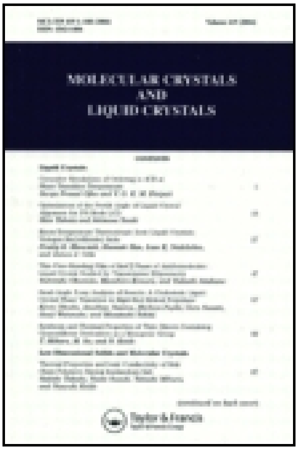

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EPR Studies of Electron Spin Polarization of Triplet Exciton and its Transfer into Triplet Traps of Naphthalene-TCNQ and Naphthalene-*p*Chloranil Guest Complexes in the Naphthalene-TCNB Host

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The EPR spectra of triplet excitons in single crystals of Naphthalene-TCNB (*N*-TCNB) charge-transfer (CT) complexes show optical electron spin polarization (OEP) which is accounted for by a spin selective populating process from the excited CT singlet into an excited triplet state localized on the acceptor. OEP is also observed for triplet traps in *N*-TCNB crystals doped with TCNQ and *p*Chloranil. The analysis of the orientation dependence of spin polarization allows one to establish that also selective decay from the trap spin sublevels is important for the onset of the observed OEP features.

INTRODUCTION

Naphthalene (*N*) and 1,2,4,5-Tetracyanobenzene (TCNB) form charge transfer (CT) complexes that in a single crystal are arranged in stacks of alternate donor and acceptor molecules with their molecular planes parallel to each other.[1] At room temperature the crystal structure is disordered and the naphthalene molecules exhibit a large amplitude libration around the molecular axis z normal to the molecular planes. At about 60 K an order-disorder phase transition is observed with the librational motion freezed in at lower temperatures.[2]

Upon irradiation with visible light of a *N*-TCNB single crystal triplet excitons are formed by the intersystem crossing process (ISC) caused by the spin-orbit interaction that allows singlet-triplet mixing. Since this interaction is spin-selective, the triplet fine structure sublevels are populated at different rates and optical electron spin polarization (OEP effect) is produced among the triplet spin levels whose populations can deviate even strongly from a Boltzmann distribution.[3]

OEP is observed when the spin-lattice relaxation time between the triplet sublevels is not too short with respect to the triplet lifetime.[4] This phenomenon is observed in *N*-TCNB when a crystal of *N*-TCNB is irradiated at room temperature inside the resonant cavity of an EPR spectrometer, the spectrum of the triplet exciton consisting of one pair of lines with opposite phases, one line being in emission and the other in absorption.

In triplet excitons the decay rate constants of the annihilation or of the trapping processes are almost independent of the triplet sublevels[5,6] and the extent of spin polarization observed in the EPR spectra depends on the anisotropy of the populating rate constants.

When guest molecules are present in the host crystal lattice the mobile excitations can be trapped at the guest sites. If the transfer of the excitation occurs by preserving the preferential spin alignment of the exciton substates, also the EPR signals of the shortlived triplet trap can be polarized. However, in the case of localized excitation, in addition to the populating process, the decay too can be spin selective so that the spin polarization features may be different from those of the exciton.

The kinetic parameters that drive the relative populations of the triplet sublevels may be obtained from a detailed analysis of the EPR line intensities as the orientation of the crystal is changed with respect to the spectrometer magnetic field B. In fact, the intensity of the EPR lines of a spin polarized triplet depends on the orientation of the magnetic field with respect to the principal axes of the spin-spin dipolar interaction. At certain orientations of B an inversion of the signal phase is observed. These singular points, which in some cases can be determined with a rather good precision, are related to the relative values of the populating and decaying rates of the zero-field triplet sublevels. A detailed analysis of these effects can give valuable information on the energy transfer process that involves optically excited triplet species.

