Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

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Version of record first published: 20 Apr 2011.

To cite this article: V. Ern & A. Fort (1983): Zero Field Splitting of Triplet Excitons in p-Terphenyl Crystals, Molecular Crystals and Liquid Crystals, 100:1-2, 1-15

To link to this article: http://dx.doi.org/10.1080/00268948308073714

Mol. Cryst. Liq. Cryst., 1983, Vol. 100, pp. 1–15
0026-8941/83/1002–0001/$18.50/0

Printed in the United States of America

Zero Field Splitting of Triplet Excitons in *p*-Terphenyl Crystals

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(*Received December 13, 1982*)

The zero field splitting (ZFS) of triplet excitons has been investigated in *p*-terphenyl crystals at room temperature via a detailed study in a family of planes of the position of high-field resonances of the modulation by a magnetic field of delayed fluorescence due to triplet-triplet annihilation. The ratio of the crystal ZFS parameters is $D^*/E^* = +0.14 \pm 0.02$ and the x^*, y^* principal axes of the tensor in the *ac* plane make an angle of $\alpha^* = 16° \pm 1°$ with the *a*, *c'* crystal axes. One of the principal axes is thus oriented along the long axes of the molecules in good agreement with the predictions of Sternlicht-McConnell's average spin Hamiltonian for the exciton.

INTRODUCTION

Crystals of polyphenyl molecules, notably the biphenyl, *p*-terphenyl, *p*-quaterphenyl series, have been attracting an increasing interest in the last years because of the non-rigidity of these molecules with respect to the torsional angle about the long molecular axis between planes of the phenyl rings. Due to the delicate balance that may exist between competing *intra*molecular (interphenyl-ring) and *inter*molecular forces, this torsional angle and hence the equilibrium molecular conformation strongly depends on the environment, that is, on the physical state and on the temperature of the aggregate. Typically, in the gaseous state the molecules are strongly non-planar, the torsional angle being reduced in the liquid phase. In the solid state at room temperature the *p*-polyphenyl molecules can be considered as effec-

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tively planar, the planarity being thought to result from a time-averaged, large amplitude, torsional libration about the long axis of the molecule. The high-temperature X-ray or neutron-diffraction detected crystal structures appear as consisting of planar molecules of D_{2h} symmetry with a well defined mean molecular plane. The molecules are packed in the usual $C_{2h}^5(P2_1/a)$ monoclinic space group with two translationally inequivalent molecules in the unit cell as is typically the case for "rigid" organic molecules of similar size like naphthalene and anthracene. However, in *p*-polyphenyl crystals, as damping of the torsional mode takes place upon cooling, the high temperature structure is unstable and at low temperatures the solids undergo characteristic reversible "antiferrodistortive type" phase transitions at which the molecules become stabilized in non-planar configurations accompanied with changes in the unit cell dimensions. For details and quantitative aspect of the X-ray and neutron diffraction structural work on these materials, the reader is referred to Refs. 1–4 for biphenyl, Refs. 5–10 for *p*-terphenyl, and Refs. 11–12 for *p*-quaterphenyl crystals, as well as to references given therein.

These features of *p*-polyphenyl solids make them ideal prototypes for studies of critical phenomena in the organic solid state induced by order-disorder or soft-mode condensation structural transitions. Closely related to the diffraction work cited above, extensive work can be found now in the literature reporting studies of infrared and Raman spectra,[13–15] Brillouin scattering,[16] sound velocities and elastic constants,[16,17] optical indicatrix and diamagnetic anisotropies,[18–20] dislocations and rotational disorder,[8,21,22] transitional heat capacities and hydrostatic pressure effects,[23,24] as well as of inelastic and critical quasi-inelastic neutron scattering.[24–27] Excited electronic states of *p*-polyphenyl crystals have been also attracting increasing interest in recent years. Specially, neat and mixed biphenyl crystals have been already extensively studied, notably by absorption, prompt fluorescence and phosphorescence emission spectra,[28–30] and by EPR-ENDOR work[31–33] on the lowest photoexcited triplet state. Recently, the detailed work of Hutchison *et al.*[33] has shown that at low temperature the biphenyl molecules which are twisted in their ground state, tend to the planar configuration even in the crystalline environment upon excitation in their lowest triplet state. Fluorescence and singlet exciton energy transfers have been recently studied in *p*-terphenyl crystals.[34–36] The phase transition in this material has been also studied by following the temperature dependence of the electron- and hole-mobility tensor[37] as well as by changes induced in the delayed

fluorescence dependence on a magnetic field applied along certain directions in the crystal,[38] the effect showing in the transition region around 180 K a qualitatively similar behaviour as that observed for the Raman scattering data.[38,15]

