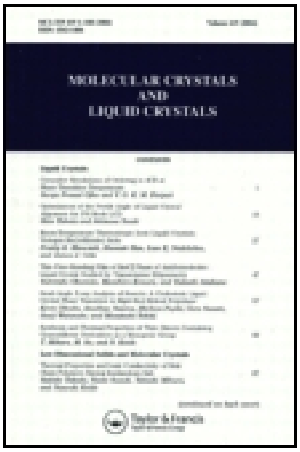

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A Study of Biphenyl Crystal Phosphorescence Induced by Impurities‡

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Abstract—An intense blue phosphorescence was observed at 6 °K in a biphenyl crystal following the deliberate addition of either carbazole or dibenzothiophene. In both cases the emitting species was biphenyl since the spectrum was essentially the same as that observed for biphenyl in paraffin solvents by other workers. Pure biphenyl itself did not phosphoresce and the luminescence originated from energy trapping centres created in the crystal lattice adjacent to the impurity molecule. Preliminary temperature dependence studies of the phosphorescence and delayed fluorescence were made and some of the energetics estimated for the biphenyl system. The energy of the triplet band above the ground state deduced in this way is in satisfactory agreement with Hirota's independent measurement.

1. Introduction

There are very few examples known of phosphorescence from carefully purified single crystals of aromatic compounds and the reason for this lies in the now well-investigated phenomenon of triplet-triplet annihilation.[1] Weak exciton phosphorescence has been reported for benzophenone,[2] some *p*-dihalogenobenzenes[3] and anthracene[4–6] crystals. At low temperatures the phosphorescence intensifies[6,7] when it is postulated that the emission originates at a trap, usually taken to be some (unspecified) lattice imperfection. The purpose of this communication is to show that

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phosphorescence may be induced *from the matrix* by residual impurities that themselves cannot act as acceptors of the triplet energy.

2. Experimental

Some care was taken in the purification of the biphenyl used in this work as a matrix. It was treated with maleic anhydride to remove anthracene, shaken with concentrated sulphuric acid to remove a second impurity (possibly carbazole) followed by a slow sublimation procedure to separate any involatile impurities and chromatography on silica gel using petroleum ether as eluent. This final material was zone refined through 46 passes. The carbazole was treated with maleic anhydride and chromatographed, while the dibenzothiophene was simply zone-refined, undergoing 204 passes. The spectra were measured of samples suspended freely in helium gas which acted both as a heat exchanger and a gas thermometer[8]; in this way, temperatures were measured to within about one degree in the range 6–50 °K. Delayed fluorescence and phosphorescence spectra were recorded about 10^{-2} sec after the sample was shielded from the exciting light by the use of a phosphoroscope.

3. Carbazole in Biphenyl

In a crystal of biphenyl doped with carbazole, the absorption and fluorescence spectra were characteristic of carbazole since the vibrational analyses were essentially identical to those already given[9] with fluorene as matrix. Following arguments presented by Hochstrasser and Small,[10] there is evidence that carbazole may occupy several different sites in the biphenyl lattice. For example, in a *bc′* section two prominent origin bands are active both in absorption and fluorescence at 29 672 and 29 698 cm^{-1} with a third weaker line at 29 678 cm^{-1}. Complete spectra were built on each line. However, using the $(20\bar{1})$ secondary cleavage plane, there were only two origins at 29 678 and 29 698 cm^{-1}. This variation in intensity was noted but not understood, although it may have been related to the fact that the *bc′* sections were prepared by surface grinding. The lines were about 5 cm^{-1} wide at a temperature of about 10–15 °K, corresponding to conditions of strong irradiation.