In this paper we report a study of the spin polarization of the triplet exciton in *N*-TCNB and of polarized triplet traps in the host crystal of *N*-TCNB doped with the guest acceptors Tetracyanoquinodimethane

(TCNQ) and Tetrachloro-*p*-benzoquinone (*p*Chl), which are expected to substitute for the TCNB molecules in the crystal lattice. In the latter trap EPR polarized spectra have been already reported although no account was made of the OEP features.[7]

EXPERIMENTAL AND RESULTS

Naphthalene was vacuum sublimed and zone refined. TCNB was prepared as described in the literature[8] and purified by repeated recrystallizations from ethanol and vacuum sublimed. Also TCNQ and *p*Chl were purified by vacuum sublimation. The crystals were grown by slow evaporation of spectrophotometric grade acetone (Merck UVASOL) solution. Single crystals of the *N*-TCNB complexes doped with TCNQ and *p*Chl were obtained from acetone solutions containing the dopant at the molar ratio of 2%.

The EPR measurements were done using a conventional JEOL PE-3X spectrometer operating in the X-band and equipped with a nitrogen gas cryostat. The light source was a high-pressure mercury lamp (HBO 500W) and filters were applied to single out the spectral range 320 to 600 nm.

Time resolved EPR experiments for measuring the kinetic parameters of the decay process and of the spin-lattice relaxation were carried out by a nitrogen pulsed laser (Lambda Physik K 600) as light source whose pulse duration was 5 ns. The transient signal was fed into a boxcar averager (EG and G mod. 162) equipped with a gated integrator (EG and G mod. 164) and triggered at the modulating frequency of the laser pulse (~ 100 Hz).

The *N*-TCNB complexes crystallize in the monoclinic system, with space group $C2/m$, $a = 9.39$, $b = 12.66$, $c = 6.87$ Å, $\beta = 107.2°$ and $Z = 2$. The constituent molecules are stacked alternately along the c axis while b is the two-fold symmetry axis.[1] At room temperature the two complexes in the unit cell undergo a high frequency librational motion around the Z axis normal to the molecular plane. At low temperature below the phase transition at 60 K the two complexes are inequivalent as revealed by ESR measurements on the X-trap triplets.[9,10]

In our experiments the measurements of the resonant fields of the EPR lines and the identification of their phases according to their emissive or absorptive character were performed by rotating the magnetic field B in the planes of the crystallographic axes $a'bc$ where a' is perpendicular to the bc plane. The angular variation of the fine structure splitting was fitted by a least squares procedure to a curve of the type

$$\Delta = D_{ii}\cos^2\alpha + D_{jj}\sin^2\alpha - 2D_{ij}\sin\alpha\cos\alpha \tag{1}$$

where the indices i and j refer to the particular plane in which the magnetic field is rotated. $D_{ij}/3$ are the elements of the fine structure tensor. Diagonalization of the tensor gives the principal values and directions of the zero-field splitting Hamiltonian

$$\mathbf{H}_{\mathrm{ZFS}} = -X_e S_x^2 - Y_e S_y^2 - Z_e S_z^2 \tag{2}$$

which describes the dipole-dipole interaction between the two electron spins of the triplet.

The EPR spectrum of the triplet exciton in the single crystal of the *N*-TCNB complex was detected at room temperature and it consisted of a single pair of motional narrowed and spin polarized lines. The signal intensity decreased with lowering temperature because of the efficient trapping process.[9] The ZFS parameters measured at 280 K are

$$X_e = \pm 325 \pm 2\ \mathrm{G}; \qquad Y_e = \pm 161 \pm 2\ \mathrm{G}; \qquad Z_e = \mp 486 \pm 2\ \mathrm{G}$$

which are in good agreement with the values reported in ref. 11. The principal directions coincide with the a', b, c axes within the experimental errors.

N-TCNB crystals doped with TCNQ showed EPR lines due to a single triplet trap. The linewidth is 4.1 G, almost independent of the crystal orientation and no hyperfine structure is resolved. The ZFS principal values are $X = \pm 393 \pm 2$ G, $Y = \mp 142 \pm 2$ G and $Z = \mp 251 \pm 2$ G with the principal directions aligned with the crystallographic axes within the experimental errors.

TABLE

Direction cosines of the fine structure principal axes x, y, z of *N*-*p*Chl triplet trap with respect to the a', b, c crystal axes in the *N*-TCNB crystal host

	a'	b	c
x	1	0	0
y	0	0.9914	±0.1301
z	0	∓0.1301	0.9914

N-TCNB crystals doped with *p*Chl give the EPR spectra of triplet species trapped at two translationally inequivalent sites in the crystal lattice. The two sites are connected by a twofold rotation about the symmetry axis *b*. Principal values and directions of the fine structure tensor are reported in the Table. Also, in the case of the *p*Chl traps, the EPR lines are polarized.

