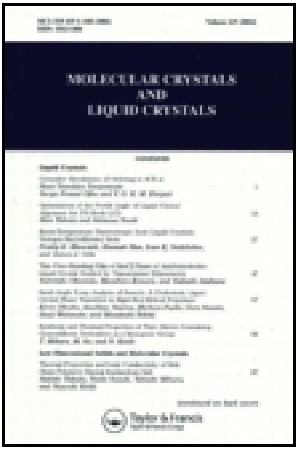

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Migration and Annihilation of Triplet Excitation Energy in the Charge-Transfer Anthracene-Tetrachlorophtalic Anhydride Crystal

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Migration and Annihilation of Triplet Excitation Energy in the Charge-Transfer Anthracene-Tetrachlorophtalic Anhydride Crystal

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The emission spectra of the charge-transfer crystal of anthracene-tetrachlorophtalic anhydride were studied in the 1.7–300 K temperature range. Delayed fluorescence was observed over the whole temperature range. At temperatures below ~40 K it results from heterogenous (mobile exciton–trapped exciton) triplet-triplet annihilation. At higher temperatures it is due to homogenous triplet-triplet annihilation. The existence of mobile excitons is also proved by the character of the ESR lines which are very narrow Lorentzians. The phosphorescence, observed only in the range 1.7–40 K, originates from at least two different kinds of traps with energies ~6 cm^{-1} and ~140 cm^{-1}, respectively. The vibrational structure of the phosphorescence is identical to that of anthracene, with 0—0 band blue-shifted by ~400 cm^{-1}. A kinetic model of trapping and detrapping of triplet excitons as well as the nature of the traps are discussed.

1 INTRODUCTION

A great deal of experimental effort has been spent, in recent years, on investigations of the properties of the triplet excitons in crystals of weak charge-transfer (CT) complexes. However, the optical and ESR studies have been almost exclusively devoted to such CT crystals whose triplet excitons are formed primarily as a product of locally excited triplet states of the donor molecules, although in some cases a relatively large admixture of CT character to the lowest triplet state can occur.[1–16]

In the present work we have undertaken detailed optical studies of emission of anthracene-tetrachlorophthalic anhydride (A-TCPA) CT crystals over a wide temperature range, from 1.7 to 300 K. The aim of these studies, supplemented by ESR measurements (in a limited temperature range, 100 to 300 K), was to obtain a detailed insight into the migration and annihilation of triplet excitons and into the role of traps in controlling and governing these processes in CT crystals. These studies have been stimulated, at least partially, by the conclusions of our recent work,[17] that has dealt with CT crystals in which the lowest triplet state is of pure charge-transfer nature and where we have noticed a qualitatively different behavior of the triplet excitons as compared to that in the above-mentioned class of CT crystals.

2 EXPERIMENTAL

Tetrachlorophthalic anhydride (TCPA) was vacuum-sublimed. Anthracene (A) was twice zone refined for 60 passes. Single (1 : 1) crystals were grown by the slow evaporation of spectroscopically pure CCl_4 solution containing equimolar amounts of TCPA and A. Needle-like, dark-yellow crystals had typical size: 10 × 1 × 0.5 mm.

Emission spectra were measured by a standard spectrophosphorometry technique.[18] In all cases excitation of the crystal was effected by 404 nm Hg line isolated by appropriate filters from HBO-200 mercury lamp.

The decay curves of long-lived emission were averaged with the aid of a wave-form eductor (PAR-TDH9). A "third chopper"[19] method was used for decay times longer than 10 ms.

The ESR experiments were performed at X-band frequencies on a Bruker 418 S spectrometer equipped with a nitrogen flow cryostat. Excitation within the CT absorption band of A-TCPA complex was obtained with radiation from a mercury HBO-200 lamp appropriately filtered.

3 RESULTS

Emission of the A-TCPA crystal, at 1.7 K, is composed of three different emission spectra, i.e. prompt fluorescence, phosphorescence and delayed fluorescence (Figure 1). All these spectra, as well as the other spectral characteristics of each of these emissions are subject to changes upon changes in temperature. In the following we summarize briefly the results of the detailed temperature studies of the emission spectra.

