

**689.** *The Effect of Impurities on the Fluorescence of Anthracene Crystals containing Tetracene.*

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The temperature-dependence of energy transfer in mixed crystals of tetracene in anthracene is shown to be dependent on the concentration of impurities in the host crystal. The effect of impurities on the temperature-dependence of energy transfer is similar to their effect on the temperature-dependence of anthracene luminescence. When extremely pure zone-refined anthracene is used, both the energy transfer and the anthracene luminescence cease to be markedly temperature-dependent. The explanation is discussed in terms of excitons and impurity levels which act as traps for the excitation energy at sufficiently low temperatures.

In recent years the transfer of excitation energy to tetracene molecules embedded in an anthracene lattice has been examined extensively,<sup>1-10</sup> and several different explanations have been offered. It has been known for some time that the energy transfer from excited anthracene molecules to tetracene is notably temperature-dependent, the tetracene fluorescence being quenched at low temperatures. This has been attributed (i) to imperfections in the anthracene lattice,<sup>6</sup> (ii) to lattice vibrations,<sup>8,9</sup> and more recently (iii)

<sup>1</sup> Bowen, *Nature*, 1938, **142**, 1081; 1943, **153**, 653; *J. Chem. Phys.*, 1945, **13**, 306; Bowen and Mikiewicz, *Nature*, 1947, **159**, 706.

<sup>2</sup> Bowen, Mikiewicz, and Smith, *Proc. Phys. Soc.*, 1949, **62A**, 26.

<sup>3</sup> Geschwendfer and Wolf, *Naturwiss.*, 1961, **48**, 42.

<sup>4</sup> Avakian and Wolf, *Z. Phys.*, 1961, **165**, 439.

<sup>5</sup> Choudhury and Ganguly, *Proc. Roy. Soc.*, 1960, *A*, **259**, 419.

<sup>6</sup> Ferguson and Schneider, *Canad. J. Chem.*, 1958, **36**, 1070.

<sup>7</sup> Sidman, *J. Chem. Phys.*, 1956, **25**, 122.

<sup>8</sup> Lyons and White, *J. Chem. Phys.*, 1958, **29**, 447.

<sup>9</sup> White, M.Sc. Thesis, University of Sydney, 1959.

<sup>10</sup> Ferguson, *Austral. J. Chem.*, 1956, **9**, 160, 172.

to levels lying below the free exciton level, in which the excitation energy is trapped and from which it can be liberated at a sufficiently high temperature.<sup>4,11</sup> Nevertheless, a conclusive explanation for the temperature-dependence has not been established.

In this work we show that the temperature-dependence of the energy transfer is associated with the presence of minute concentrations of impurities in the anthracene, which are not removable by such standard methods of purification as chromatography, recrystallisation, sublimation, and distillation with ethylene glycol.

#### EXPERIMENTAL

Anthracene was purified by (i) chromatography, (ii) distillation with ethylene glycol, sublimation, and chromatography, and (iii) zone refining, the column being subjected to 120 passes of the zone heater.<sup>12</sup>

Mixed crystals were then prepared by subliming the anthracene with a small quantity of Eastman Kodak tetracene in a dark inert atmosphere. The resulting crystals were examined under a polarising microscope to determine their thickness and extinction directions. The crystals were mounted on to a copper disc fitted into the helium cryostat, and their fluorescence spectra were recorded on a Hilger Littrow mounting quartz spectrograph at 4°K, 80°K, and 300°K, or else on a spectrophotometer. The fluorescence was excited by a high-pressure Mazda 250-w mercury lamp, the 3660 Å line being selected with a Hilger D-292 monochromator. Because a spectrophotometric method was used to record those spectra shown in Fig. 2a the frequency measurement in these cases was no more accurate than  $\pm 80$  cm.<sup>-1</sup>.

#### RESULTS

*Anthracene Distilled with Ethylene Glycol and Chromatographed.*—Mixed crystals grown from distilled and chromatographed anthracene exhibited a marked decrease in energy transfer below 40°K (Figs. 1b, c, and 2a), in agreement with previous workers.<sup>4,6,8</sup> Closer examination of chromatographed samples showed there are certain ranges of temperature in which the efficiency of energy transfer, as measured by the ratio of the peak heights  $T_0/A_2$ , changes markedly (Fig. 1c). These temperature ranges are seen to correlate very well with the ranges in which the luminescence of anthracene itself changes markedly<sup>11</sup> (Fig. 1a).

In the purest sample of anthracene containing tetracene the highest energy band of the anthracene fluorescence was at 25,050 cm.<sup>-1</sup>, which is at higher energy than any of the bands in fluorescence of less pure anthracene, indicating the possible presence of traps in the impure anthracene.

