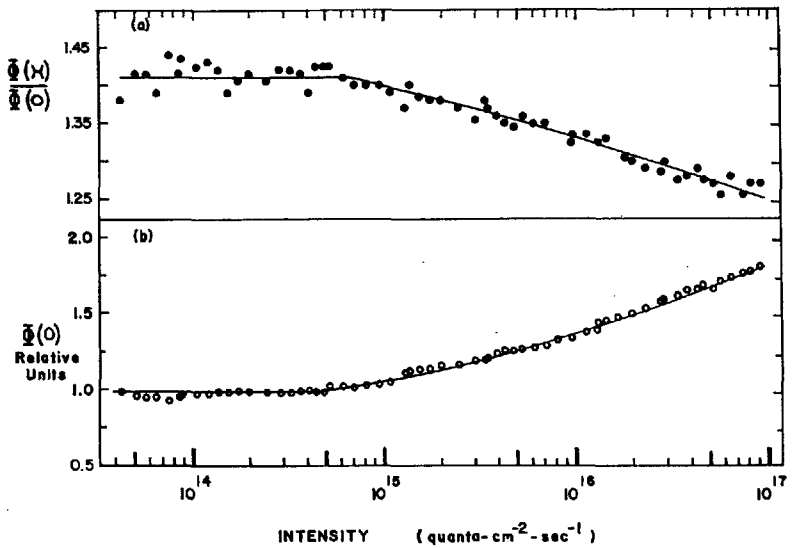

Figure 1. The fluorescence quantum efficiency Φ (in relative units) of crystalline tetracene ($\sim10\mu$ thick sublimation flake) as a function of light intensity (366 mμ excitation). (*a*) $\Phi(\mathbf{H})/\Phi(0)$—enhancement of the fluorescence in a magnetic field $\mathbf{H}=4000$ gauss oriented in ab plane, " on resonance " orientation; (*b*) relative quantum efficiency $\Phi(0)$ in absence of applied magnetic field.

With increasing I, $\Phi(0)$ increases gradually and there is a concomitant decrease in $\Phi(\mathbf{H})/\Phi(0)$. No change in $\Phi(0)$ as a function of I was observed at a temperature of 210 °K and below. At 77 °K, $\Phi(\mathbf{H})/\Phi(0)$ is unity.[1]

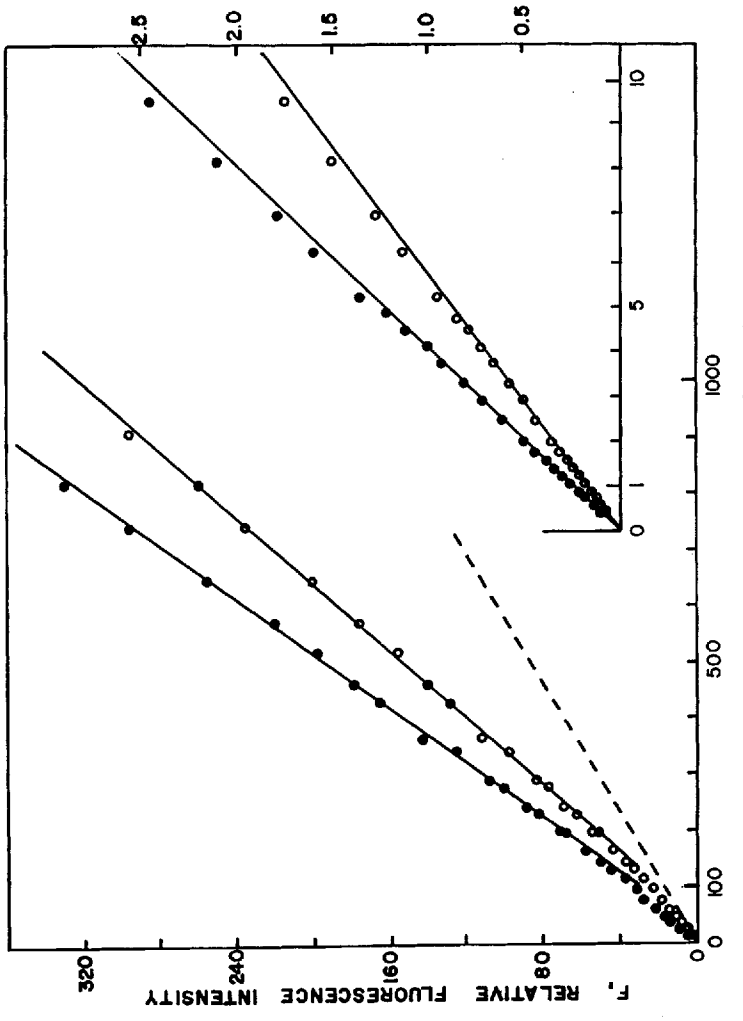

Figure 2. Relative fluorescence intensity F as a function of excitation intensity; same conditions and crystal as in Fig. 1. ● . . . Magnetic field H = 4000 gauss applied, ○ . . . No magnetic field applied. — — — — — . . . . F extrapolated from the low intensity region ($1 \times 10^{14} - 5 \times 10^{14}$ quanta-cm^{-1}-sec^{-2}), which is shown in the insert.