Because of the possibility of long lifetimes and migration lengths, triplet excitons constitute a sensitive tool to probe molecular solid state properties.[39] The cooperative effects like triplet-triplet exciton annihilation leading to observable delayed fluorescence, notably its magnetic field dependence, can yield information on triplet exciton zero-field splittings, transport, and spin relaxation.[40-42] In *p*-terphenyl crystals, triplet exciton populations can be easily created by direct excitation in the first triplet band with commercially available lasers. Delayed fluorescence has been already used in this material to study the wavelength dependence of the $S_0 \rightarrow T_1$ absorption,[43] the temperature effects of triplet exciton trapping by deep chemical and shallow structural traps,[44,45] and the triplet exciton-diffusion tensor components at room temperature.[46] Recently, Altwegg *et al.*[47] have reported zero-field splitting (ZFS) parameters for the triplet exciton of *p*-terphenyl crystals at room temperature in a paper dealing essentially with the general problem of the applicability of Suna's theory[41] and the spin relaxation effect in naphthalene crystals.[48] From the experimental data obtained in two planes of a *p*-terphenyl crystal an exciton ZFS parameters ratio $d^* = D^*/E^* = -0.18$, and an angle of $\alpha^* = 1°$ for the x^*, y^* principal ZFS tensor axes in the *ac* plane were reported in Ref. 47. The x^*, y^* axes appear thus as nearly coinciding with the crystallographic *a*, *c'* axes. Now, such position of ZFS principal axes is inconsistent with the *p*-terphenyl crystal structure[5-7] and the average spin Hamiltonian picture of Sternlicht–McConnell[49] for the triplet exciton. As is seen in the next section, the average Hamiltonian picture predicts that in *p*-terphenyl crystals one of the exciton ZFS principal axes coincides with the direction of the long molecular axes in the crystal and hence one should expect a value of $\alpha^* \simeq 17°$. This discrepancy appeared to us as rather puzzling since Sternlicht–McConnell's approach has been found to be a good approximation for many molecular solids studied up to now. In *p*-terphenyl crystals the exciton hopping rates in the *ab* plane[46] have a similar order of magnitude as those found for other monoclinic crystals, for instance, naphthalene,[50] and it was felt that the problem posed here should be further investigated in more detail.

In this paper we report a detailed study of the high-field resonance positions of magnetic field modulated delayed fluorescence in a family

of planes of *p*-terphenyl crystals at room temperature. The work indicates that for this material one indeed has a value of $\alpha^* = 16° \pm 1°$ for the ZFS axes position in the *ac* plane, the ZFS parameters ratio for the exciton being actually $D^*/E^* = +0.14 \pm 0.02$.

THE TRIPLET EXCITON ZFS TENSOR IN *p*-TERPHENYL CRYSTALS

As mentioned above, X-ray and neutron diffraction work by several authors[5-7] indicates that *p*-terphenyl crystals at room temperature belong to the $C_{2h}^5(P2_1/a)$ monoclinic space group with two effectively planar translationally inequivalent molecules in the unit cell. The molecular packing is determined by the angles[5-7]

	a	b	c'
$L(x)$	106.5°	90°	16.9°
$M(y)$	58.0°	33.5°	80.7°
$N(z)$	142.9°	56.5°	104.1°

(1)

that the L (long), M (medium), N (normal to the mean molecular plane) axes, chosen as the x, y, z molecular axes in the D_{2h} symmetry, make with the crystallographic a, b, c' axes, c' being the normal to the ab plane. A peculiarity of the packing is that the long molecular axis (L) lies in the ac plane, nearly coinciding (within 1°) with the $\{\bar{1}02\}$ direction. Hence, as required by the point group symmetry, the two translationally inequivalent molecules in the unit cell have parallel long axes.

In the average Hamiltonian picture for the exciton spin of Sternlicht–McConnell[49] for a monoclinic C_{2h}^5 space group crystal, the exciton ZFS tensor components in the crystal a, b, c' coordinate system are given by

$$T_{ii} = \left(\tfrac{1}{3}D - E\right)L_i^2 + \left(\tfrac{1}{3}D + E\right)M_i^2 - \tfrac{2}{3}DN_i^2 \qquad (i = a, b, c')$$

$$T_{ac'} = \left(\tfrac{1}{3}D - E\right)L_aL_{c'} + \left(\tfrac{1}{3}D + E\right)M_aM_{c'} - \tfrac{2}{3}DN_aN_{c'}$$

$$T_{ab} = T_{bc'} = 0$$

where D, E are the single molecule ZFS parameters[51] and L_i, M_i, N_i, $i = a, b, c'$ are the cosine directors of the angles given in (1) that L, M, N make with the crystallographic a, b, c' axes.

Using for the tensor principal axes (x^*, y^*, z^*) the nomenclature convention shown in Figure 1, as usually used in triplet exciton ESR

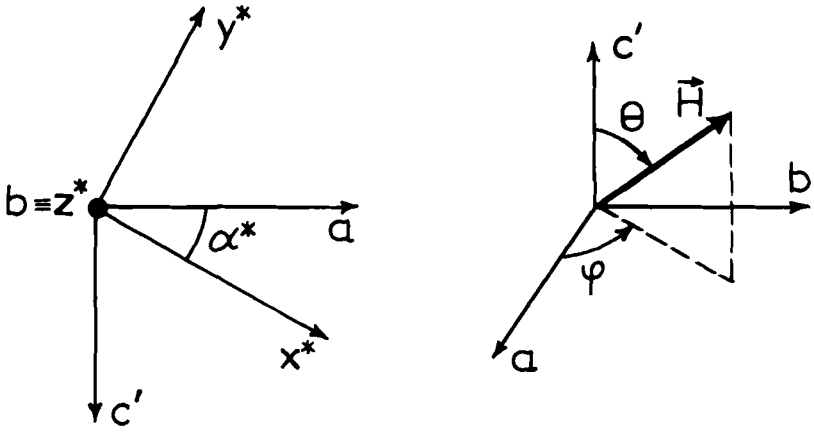

FIGURE 1 On the left: convention for the labelling of the x^*, y^* exciton principal ZFS tensor axes in the ac plane of a monoclinic crystal. The z^* axis is normal to the figure's plane and taken to coincide with the b crystal symmetry axis (see Ref. 52 in text). On the right: convention used for the polar (ϕ, θ) angles to specify the orientation of the applied magnetic field relative to the crystallographic axes a, b, c'.