Pure biphenyl crystals did not phosphoresce even at the lowest temperatures reached (about 6 °K). However, when biphenyl was doped with carbazole an intense, blue phosphorescence was easily recorded. A study of the vibrational intervals and of the relative line strengths showed that the emitting species was biphenyl and not carbazole. The main features of the analysis are shown on the densitometer tracing of the spectrum in Fig. 1 and this may be compared with the phosphorescence spectrum of biphenyl in paraffin solvents.[11] However, the spectrum displayed the same type of multiplet structure that was evident in the fluorescence and absorption spectra of carbazole at shorter wavelengths. The *bc′* sections showed two phosphorescence origin bands at 22 939 and 22 970 cm^{-1} and in the four $(20\bar{1})$ sections studied, there were three at 22 934, 22 960 and 22 985 cm^{-1}. Thus we conclude that the several ways that carbazole may substitute in the host perturb *the biphenyl molecules of the lattice adjacent to the impurity site* so as to create corresponding energy minima in the local triplet band structure. Although the triplet level of carbazole is about 1700 cm^{-1} above the biphenyl triplet band, there is no evidence from the temperature dependence studies described later to suggest that the minima represent metastable levels but are, indeed, energy traps below the band. The traps mentioned so far were of one type since they showed a similar behavior as the temperature was raised. The set of origin bands grew weaker, broadened and rapidly merged into a single line that appeared to shift slowly to lower wavelengths presumably because the higher energy traps were the first to empty into the band. These levels were treated as though degenerate and will be referred to collectively as traps of type 1 (T_1) in the subsequent discussion.

A second type of trap (T_2) was located by the appearance of another biphenyl phosphorescence origin at 22 886 cm^{-1} to the

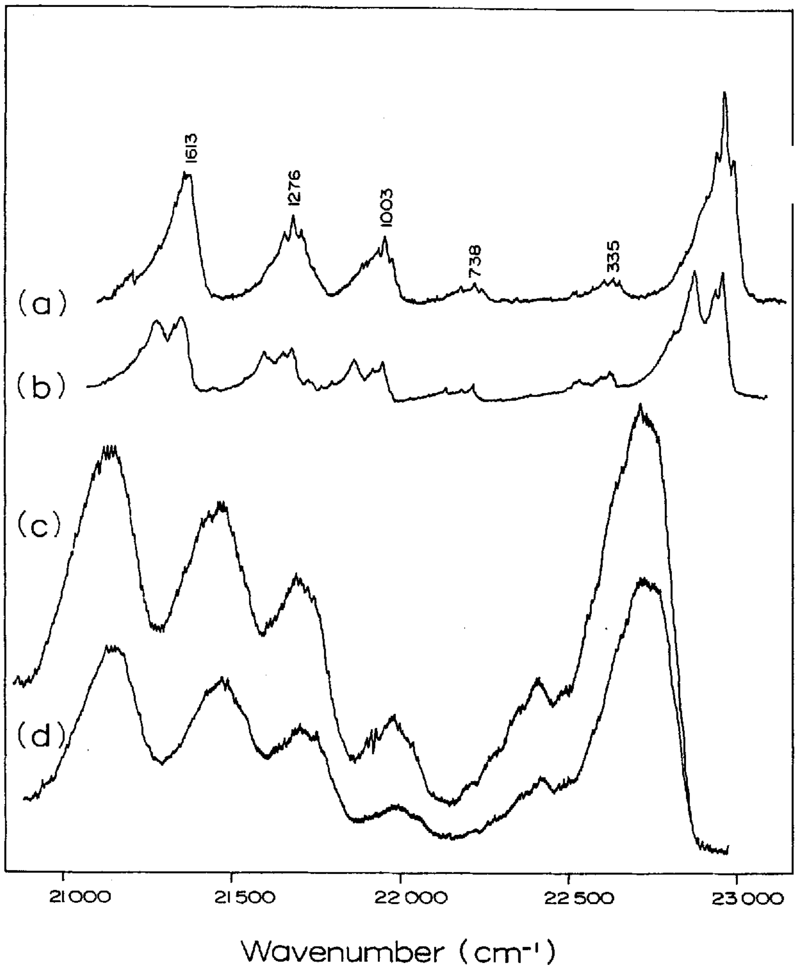

Figure 1. Phosphorescence spectra of biphenyl crystals doped with (a) carbazole at ~ 6 °K, (b) carbazole at ~ 15 °K showing a second trap coming into prominence, (c) dibenzothiophene-h_8 at ~ 6 °K, and (d) dibenzothiophene-d_8 at ~ 6 °K.