In Fig. 2, the data of Fig. 1 are plotted in a different manner for reasons which will become apparent. F is the measured fluorescence intensity in relative units. If both F and I are expressed in the proper units, then $\Phi = F/I$. As is evident from Fig. 2, a plot of F against I yields straight lines with different slopes for $I < 5 \times 10^{14}$ and $I > 2 \times 10^{16}$ quanta-cm^{-2}-sec^{-1}. The intensity interval in which F is not linearly proportional to I covers a range of roughly $5 \times 10^{14} - 2 \times 10^{16}$ quanta-cm^{-2}-sec^{-1}. The dashed line in Fig. 2 represents the extrapolated value of F from the low intensity region, which is shown in the insert in Fig. 2.

An attempt was made to measure the fluorescence decay time of tetracene at 300 °K using freshly grown crystals which were kept in a vacuum. The decay time at room temperature was faster than the resolution of the apparatus (TRW Decay Time Fluorometer ~2 nanoseconds). At 77 °K, however, an average of 10 ± 0.5 nanoseconds was measured. The fluorescence intensity ratio Φ_{77}/Φ_{300}, where 77 and 300 refer to the temperature in °K, was 50. As the samples were allowed to warm up, the decay time and fluorescence intensity decreased gradually.

Discussion

Singlet exciton fission in tetracene is a very efficient intersystem crossing mechanism at room temperature since it is not forbidden by spin angular momentum conservation rules. Since triplet excitons normally have longer lifetimes than the singlets, high densities of triplets can be formed when the fission process is the dominant decay channel for the singlets. The interpretation of our results is based on the assumption that at high intensities, the triplet exciton densities are sufficiently high to give rise to triplet-triplet fusion or bimolecular annihilation. This constitutes an additional radiative decay channel at high light intensities and the quantum efficiency of fluorescence increases.

The magnetic field **H** decreases the coupling between the singlet and triplet manifold of states. **H** (~4000 gauss) therefore decreases the singlet exciton fission and radiative triplet-triplet fusion

rates. Consequently, at high light intensities when the fusion process is operative, the increase in Φ is accompanied by a decrease in the ratio $\Phi(\mathbf{H})/\Phi(0)$ (Fig. 1a). The fusion process has been observed in crystalline anthracene[7] by a number of workers but until now has not been seen in tetracene.

The following kinetic scheme is proposed to account for our observations, where the symbol γ (cm^3-sec^{-1}) denotes bimolecular, and k (sec^{-1}) unimolecular rate constants. S and S_0 are the excited and ground singlet states, respectively, and T represents triplet excitons.

(a) Light absorption

(1) $S_0 + h\nu \rightarrow S$ (absorption coefficient ϵ (cm^{-1}))

(b) Singlet decay

(2) $S + S_0 \xrightarrow{\gamma_S} T + T$ (exciton fission, magnetic field sensitive)

(3) $S \xrightarrow{k_F} S_0 +$ fluorescence

(4) $S \xrightarrow{k_{IS}} T$ (first-order intersystem crossover)

(5) $S \xrightarrow{k_{SG}} S_0$ (radiationless decay)

(c) Triplet decay

(6) $T + T \xrightarrow{\gamma_{TS}} S + S_0$ (radiative recombination or fusion, magnetic field sensitive)

(7) $T + T \xrightarrow{\gamma_{TT}} T + S_0 +$ lattice energy (nonradiative recombination or fusion)

(8) $T \xrightarrow{k_T} S_0 +$ lattice energy (k_T^{-1} = triplet lifetime)

We have omitted the step $T + T \rightarrow S_0 +$ lattice energy, since this transition should be much less probable than (6) because of unfavorable Franck–Condon factors. The triplet-pair states (triplet excitons on neighboring molecules) which are intermediates in the fusion process may aso have quintet character, but there are of course no quintet states in tetracene at 2.4 eV (the energy of one triplet exciton is about 1.20 eV).[1] We have also omitted the step $S + S_0 \rightarrow T +$ lattice energy, i.e. intersystem crossover with the triplet pair state as an intermediate (such as might occur in an otherwise geminate recombination of triplet excitons) and therefore a parallel pathway to (2) for the disappearance of excited singlet states. This step would require a spin reversal within the lifetime of the triplet-pair state (formed during the fission process); the lifetime of this pair state is thought to be much smaller than the spin-lattice relaxation time.[8] Furthermore, even if this step does occur, it can be shown that the inclusion of this process in the kinetic scheme in a manner consistent with the experimental results does not alter any of the results and the calculated rate constants by more than a factor of two.

We proceed now to the analysis of (1) through (8). Steady-state considerations apply to our experiments. In any thin section of the crystal at a distance x from the illuminated surface, the concentration dependence of S and T may be described by the following equations:

$$\frac{dS(x)}{dt} = \epsilon I(x) - (\gamma_S S_0 + k_{SG} + k_{IS} + k_F) S(x) + \gamma_{TS} T^2(x) + D_S \frac{\partial^2 S(x)}{\partial x^2} = 0 \qquad (9)$$

$$\frac{dT(x)}{dt} = 2\gamma_S S_0 S(x) - (2\gamma_{TS} + \gamma_{TT}) T^2(x) - k_T T(x) + D_T \frac{\partial^2 T(x)}{\partial x^2} = 0 \qquad (10)$$

where D_S and D_T stand for the diffusion coefficient of the singlet and triplet excitons, respectively. We shall denote the fission

process by a first-order rate constant k_S, such that $k_S = \gamma_S S_0$, where $S_0 = 3.4 \times 10^{21}$ is the number of molecules per cm^3 in crystalline tetracene.