work[52] on monoclinic crystals, the principal values and the position of the x^*, y^* axes in the ac plane are obtained through a rotation about $b \equiv z^*$ by an angle α^* that will be given by

$$\tan 2\alpha^* = 2T_{ac'}(T_{aa} - T_{c'c'})^{-1}.$$

In p-terphenyl crystals, as $L_b = 0$, this expression simplifies after some straightforward trigonometry to the simple result

$$\alpha^* = \arccos L_{c'} \tag{2}$$

that is, the position of the ZFS tensor axes in the ac plane is *independent* in this material of the D, E values of the molecule, being directly given by the crystallographic data, namely, by the angle that the long molecular axis makes with c'. This feature also allows one to express the ZFS exciton D^*, E^* parameters in terms of the molecular values in the simple form

$$\begin{aligned} D^* &= \tfrac{1}{2}D(3N_b^2 - 1) - \tfrac{3}{2}E(1 - N_b^2) \\ E^* &= \tfrac{1}{2}D(1 - N_b^2) - \tfrac{1}{2}E(1 + N_b^2) \end{aligned} \tag{3}$$

and their ratio $d^* \equiv D^*/E^*$ as

$$d^* = \frac{(3N_b^2 - 1)d - 3(1 - N_b^2)}{(1 - N_b^2)d - (1 + N_b^2)} \tag{4}$$

where d is the ratio D/E for the single molecule and N_b the cosine of the angle that the normal to its plane makes with the b symmetry axis of the crystal.

The result given by (2) can be arrived at intuitively if one realizes that, as in p-terphenyl crystals[53] the molecules are packed with their long axis L in the ac plane, the two inequivalent molecules in the unit cell have these axes parallel and the average Hamiltonian must conserve this symmetry direction as one of the principal exciton ZFS axes. In the axes convention of Figure 1, the y^* exciton axis thus coincides with the direction of the long molecular axes and x^* must make according to diffraction data (1) an angle with a of $\alpha^* = 16.9°$. Hence the experimental value of $\alpha^* \simeq 1°$ reported previously[47] appears as inconsistent with the crystallographic data and with the average Hamiltonian picture of Sternlicht–McConnell[49] which was found up to now to give a good approximation for the experimental triplet exciton zero-field splittings in many molecular solids. The experimental work reported in the next section shows that such is also the case for p-terphenyl.

EXPERIMENTAL AND RESULTS

Samples typically 1–2 mm thick were obtained by cleavage along the ab plane from crystal boules grown by the Bridgman method from material (Merck, scintillation grade) highly purified by two-step 100 zone-refinement passes.[54] Room temperature triplet exciton lifetimes measured either from buildup or decay of delayed fluorescence, ranged between 20–22 msec and no impurity fluorescence could be detected. The platelets were oriented by X-rays or conoscopy. The samples exhibited high-quality conoscopic patterns, which as expected for an ab plane platelet (the optical plane is the (010) plane) showed clearly the optical axis along the a direction making an angle of $\sim 17°$ with the c', perpendicular to the ab plane direction.[18]

The modulation of delayed fluorescence as a function of the orientation of a 6kOe magnetic field was recorded by placing the samples in a fixed orientation between the poles of a slow, uniformly rotating

electromagnet whose angular positions in the horizontal plane were followed by an optical decoder whose output drove the recorder's X-axis with a reproducibility of $\pm 1°$. The crystals were excited in the triplet band by the 4765 Å line of an argon laser (Spectra Physics 164) through a stack of Schott OG455 and BG12 filters and the delayed fluorescence was collected by a quartz light guide and detected through a stack of CS7-37 filters by an EMI 9635 QB photomultiplier whose output fed recorder's Y-axis after amplification. In order to obtain the highest signal-to-noise ratio and reproducibility of the signal with the lowest excitation intensities, assuring a negligible contribution of the bimolecular term to triplet decay,[39] the samples were excited by a collimated, uniformly expanded (to *ca.* 1 cm dia.), vertical laser beam which, for all crystal orientations, fell onto the *ab* plane of the platelets. This was achieved with a sample holder consisting of a small 90° totally reflecting prism in front of which the *ab* plane platelets were mounted vertically (c' horizontal in the plane of magnetic field rotation) on a holder which, in turn, allowed a rotation of the crystal in settings of 5° ($\pm 1°$) steps around the c' axis, thus allowing scans of the anisotropy of delayed fluorescence in planes at a chosen angle ϕ (see convention on the right in Figure 1) in going from the *ac* to the bc' crystallographic planes. To avoid strains the crystals were held to the holder's plate by suction with a small air pump. The setup allowed one, in this way, to perform the study of the anisotropy in all planes under identical spatially uniform-low intensity conditions of excitation.