3.1 Fluorescence

The fluorescence band, which is identified as the charge-transfer fluorescence of the A-TCPA complex and which always lacks any vibrational structure in solutions,[20] appears in the crystal as a structured band with 1400 cm^{-1} frequency that is characteristic of a local vibration within the anthracene molecule.[21,22] The intensity of fluorescence decreases continuously with increasing temperature, but contrary to the intensity changes of two others observed emis-

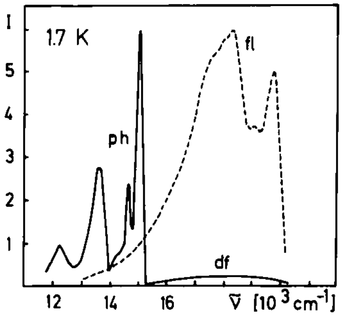

FIGURE 1 Emission spectra of A-TCPA crystal at 1.7 K: fl—prompt fluorescence, df—delayed fluorescence and ph—phosphorescence (Intensity scale in arbitrary units).

sions, this decrease is rather small in the temperature range considered (about 30% decrease in intensity between 1.7 and 300 K).

3.2 Phosphorescence

The phosphorescence spectrum, at 1.7 K (Figure 1), closely resembles molecular phosphorescence of the donor, i.e. anthracene. It shows the well-known vibrational structure of anthracene phosphorescence.[21,22] This observation confirms the expectation that, in CT crystal of A-TCPA, triplet excitons of the lowest energy are those localized on the anthracene molecules.

The O—O transition of the phosphorescence band in the A-TCPA crystal observed at 15110 ± 20 cm^{-1} (at 1.7 K) is shifted toward higher energies as compared either to O—O transition of the phosphorescence band in crystalline anthracene (14741 cm^{-1},[21]) or to the O—O transition of phosphorescence of anthracene embedded in glassy solution (14930 cm^{-1},[22]). Such a blue shift of the donor phosphorescence is usually observed in CT crystals and is accounted for as being due to the charge-transfer stabilization of the ground state.[23]

The separation between the O—O transition in the phosphorescence band (15110 cm^{-1}) and the highest-energy vibrational component of the fluorescence band (19750 cm^{-1}) can be approximately treated as the separation between singlet and triplet excitonic bands in our crystal and this amounts to about 4600 cm^{-1}.

Increase of the temperature causes a red shift of the phosphorescence band. For instance, O—O transition located at 15110 cm^{-1}, at 1.7 K, shifts to 15040 cm^{-1} at 10 K and to 14970 cm^{-1} at 25 K (cf. Figure 1 and Figure 2). For temperatures higher than 25 K no further changes in the position of the phosphorescence band are observed.

Temperature changes are also influencing, in a rather complicated way, the integral intensity of phosphorescence, as well as the intensity distribution

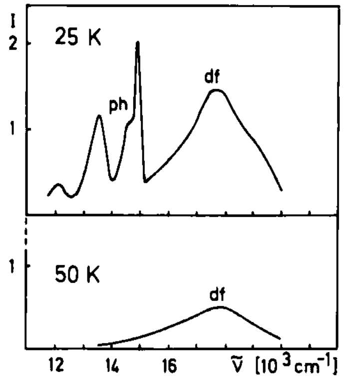

FIGURE 2 Long-lived emission spectra of A-TCPA crystal at 25 and 50 K.

amongst different vibrational components. Temperature changes of the integral intensity of phosphorescence are illustrated in Figure 3. It is seen that increasing the temperature, in the range 1.7–11 K, leads to increase of the integral intensity by a factor more than two. Above 11 K the intensity of the phosphorescence gradually decreases with increasing temperature and eventually, above 40 K, phosphorescence is no longer observed (cf. also Figure 2).

Observed decays of phosphorescence are nonexponential in the whole temperature range (Figure 4). At 1.7 K decay curves can be satisfactorily approximated by the two one-exponential decays with decay times 73 and 10 ms respectively. The long-lived component is very sensitive to temperature, especially between 1.7–15 K.

Both, the intensity changes and the changes of the decay of phosphorescence (and also the nonexponential character of the decay) with the tempera-

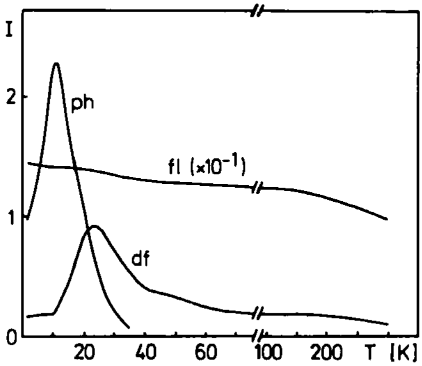

FIGURE 3 Temperature dependences of the integral intensities of prompt fluorescence (fl), delayed fluorescence (df) and phosphorescence (ph).