red of the first origin (see Fig. 1). These were detected only at higher temperatures where traps of type 2 became more active at the expense of those of type 1. T_2 probably occurs through the presence either of a second unsuspected impurity with levels above the corresponding ones of biphenyl, or of two carbazole molecules in close proximity. The observation of deeper traps that showed an analogous behavior in biphenyl doped with dibenzothiophene suggests that the latter explanation is correct.

The temperature dependence of the phosphorescence intensity from T_1 and T_2 (I_{p_1} and I_{p_2}, respectively) and delayed fluorescence from carbazole (I_{DF}) is shown in Fig. 2. The maximum in I_{DF} indicated that traps of one type were emptying into the band, with triplet-triplet annihilation subsequently occurring. The emptying trap was identified by observing a rapid decrease in the corresponding I_p, in this case I_{p_1}. The recombination process may be described[1,12] in terms of the concentrations of singlet excited carbazole molecules $[S]$ and of occupied traps of types 1 and 2 $[T_1]$ and $[T_2]$, respectively, by the equation

$$\frac{d}{dt}[S] = k_1[T_1]^2 + k_2[T_1][T_2] + k_3[T_2]^2 - k_4[S]$$

The temperature dependent annihilation rate constants k_1 and k_2 involve the smaller trap depth and k_3, the larger trap depth, exponentially. The rate constant k_4 is the sum of several less temperature-dependent terms. The first term on the right hand side of the rate equation refers to the annihilation of T_1 at another T_1 site, the second term to T_1 annihilating at T_2 and the third to T_2 annihilating at another T_2. Each of these terms might be expected to dominate in different temperature regions. In particular, at low temperature where $[T_2]$ was observed to be very small the first should be the important second-order term. Then the stationary-state approximation may be applied to $[S]$ to give the relation

$$\log (I_{DF}/I_{p_1}^2) = \text{constant} \ (-\Delta E/kT)$$

The slope of the linear portion of such a plot yielded a depth for the set of shallow traps of about 250 cm^{-1} (see Fig. 3). This may