Figure 2 exhibits some of the typical experimental anisotropies of the modulation of delayed fluorescence by a 6kOe magnetic field observed for a *p*-terphenyl sample at room temperature. The *ac* plane ($\phi = 0°$) modulation is characterized by the usual sharp high-field resonance peaks whose angular separations should be bisected[40,41] by the exciton ZFS principal axes. In the portion of the curve shown, the bisectrix of the two peaks (indicated by arrows in Figure 2) corresponds to the exciton's x^* axis which, as expected from the general symmetry considerations of the previous paragraph, is indeed found at $\alpha^* = 16°$ ($\pm 1°$) from the crystallographic *a* axis. As the angle ϕ is increased in going towards the bc' plane ($\phi = 90°$) the peaks broaden and approach each other to a minimum separation of only $\Delta\theta = 32°$ in that plane, the *b* axis being now, as expected by symmetry, the bisectrix of the two peaks. For planes in the vicinity of the bc' plane the two peaks show a markedly asymmetric behaviour as shown in detail in Figure 3, with the broader resonances shifting more rapidly away from the *b* axis. For the $\phi = 90° \mp \delta$ planes the behaviour of

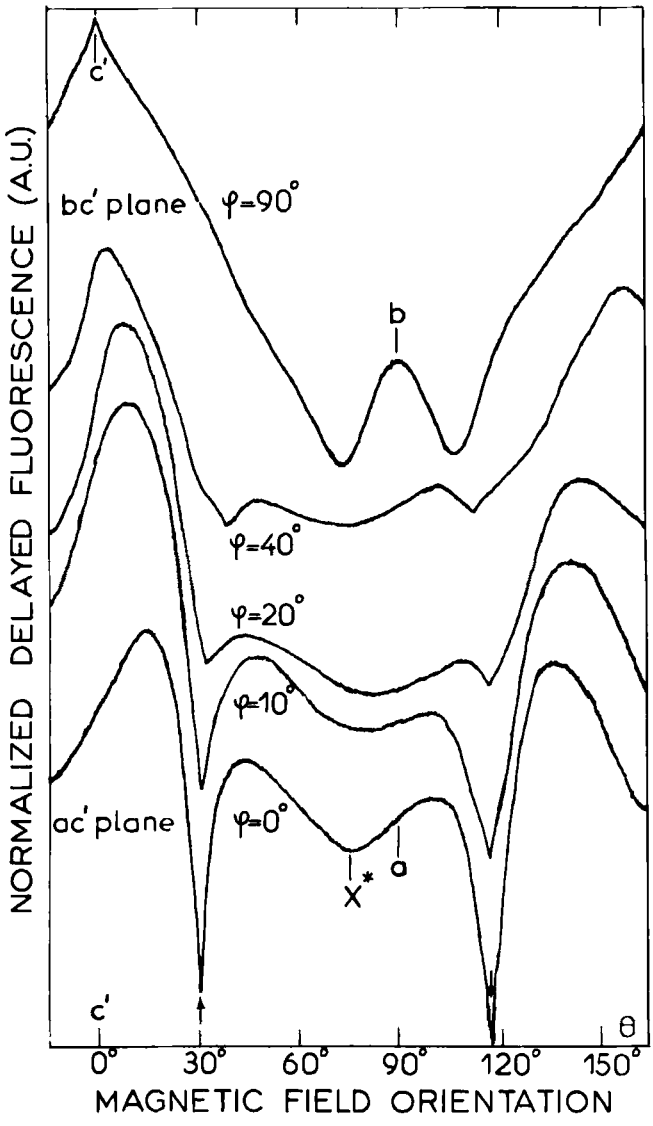

FIGURE 2 Some of the typical experimental anisotropies of the modulation of delayed fluorescence by a 6kOe magnetic field observed for a *p*-terphenyl sample at room temperature. For clarity, the anisotropies for the different planes are displaced on the vertical scale. Data for all planes are drawn using the same arbitrary unit scale for the relative size of the magnetic field effect. The $\phi = 0°$ curve corresponds to the *ac* plane in which x^* gives the position of the principal axis bisecting the two high-field resonances indicated by arrows. The $\phi = 90°$ plane is the *bc'* plane. The *c'* axis is the common origin for the angle θ (see Figure 1) for all planes.

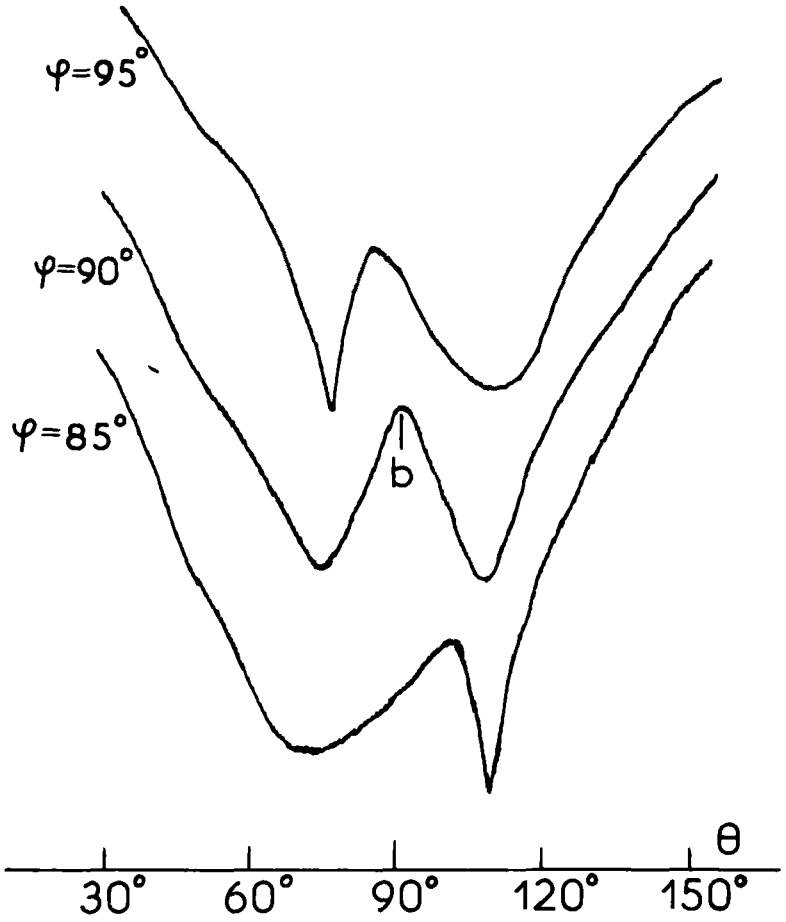

FIGURE 3 Details showing the markedly asymmetric behaviour of the resonances in the immediate vicinity of the *bc'* plane. The position of planes as given by the angle ϕ is within an $\pm 1°$ error. The magnetic field is 6kOe.