Solution of the kinetic equations

Major simplifications are achieved if we consider the two limits of low and high light intensity at room temperature. In the low intensity case, the triplet concentration is too low to give rise to triplet-triplet fusion and the $T^2(x)$ term in (9) can be dropped. In addition, it will be shown that the lifetime of the singlet is of the order of 10^{-10} seconds at room temperature and the diffusion term is therefore assumed to be unimportant in altering the singlet spatial population distribution at any light intensity since the absorption depth of the light used (366 mμ) is about one micron (singlet exciton diffusion length $\ll \epsilon^{-1}$). Under these low light intensity conditions ($I < 5 \times 10^{14}$ quanta-cm^{-2}-sec^{-1}), F should vary linearly with I, and such is the case (Fig. 2).

In the high intensity region F appears to increase linearly with I (Fig. 2). This can be explained if we assume that in this regime the triplet lifetime is determined by the $T^2(x)$ term in (10) and that triplet diffusion is not a significant process. Equation 10 has been solved by Murrell[9] for the condition that the monomolecular decay and diffusion terms in (10) are much greater than the bimolecular decay term. Using Murrell's solution, modified by the addition of the $T^2(x)$ term, it can be shown that under these conditions, F is proportional to I plus higher powers of I. Experimentally this is found to be the case in the intermediate intensity region ($5 - 200 \times 10^{14}$ quanta-cm^{-2}-sec^{-1}). We will therefore confine our discussion to the intensity region above 2×10^{16} quanta-cm^{-2}-sec^{-1}, and neglect the intermediate intensity region.

Case I: Low light intensity ($I < 5 \times 10^{14}$ quanta-cm^{-2}-sec^{-1}).

$$\gamma_{TS} T^2(x) + D_S \frac{\partial^2 S(x)}{\partial x^2} \ll k_{\mathrm{TOT}} S(x),$$

where $k_{\mathrm{TOT}} = k_S + k_F + k_{IS} + k_{SG}$.

After integrating (9) over the entire crystal thickness d, where $d \gg \epsilon^{-1}$, we obtain the following equation:

$$k_F\left(\frac{dS}{dI}\right)_l = \frac{k_F}{k_{\mathrm{TOT}}} = \Phi_l = G\left(\frac{dF}{dI}\right)_l = Gm_l \tag{11}$$

where the subscript l refers to low light intensity. The slope m_l of a F vs. I plot in Fig. 2 is proportional to the absolute quantum efficiency of fluorescence in the low light intensity region. G is a constant for any given crystal that depends on the geometry of the experiment.

Case II: High intensity ($I > 2 \times 10^{16}$ quanta-cm^{-2}-sec^{-1}).

$$(2\gamma_{TS} + \gamma_{TT})\, T^2(x) \gg k_T\, T(x) + D_T \frac{\partial T^2(x)}{\partial x^2}$$

After combining (9) and (10), integrating and arranging of terms, we obtain

$$\frac{1}{k_F}\left(\frac{dI}{dS}\right)_h = \frac{1}{k_F}\left[k_{\mathrm{TOT}} - \frac{2k_S\gamma_{TS}}{2\gamma_{TS} + \gamma_{TT}}\right] \tag{12a}$$

where the subscript h stands for high light intensity.

Under conditions in which $k_{\mathrm{TOT}} \cong k_S$, this equation can be inverted and it assumes the simple form

$$k_F\left(\frac{dS}{dI}\right)_h = \frac{k_F}{k_S}\left[1 + 2\frac{\gamma_{TS}}{\gamma_{TT}}\right] = G\left(\frac{dF}{dI}\right)_h = Gm_h \tag{12}$$

The statement that $k_{\mathrm{TOT}} \cong k_S$ at room temperature is the essence of the Swenberg–Stacy hypothesis.[5]

Since k_S is the dominant and magnetically sensitive part of k_{TOT}, a decrease in temperature should increase the fluorescence efficiency and minimize the effect of a magnetic field in a parallel fashion. This has already been shown.[1]

Calculation of k_{TOT}

k_{TOT} at 300 °K may be estimated from the 10 nsec measured fluorescence decay time at 77 °K and the measured ratio $\Phi_{77}/\Phi_{300} = 50$,

where the subscripts refer to the absolute temperatures. According to Eq. 11, we have in the low light intensity region

$$(k_{\mathrm{TOT}})_{300} = \frac{\Phi_{77}}{\Phi_{300}} (k_{\mathrm{TOT}})_{77} = 5 \times 10^{9}\ \mathrm{sec}^{-1} \tag{13}$$

This is based on the reasonable assumption that k_F is at most weakly temperature-dependent.

The lifetime of the singlet state in crystalline tetracene at room temperature is therefore about 2×10^{-10} sec. It should be noted at this point that variations in the ratio of Φ_{77}/Φ_{300} are encountered with different crystal samples. This ratio may be as low as 7 for aged crystals.[10] It is emphasized therefore that the above calculation of $(k_{\mathrm{TOT}})_{300}$ can be performed only if all the relevant quantities in (13) are obtained for the same samples.

Estimate of k_S, k_F and relative magnitudes of rate constants in k_{TOT}

It was shown previously[1] that in the low light intensity region the magnetic effect disappeared at 160 °K (i.e., $\Phi(\mathbf{H})/\Phi(0) = 1.0$). In the higher temperature region ($T > 200$ °K), the magnetic field sensitive constant k_S is therefore comparable in magnitude or larger than the sum of rate constants $k_F + k_{IS} + k_{SG} = k_t$.