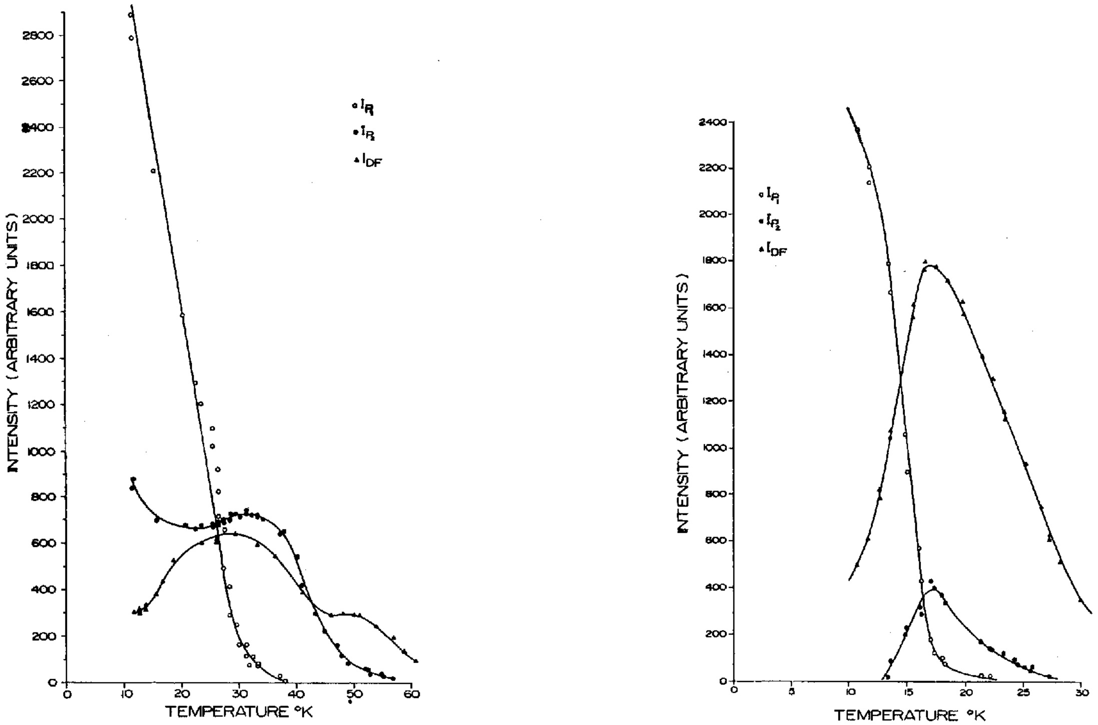

Figure 2. Temperature variation of the intensity of the phosphorescence (I_{p_1} and I_{p_2}) and of the delayed fluorescence (I_{DF}) from a biphenyl crystal doped with dibenzothiophene-h_8 (on the left) or carbazole (on the right).

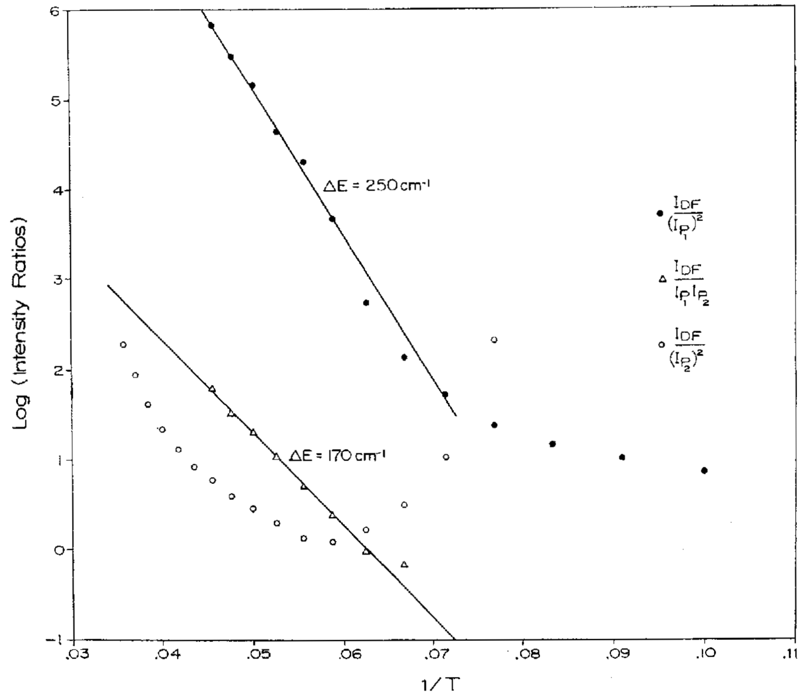

Figure 3. Plots of log (intensity ratios) against $1/T$ for the carbazole/biphenyl system.

be an over-estimate of the trap depth since there may be significant contributions to I_{DF} arising from other processes in the higher temperature region. In any event the percentage error (~ 20%) in this energy is large since it was estimated over a small temperature range using a relatively crude thermometer. If this value for the trap depth is accepted, the corresponding estimate of the energy gap to the triplet band is about 23 210 cm^{-1}. This takes the mean phosphorescence energy from the set of traps T_1 to be 22 960 cm^{-1} and assumes that any perturbation in the ground state of the biphenyl crystal is small compared with those in the triplet state. In a more direct measurement, Hirota[13] found the band gap at 78 °K to be about 23 200 cm^{-1}. This result suggests that the net repulsive effect on the ground electronic state of a biphenyl molecule caused by the insertion into an adjacent lattice site of a carbazole molecule (having a different shape) must be appropriately small. Plots formed by replacing $I_{p_1}^2$ by $I_{p_1}I_{p_2}$ or $I_{p_2}^2$ in the simplified expression above did not yield straight lines.

