Ultra-Violet Polarization Ratios in Anthracene-Tetracene Mixed Crystals

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The visible absorption and emission spectra of tetracene in anthracene host crystal have been re-investigated, and values of polarization ratio and crystal intensification factors recorded with the help of measured crystal thickness and tetracene concentration. The results are compared with theoretical expectations based on solution oscillator strengths and estimates of higher transition multipoles. The trend is correctly accounted for and the agreement for polarization ratios and intensification factors is reasonably good.

Experiments on mixed crystals in which a host molecule is replaced by a guest with the same orientation of axes are of importance for theories of intermolecular interactions in molecular crystals. Difficulties over the treatment of electromagnetic retardation of the dipole-dipole interactions, which are severe in pure crystals, appear in mixed crystals in a much weakened form, and there are experimental advantages from the fact that measurements can be made with relatively thick crystals in which the guest is present in high dilution. Mixed crystals of tetracene in anthracene provide a favourable example because the ultra-violet spectra of both host and guest are well known, and adequate theoretical models are available. Advances in technique have made it necessary to record new measurements of the polarization properties of fluorescence and absorption in these systems. Some of the present results have already been briefly reported in part [1] and compared with previously available values.[2]

The host anthracene crystals belong to space group $P2_1/a$, and both fluorescence and absorption are measured with the electric vector of the light parallel and perpendicular to the b crystal axis and the direction of propagation perpendicular to the ab plane. The extinction coefficient in absorption is different for the two directions of polarization of the light. The polarization ratio is defined as $PR(b/a) = \varepsilon_b/\varepsilon_a$ where ε_b and ε_a are extinction coefficients for the band maxima with light polarized parallel and perpendicular to the b crystal axis. Similarly, in fluorescence $PR(b/a) = E_b/E_a$ where E is the intensity of the light emitted with the indicated polarization directions. Corresponding quantities integrated over the whole bands are of more fundamental significance. The definitions are then modified by replacing ε or E by $\int\varepsilon(\bar{\nu})d\bar{\nu}$ or $\int E(\bar{\nu})d\bar{\nu}$, where $\bar{\nu}$ is the energy of absorption or fluorescence. In absorption the polarization ratio is then the ratio of oscillator strengths for absorption of the two electric vector directions of the light.

With the assumptions that tetracene replaces anthracene by a simple substitution at a lattice site, and that the directions of the corresponding molecular axes are exactly preserved, we may calculate the oriented-gas polarization ratio for a transition of any given molecular polarization property. For the first absorption system of tetracene, in which the absorbed light is polarized parallel to the shorter in-plane molecular axis the oriented-gas polarization ratio is 7·7 : 1 with the stronger component along the b crystal axis. Evidence in support of the assumption that the mixed

crystal of tetracene in anthracene forms by precise molecular substitution is lacking, but in a number of other and similar mixed crystals the correctness of the assumption has been shown by spin resonance studies of the triplet state of the impurity molecule.[3] Measurements of polarization ratios for ultra-violet absorption and fluorescence give values different from the oriented-gas ratio both in pure and mixed crystals, and the character and extent of these departures from expectation are the subject of the present investigation.

EXPERIMENTAL

The spectral measurements were made with a specially constructed single-beam recording spectrophotometer based on a Hilger-Müller monochromator with photo-multiplier detection. Fluorescence spectra were recorded continuously across the spectrum but in absorption were obtained with point-by-point measurements. The device as a whole was linear with respect to light intensity within the limits used. The apparatus was calibrated in spectral response with a standard light source. Light was polarized by passage through a Glan prism with collimation to ensure that the divergence of the light beam was less than 4° of arc. The purity of the emerging polarized light was checked by the insertion of an accurately oriented second polarizing prism.

Mixed single crystals were grown from dimethyl formamide by the method of Lipsett[4] by adding about 10^{-3} mole of tetracene for each mole of anthracene in solution. The anthracene used was B.D.H. blue fluorescence-grade zone-refined in 70 passes; tetracene was repeatedly re-crystallized from benzene. Its extinction coefficient in cyclohexane at 275 mμ was found to be $2\cdot94\pm0\cdot05\times10^5$ in excellent agreement with a recent measurement in dioxane.[5] Earlier literature reports invariably give a lower extinction coefficient probably on account of oxygen contamination.