Looking at the luminescence of anthracene, we find in the purest samples (Fig. 2d), as the temperature is raised from 4° to 300°K, that the 25,050 cm.<sup>-1</sup> peak shifts slightly to lower energy. Since this is attributed to increasing reabsorption, there is no reason to suppose that the luminescence, corrected for reabsorption, is temperature-dependent. This conclusion is confirmed by looking at the intensity of luminescence at 23,650—23,750 cm.<sup>-1</sup> which is built on the 25,050—25,150 cm.<sup>-1</sup> origin.<sup>13</sup> The 23,700 cm.<sup>-1</sup> band is unchanged in intensity from 4° to 300°K. On the other hand, the effect of temperature on the luminescence of chromatographed anthracene is pronounced.<sup>8</sup> Luminescence at 23,610 cm.<sup>-1</sup> ( $\pm 50$  cm.<sup>-1</sup>) increases with temperature (Fig. 1a) between 4° and 100°K in much the same way as does the 25,050 cm.<sup>-1</sup> band.<sup>14</sup> These observations help to show that the temperature-dependence of the luminescence, as well as that of the energy transfer, is in some way connected with the presence of impurities. Above about 150°K a gradual decrease in luminescence is attributed to thermal degradation of the excitation energy in

<sup>11</sup> Lyons, "Symposium on Electrical Conductivity of Organic Solids," held at Duke University, 1960, Interscience Publ. Inc., New York, 1961, p. 193.

<sup>12</sup> Lacey and Lyons, *Rev. Sci. Instr.*, 1963, **34**, 309.

<sup>13</sup> Lacey and Lyons, *Proc. Chem. Soc.*, 1960, 414.

<sup>14</sup> Lyons and White, *J.*, 1960, 5213.

both anthracene and tetracene. In Fig. 2b, although there is less transfer to the tetracene than with zone-refined anthracene (Fig. 2a), there is no apparent temperature-dependence of the transfer. This is not understood unless in this sample the impurities gave rise to traps all sufficiently deep not to be emptied even at 300°K.

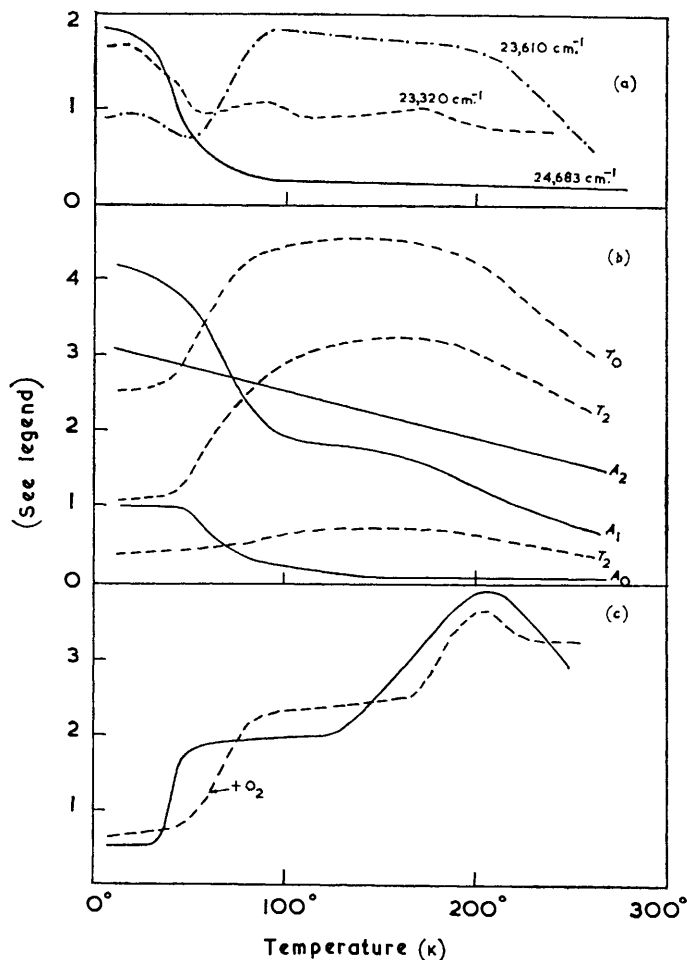


FIG. 1. Temperature-dependence of luminescence of chromatographed anthracene and anthracene distilled with ethylene glycol.

- (a) Three bands in a spectrum of a crystal of anthracene. (b) Main peaks in a spectrum of a crystal of anthracene containing tetracene. (c) Ratio of tetracene peak height,  $T_0$ , to anthracene peak,  $A_2$ .