the two peaks is interchanged giving similar behaviour for positions $\theta = 90° \pm \epsilon$ as expected for the monoclinic structure for which b is a crystal symmetry axis. In both JM's and Suna's theories[40,41] the position of the high-field resonances is determined by crossings of two triplet-pair energy levels given by

$$d^*\left(\tfrac{1}{3} - n^{*2}\right) + \left(m^{*2} - l^{*2}\right) = 0 \qquad (5)$$

where l^*, m^*, n^* are the cosine-directors of the field's direction with

respect to exciton's principal ZFS axes x^*, y^*, z^*, respectively, being expressed for monoclinic crystals as

$$\begin{aligned} l^* &= \cos\alpha^*\cos\phi\sin\theta + \sin\alpha^*\cos\theta \\ m^* &= \sin\alpha^*\cos\phi\sin\theta - \cos\alpha^*\cos\theta \\ n^* &= \sin\phi\sin\theta \end{aligned} \tag{5'}$$

in the axes convention of Figure 1. In Eqs. (5) $d^* = D^*/E^*$ is the ratio of triplet exciton ZFS parameters and α^* the angle that the x^* principal axis makes with the crystallographic a axis ($b \equiv z^*$). Figure

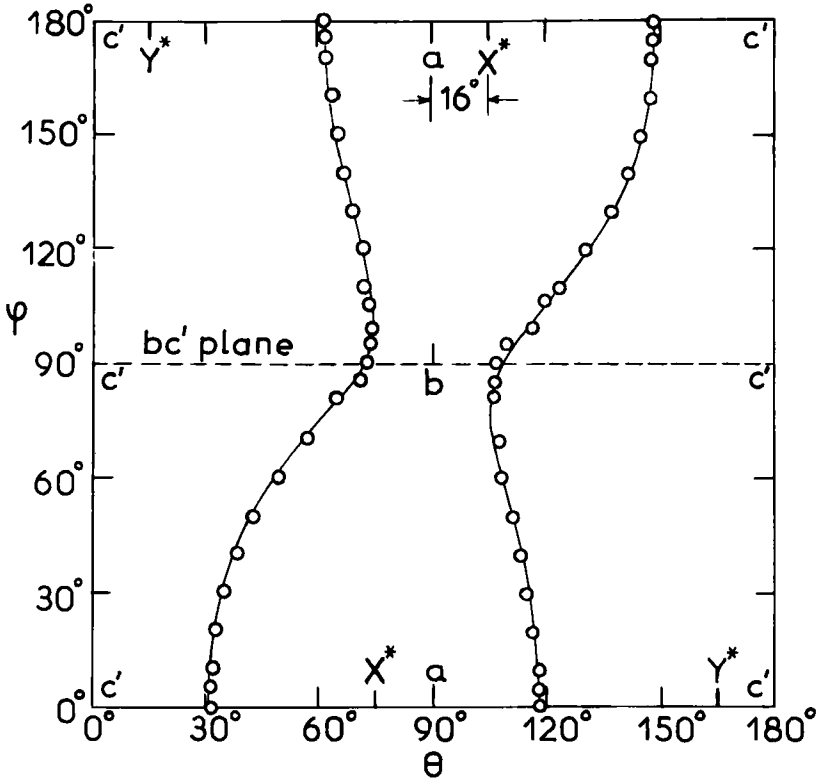

FIGURE 4 Plot of the (ϕ, θ) positions of the resonances. The open dots give the experimentally observed positions of the resonances. The solid curve is the theoretical prediction using Eqs. (5) in the text. The best fit shown is obtained for the ZFS exciton parameters $d^* = +0.14$ and $\alpha^* = 16°$; the uncertainty on these values is estimated to be ± 0.02 and $\pm 1°$, respectively.

4 shows the experimentally observed (θ, ϕ) resonance positions (open circles) for the family of planes studied, the solid curve representing the theoretical behaviour predicted by (5). The best fit shown is obtained for $d^* = D^*/E^* = +0.14$ and $\alpha^* = 16°$. The experimental uncertainty on these ZFS exciton parameters is estimated to be ± 0.02 and $\pm 1°$, respectively.