The crystals used were all of approximately the same thickness and were free from imperfections under microscopic examination. All had developed *ab* crystal faces. Crystal thickness was measured from the difference in height between the focal planes at the upper and lower surfaces of the crystal measured microscopically and corrected to true thickness using the refractive indices of anthracene of Sundararajan.[6] Crystals about 200 μ thick were used throughout, the thickness measurement being accurate to about 5 %. The tetracene concentration was estimated spectrophotometrically by dissolving a known mass of the crystal in cyclohexane, and measuring the optical densities of the solution at 310 and 275 mμ. From the values of the extinction coefficients of tetracene and anthracene at the two wavelengths the percentage tetracene to anthracene can be calculated (for anthracene, ε at 275 mμ: $3\cdot08\pm0\cdot15\times10^2$, and at 310 m$\mu$: $1\cdot26\pm0\cdot04\times10^3$; for tetracene ε at 275 mμ, as already quoted, and at 310 m$\mu \ll 1/50\ \varepsilon$ of tetracene at 275 mμ). The concentrations so found are accurate to about ±8 %. Otherwise, measurements of fluorescence and absorption polarization ratios were made by standard methods. The polarizing prism and other optical components were not moved during the experiments. In order to eliminate errors due to polarization discrimination within the optics, different polarization directions were observed by rotating the crystal between runs through 90° on a microscope stage.

RESULTS

A typical absorption spectrum is shown in fig. 1, and a table of results in table 1. The values quoted in table 1 are means of results obtained on two crystals each measured four times. The imperfect agreement between values obtained from band maxima and integrated band areas is mainly to be ascribed to the difficulty of allowing for background absorption which was troublesome even in apparently perfect crystals. The ratios of extinction coefficients measured at band maxima are, therefore, probably the more reliable. Values at 430 mμ are the least satisfactory on account of the absorption tail of the anthracene host crystal. The results in table 1 are compared with those of Choudhury and Ganguly[2] for ε_b. The new values are higher; the agreement for the weaker absorption in the direction is within 10-20 % in extinction

coefficient.   Probably Choudhury and Ganguly's values were low on account of penetration of the crystal by a small component of light with the " wrong " polarization.   This can have a large effect on measurements of the intensities of strongly absorbing systems, and must be avoided by rigorous experimental precautions to ensure that the incoming light is completely polarized.
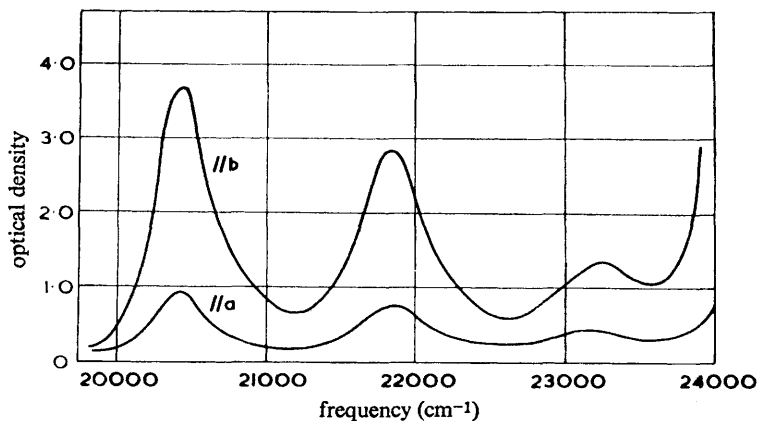

FIG. 1.—Typical absorption spectrum of tetracene in anthracene host crystal.   Tetracene concentration : $1 \cdot 03 \times 10^{-3}$ mole/mole, $\pm 8 \%$; crystal thickness 176 μ.