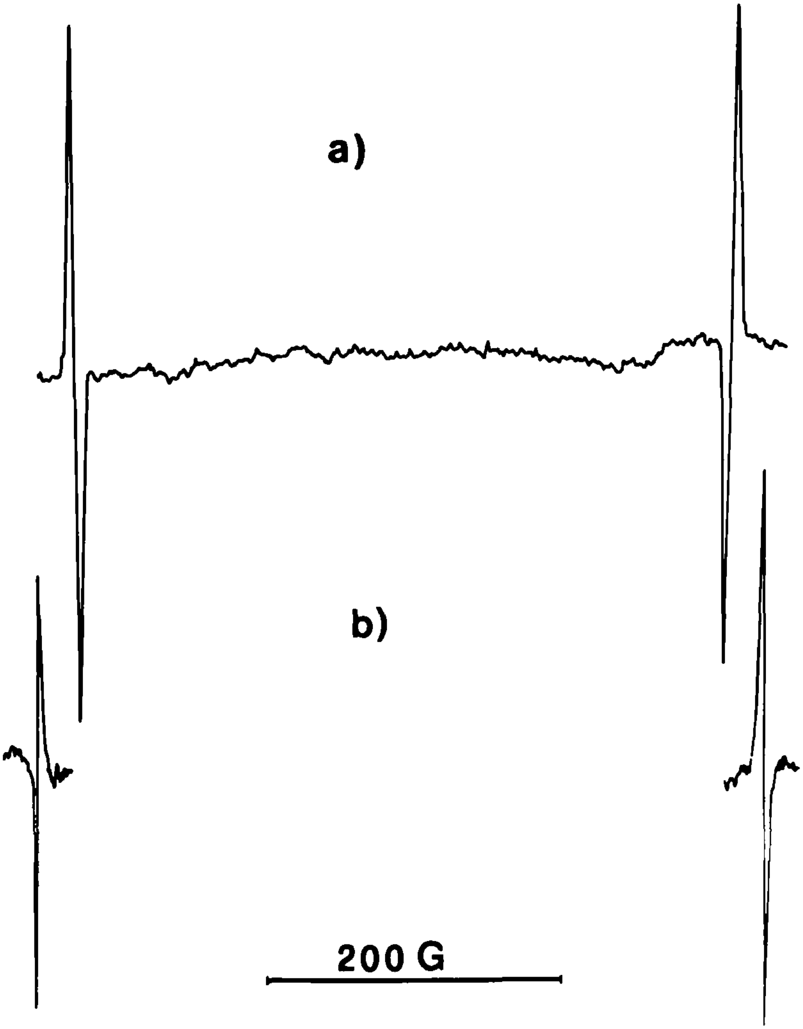

FIGURE 1 EPR spectra of the triplet exciton (b) and of the *N*-TCNQ triplet trap (a) with $B//y$. Triplet exciton lines are over modulated (2G mod.).

The spin polarization of the triplet traps does not correspond to that of the triplet exciton lines as it is clearly shown in Figure 1 where the EPR spectrum of the triplet exciton in the pure *N*-TCNB crystal is reported together with that of the *N*-TCNQ triplet trap in the doped crystal for the same orientation of the magnetic field with respect to the crystal axes. Figure 2 shows the resonant fields and the signal phases of the triplet exciton together with those of the trapped species for the same crystal orientations.