The value obtained for α^* is in good agreement with the value expected using the average spin Hamiltonian picture and the known crystallographic data as discussed above. The experimental d^* value could be, in principle, checked via (4) if the single molecule ZFS ratio d were known. Unfortunately for the p-polyphenyls series, only the biphenyl molecule has been up to now studied extensively,[31-33] and its D, E parameters are now known with great precision from the recent EPR-ENDOR work of Hutchison *et al.*[33] To our best knowledge, the only experimental data reported for the p-terphenyl molecule is the $D' \equiv (D^2 + 3E^2)^{1/2} = 9.6 \times 10^{-2}$ cm^{-1} value obtained from work in rigid glass at 77 K.[55] Orloff and Brinnen[56] have made theoretical calculations of the ZFS parameters for the polyphenyl series. As pointed out by them, while their calculated molecular D values can be considered as reliable, deviating typically only by 5% from the experimental values, the, typically small, E theoretical values should be considered as only qualitative. Indeed, for biphenyl the calculated D value[55] differs from the experimental one[33] by only 0.5%, but the experimental E value has the sign opposite to the calculated one using the same coordinate system. The experimental molecular ZFS ratio $d = D/E$ for biphenyl is negative ($D > 0$, $E < 0$) in the coordinate convention $L(x)$, $M(y)$, $N(z)$ used also in this work for the D_{2h} symmetry. The reported exciton value $d^* = 0.14 \pm 0.02$ for the p-terphenyl crystal would also predict a negative d ($D > 0$, $E < 0$) ratio for this molecule. Figure 5 shows a plot of Eq. (4), the insert expanding the region of interest here. For $d^* = 0.14 \pm 0.02$ and using the room temperature X-ray diffraction measured angle between the b axis and the normal to the mean molecular plane of $56.5° \pm 0.5°$[5-7] one predicts a molecular ZFS ratio $d = D/E = -11 \pm 2$ for the p-terphenyl molecule. This value seems reasonable, being intermediate between the biphenyl value and some typical values for polyacene molecules (e.g. -6.0 for naphthalene and -8.5 for anthracene). Using the theoretically calculated value[56] of $D \simeq 10.3 \times 10^{-2}$ cm^{-1} one estimates $E \simeq -0.9 \times 10^{-2}$ cm^{-1} for the p-terphenyl molecule. For these parameters and using Eqs. (3) one predicts, with an uncertainty estimated to be at least 20%, the crystal ZFS parameters $D^* \simeq 0.6 \times 10^{-2}$ cm^{-1} (64 Oe) and $E^* \simeq 4.2 \times 10^{-2}$ cm^{-1} (450 Oe), that is, the

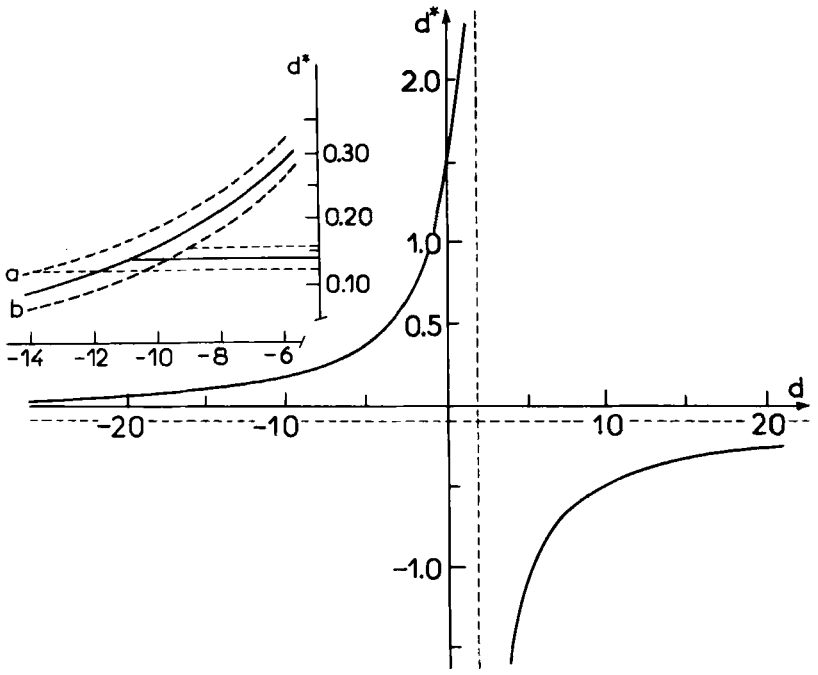

FIGURE 5 Plot of Eq. (4) in text, the insert on the left expanding the region of interest here. The solid curves are for $N_b = \cos 56.5°$ as given by the crystal data matrix (1) in the text. The dashed curves (a) and (b) are drawn for $N_b = \cos 56°$ and $N_b = \cos 57°$, respectively, to take into account a possible uncertainty of $\pm 0.5°$ for the X-ray diffraction determined position of the mean molecular plane. The asymptotes indicated by the dashed axes correspond to the values $d^* = -0.12$ ($d \to \pm\infty$) and $d = 1.90$ ($d^* \to \pm\infty$). The horizontal lines in the insert are drawn to indicate the possible uncertainty range for the d value.

ordering $Y^* \simeq +4.4 \times 10^{-2}\ \text{cm}^{-1}$, $Z^* \simeq -0.4 \times 10^{-2}\ \text{cm}^{-1}$, $X^* \simeq -4.0 \times 10^{-2}\ \text{cm}^{-1}$ for the crystal[57] triplet spin sublevels in p-terphenyl, similar to that found for anthracene.[52]