*Chromatographed Anthracene.*—Mixed crystals prepared from anthracene purified only by chromatography over alumina were examined. This anthracene was known to contain small amounts of different impurities from the edge band absorption and fluorescence spectra.<sup>15</sup>

The fluorescence at 300°K exhibited a tetracene : anthracene ( $T/A$ ) intensity ratio of approximately 1.5 : 1 for a molar concentration ratio of  $\sim 8 \times 10^{-5} : 1$  (Fig. 2b). Cooling to 4°K hardly changed the tetracene intensity, but the anthracene intensity increased

<sup>15</sup> Alexander, Lacey, and Lyons, *J. Chem. Phys.*, 1961, **34**, 2200.

slightly. In this instance it appears that the presence of certain impurities (which in anthracene are known to include perylene, carbazole, methylanthracene, and anthraquinone<sup>16</sup>) in some way prevents the energy transfer from being temperature-dependent,

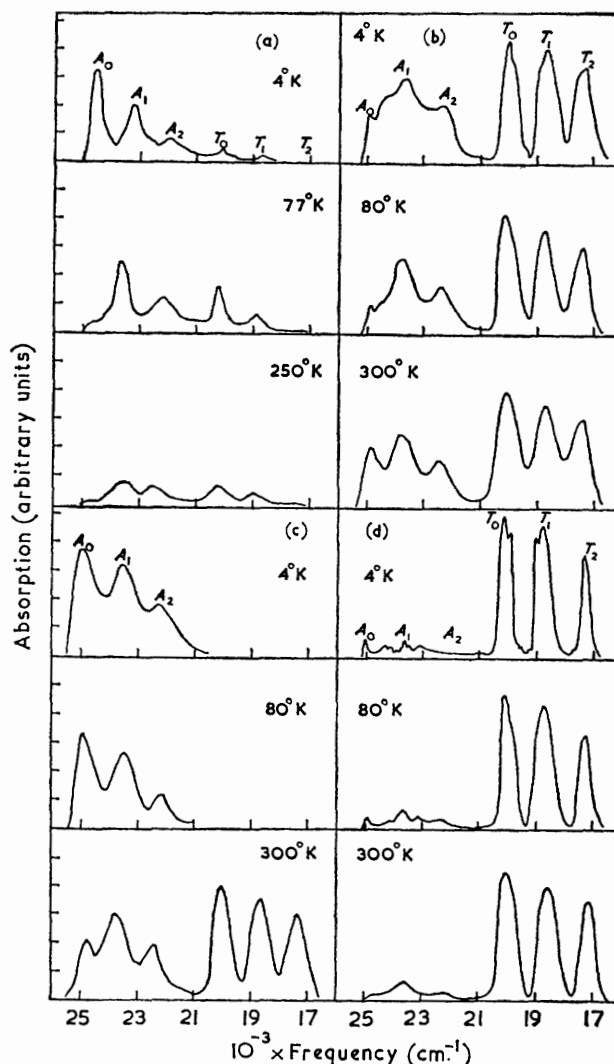


FIG. 2. Luminescence of anthracene (various purities) containing tetracene in concentrations:

(a)  $ca. 10^{-5}$ ; (b)  $8 \times 10^{-5}$ ; (c)  $4 \times 10^{-5}$ ; (d)  $5 \times 10^{-5}$  mole/mole.

- (a) Anthracene distilled with ethylene glycol and chromatographed but not zone-refined. (b) Anthracene chromatographed but not zone-refined. (c) Anthracene zone-refined, then oxidised. (d) Zone-refined anthracene.

although the impurities caused a decrease in the ratio of the tetracene-anthracene luminescence compared with the ratio when the anthracene had been zone-refined (Fig. 2d).

*Zone-refined Anthracene Allowed to Oxidise.*—A mixed crystal was prepared from a column of anthracene that had been subjected to 90 passes of the zone heater and then allowed

<sup>16</sup> Hutchinson and Lapage, U.K. Atomic Energy Authority, A.W.R.E., 1955, Report No. 0-73/S4.

to remain open to air for 12 months. This anthracene could be expected to contain only oxidation products as impurities. The fluorescence spectrum of such a crystal showed an intensity ratio ( $T/A$ ) of approximately 1.5 : 1 at 300°K, but at 80°K and 4°K the tetracene fluorescence was quenched completely (Fig. 2c). Absorption spectra showed the molar concentration ratio of tetracene to anthracene to be  $\sim 4 \times 10^{-5} : 1$ . Thus it seems that the oxidation impurities have so completely trapped the energy that it can no longer be transferred by thermal activation.