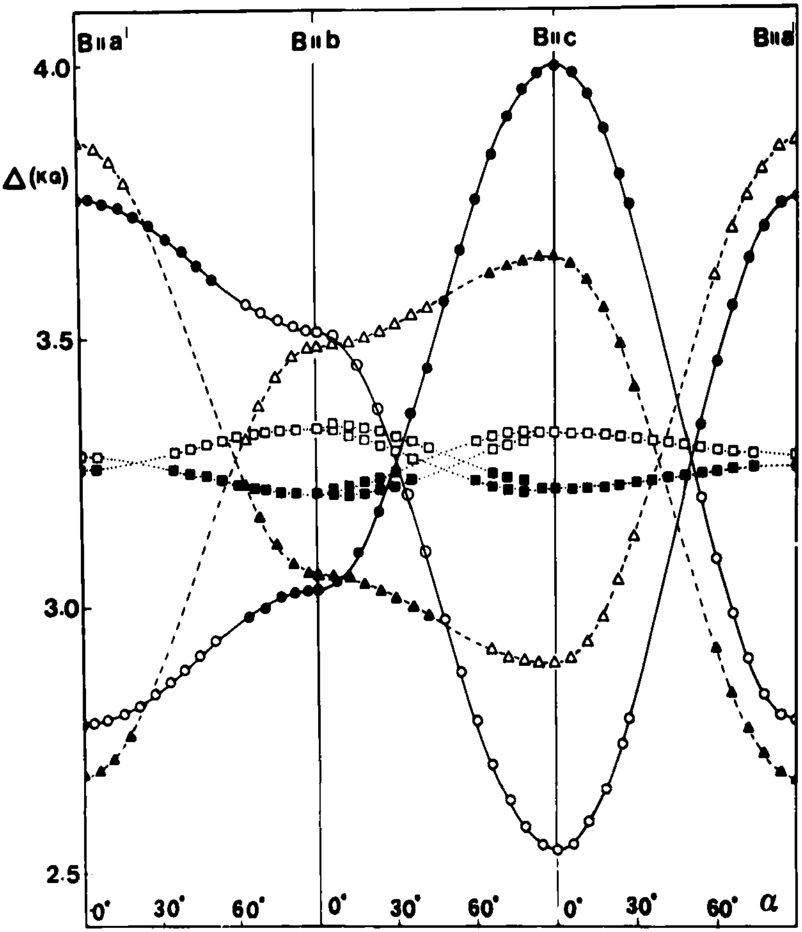

FIGURE 2 Resonant fields with their least squares fitting curves and signal phases. Empty and full symbols represent emission and enhanced absorption lines, respectively. Circles refer to the *N*-TCNB exciton, triangles to the *N*-TCNQ and squares to the *N*-*p*Chl traps.

DISCUSSION

In the *N*-TCNB crystal lattice stable at high temperature ($T > 60$ K) the TCNB molecules are located at translationally equivalent positions while the naphthalene molecules occupy statistically two translationally inequivalent sites *A* and *B* differing by a rotation of $\pm 18°$[9] around the *c* axis which coincides with the direction *z* perpendicular to the molecular plane. A high amplitude librational motion allows a naphthalene at *A* to jump to site *B*. Although details on the crystal structure at temperatures below the phase transition are not known; an EPR and ENDOR investigation on X-trap at 4.2 K indicates that the jumping process is frozen and moreover the two triplet traps at *A* and *B* have their molecular axes Z_A and Z_B making an angle of $\pm 7°$ with *c*.[11]

The triplet exciton spectra of the *N*-TCNB crystals show two lines for any orientation of the crystal in the magnetic field. The principal directions of the dipolar interaction tensor are along the mean values of the two sites *A* and *B*. This fact however cannot give information on the lattice dynamics since it could derive either from a fast $A \leftrightarrow B$ exchange motion or from a fast motion of the triplet exciton among differently oriented complexes.

In *N*-TCNB crystals doped with TCNQ or *p*Chl, the guest molecules are expected to substitute for TCNB and to assume an orientation in the lattice with their long axes parallel to the TCNB long axis. The structure of the *N*-TCNQ and *N*-*p*Chl complexes results to be similar to that predicted for the analogous complexes of Anthracene-TCNQ and *N*-*p*-benzoquinone.[12]

Since TCNQ and *p*Chl are better acceptors than TCNB, their CT complexes with naphthalene act as traps for triplet excitons in *N*-TCNB crystals[13] and the EPR signals we observe are to be attributed to *N*-TCNQ and to *N*-*p*Chl complexes in their first excited triplet state. For *N*-TCNQ traps the principal directions of the dipolar interaction tensor coincide, within experimental errors, with those of the triplet exciton; this fact indicates that naphthalene in the complex is either symmetrically localized with respect to the TCNQ acceptor or that it undergoes a fast motion between the two potential wells corresponding to the above mentioned sites *A* and *B* of the host.