TABLE 1.—ABSORPTION BY TETRACENE IN ANTHRACENE SINGLE CRYSTAL

λ(mμ)	ν(cm^{-1})	ε_b^{*}†	f_b^{*}†	$\varepsilon_b/\varepsilon_a$	f_b/f_a
490	20,410	$2 \cdot 88 \times 10^4$ $(2 \cdot 23 \times 10^4)$	0·024	4·0	3·6
459	21,790	$2 \cdot 27 \times 10^4$ $(1 \cdot 72 \times 10^4)$	0·023	3·9	3·7
430	23,260	$1 \cdot 05 \times 10^4$ $(1 \cdot 15 \times 10^4)$	0·012	3·1	3·1

  * The uncertainty in the extinction coefficients and oscillator strengths is about $\pm 12 \%$.   Polarization ratios, in which the errors due to crystal thickness and concentration measurements do not arise, should be better than $\pm 10 \%$.   Bracketed values are those of Choudhury and Ganguly.[2]
  ** oscillator strength.
  † Values revised from those given in a preliminary communication [1] to take account of new values of extinction coefficients of rigorously oxygen-free anthracene solution, on which the estimation of crystal concentration depends.   We are indebted to Dr. Gad Fischer for new measurements.
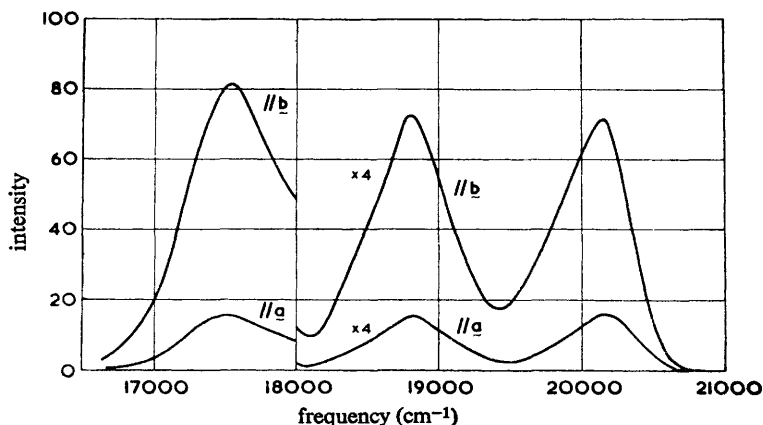

FIG. 2.—Fluorescence emission spectrum of tetracene in anthracene host.

Fig. 2 and table 2 show the results obtained in fluorescence. The values quoted are means of a large number of determinations carried out on several different crystals. A comparison with the results of Choudhury and Ganguly given in table 2 discloses values that are lower, and closer to those obtained in absorption.

TABLE 2.—FLUORESCENCE OF TETRACENE IN ANTHRACENE CRYSTAL

λ(mμ)	v(cm^{-1})	E_b/E_a^*	$\int E_b \mathrm{d}v / \int E_a \mathrm{d}v$
495	20,200	4·4 ±0·2 **	4·9 ±0·2 ** (5·7)
532	18,800	4·6 ±0·2	4·7 ±0·2 (5·2)
571	17,510	5·0 ±0·2	5·6 ±0·2 (5·7)

* ratio of maximum intensities.
** affected by re-absorption; bracketed values are those of Choudhury and Ganguly.[2]

COMPARISON WITH THEORY

A general understanding of the results may be had with the help of theoretical studies of the mixing of states of the guest molecule with those of the host by inter-molecular forces.[7,9] Let us suppose that the guest-host interactions are the same as those of host and host, implying not only accurate alignment of the guest on a site left vacant by a host molecule, but also equal host and guest transition moments for corresponding transitions. Then, if w is the difference between the excitation energy of the lowest transitions of guest and host, i.e., the trap depth, the transition energies in the mixed crystal are given by the values of E solving eqn. (1),

$$1 - \frac{w}{N} \sum_{\mathbf{k}} \frac{1}{E - e(\mathbf{k})} = 0, \tag{1}$$

where N is the number of lattice sites in the finite crystal block used to calculate the pure host energy spectrum $e(\mathbf{k})$, $\mathbf{k}$ being the wave vector. The N sites in the mixed crystal are occupied by $N-1$ host molecules and one guest. The lowest of the energy levels from eqn. (1) applies to an excitation essentially localized in the guest (trap level), and the other solutions apply to delocalized, or free, excitons in the host. Presently we are concerned only with the trap level, here well separated from all the others. We now re-write eqn. (1) with the energy variable e referring to the centre of gravity of the host band e^r, where

$$e(\mathbf{k}) = e^r + I(\mathbf{k}),$$
$$I(\mathbf{k}) = \sum_q e^{i\mathbf{k}.\mathbf{q} - \mathbf{p}} \mathbf{V}_{pq} \tag{2}$$