*Zone-refined Anthracene.*—A 10.3  $\mu$  mixed crystal of purest anthracene, which exhibited an overall intensity ratio of tetracene fluorescence to anthracene fluorescence of approximately 5 : 1 at 300°K, showed no change in energy transfer on cooling to 4°K; if anything, the tetracene fluorescence was slightly enhanced (Fig. 2d). From absorption measurements the molar concentration ratio tetracene:anthracene was estimated to be  $\sim 5 \times 10^{-5} : 1$ .

This lack of temperature-dependence of the energy transfer was verified by using a 1.9  $\mu$  crystal grown from another batch in which the tetracene concentration was further reduced until the fluorescence intensities of tetracene and anthracene were equal at 300°K. Again, the tetracene fluorescence was enhanced slightly on cooling to 4°K.

Previous workers<sup>2,8,17</sup> have found that equal intensities of tetracene and anthracene fluorescence, at 300°K, were obtained with a molar ratio of  $\sim 3 \times 10^{-5} : 1$ . Yet in this instance, with a concentration of  $5 \times 10^{-5} : 1$ , the intensity ratio, estimated visually, was  $\sim 5 : 1$  showing that with extremely pure anthracene the energy transfer is considerably enhanced. Even if the apparent enhancement is a function of crystal thickness<sup>18</sup> and requires further study, the temperature-dependence of energy transfer should be independent of thickness, for as the temperature was raised the spectra were always observed on the one crystal.

An unexpected observation was that of the polarisation ratio for the tetracene spectrum in the mixed crystal. The  $b:a$  ratio for anthracene was always greater than 1, as expected, but the  $b:a$  ratio for tetracene was always less than 1, where  $b$  and  $a$  signify the intensity of the fluorescence polarised parallel and perpendicular to the  $b$  crystal axis, respectively. The latter observation is contrary to the polarisation ratio observed by other workers.<sup>5,6,19,20</sup> We attribute this in part to partial oxidation of the tetracene to the mono- or di-quinone, both of which would be expected to give rise to long-axis polarised transitions<sup>21</sup> in this spectral region, although infrared spectra of a tetracene sample failed to show strong carbonyl absorption (Sidman<sup>7</sup> observed the tetracene fluorescence in a mixed crystal with anthracene to be depolarised at 20°K, and similarly for anthracene in phenanthrene,<sup>22</sup> but offered no explanation for his findings.) A mixed crystal grown from tetracene, which had previously been partly oxidised by sublimation in air, exhibited a marked increase in  $a$ -polarised tetracene fluorescence relative to  $b$ -polarised fluorescence. With successive sublimation of the tetracene in air the  $a$ -polarisation intensity continued to increase, giving strength to our assumption. Regardless of the degree of oxidation of the tetracene, the anthracene spectrum and polarisation ratio were constant.

## DISCUSSION

From the foregoing results it appears that in samples made from pure anthracene the energy transfer is due entirely to a mechanism which is independent of temperature. It is, therefore, independent of lattice vibrations that are quenched at 4°K. For small concentrations of impurity, the resultant imperfections which are at distances from tetracene molecules greater than 44 Å (the critical intermolecular distance<sup>6</sup> for transfer

<sup>17</sup> Ferguson, Ph.D. Thesis, University of Sydney, 1955.

<sup>18</sup> Faidysh and Zima, *Optika i Spektroskopiya*, 1959, **7**, 98.

<sup>19</sup> Craig and Thirunamachandran, *Proc. Chem. Soc.*, 1961, 253.

<sup>20</sup> Bree and Lyons, *J.*, 1960, 5206; *J. Chem. Phys.*, 1954, **22**, 1630.

<sup>21</sup> Sidman, *J. Amer. Chem. Soc.*, 1956, **78**, 4567.

<sup>22</sup> Sidman, *J. Chem. Phys.*, 1956, **25**, 115.

of energy between anthracene and tetracene) act as efficient traps for the excitation energy at low temperatures.<sup>12,14,23</sup>

The results with zone-refined anthracene differ slightly from those of Bowen, Mikiewicz, and Smith.<sup>2</sup> The molar concentration ratio at which 50% of the emitted energy comes from the tetracene now seems to be less than their figure of  $3 \times 10^{-5} : 1$ . However, for an accurate correlation of results one needs to know the thicknesses of the crystals used by them since the tetracene : anthracene fluorescence ratio is now known to be thickness-dependent.<sup>18</sup> When the fluorescence intensities were equal we were not able to determine with our apparatus the very low concentration of tetracene in the sample.

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<sup>23</sup> Hochstrasser, *J. Mol. Spectroscopy*, 1962, **8**, 485; Wolf, Abs. Organic Crystal Symposium, Nat. Res. Council, Ottawa, Canada, 10—12th October, 1962.

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