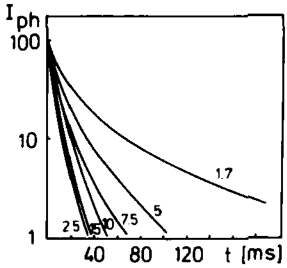

FIGURE 4 Decay curves of phosphorescence of A-TCPA crystal in the 1.7–25 K temperature range.

ture seem to indicate that the observed phosphorescence spectrum is a complex one and originates from several different emitting species (different anthracene traps). We shall discuss this problem in detail in the next section.

Finally, let us mention that the dependence of the integral intensity of phosphorescence, I_{ph}, on the intensity of the exciting light, I_{ex}, was observed to confirm to the relation $I_{ph} \sim (I_{ex})^n$, with $n = 0.95$ at 1.7 K and slightly decreasing at higher temperatures (down to $n = 0.7$ at 35 K).

3.3 Delayed fluorescence

Delayed fluorescence is observed over the whole investigated temperature range, from 1.7 to 300 K (Figures 1, 2). It has very weak but constant intensity between 1.7 and 10 K. In the range 10–24 K its integral intensity increases (notice that this temperature range corresponds to a very fast decrease of the intensity phosphorescence)—Figure 3. Above 24 K it is gradually decreasing and becomes very weak (tough still observable) around room temperatures.

Decay curves of delayed fluorescence are non-exponential at each temperature and are very sensitive to the temperature changes, as illustrated by Figure 5.

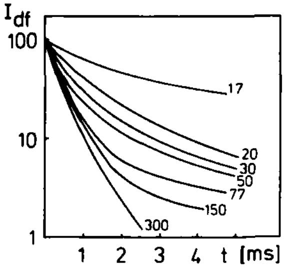

FIGURE 5 Decay curves of delayed fluorescence of A-TCPA crystal in the 1.7–300 K temperature range.

The intensity of delayed fluorescence, I_{df}, depends on the intensity of the exciting light in the following manner: $I_{df} \sim (I_{ex})^n$ with $n = 1.7$ at 1.7 K. For higher temperatures n decreases, reaching a constant value $n = 1.0$ for 40 K and all higher temperatures.

These observations clearly indicate that delayed fluorescence is controlled by the triplet-triplet annihilation process (thermal activation of the triplet excitons to the singlet exciton band is prevented, at least at low temperatures, by the very large separation, of ~4600 cm^{-1}, between singlet and triplet excitonic bands—more detailed discussion in the next section).

3.4 ESR results

Figure 6 shows a typical ESR spectrum of the A-TCPA crystal. The observed ESR signal consists of two lines, one of which corresponds to absorption (low-field line) and the other one to emission (high-field line). The lineshapes are Lorentzian with very small widths—less than 2 Gs at 200 K. Both these facts indicate clearly that the ESR signal is due to mobile triplet excitons in the temperature range considered (100–300 K).

Rotation of the crystal in the principal planes of the zero-field-splitting (ZFS) tensor yields an angular dependence of ESR lines illustrated in Figure 7.

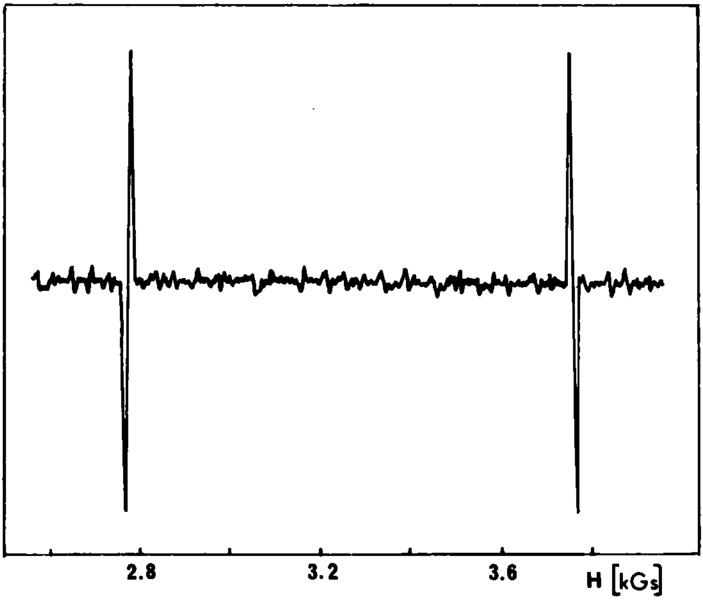

FIGURE 6 The ESR spectrum of A-TCPA single crystal at 120 K, observed for magnetic field parallel to the x-axis of the ZFS tensor (see next figure). The microwave frequency was 9.187 GHz.