Below 160 °K, k_t dominates and is insensitive to an applied magnetic field as is shown by the fact that $\Phi(\mathbf{H})/\Phi(0)$ is unity below 160 °K.[1] An estimate of the relative magnitudes of $k_S(0)$ and k_t can be made according to (11) by plotting $k_F/\Phi(0) = k_{\mathrm{TOT}}$ as a function of the reciprocal absolute temperature on a semi-logarithmic scale (Fig. 3a). Since $k_S(0) > k_t$ at elevated temperatures and $k_t > k_S$ at low tempreatures, we assume that the two straight-line portions of this curve represent the temperature dependence of k_S in the high temperature and k_t in the low temperature regions, respectively. The two lines, when extrapolated, intersect at 204 °K, at which temperature $k_S \approx k_t$. At 300 °K, it is estimated that $k_S \approx 34k_t$ or $k_t \approx 0.03k_S$, which supports the Swenberg–Stacy hypothesis.[5] Therefore from $k_S \approx k_{\mathrm{TOT}}$

at 300 °K and from (13),

$$k_S = 5 \times 10^9 \text{ sec}^{-1}, \qquad \gamma_S = \frac{k_S}{S_0} = 1.5 \times 10^{-12} \text{ cm}^3\text{-sec}^{-1} \tag{14}$$

The temperature dependence of k_S follows the relation:

$$k_S = k_0 \exp\left(-\frac{\Delta E}{kT}\right) \tag{15}$$

The value of ΔE was previously given as 1300 cm^{-1} or 0.16 eV.[1] Repeated measurements since then, however, have shown that a more accurate value for ΔE is 1660 $\pm$ 50 cm^{-1} or 0.207 $\pm$ 0.007 eV. Below about 160 °K the fluorescence increases also exponentially but with an activation energy of only 65 $\pm$ 5 cm^{-1} (0.0081 eV). From (14) and the measured value of ΔE, $k_0 = (1.5 \pm 0.5) \times 10^{13}$ sec^{-1}.

The radiative rate constant k_F can be estimated from the absolute quantum efficiency value of Bowen *et al.*; at 293 °K, $\Phi \sim 0.002$.[3] Using (11) we estimate that $k_F \sim 10^7$ sec^{-1}, whereas for the isolated molecule k_F is 1.4×10^8 sec^{-1}.[11] The crystal value of k_F is smaller than the analogous value in anthracene. This result is consistent with the suggestion that the emitting state in tetracene is a dimer[12] or excimer. For example, in pyrene crystals the dimer emission rate constant has a value of 5.55×10^6 sec^{-1},[13] and in hexane solution the emission rate constant of the pyrene excimer is 1.16×10^7 sec^{-1}. Nevertheless, it is cautioned that the tetracene value of k_F calculated above is based on a perhaps inaccurate value[3] of Φ. A remeasurement of this quantity would be highly desirable.

On the magnitude of the fluorescence quantum efficiency in the high intensity region

It is instructive to examine the ratio of Eqs. 12 to 11 ($\mathbf{H} = 0$). We obtain

$$\frac{m_h}{m_l} = (k_S + k_l) \Big/ \left\{ k_S \left[1 - \frac{2\gamma_{TS}}{2\gamma_{TS} + \gamma_{TT}} \right] + k_t \right\} \tag{16}$$

after a slight rearrangement of terms. In the high intensity region $F_h = m_h I_h - F_0$ according to Fig. 2, where F_0 is the F axis intercept for $I = 0$. Since $\Phi_h = F_h/I_h$, the ratio (16) is the maximum possible value of Φ_h/Φ_l. It is thus predicted that the quantum efficiency should become a constant with increasing I at sufficiently high light intensities (which were not available in our experiments), and the Φ curve in Fig. 1b should level off at some higher intensity value. The slope ratio m_h/m_l can be obtained directly from the experimental curves shown in Fig. 2 and from this ratio γ_{TS}/γ_{TT} can be calculated using (16). Eight measurements of this slope ratio on eight different crystals gave an average value of 1.87 and $\pm 15\%$ as an average deviation. Using the approximation $k_S \gg k_t$ which introduces a negligible error at 300 °K, and rearranging (16) we obtain at zero magnetic field:

$$\frac{m_h}{m_l} = 1 + \frac{2\gamma_{TS}}{\gamma_{TT}} = 1.87 \pm 0.28 \tag{17}$$

$$\frac{\gamma_{TS}}{\gamma_{TT}} = 0.44 \pm 0.14 \tag{18}$$

EVALUATION OF γ_{TS} FROM γ_S

γ_{TS} can be evaluated from γ_S by making use of the thermodynamic equilibrium constant that connects these rate constants. Thus, considering the hypothetical case of thermodynamic equilibrium between S, S_0 and T, we have

$$S + S_0 \underset{\gamma_{TS}}{\overset{\gamma_S}{\rightleftharpoons}} T + T \tag{19}$$

For this equilibrium, Merrifield *et al.*[2] have written (20):

$$\frac{\gamma_S}{\gamma_{TS}} = 9 \exp\left(-\frac{\Delta E}{kT}\right) = K \tag{20}$$

where

$$K = \exp\left(\frac{\Delta S}{k}\right) \exp\left(\frac{-\Delta E}{kT}\right) \tag{21}$$

where $\Delta E = 2E_T - E_S = 1660 \pm 50$ cm^{-1} and E_T and E_S are the relaxed triplet and singlet exciton energies, respectively; k is the Boltzmann constant in (20)–(21). The thermodynamic equilibrium constant K contains the entropy (ΔS) term, which gives rise to the spin factor 9 in (20).