A different situation is encountered with *p*Chl doped crystals where the EPR spectra show that the excitation is trapped at two magnetically inequivalent sites connected by a twofold rotation about the symmetry axis *b* of the monoclinic crystal. It is to be noted that the *z* principal directions of the two fine structure tensors coincide with those (z_A and z_B) of the X-traps in Nd$_8$-TCNB (in the low temperature phase). Instead the x principal directions of the two N-pChl sites tensor, are coincident with the x direction of the exciton, i.e. they are along the mean x direction of the sites A and B.

The above results indicate that the substitution of TCNB molecules by pChl ones causes a distortion of the high temperature lattice, in the neighbourhood of the guest, in such a way that it assumes the characteristics of the low temperature phase. Nevertheless in this distorted lattice the naphthalene in-plane motion characteristic of the high temperature phase is still operative. The zero field splitting parameters measured for the triplet exciton when compared with those of a free naphthalene molecule show that the triplet excitation in the N-TCNB complex resides mainly on naphthalene and the CT character χ_{CT} is about 25%.[9]

This value was calculated according to the equation

$$Z_c = (1 - \chi_{CT})Z_{loc} + \chi_{CT}Z_{ion} \tag{3}$$

with $Z_{loc} = Z_{naphth.} = -707$ G[14] and $Z_{ion} = +153$ G. Since the local and ionic contributions have opposite signs and Z_c is found to be larger than Z_{ion}, the sign of Z_c must be negative as that of Z_{loc}. This point is relevant for the assignment of the EPR lines to the $|0\rangle \rightarrow |+\rangle$ and $|-\rangle \rightarrow |0\rangle$ transitions, whose polarization is discussed in the following.

The same arguments when applied to the case of the N-TCNQ triplet trap give a CT character of 0.53. This value is obtained with the assumption that also in the complex with TCNQ the local excitation resides on naphthalene, a CT character close to 0.5 indicating that the two zero-order states ψ_{loc} and ψ_{CT} have approximately the same energy. Concerning the sign of the parameter Z_{loc} it is expected to be negative even in the less plausible case of a triplet excitation localized on TCNQ.

The ZFS parameters of N-pChl are surprisingly small indicating a quite high CT character. Assuming here too a local contribution on naphthalene and taking the estimated value of 160 G for Z_{ion}, the CT character is $\chi_{CT} = 0.85$ for a positive choice of the sign of Z_c, and $\chi_{CT} = 0.77$ if Z_c is negative. Such high values of χ_{CT} indicate that the CT state here is lower in energy than the neutral triplet, at difference with the previous results on the N-TCNQ complex. This fact contrasts with the lower electron affinity of pChloranil with respect to TCNQ[13] and points to a stronger CT interaction of naphthalene with chloranil due to a larger overlap in the latter complex.[12]

The assumption of a neutral state mostly localized on the donor seems to be supported by the observation of a CT trap with the same ZFS parameters when *N*-TCNB is doped with *p*-bromanil.

The OEP effect is produced whenever the photoexcited triplet state has populating and/or decay rates that are selective for the triplet sublevels and the latter faster than, or of the same order, as the spin lattice relaxation rate.[3] In the presence of the magnetic field B the populating and the decay rates of the individual sublevels are given by the relations

$$P_i = \sum_u |c_{iu}|^2 P_u$$

$$K_i = \sum_u |c_{iu}|^2 K_u \tag{4}$$

where $i = 0, 1, -1$ and $u = x, y, z$. P_u and K_u are the values pertaining to the zero field conditions. Mixed terms $c_{iu}c_{iv}P_u^{1/2}P_v^{1/2}$ should be also included when the triplet is generated in a superposition of spin states.[15] However this does not occur in our case.

