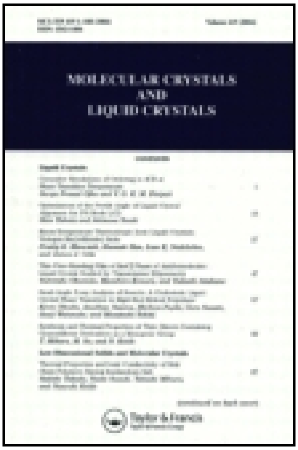

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M. Chabr [a] & I. Zschokke-gränacher [a]

[a] Institute of Physics, the University of Basel, Switzerland

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Determination of the Orientation of Guest Molecules in the Host Lattice of Organic Crystals

M. CHABR and I. ZSCHOKKE-GRÄNACHER

Institute of Physics, the University of Basel, Switzerland

It is a well known fact that the rate constant for mutual triplet annihilation in organic crystals depends on the magnitude of the magnetic field and on its direction relative to the crystallographic axes. The dependence of the delayed fluorescence on the magnetic field direction displays resonance minima, which are caused by energy level crossings of the annihilating triplet pair. For the annihilation between free excitons (homofusion) in undoped crystals this has been first observed and theoretically explained by Johnson, Merrifield *et al.*[1,2] The theory has been further extended by Suna.[3]

In doped crystals, where triplet annihilation between free host excitons T_H and localized guest excitons T_G occur (heterofusion), both the host S_{1H} and the guest S_{1G} fluorescent singlet states are excited:

$$\begin{tikzcd}
 & & S_{1H} \arrow[r] & h\nu_H \text{ Host del. fl.} \\
T_H + T_G \arrow[r, shift left] & (T_H T_G) \arrow[l, shift left] \arrow[ur] \arrow[dr] & & \\
 & & S_{1G} \arrow[r] & h\nu_G \text{ Guest del. fl.}
\end{tikzcd}$$

In the case of heterofusion the minima in the delayed fluorescence intensity appear at different magnetic field directions than for homofusion, which depend on the orientation of the molecular fine structure tensor of the guest triplet state with respect to the host lattice. From the magnetic field anisotropy of guest delayed fluorescence the orientation of the guest molecules relative to the host lattice can be experimentally determined.[4]

The following systems have been investigated at different doping levels:

$$\text{anthracene doped with tetracene} \left(10^{-8}\,\frac{\text{mol}}{\text{mol}} - 10^{-5}\,\frac{\text{mol}}{\text{mol}}\right)$$

$$\text{naphthalene doped with pyrene} \left(\textit{ca. } 10^{-3}\,\frac{\text{mol}}{\text{mol}}\right)$$

The crystals were grown in vacuum from the melt by the Bridgman technique. For excitation of the triplet excitons the light from a 1 Watt Krypton laser was used. The intensity of the guest delayed fluorescence emission was measured by conventional methods. The magnetic field (9 kGauss) could be rotated in any plane perpendicular to the crystallographic *ab*-plane. The orientation of the magnetic field is measured in polar coordinates. The azimuth in the *ab*-plane will be denoted by the angle φ and the elevation by ϑ. The measurements were performed at room temperature.

For heterofusion in tetracene doped anthracene the directions of the tetracene delayed fluorescence intensity minima as calculated for a substitutional guest are shown together with the experimental results in Figure 1. For anthracene single crystals there are two molecules per unit cell. Each of the two dashed curves in Figure 1 corresponds to one of the two possible

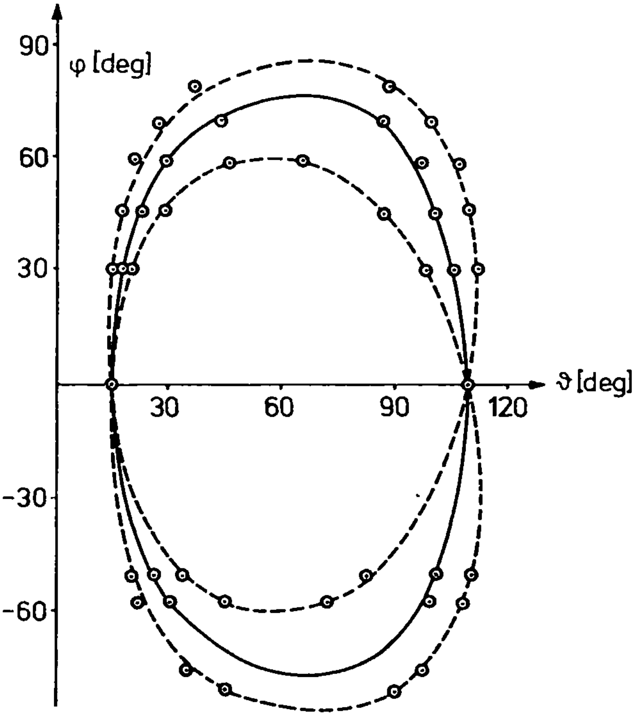

FIGURE 1 High field level-crossing resonance directions in a magnetic field of $H = 9$ kG for a tetracene doped anthracene crystal. φ and ϑ are the spherical angles of the magnetic field relative to the crystallographic axes *a*, *b*, c^* (see Ref. 4).
Solid lines: calculated for homofusion.
Broken lines: calculated for heterofusion with substitutional guest.
Points: experimental data.

orientations of the guest in the anthracene host lattice. The center curve—solid line—shows the angular dependence of the delayed fluorescence resonance minima for homofusion in anthracene. As can be seen from the correspondence between experiment and theory, the tetracene molecules enter the anthracene lattice substitutionally at all doping levels.[4] This is to be expected since for this particular system the size and shape of the host and guest molecules are similar.

In naphthalene doped with pyrene the measured resonance directions of the pyrene delayed fluorescence do not coincide with the curves calculated for a substitutional guest. By a least square fit to the experimental points the orientation of the guest has been evaluated. With respect to the naphthalene molecules the pyrene molecules are rotated by 10 degrees about the vertical to the molecular plane. Pyrene and naphthalene are quite different in size and shape. The almost substitutional orientation of pyrene in the naphthalene host is therefore rather surprising.

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