It should be kept in mind that in our experiments we do not have thermodynamic equilibrium between S and T states; instead we have the steady state conditions expressed in (9) and (10). Nevertheless, once γ_S is known, regardless of whether thermodynamic equilibrium exists or not, γ_{TS} can be calculated from (20) if the equilibrium constant K is known. The latter can be calculated using the experimental value of ΔE and the calculated value for ΔS. We then have

$$\frac{\gamma_S}{\gamma_{TS}} = (3.2 \pm 0.8) \times 10^{-3} \tag{22}$$

$$\gamma_{TS} = (4.8 \pm 1.2) \times 10^{-10} \text{ cm}^3\text{-sec}^{-1} \tag{23}$$

and

$$\gamma_{TT} = (11 \pm 5) \times 10^{-10} \text{ cm}^3\text{-sec}^{-1} \tag{24}$$

In order to make comparisons between the results obtained for γ_{TS} and γ_{TT} with tetracene and those found with anthracene as described by Avakian and Merrifield (henceforth referred to as AM), it should first be made clear that the definition of the bimolecular rate constant for the formation of a singlet state from 2 triplet states, γ_{TS} is different from that of the comparable term, $\gamma_{\text{radiative}}$ used by AM. The relation between the two is $\gamma_{TS} = 2\gamma_{\text{radiative}}$ (AM); thus, on an equivalent basis, $\gamma_{TS}/2 = (2.4 \pm 0.6) \times 10^{-10}$ cm^3/sec for tetracene, as compared to an estimate of $\gamma_{\text{radiative}} = 8 \times 10^{-12}$ cm^3/sec for anthracene. Delayed fluorescence in tetracene generated by direct excitation of triplet excitons, is probably difficult to observe because of the low quantum efficiency of fluorescence in tetracene. In crystalline anthracene the fraction f of triplet-triplet annihilations giving rise to

singlets is estimated to be ~ 0.4.[14] f in tetracene according to our data is 0.36 ± 0.13.

Theoretical calculations of the radiative fusion constants in anthracene[15–17] and tetracene[17] indicate that the triplet-triplet annihilation proceeds via charge-transfer (CT) intermediates, which promptly decay to the lowest excited singlet. The existence of a CT state in tetracene at 2.9 eV has been proposed by one of us.[18] Swenberg has calculated γ_{TS} for tetracene, assuming that the annihilating triplet state is coupled to the singlet indirectly via this CT state at 2.9 eV. Since $E_{CT} - 2E_T$ in tetracene is 0.5 eV, Swenberg obtained a very small value of γ_{TS} ($\sim 3 \times 10^{-16}$ cm^{-3} sec^{-1}). As Swenberg himself pointed out, however, the calculated value of γ_{TS} is critically dependent on $E_{CT} - 2E_T$ and the high value for γ_{TS} implies a lower value for E_{CT} than 2.9 eV. The energy of the CT level used by Swenberg in the calculation of γ_{TS} is that of a nearest neighbor charge-transfer state. It may be that the proposed dimeric or excimeric nature of excited tetracene accounts for this discrepancy. As Azumi and McGlynn[19] have pointed out, an excimer can be described as having partial charge resonance character, so perhaps a higher-lying pure CT state need not be invoked in a calculation of the type that Swenberg has performed.

Temperature dependence of the magnetic field effect

We have previously defined $k_{TOT} = k_S + k_t$. Since k_S is magnetically sensitive, we can incorporate the magnetic field dependence of k_S in a function χ, such that

$$k_{TOT} = k_S(\mathbf{H}) + k_t \tag{25}$$

where

$$k_S(\mathbf{H}) = \chi k_S(0), \tag{26}$$

χ is less than unity and represents the specific effect of the magnetic field on the coupling between the singlet and double-triplet exciton manifold of states.

In the low light intensity case the magnetic field enhancement in the fluorescence as a function of temperature, based on (11),