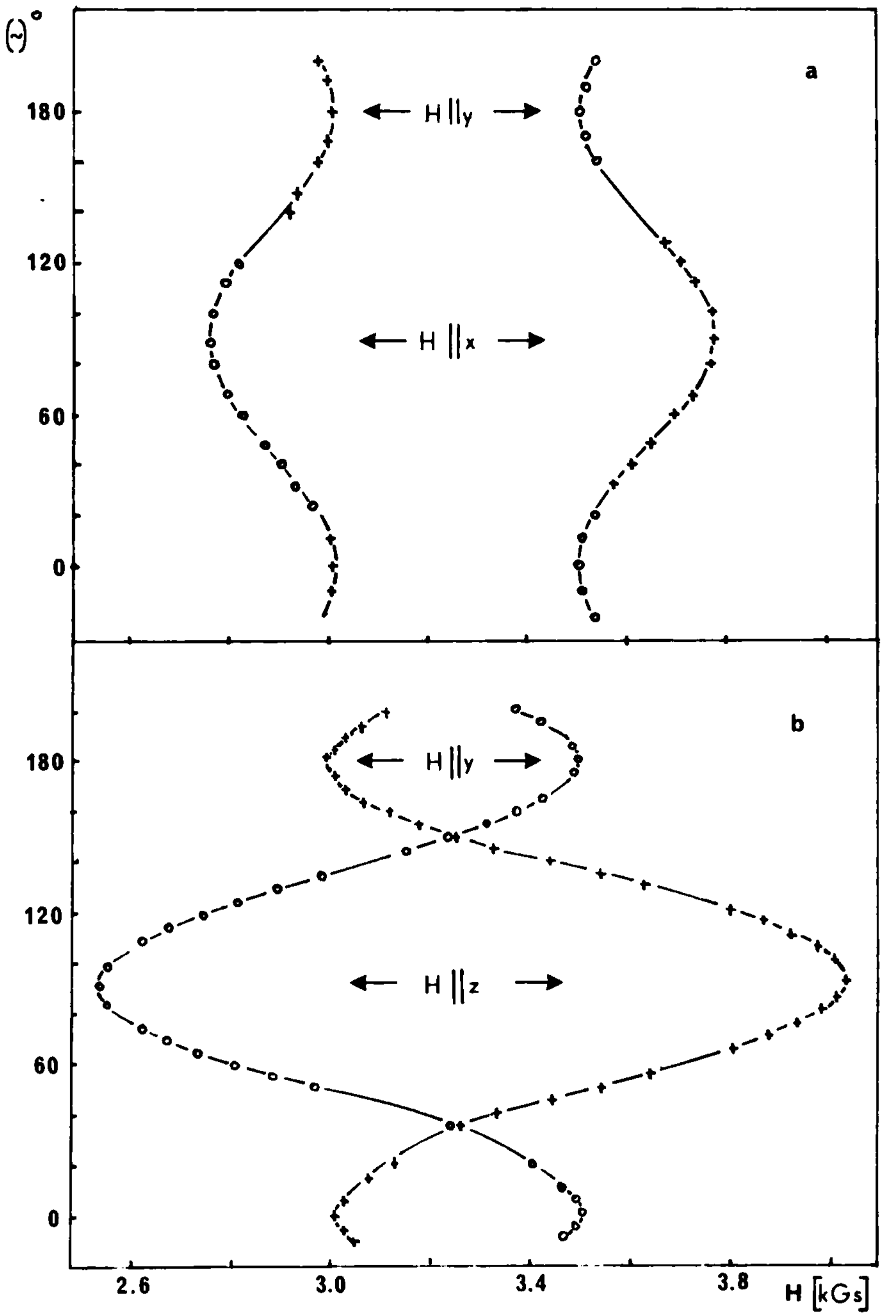

FIGURE 7 Angular dependence of the ESR lines of A-TCPA crystal at 120 K: rotation of the crystal about the *z*-axis of the ZFS tensor (a) and about the *x*-axis of the ZFS tensor (b) *z*-axis direction found experimentally coincides with the needle axis of the crystal. Crosses and circles correspond to the observed microwave absorption and microwave emission, respectively. Solid lines were calculated with the ZFS parameters given in the text. The microwave frequencies were: 9.202 GHz (a) and 9.185 GHz (b).