CONCLUSIONS AND DISCUSSION

Present detailed experimental analysis of the position of high-field resonance peaks of triplet-triplet annihilation in a family of planes of p-terphenyl crystals has allowed us to account for the puzzling discrepancy that existed up to now between the theory using the usual Sternlicht-McConnell's averaged spin Hamiltonian and the previously reported[47] near-coincidence $\alpha^* = 1°$ of the exciton ZFS principal axes

x^*, y^* with the crystallographic a, c' axes. Also, the values $\alpha^* = 1°$ and $d^* = -0.18$ as given previously would imply a positive molecular d ratio, which seems unlikely from what is known now on the polyphenyl series.[33,55] The origin of the discrepancy raised by these ZFS parameters, reported from the analysis of just two planes for a solution grown crystal,[47] is not clear. One possible explanation, however, could lie in the fact that p-terphenyl is known to occasionally also grow from solution with a well developed {201} plane.[5] Such plane contains the b axis and exhibits thus a two-fold symmetry as the ab plane the normal to the b axis being actually the $(10\bar{2})$ direction, which coincides, within 1°, with the long molecular axis,[5-7] and hence with the exciton y^* axis. The normal to such plane is not the c' axis as for a {001} platelet but the exciton's x^* axis, and a plane labeled as ac plane will be indeed an ac plane but in which the angle θ is actually measured from the exciton x^* axis. Hence, the $\theta = 90°$ direction would correspond to the y^* axis which bisects the two high-field resonances, the plane exhibiting thus a symmetry with an apparent $\alpha^* \simeq 0°$ value. If such were the case, the exciton ZFS parameters $\alpha^* = 16°$ and $d^* = +0.14$ reported in this work will predict using (5) for the two planes reported in Ref. 47 high-field resonances at $\phi = \pm 72°$ ($\pm 18°$ from b), and $\theta = 44°$ and 137°, which indeed agree, within the experimental error of $\pm 1°$, with the resonance positions reported in Ref. 47.

In view of the fact that in p-terphenyl triplet diffusion is anisotropic[46] in the ab plane so that Suna's approach using the smooth approximation[41] with an isotropic, average lattice spacing $\bar{R}$ may lead to an appreciable error, and as additional spin relaxation mechanisms[47,58] may also contribute to the resonance lineshapes, it was felt that at this stage a computing effort using several adjustable parameters and questionable approximations to obtain a fit for the overall magnetic field dependence of delayed fluorescence was premature, at least, until additional experimental information on p-terphenyl, for instance, a detailed ESR linewidth study, becomes available. It is hoped that present work will spur additional interest in this direction on this material, as well as on other solids of the p-polyphenyl molecules.

Acknowledgement

We are grateful to Dr. M. Schott of the Groupe de Physique des Solides de l'E.N.S., Paris, for stimulating discussions, and to Dr. G. Klein of the PREN, Strasbourg, for providing most crystal boules.

References

1. J. Trotter, *Acta Cryst.*, **14**, 1135 (1961); A. Hargraves and S. H. Rizvi, *Acta. Cryst.*, **15**, 365 (1962).
2. V. M. Koshin and K. V. Mirskoya, *Sov. Phys. Cryst.* **14**, 938 (1970).
3. G. P. Charbonneau and Y. Delugeard, *Acta Cryst., B* **32**, 1420 (1976); G. P. Charbonneau and P. Rivet, *Acta Cryst., A* **36**, 51 (1980).
4. H. Cailleau, J. L. Baudour, and C. M. E. Zeyen, *Acta Cryst., B* **35**, 426 (1979); H. Cailleau, F. Moussa and J. Mons, *Solid State Comm.*, **31**, 521 (1979).
5. L. W. Pickett, *Proc. Roy. Soc. A* **142**, 333 (1933).
6. J. Dejace, *Bull. Soc. Fr. Minéral. Cristallogr.*, **92**, 141 (1969).
7. H. M. Rietveld, E. N. Maslen, and C. J. B. Clews, *Acta Cryst. B* **26**, 693 (1970).
8. W. Jones, J. M. Thomas, J. O. Williams, and L. W. Hobbs, *J.C.S. Faraday II*, **71**, 138 (1975).
9. J. L. Baudour and G. P. Charbonneau, *Acta Cryst. B* **30**, 1379 (1974).
10. J. L. Baudour, Y. Delugeard, and H. Cailleau, *Acta Cryst. B* **32**, 150 (1976).
11. Y. Delujeard, J. Desuché, and J. L. Baudour, *Acta Cryst. B* **32**, 702 (1976).
12. J. L. Baudour, Y. Delugeard, and P. Rivet, *Acta Cryst. B* **34**, 625 (1978).
13. S. Friedman, R. Kopelman, and N. Prasad, *Chem. Phys. Letters*, **24**, 15 (1974).
14. A. Bree and M. Edelson, *Chem. Phys. Lett.*, **46**, 500 (1977); ibid. **55**, 319 (1978).
15. A. Girard, H. Cailleau, Y. Marqueton, and C. Ecolivet, *Chem. Phys. Lett.*, **54**, 479 (1978).
16. C. Ecolivet and M. Sanquer, *J. Chem. Phys.* **72**, 4145 (1980); C. Ecolivet, B. Toudic, and M. Sanquer, *J. de Phys.*, (*Paris*), **42** (C6), 779 (1981).
17. C. Ecolivet, *J. de Phys.*, (*Paris*), **42** (C6), 578 (1981).
18. K. S. Sundarajan, *Z. Krist.*, **93**, 238 (1936).
19. K. Lonsdale and K. S. Krishnan, *Proc. Roy. Soc. London Ser.*, **A156**, 597 (1936).
20. G. P. Charbonneau and P. Rivet, *Acta Cryst. A*, **36**, 51 (1980).
21. W. Jones, J. M. Thomas, and J. O. Williams, *Mat. Res. Bull.*, **10**, 1031 (1975).
22. S. Ramdas and J. M. Thomas, *J. Chem. Soc. Faraday II*, **72**, 1251 (1976).
23. D. Dworkin and H. Cailleau, *J. Phys. Letters*, **41**, L83 (1980).
24. H. Cailleau, J. L. Baudour, and J. Meinnel, A. Dworkin, F. Moussa, and C. M. E. Zeyen, *Far. Discussions Roy. Soc. Chem.*, **69**, 9 (1980).
25. H. Cailleau, A. Heidemann, and C. M. E. Zeyen, *J. Phys. C, Sol. State Phys.*, **12**, 411 (1979).
26. H. Cailleau, A. Girard, F. Moussa, and C. M. E. Zeyen, *Solid State Comm.*, **29**, 259 (1979).
27. H. Cailleau, F. Moussa, C. M. E. Zeyen, and J. Bouillot, *Solid State Comm.*, **33**, 407 (1980); *J. Phys.*, (*Paris*), **42**, (C6), 704 (1981).
28. K. Razi Naqvi, J. Donatsch, and U. P. Wild, *Chem. Phys. Lett.*, **34**, 285 (1975).
29. R. M. Hochstrasser, R. D. McAlpine, and J. D. Whiteman, *J. Chem. Phys.*, **58**, 5078 (1973).
30. R. M. Hochstrasser and H. N. Sung, *J. Chem. Phys.*, **66**, 3265 (1977), and references given therein.
31. A. S. Cullick and R. E. Gerkin, *Chem. Phys. Lett.*, **23**, 217 (1977).
32. H. C. Brenner, C. A. Hutchison, and M. D. Kemple, *J. Chem. Phys.*, **60**, 2180 (1973); C. A. Hutchison and V. H. McCann, ibid. **61**, 820 (1974).
33. C. A. Hutchison and M. D. Kemple, *J. Chem. Phys.*, **71**, 866 (1979).
34. J. O. Williams, *Chem. Phys. Lett.*, **42**, 171 (1976).
35. J. O. Williams and A. C. Jones, *J. Luminescence* **24/25**, 723 (1981).
36. A. C. Jones, K. Janecka-Styrcz, D. A. Elliott, and J. O. Williams, *Chem. Phys. Letters* **80**, 413 (1981), and references given therein.
37. Z. Burshtein and D. F. Williams, *J. Chem. Phys.*, **68**, 983 (1978).
38. J. Fünfshilling, L. Altwegg, I. Zschokke-Gränacher, M. Chabr, and D. F. Williams, *J. Chem. Phys.*, **70**, 4622 (1979).