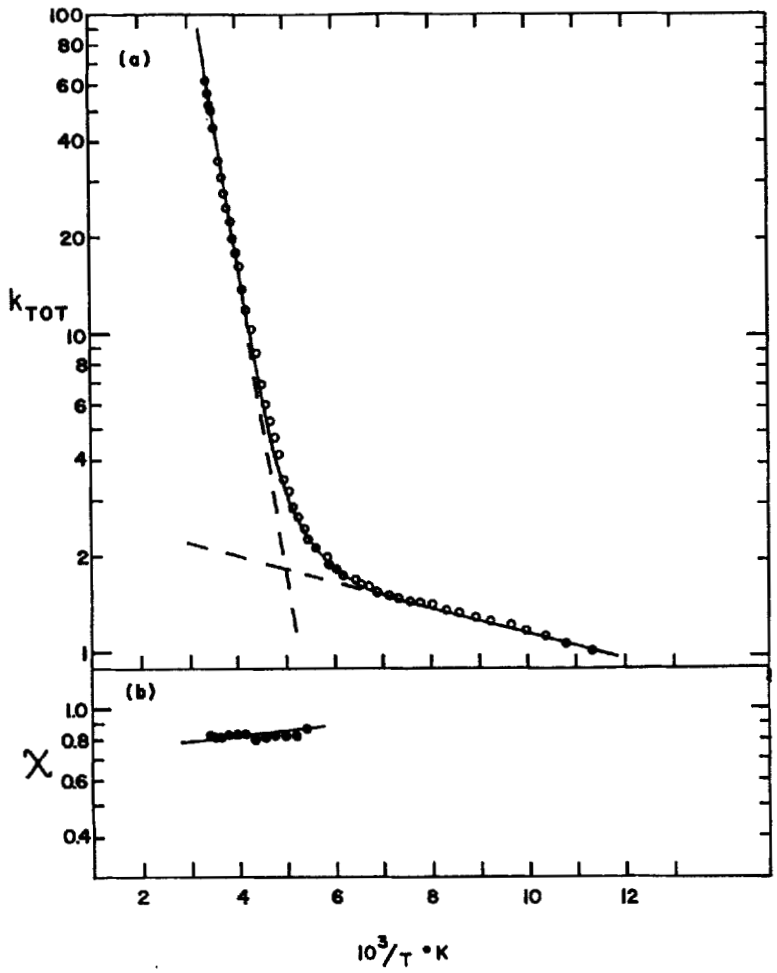

Figure 3. (*a*) $k_{\mathrm{TOT}}\,(\mathrm{sec}^{-1}) = k_F/\Phi(0)$ (defined in Eq. 11), overall decay constant of excited singlet in relative units, plotted as a function of temperature. (*b*) Temperature dependence of the magnetic field decoupling (singlet → triplet pair state) constant χ (defined in Eq. 26).

may be written

$$\left[\frac{\Phi_t(\mathbf{H})}{\Phi_t(0)}\right]_T = \frac{k_S(T) + k_t(T)}{\chi k_S(T) + k_t(T)} \tag{27}$$

For the crystal of Fig. 2, this ratio varies from 1.41 at 300 °K to 1.0 at 160 °K. Using these values and estimating the relative magnitudes of $k_S(T)$ and $k_t(T)$ from Fig. 3a, χ can be calculated as a function of temperature. At 300 °K, for example, $\chi = 0.82$ in an " off resonance " orientation (see below); the exact value of χ depends on the orientation of the magnetic field vector in the ab crystal plane.[1] As the temperature is lowered the calculated values of χ increase slightly (Fig. 3b), exhibiting an activation energy of $31 \pm 8\ \text{cm}^{-1}$. This indicates that the magnetic field is somewhat less efficient in decoupling the singlet and triplet pair states at lower temperatures. The temperature dependence in (27) is of course not the same as in (11), which is due to the $k_S(T)$ term. The temperature dependence of $k_S(T)$ in (27) is not important as long as $k_S \gg k_t$.

The form of Eq. 27 suggests an explanation for the variation of $\Phi(\mathbf{H})/\Phi(0)$ which is observed with different crystals and in different laboratories. This ratio varies from 1.28–1.43[1,2] and has been reported to be as low as 1.06.[4] The magnetic effect (27) is strongly dependent on the relative magnitudes of $k_S(T)$ and $k_t(T)$. The larger k_t is relative to k_S (the former may be a function of impurities, defects, etc.), the smaller is (27) even though χ may be constant from crystal to crystal; (however, the presence of stray light may also lead to spurious low values of (27)). The same explanation is offered for the previously mentioned variation in the fluorescence efficiency ratio Φ_{77}/Φ_{300} observed with different crystals.

Effect of magnetic field H on γ_S, γ_{TS} and γ_{TT}

It was shown previously that $\Phi_t(\mathbf{H})/\Phi_t(0)$ is highly anistropic with respect to the orientation of **H** in the ab plane of the crystals.[1] It exhibits a maximum ($\sim$1.4) at an orientation for which the triplet pair states with singlet character $|0, 0\rangle$, $|+1, -1\rangle$ and

$|-1, +1\rangle$ are degenerate in a field of $\mathbf{H} > 2000$ gauss; this is referred to as the " on resonance " condition. At other particular orientations only the $|+1, -1\rangle$ and $|-1, +1\rangle$ pair states with singlet character are degenerate and $\Phi(\mathbf{H})/\Phi(0)$ exhibits a minimum value of about 1.2. This orientation will be referred to as the " off resonance " orientation. The symbols i, j in $|i, j\rangle$ refer to the spin angular momenta components of the paired triplet excitons along the direction of $\mathbf{H}$.

The effect of $\mathbf{H}$ on the rate constants γ_{TS} and γ_{TT} may be determined from the slope ratios of the linear portion of the curves in Fig. 2. We shall denote $\gamma_{TS}(\mathbf{H})$ by γ'_{TS}, $\gamma_{TT}(\mathbf{H})$ by γ'_{TT} and $\gamma_S(\mathbf{H})$ by γ'_S. We shall again write $k_{\mathrm{TOT}} \approx k_S$ at 300 °K. Using Eqs. 11 and 12, we can write down the following ratios of slopes (where $m(\mathbf{H}) = m', m(0) = m$), which are valid at 300 °K:

$$\frac{m'_l}{m_l} = \frac{\gamma_S}{\gamma'_S} \tag{28}$$

$$\frac{m'_h}{m_h} = \frac{\gamma_S}{\gamma'_S}\frac{[1 + 2\gamma'_{TS}/\gamma'_{TT}]}{[1 + 2\gamma_{TS}/\gamma_{TT}]} \tag{29}$$

Taking the ratio of (29) to (28), we obtain

$$\frac{m_l m'_h}{m'_l m_h} = \frac{1 + 2\gamma'_{TS}/\gamma'_{TT}}{1 + 2\gamma_{TS}/\gamma_{TT}} \tag{30}$$

The ratio of $(\gamma'_{TS}/\gamma_{TS})$ $(\gamma_{TT}/\gamma'_{TT})$ can be calculated from the experimental data such as shown in Fig. 2 and (30), which can then be compared to γ'_S/γ_S. This was done for three different crystals in two different orientations and the results are summarized in Table 1.