The ZFS parameters obtained from these results, in the usual manner, are the following: $D = 0.0700\ \mathrm{cm}^{-1}$, $E = 0.0080\ \mathrm{cm}^{-1}$, $D^{m} = (D^2 + 3E^2)^{1/2} = 0.0714\ \mathrm{cm}^{-1}$. These values are practically identical with the corresponding values for pure anthracene[24] and very close to the values for the isolated A-TCPA complex.[25] Thus, these results strongly support the conclusion drawn from optical observations, that the lowest triplet state in A-TCPA crystal is that of the locally excited triplet of the anthracene molecule.

4 DISCUSSION

The observed temperature changes of phosphorescence (i.e. red shift and the changes in the relative intensity distribution) as well as the non-exponential nature of the phosphorescence decay, indicate that the phosphorescence emission is a complex one and composed of more than one component. It originates from at least two (but probably from several) anthracene traps of different depth. In order to simplify our discussion we will assume the presence of two active traps: very shallow, T_1 and deep, T_2, as illustrated by the scheme in Figure 8.

4.1 Proposed mechanism

We shall consider the following processes which control and govern concentrations of free triplet excitons (T_e) and trapped excitons (T_1 and T_2):

$$S_O \xrightarrow{I_{exc}\sigma_{abs}\phi_{isc}} T_e \tag{1}$$

$$T_e \underset{\epsilon_1^{*}}{\overset{\epsilon_1}{\rightleftarrows}} T_1 \tag{2}$$

$$T_e \underset{\epsilon_2^{*}}{\overset{\epsilon_2}{\rightleftarrows}} T_2 \tag{3}$$

$$T_e + T_e \xrightarrow{\gamma_e} S_{CT} + S_O \tag{4}$$

$$T_e + T_1 \xrightarrow{\gamma_1} S_{CT} + S_O \tag{5}$$

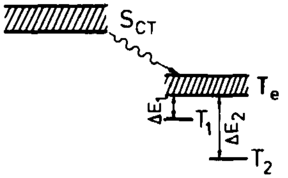

FIGURE 8 Excitonic bands and trap energy levels for A-TCPA crystal (details in the text).

$$T_e + T_2 \xrightarrow{\gamma_2} S_{CT} + S_O \tag{6}$$

$$T_1 \xrightarrow{k_1} S_O \tag{7}$$

$$T_2 \xrightarrow{k_2} S_O \tag{8}$$

Process (1) is the excitation process, within the *CT* absorption band, followed by population of the triplet exciton band via intersystem crossing. Triplet excitons, created in this way, can either be trapped, processes (2) and (3), or can collide with another free exciton (4), or trapped excitons (5) and (6). Processes (4)–(6) lead to delayed fluorescence. Processes (7) and (8) which denote all unimolecular modes of decay (radiative and non-radiative) of trapped excitons, are responsible also for the phosphorescence.

In the following we will assume that, in the first approximation, thermally assisted detrapping processes of T_1 and T_2 traps differ by the Boltzman factor, i.e. $\epsilon_1^* = \eta e^{-\Delta E_1/kT}$ and $\epsilon_2^* = \eta e^{-\Delta E_2/kT}$ and that homogenous and heterogenous annihilation processes are equally probable, i.e. $\gamma_e = \gamma_1 = \gamma_2 = 2\gamma$.

According to the proposed mechanism, and under steady-state approximation, the following relation between intensity of exciting light and the concentrations of free and trapped excitons is obtained:

$$I_{\mathrm{exc}}\,\sigma_{\mathrm{abs}}\,\phi_{\mathrm{isc}} = k_1[T_1] + k_2[T_2] + 2\gamma[T_e]([T_e] + [T_1] + [T_2]) \tag{9}$$

Now we will focus on explaining the observed temperature dependence of phosphorescence and delayed fluorescence in terms of the proposed mechanism.

4.2 Temperature dependence of phosphorescence and of delayed fluorescence

At 1.7 K the intensity of phosphorescence is larger by almost one order of magnitude than that of delayed fluorescence. Triplet excitons, T_e, produced upon excitation, followed by intersystem crossing, are effectively trapped on T_1 and T_2 traps. Thermal detrapping of T_1 and especially of T_2 traps is of low efficiency, hence the population of the triplet excitons band is relatively small and the intensity of phosphorescence (originating from T_1 and T_2 traps) is much larger than the intensity of delayed fluorescence. This latter is practically due to the heterogenous triplet-triplet annihilation processes (5) and (6).