It is possible to postulate other ways in which the triplet band may become distorted. For example, if the solute concentration were made high enough, the traps could become connected thermally through clustering without involving the triplet exciton band directly. The nominal concentrations in the samples used ranged from 5×10^{-4} to 4×10^{-3} M/M and the actual concentrations may well have been less, when clustering should be unimportant.

4. Dibenzothiophene in Biphenyl

The same general behavior was observed when biphenyl was doped with dibenzothiophene. In this case, the biphenyl phosphorescence bands (as well as the dibenzothiophene fluorescence and absorption bands) were unusually broad (about 250 cm^{-1}) and no multiplets could be found (see Fig. 1). Apparently the diffuse nature of the spectrum was not a characteristic of the dibenzothiophene molecule since its spectrum in the pure crystal[14] or paraffin matrices[15] was sharp. Possibly dibenzothiophene occupies a large number of different sites in the host lattice, or even some form of hindered rotation may occur if two biphenyl molecules are replaced.

The change of solute from carbazole to dibenzothiopene caused the highest energy phosphorescence band of the bc' section to redshift by 80 cm^{-1}. Traps of type 2 were readily observed above about 20 °K when another broad phosphorescence origin, about 320 cm^{-1} to the red of the first, gradually increased in strength (see Fig. 2). The double maxima in I_{DF} was apparently a consequence of the traps T_1 emptying in the temperature range 20–30 °K and T_2 in the range 40–50 °K.

From the various plots shown in Fig. 4, the only satisfactory trap depth was for T_2 which was found to be 670 cm^{-1}. The

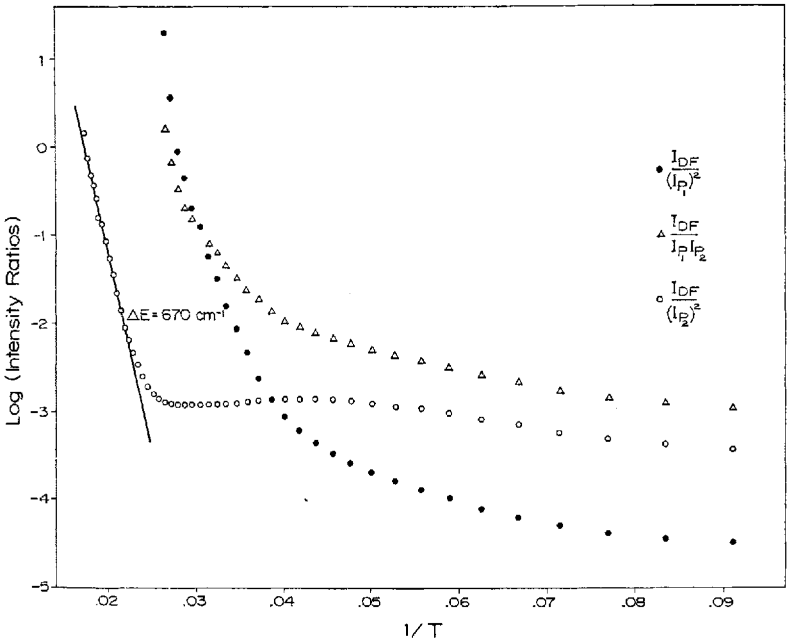

Figure 4. Plots of log (intensity ratios) against $1/T$ for the dibenzothiophene-h_8/biphenyl system.

corresponding (broad) phosphorescence origin band was at 22 580 cm^{-1} leading to an independent estimate for the band gap of 23 250 cm^{-1}. However, because of the extreme width of the phosphorescence bands, it is probably an unsatisfactory approximation to assume that all the traps lie at the same energy below the band in this case. This may account for the non-linearity of the other plots in Fig. 4.