According to (20), the thermodynamic equilibrium constant K should be independent of $\mathbf{H}$ because at sufficiently high temperatures all the spin states will be equally populated and the change in ΔE with $\mathbf{H}$ is negligible compared to its value of 1660 cm^{-1}. Therefore, the ratio γ_S/γ_{TS} should be independent of $\mathbf{H}$ and the orientation of $\mathbf{H}$. Accordingly, the ratios γ'_S/γ_S and γ'_{TS}/γ_{TS} should be the same.[2] The data in Table 1 in the " off resonance "

TABLE 1 Comparison of Rate Constants γ_S, γ_{TS}/γ_{TT} in the Presence and Absence of a Magnetic Field‡ of 4000 gauss at 300° K

	" on resonance "		" off resonance "	
Crystal	$\frac{\gamma'_S}{\gamma_S}$	$\frac{\gamma'_{TS}}{\gamma_{TS}}\frac{\gamma_{TT}}{\gamma'_{TT}}$	$\frac{\gamma'_S}{\gamma_S}$	$\frac{\gamma'_{TS}}{\gamma_{TS}}\frac{\gamma_{TT}}{\gamma'_{TT}}$
A	0.70	0.74	0.82	0.81
B	0.70	0.74	0.80	0.80
C	0.71	0.74	0.83	0.83

‡ The primed quantities refer to values in the presence of **H**.

orientation is consistent with this assumption which implies that γ'_{TT}/γ_{TT} is unity. There is, however, a small discrepancy for the " on resonance " data which cannot yet be explained. Maintaining the assumption that γ_S/γ_{TS} is independent of **H**, then in the " on resonance " condition $\gamma'_{TT} = 0.95\gamma_{TT}$. Based on a ratio of $\gamma'_{TT}/\gamma_{TT} = 1.0$, the ratio of $\gamma'_{TS}/\gamma_{TS} \cong 0.80$ " off resonance " is about the same as is observed in anthracene.[20] " On resonance " this ratio undergoes a dip of about 7–10% to 0.74 which is also observed in anthracene.[20] In this respect also, anthracene and tetracene exhibit markedly similar behavior.

We now return to a consideration of γ_{TT}, the rate of production of one triplet exciton from a pair of annihilating triplets. Thermodynamic considerations[2] for the ratio γ_S/γ_{TS} from (20) coupled with the form of our kinetic equations such as (30) indicate γ_{TT} should be practically independent of **H** and of the orientation of **H**.

Merrifield has shown that γ_{TS} is greater the more uniformly the singlet character is spread over the nine annihilating pair states.[21] The same considerations should apply to γ_{TT}, the annihilation rate of the triplet pair states to form a single excited triplet state. One should therefore consider the spin functions when (1) $\mathbf{H} = 0$, (2) **H** is in an " off resonance ", and (3) is in an " on resonance " orientation.

When $\mathbf{H} = 0$, the triplet spin functions are referred to the principal axes x, y, z of the crystal dipolar tensor[22] and are denoted

by $|x\rangle$, $|y\rangle$ and $|z\rangle$.[23] Nine pair states $|xx\rangle$, $|xy\rangle$, $|yx\rangle \ldots$, etc. are possible. The degeneracy of the pair states $|i,j\rangle$ and $|j,i\rangle$ is lifted by a weak intertriplet interaction.[21] The proper functions are then $\pm$ combinations of these degenerate pairs. The + combinations are pure quintets and the − combinations are pure triplets. At $\mathbf{H} = 0$ therefore there are three pure triplets $2^{-1/2}(|yx\rangle - |xy\rangle)$, $2^{-1/2}(|yz\rangle - |zy\rangle)$ and $2^{-1/2}(|xz\rangle - |zx\rangle)$, and three pair states $|xx\rangle$, $|yy\rangle$ and $|zz\rangle$ with singlet character.

When $\mathbf{H} \approx 4000$ gauss, the triplet excitons are quantized along the magnetic field and can be described by the quantum numbers $M_S = 0, \pm 1$. " Off resonance " there are again three triplets $2^{-1/2}(|0,1\rangle - |1,0\rangle)$, $2^{-1/2}(|0,-1\rangle - |-1,0\rangle)$ and $2^{-1/2}(|+1,-1\rangle - |-1,+1\rangle)$, and two states[21] with singlet character.

" On resonance " the $|+1,-1\rangle$, $|-1,+1\rangle$ and $|0,0\rangle$ are degenerate and the eigenstates are different linear combinations of these three pair functions. Out of the three linear combinations, one is a pure quintet, one a pure singlet—

$$3^{-1/2}(|0,0\rangle - |+1,-1\rangle - |-1,+1\rangle),$$

and one a pure triplet—

$$2^{-1/2}(|+1,-1\rangle - |-1,+1\rangle).$$

Therefore there are still three triplets, but only one singlet in the " on resonance " orientation.