The intensities of phosphorescence and of delayed fluorescence are $I_{\mathrm{ph}} \sim (k_1^r[T_1] + k_2^r[T_2])$ and $\mathrm{I}_{\mathrm{df}} \sim ([T_e] + [T_1] + [T_2])[T_e]$, respectively; here k_1^r and k_2^r are the radiative parts of the total unimolecular decay rates k_1 and k_2 of processes (7) and (8). At 1.7 K bimolecular annihilative events are of minor importance as compared to the unimolecular processes. Considering Eq. (9) under this limiting case and combining it with the above given relations for I_{ph} and I_{df} leads to the exciting light dependence of the intensity phosphorescence and of delayed fluorescence as: $I_{ph} \sim I_{exc}$ and $I_{df} \sim I^2_{exc}$, respectively. The observed values of $I_{ph} \sim I^{0.95}_{exc}$ and $I_{df} \sim I^{1.7}_{exc}$ seem to indicate that $[T_e]$ is practically controlled by the transfer of triplet excitons to T_1 and/or to T_2 traps.

In the temperature range 1.7–11 K the intensity of phosphorescence increases while the intensity of delayed fluorescence is practically constant (see Figure 3). The observed exciting light dependences of I_{ph} and of I_{df} are in this temperature range unchanged (relative to 1.7 K), thus indicating that the basic mechanism controlling both emissions is unchanged. Moreover, in this temperature range, red shift of the phosphorescence is observed (O—O transition shifts by about 70 cm^{-1}) as well as the redistribution of the relative intensities within the phosphorescence band.

In terms of the proposed mechanism, these observations show that the increase of temperature leads to the depletion of shallow T_1 traps populated initially at 1.7 K. This thermal detrapping, however, does not result in the increased rate of triplet-triplet annihilation, as the observed intensity of the delayed fluorescence is unchanged in the temperature range considered. It is increasing trapping of triplet excitons by deeper T_2 traps that is responsible for the observed red shift of phosphorescence with increasing temperature.

The process of repumping of trapped excitons from shallow to deeper traps, via exciton band, with increasing temperature has been previously observed in molecular as well as in CT crystals.[26–28]

There is, however, one striking observation that can not be accounted for in terms of the processes of the proposed mechanism. Namely, the temperature increase should never lead to the increase of ($[T_1] + [T_2]$). However, the intensity of phosphorescence is continuously increasing in this temperature range (see Figure 3), and at the same time the longlived component (73 ms at 1.7 K) of the phosphorescence decay decreases in intensity and eventually at ~15 K, disappears completely (see Figure 4). In order to explain these observations one has to assume that the quantum yield of phosphorescence originating from T_2 traps is much larger than that originating from shallow T_1 traps. As this is directly connected with the problem of the nature of traps, we will discuss it in more detail later on.

In the temperature range 11–25 K, red shift of the phosphorescence is continued, but the intensity of the phosphorescence is decreasing. The intensity of the delayed fluorescence is increasing with increasing temperature and reaches a maximum value at ~25 K (see Figure 3).

In this temperature range $[T_2]$ is continuously and strongly diminished with an increase of temperature. Increasing the population of the exciton band, $[T_e]$, results in increasing the triplet-triplet annihilation, thus leading to the observed increase of the delayed fluorescence intensity. At ~25 K, the observed exciting light dependence of phosphorescence and of delayed fluorescence, is: $I_{ph} \sim I_{exc}^{0.7}$ and $I_{df} \sim I_{exc}^{1.1}$, thus becoming close to $I_{exc}^{0.5}$ and $I_{exc}^{1.0}$, respectively, i.e. values that are expected in the limiting case of $[T_e]$ being controlled by the triplet-triplet annihilation (heterogenous, $T_e - T_2$). Additional evidence supporting the suggestion that delayed fluorescence is controlled by triplet-triplet annihilation comes from the activation energy obtained for this process in the temperature range considered (cf. next section).

Increase of the temperature above 25 K does not cause any further red shift of phosphorescence, thus indicating that the phosphorescence now originates exclusively from T_2 traps. The intensity of phosphorescence is continuously decreasing and at ~40 K phosphorescence can no longer be detected, which is connected (at least for higher temperatures) with the complete thermal depopulation of these traps.