Triplet-triplet absorption was observed in the biphenyl crystal doped with dibenzothiophene and the spectra (at about 10 °K) are shown in Fig. 5. For comparison the spectrum observed by Ramsay and Munro[16] of biphenyl in a rigid glass at 77 °K is also given. Although the bands were broad they were split sufficiently to indicate the presence of two electronic transitions of opposite polarization. No reliable assignment of the symmetry of the lowest triplet state has been made. However, if the symmetry

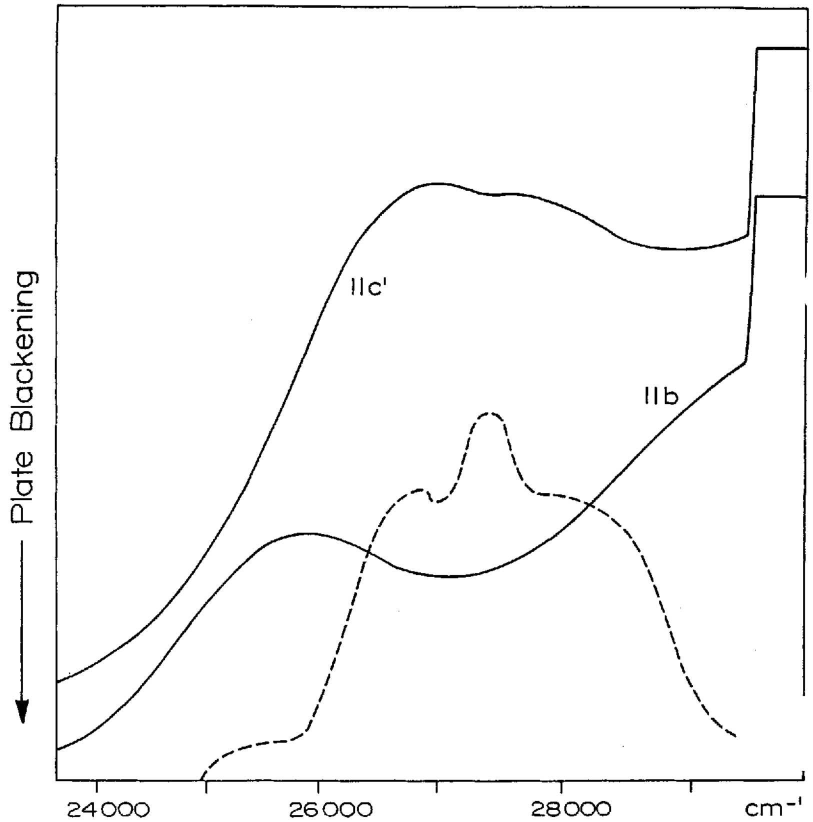

Figure 5. Triplet-triplet absorption of biphenyl in a single crystal doped with dibenzothiophene-h_8 at ~ 10 °K (full lines) and in a rigid glass at 77 °K taken from reference 16 (broken line).

$^3B_{2u}$ (whose orbital component transforms like an in-plane vector normal to the molecular length) calculated for planar biphenyl[17] is accepted, then the vibronic assignments are: $^3A_g \leftarrow {}^3B_{2u}$, parallel to the short in-plane axis at low energy and $^3B_{3g} \leftarrow {}^3B_{2u}$, parallel to the long axis at higher energy.

Some experiments were also carried out on biphenyl doped with dibenzothiophene-d_8, the deuterated compound being synthesized from biphenyl-d_{10} supplied by Merck, Sharp and Dohme of Canada Ltd. There was no measureable shift in the wavelength of the induced biphenyl phosphorescence from that observed with dibenzothiophene-h_8 as guest and the temperature dependence of the intensity of the light emission was qualitatively similar. However, a pronounced delayed fluorescence from phenanthrene and to a lesser extent from anthracene became evident above about 25 °K and the system was not studied further. The phenanthrene and anthracene were present in the commercial biphenyl-d_{10} and there was insufficient starting material for complete purification and synthesis.

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