According to the above, γ_{TS} and therefore γ_S should decrease in the sequence (1) $H = 0$, (2) $H \approx 4000$ gauss, " off resonance " and (3) $H \approx 4000$ gauss, " on resonance ". Since the number of triplets does not change in this sequence, it is expected that γ'_{TT} should be equal to γ_{TT} at all orientations of $\mathbf{H}$.

Merrifield has calculated[21] that in anthracene one out of every 25 triplet-triplet collisions yields a singlet. Repeating his calculation with our data we find in tetracene one out of 27 collisions giving rise to a singlet. Furthermore, we calculate that one out of 8–15 collisions leads to triplet-triplet annihilation. According to the assumptions made previously, the result of an annihilation is either one triplet or one singlet exciton. The uncertainty in the

fraction of collisions leading to annihilation stems from the experimental uncertainty in the ratio γ_{TS}/γ_{TT}.

Summary and Conclusions

The exciton fission process in crystalline tetracene is a very efficient intersystem crossing mechanism at room temperature. At light intensities above $\sim 2 \times 10^{16}$ quanta-cm^{-2}-sec^{-1}, the lifetime of the triplet excitons formed from the fission process appears to be governed by bimolecular annihilation or fusion. This leads to an increasing quantum efficiency of fluorescence with increasing light intensity. A fraction of 0.36 ± 0.13 of these annihilations generates an excited singlet. It is estimated that the quantum efficiency at intensities above 10^{17} quanta-cm^{-2}-sec^{-1} should reach a limit of approximately double its value at low light intensities. A magnetic field of about 4000 gauss gives rise to a decrease in both the singlet exciton fission and triplet exciton fusion rate constants. At light intensities at which the fusion process is operative, the increase in the fluorescence when a magnetic field is applied is less than at low light intensities. At low light intensities the fusion process is insignificant because of low triplet exciton densities, and the effect of the magnetic field on the fluorescence enhancement is largest. It is estimated that one out of 12 ± 4 triplet exciton collisions leads to annihilation.

The following is a summary of the rate constants. These values are based on the experimental data and assumptions which are pointed out in each case below:

(*a*) Decay constant at 77 °K $k_t = k_{IS} + k_{SG} + k_F = (10 \pm 0.5) \times 10^7$ sec^{-1} (based on measurement).

(*b*) Fission rate constant at 300 °K, $\gamma_S = 1.5 \times 10^{-12}$ cm^3-sec^{-1} (or $k_S = \gamma_S/S_0 = 5 \times 10^9$ sec^{-1}), based on (*a*) and Eqs. 11 and 13 (both values within $\pm$ 5%).

(*c*) Radiative decay constant $k_F \approx 10^7$ sec^{-1}, based on Bowen *et al.*'s quantum efficiency,[3] Eq. 11 and (*b*).

(*d*) Bimolecular triplet-triplet annihilation or fusion constants at 300 °K (based on (*a*), (*b*) and model proposed to account for experimental observations):

$T + T \rightarrow S$, $\gamma_{TS} = (4.8 \pm 1.2) \times 10^{-10}$ cm^3 sec^{-1};
$\gamma_{TS}/2 = (2.4 \pm 0.6) \times 10^{-10}$ cm^3/sec
$T + T \rightarrow T$, $\gamma_{TT} = (11 \pm 5) \times 10^{-10}$ cm^3 sec^{-1}.

The tetracene value $\gamma_{TS}/2$ should be directly comparable to the analogous rate constant $\gamma_{\text{radiative}}$ as defined by Avakian and Merrifield[7] for anthracene. $\gamma_{\text{radiative}}$ is estimated to be approximately 30 times greater in tetracene than in anthracene.

(*e*) Effect of magnetic field **H** = 4000 gauss on bimolecular constants (300 °K)
$\gamma_S(\mathbf{H})/\gamma_S = 0.70$, " on resonance ".
$\gamma_S(\mathbf{H})/\gamma_S = 0.81 \pm 0.01$, " off resonance ".
The effect of **H** on γ_{TS} is similar in magnitude to the effect observed in anthracene. There appears to be no effect of **H** on γ_{TT} in the " off resonance " orientation of **H**.

Recent experiments in our laboratory using 436 mμ light have enabled us to arrive at a preliminary estimate of the values of the triplet diffusion length l, diffusion coefficient D, and lifetime k_T^{-1}. These are $l \cong 0.4\mu$, $D \cong 7 \times 10^{-5}$ cm^2/sec, and $k_T^{-1} = 13$ μsec. The best estimate of the probable error in these values at this time is that they are within a factor of 3 of what our more refined measurements and calculations will yield. These results will be reported in a later publication.

Appendix

As a result of the experiments performed with 436 mμ light, which provide information on l, D and k_T, we have been able to obtain a numerical solution of (10), including the triplet exciton diffusion term (and neglecting the singlet exciton diffusion). This solution indicates that a more accurate experimental value for (17) would be 2.30. In other words, with our present maximum light intensity, we were not quite in the linear high light intensity region. This introduces an error only in the absolute value of γ_{TT}. More accurate values for D and k_T may result in further alteration of the value of (17) and hence γ_{TT}, but indications are that any future changes in the magnitude of γ_{TT} will be within the range of error indicated in this paper.

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