Only free mobile excitons, T_e, are present at temperatures higher than 40 K. The ESR results (relevant to the range 100–300 K) strongly support this conclusion, as both the small linewidth and the Lorentzian lineshape are indications of the motional (or exchange) interactions between mobile excitons.[24] Therefore, the intensity of delayed fluorescence at higher temperatures is governed and controlled by the triplet-triplet annihilation (homogenous, $T_e - T_e$) process. From 25 K the intensity of delayed fluorescence is observed to decrease, at first fast (25–40 K) and then slowly. This decrease might be due, at first to the transfer of excitation to very deep impurity traps (which decay nonradiatively) and secondly (at higher temperatures) to increasing dissipation of the energy by exciton-phonon interactions.

The above discussion satisfactorily explains the experimental results in terms of the proposed mechanism and by the same token justifies this mechanism itself. Some observations, however, can not be explained in terms of the kinetic model and need detailed knowledge of the nature of traps.

4.3 The nature of the traps

The activation energy of the emitting T_1 traps can be found from the temperature dependence of the phosphorescence decay time in the 1.7–10 K temperature range, given as: $\beta_1(T) = k_1 + \eta e^{-\Delta E_1/kT}$. With the assumption that, at 1.7 K thermal activation of T_1 to the exciton band is negligable as compared to the unimolecular decay of T_1 (which is justified by the very weak delayed fluorescence), one finds the activation energy of the T_1 traps: $\Delta E_1 = 6 \pm 2\ \mathrm{cm}^{-1}$ (see Figure 9).

The very shallow T_1 traps are strongly depleted with an increase in temperature. As we recall (cf. Section 3.2), the long-lived component of the phosphorescence decay (73 ms at 1.7 K) looses fast its intensity (as compared to the short-lived component) with increasing temperature and at ~15 K it can no longer be measured (cf. Figure 4). Hence, we identify the long-lived component of phosphorescence as that originating from T_1 trap.

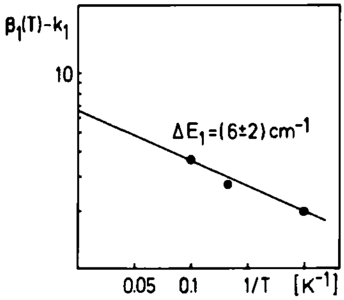

FIGURE 9 Inverse temperature dependence of the rate constant for unimolecular decay of T_1 traps (given as $1/\tau_1 = \beta_1(T) = k_1 + \eta e^{-\Delta E_1/kT}$, with assumption $1/k_1 = 73\ \mathrm{ms}^{-1}$).

The activation energy of the T_2 traps can be obtained, in the usual manner,[29] from the temperature dependence of the ratio of intensity of delayed fluorescence to the square of the intensity of phosphorescence. Figure 10 illustrates this dependence and yields an activation energy $\Delta E_2 = 140 \pm 10\ \mathrm{cm}^{-1}$. The characteristic decay time of phosphorescence originating from T_2 trap can either be identified with the short-lived component at 1.7 K or with the decay at 25 K (at this temperature phosphorescence is exclusively connected with the emission from T_2 trap). In both cases this decay time is 10 ± 2 ms (see Figure 4).

Now we can try to specify the nature of the traps. The crystal structure of CT crystals is usually that of a linear stacking arrangement with donor and acceptor molecules arranged within the stack in an alternate fashion with their molecular planes being nearly parallel (a "sandwich" structure of the donor-acceptor pair).[30] In connection with the crystal structure of this kind one could propose the following:

1. The T_1 trap ($\Delta E_1 \sim 6\ \mathrm{cm}^{-1}$, with $\tau_{ph} = 73$ ms) might be formed due to the error in the alternation order of the donor and the acceptor molecules within the linear stack of the CT crystal.

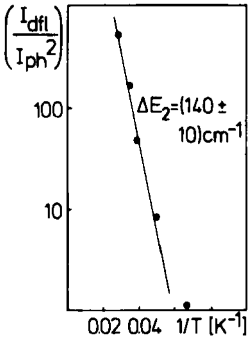

FIGURE 10 Inverse temperature dependence of log (I_{df}/I^2_{ph})

The presence of very shallow traps of this kind has been postulated in CT crystals of anthracene-pyromellitic dianhydride,[1] based on the observation that the decay time of phosphorescence originating from these traps is very close to the phosphorescence decay time of pure anthracene crystals.[21,31,32]