In expressions (2), $\mathbf{V}_{pq}$ is the interaction energy between the guest molecule at site p, and hosts at sites q. For the trap level, assumed widely separated from the host band, we expand in powers of $I(\mathbf{k})/e$,

$$0 = 1 - \frac{w}{N} \sum_{\mathbf{k}} \frac{1}{E - e(\mathbf{k})} = 1 - \frac{w}{Ne} \sum_{\mathbf{k}} \frac{1}{1 - I(\mathbf{k})/e}$$

$$= 1 - \frac{w}{Ne} \sum_{\mathbf{k}} \{1 + I(\mathbf{k})/e + (I(\mathbf{k})/e)^2 + \ldots\}. \tag{3}$$

Application of the closure properties of sums over the wave vector $\mathbf{k}$ gives, for the leading term

$$e = w + \sum_q \mathbf{V}_{pq}^2 / e + \ldots$$

which may be written approximately, for large e,

$$e = w + \sum_q \mathbf{V}_{pq}^2 / w + \ldots \tag{4}$$

This agrees with the result of a straightforward application of perturbation theory in ref. (9) but depends on the assumed equality of the host-guest and host-host inter-actions. In the limit of perturbation theory, result (4) applies with no such restriction. The appearance of the sum of squared interactions in expression (4) shows that the host-guest coupling falls off rapidly with distance, and retardation effects can be neglected. For the same reason, however, consideration of higher multipole inter-actions should be included, a problem not considered in earlier work. The calculation of polarization ratio depends upon the wave function for the guest molecule. These are obtained, as in ref. (9) by consideration of the mixing of the first two excited states of the host with the guest. In table 3 the results of calculations are compared with experimental results ; the dipole calculations are those of ref. (9), while the effects of including higher multipole moments have been newly worked out by Dr. T. Thirunamachandran.[10] Table 3 includes values for the *intensification factors*, not so far defined. They are the ratios of the measured oscillator strengths to those calculated from the solution spectrum with the oriented gas assumption. They are thus indices of the degree to which intensity transfers are induced between different free molecule transitions under the influence of intermolecular forces. They depend upon the measurement of absolute absorption strengths in the crystal, and are less accurately known than the ratio of measured intensities given by the polarization ratio.

TABLE 3.—CALCULATED AND EXPERIMENTAL POLARIZATION RATIOS
AND INTENSIFICATION FACTORS

progression member	PR † (expt.)	PR (calc. A)*	PR (calc. B)*	I_a (expt.)	I_a (calc. A)	I_a (calc. B)*
$n = 0$	3·6	2·77	4·17	2·2	1·7	2·36
$n = 1$	3·7	2·68	4·10	1·5	1·5	2·42
$n = 2$	3·1	2·57	4·0	1·8	1·8	2·50

* calculation A: based upon solution values of transition dipole moment, and zero values of higher multipoles.

calculation B: solution values of transition dipole moment, and values of tetracene octupole moment to fit the crystal spectrum of *pure* tetracene, viz., $O_{1s} = 4e\text{Å}^3$, $O_{3s} = -130e\text{Å}^3$.

† see table 1.

The experimental intensification factors in table 3 have been calculated from the crystal intensities in table 1 and solution values of oscillator strengths for the successive absorption maxima of 0·0291, 0·0398 and 0·0224. The experimental results fall between those calculated on the basis of purely dipole coupling, and the basis including realistic values of higher moments. The agreement is generally satisfactory while, however, not favouring one or other basis decisively.

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