The coefficients c_{iu} are obtained by diagonalizing the spin hamiltonian

$$\mathbf{H} = g\beta\bar{B}\cdot\bar{S} + \bar{S}\cdot D\cdot\bar{S} \tag{5}$$

and thus they depend on the strength and direction of B with respect to the fine structure principal axes. Once obtained for a particular orientation the values of P_i and K_i, the steady state populations n_i of the individual spin levels under continuous irradiation are derived by solving the appropriate set of linear equations:

$$\begin{aligned} \dot{n}_+ &= (-K_+ - 2W)n_+ + We_1n_0 + We_2n_- + P_+n_s \\ \dot{n}_0 &= Wn_+ + [-K_0 - W(1 + e_1)]n_0 + We_1n_{-1} + P_0n_s \\ \dot{n}_- &= Wn_+ + Wn_0 + [-K_- - W(e_1 + e_2)]n_- + P_-n_s \end{aligned} \tag{6}$$

where $W = 1/3T_1$ is the frequency of spin-lattice relaxation, n_s is the population of the excited singlet state and $e_1 = \exp(-g\beta B/KT)$ and $e_2 = \exp(-2g\beta B/KT)$ are Boltzmann factors.

The EPR transitions $|-\rangle \rightarrow |0\rangle$ and $|0\rangle \rightarrow |+\rangle$ have an intensity I_- and I_+ proportional to the difference in the population of the two levels involved. However, the experimental determination of the line intensity as a function of the crystal orientation is rather difficult because the linewidth depends on orientation and moreover the non-cylindrical shape of the crystals prevents a constant quantum yield of the optical excitation. Nevertheless, the absorptive or emissive character of the lines is immediately identified and orientations of B where a line changes from emission to absorption are easily measured. These features can be compared with those of the curves of I_+ and I_- calculated for a particular set of the populating and decay rates.

For the choice of the appropriate set of kinetic parameters we rely on the following considerations. The most important decay mechanisms of triplet excitons in our molecular crystals are the trapping into impurity centers or lattice defects and the triplet-triplet annihilation process. The spin dependence of the latter is known to be very small[5] and in the former there is no reason for spin selection. Therefore the OEP effect in triplet excitons is produced only by the selective populating process.

Recent studies[16,17] on the CT complexes of TCNB with aromatic hydrocarbons have pointed out the importance of the matrix element $\langle {}^1\psi(D^+A^-)|\mathbf{H}_{\mathrm{so}}|{}^3\psi(DA^*)\rangle$ involving the spin orbit operator $\mathbf{H}_{\mathrm{so}}$, in determining the selective population of the triplet sublevels. The matrix element connects the almost ionic low-lying excited singlet state ${}^1\psi(D^+A^-)$ with a neutral triplet state where the excitation resides on the acceptor molecule.

In previous EPR investigations concerning the spin polarization properties of triplet excitons in anthracene-TCNB[18] and biphenyl-TCNB[15] we have found that the populating rates of the triplet sublevels are quite close to those measured for a triplet localized on a isolated TCNB molecule[19] confirming that this triplet is really involved in the ISC process of TCNB CT complexes.

Under the assumptions of i) spin independent decay and ii) populating rate constants in the same ratio as for the TCNB triplet, the stationary populations ($\dot{n}_i = 0$) obtained from Eqs. (6) depend only on the ratio K/W (decay rate constant over frequency of spin-lattice relaxation). The first quantity was measured from the decay of the optical emission in a time-resolved experiment and its value was of about $3 \cdot 10^3$ s^{-1}. W was taken one order of magnitude larger in analogy with the anthracene-TCNB crystal.[18] The calculated curves of the intensity I_+ for the $|0\rangle \rightarrow |+\rangle$ transition in N-TCNB triplet excitons are shown in Figure 3a. In the ranges of orientations of B where the signals could be detected, the spectral features are fully reproduced, indicating the reliability of the above assumptions.