39. For an introductory review, see for example: P. Avakian and R. E. Merrifield, *Mol. Cryst. Liq. Cryst.*, **5**, 37 (1968); C. W. Swenberg and N. E. Geacintov, in *Organic Molecular Photophysics*, ed. by J. B. Birks (Wiley) 1973, Ch. 10; V. Ern and M. Schott, in *Localization and Delocalization in Quantum Chemistry II*, ed. by O. Chalvet *et al.* (Reidel) 1976, p. 249.
40. R. C. Johnson and R. E. Merrifield, *Phys. Rev. B*, **1**, 896 (1970).
41. A. Suna, *Phys. Rev. B*, **1**, 1716 (1970).
42. M. Chabr and I. Zschokke-Gränacher, *J. Chem. Phys.*, **64**, 3093 (1976).
43. N. I. Wakayama, *Chem. Phys. Letters*, **70**, 397 (1980).
44. S. Kobayashi, K. Janecka-Styrcz, and J. O. Williams, *Mol. Cryst. Liq. Cryst.*, **75**, 1 (1981).
45. J. O. Williams, private communication.
46. A. Fort and V. Ern, *Chem. Phys. Lett.*, **74**, 519 (1980).
47. L. Altwegg and I. Zschokke-Gränacher, *Phys. Rev. B*, **20**, 4326 (1979).
48. L. Altwegg, *Chem. Phys. Lett.*, **63**, 97 (1979).
49. H. Sternlicht and H. M. McConnell, *J. Chem. Phys.*, **35**, 1793 (1961).
50. V. Ern, *J. Chem. Phys.*, **56**, 6259 (1972).
51. $D = -\frac{3}{2}Z$ and $E = \frac{1}{2}(Y - X)$ where X, Y, Z are the eigenvalues of the dipolar molecular spin Hamiltonian with $X + Y = -Z$.
52. See, for instance, D. Haarer and H. C. Wolf, *Mol. Cryst. Liq. Cryst.*, **10**, 359 (1970); H. Port and D. Rund, *Chem. Phys. Lett.*, **69**, 406 (1980); S. H. Tedder, *Chem. Phys.*, **14**, 455 (1976), ibid. **24**, 287 (1977); C. P. Poole Jr., H. A. Farach, and W. K. Jackson, *J. Chem. Phys.*, **61**, 2220 (1974).
53. It is worth noting that the conclusions given here are also applicable for the other two members of the *p*-polyphenyls series. For both biphenyl (Refs. (1–4)) and *p*-quaterphenyl (Ref. (11)) the molecular packing is also with long molecular axes in the *ac* plane, and one should find one of exciton's ZFS axes at about 17° from *a*.
54. G. J. Sloan and V. Ern, *Chem. Eng. Prog. Symp.*, Series **65**, 122 (1969).
55. B. Smaller, *J. Chem. Phys.*, **37**, 1578 (1962).
56. M. K. Orloff and J. S. Brinnen, *J. Chem. Phys.*, **47**, 3999 (1967).
57. From the considerations given in text and with the axes convention of Figure 1, the crystal Y^* level must coincide in this material with the long molecular axis (X) eigenvalue.
58. J. Rosenthal, L. Yarmus, and N. F. Berk, *Phys. Rev. B*, **24**, 1103 (1981), *Phys. Rev. B*, **23**, 5673 (1981), and references therein.