There are, however, some difficulties which accompany an acceptance of the shallow trap as due to the mistakes in the order of alternation within the stack. If the donor (anthracene) molecule could replace the acceptor molecule, then it would have two other donor anthracenes molecules as the closest neighbors within the stack. Then, after excitation, the situation would resemble that of "a prepared excimer" (or more strictly "a prepared triple excimer"). Such a presumable anthracene excimer would require at least two properties in order to assure the experimentally observed spectral characteristics of the T_1 traps. First, it must have a very small stabilization energy of its triplet state (in order to agree with the rather large blue shift of the O—O transition at 1.7 K, as there would not be any stabilization in the excimer's ground state). Secondly, the radiative as well as the non-radiative properties of the excimer's triplet state would have to be close to that of the locally excited state of anthracene (in order to agree with the observed decay time very close to that of the phosphorescence decay time of anthracene crystal).

It is difficult to argue, at the moment, as to whether the above mentioned properties can be achieved in "a prepared excimer" (or in "a prepared triple excimer"), as no relevant data concerning this issue exist. We have also to notice that any phosphorescence from the excimer's triplet state would be lacking any vibrational structure, characteristic for molecular (monomer) phosphorescence. Thus, the nature of very shallow traps, observed in A-TCPA crystals, as well as those observed in anthracene-pyromellitic dianhydride[1] and in anthracene-tetracyanobenzene,[15] seems to be far from being understood and it still needs much more experimental work to be explained.

2. The T_2 trap ($\Delta E_2 = 140\,\mathrm{cm}^{-1}$, with the phosphorescence decay time ~ 10 ms) may be formed on the anthracene molecule in the donor-acceptor pair with the structure strongly distorted from a "sandwich" structure. Such deviations may be caused by the presence of dislocations or impurities (non-trapping) in the vicinity of CT pair under consideration. As the energy of locally excited states is usually only slightly influenced by the changes of relative geometry of the donor-acceptor pair,[33] rather large geometrical changes would be necessary in order to assure the observed depth of T_2 trap.

Finally, let us return to the discussion of the puzzling temperature dependence of phosphorescence intensity in the temperature range 1.7–11 K. As we recall (cf. Figure 3), the phosphorescence intensity in this temperature range is increasing, though the sum of the concentration of the trapped excitons $[T_1] + [T_2]$ could only decrease with increasing temperature. As we briefly mentioned in the preceding section, this observation could be explained if one assumes that the quantum yield of phosphorescence from T_2 traps is larger than that from T_1 traps. This implies that:

$$k_2^r/(k_2^r + k_2^{nr}) \gg k_1^r/(k_1^r + k_1^{nr})$$

On the other hand, experimental observations show that the decay time of phosphorescence from T_2 traps (10 ms) is much shorter than the decay time of phosphorescence from T_1 traps (73 ms). Hence:

$$1/(k_2^r + k_2^{nr}) \ll 1/(k_1^r + k_1^{nr})$$

It is a well-established fact that in CT complexes of acceptors containing heavy (halogen) atoms a large decrease of the decay time of molecular phosphorescence (i.e. phosphorescence of the donor) is observed and this is due to the external heavy-atom effect on the rate constant of the radiative transition k^r.[34] The T_2 trap in our crystal consists of the donor-acceptor pair, in which heavy chlorine atoms are present in the acceptor (TCPA) molecule (contrary to the T_1 trap that consists of an anthracene molecule with two other anthracene molecules as its closest neibourghs). Thus, the heavy-atom effect on the rate constant of the radiative transition, k_2^r, is responsible for the observed large decrease of the decay time of phosphorescence from T_2 traps as compared to that from T_1 traps (in this last case the decay time of phosphorescence is practically the same as that of pure anthracene phosphorescence, as one would expect in view of the suggested microscopic nature of the T_1 trap). Therefore, $k_2^r \gg k_1^r$ and this is the reason for the large difference in the decay times of emission from T_1 and T_2 traps, as well as the reason for the much larger quantum yield of phosphorescence from the T_2 trap, and of the observed temperature dependence of phosphorescence intensity in the 1.7–11 K temperature range. In our opinion this observation seems strongly to support the suggested nature of the T_2 traps in A-TCPA crystals.

Summarizing this discussion we want to emphasize once more that, although the proposed physical origin of T_1 and T_2 traps seems to be consistent with the experimental observations, the specific microscopic nature of the traps in A-TCPA crystals, especially in the case of the shallow T_1 traps, must wait for further and more direct evidence.

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