Concerning the case of the N-TCNQ and N-pChl triplets, if the exciton is trapped by a spin conserving process,[20] we expect that

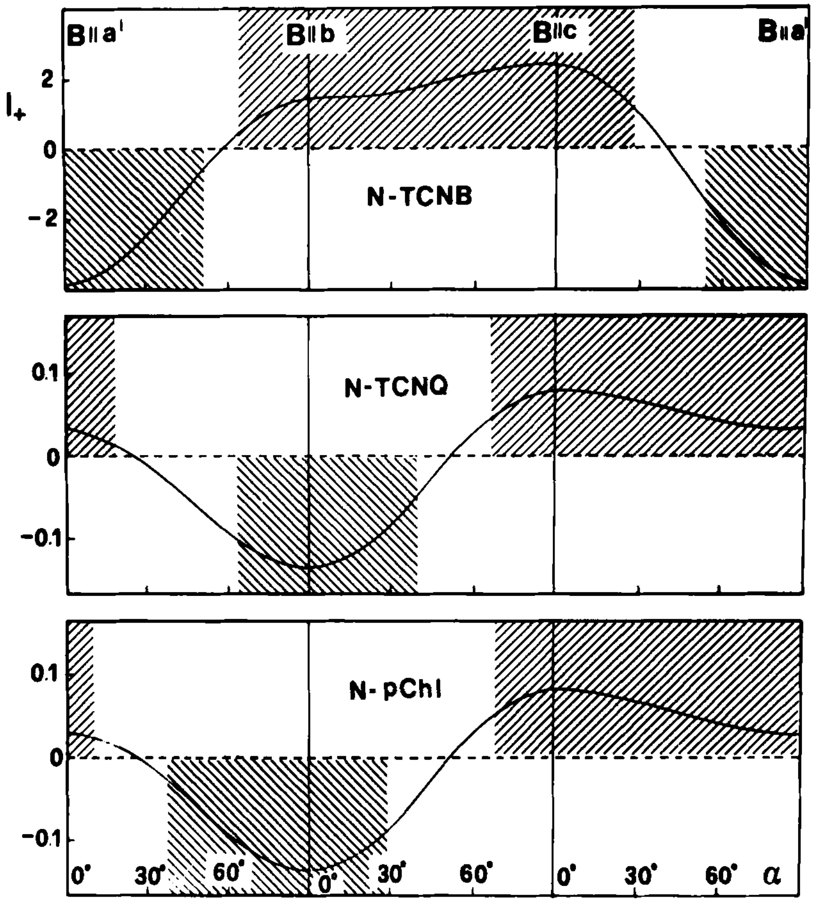

FIGURE 3 Calculated curves of I_+ for the *N*-TCNB triplet exciton, the *N*-TCNQ and the *N*-*p*Chl triplet traps. Experimental points for the $|0\rangle \rightarrow |+\rangle$ transition fall into the shaded areas.

the relative populating rates of the trap sublevels reflect those of the exciton. Figure 3; shows however that the angular dependence of the OEP is different for the exciton and traps. Moreover, we note that the difference cannot be due to an incorrect choice of the sign of the ZFS parameters, since it still remains if we assign the other EPR line of the spectrum to the $|0\rangle \rightarrow |+\rangle$ transition. The OEP of the triplet traps calls for explanation the consideration of the decaying process.

We have performed a series of calculations of the intensity I_+ of the $|0\rangle \rightarrow |+\rangle$ transition, by taking the same set of populating rates as obtained for the *N*-TCNB exciton. Time resolved EPR experiments gave the value of $T_1 = 0.03$ ms and of 0.3 ms for the mean triplet lifetime $\tau = 3(K_x + K_y + K_z)^{-1}$. Anisotropy among the decaying parameters was allowed to vary and the best agreement with the experiment was obtained for both traps *N*-TCNQ and *N*-*p*Chl by taking the values $K_x : K_y : K_z = 1 : 0.25 : 0.25$. In the case of the *N*-*p*Chl trap a positive sign of the Z_c fine structure principal component had to be taken. The fact that the same set of K_i parameters accounts for the OEP orientation dependence of both traps could be an indication that the donor molecule is responsible for the decay process. The small value of K_z is consistent with a decay from a $\pi\pi^*$ triplet state, caused by the spin-orbit coupling interaction.

In conclusion, we have found that the spin polarization displayed by the triplet exciton in *N*-TCNB crystal depends on the populating rates of the TCNB triplet molecule although the ZFS parameters indicate that the triplet excitation resides mainly on the naphthalene molecule. Spin polarization in the *N*-TCNQ and in *N*-*p*Chl triplets trapped in the host lattice of *N*-TCNB is accounted for by allowing that also the decay process is anisotropic.

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