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Crystal Structure of Diphenylacetylene- Tetracyanobenzene 1 : 1 CT Complex and Spin Polarization of Triplet Exciton and of Trans-Stilbene Triplet Trap

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The crystal structure of diphenylacetylene and 1, 2, 4, 5-tetracyanobenzene 1 : 1 charge transfer complex has been determined at room temperature. The crystals belong to the monoclinic system with space group $C2/m$, $a = 9.632(4)$ Å, $b = 12.403(6)$ Å, $c = 8.131(4)$ Å, $\beta = 101.59(4)^\circ$ with two translationally equivalent complexes per unit cell. EPR spectra of photoexcited mobile and trapped triplet species were recorded. The nature of the trap has been investigated and attributed to the trans-Stilbene-TCNB 1 : 2 CT complex. The analysis of the orientation dependence of polarized spectra of exciton and trap has shown that spin polarization is provided by ISC in which the TCNB is involved. Excitation transfer to the trap takes place by preserving alignment of the spin states.

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INTRODUCTION

In a recent paper we reported an EPR study of localized and delocalized excited triplet states of charge-transfer (CT) complexes in diphenylacetylene-1,2,4,5 tetracyanobenzene (DPA-TCNB) crystals.¹ The EPR spectra consisted of the superposition of broad signals due to two triplet molecules, localized at two translationally nonequivalent sites in the DPA-TCNB monoclinic lattice and of narrow signals due to a single species of delocalized triplet exciton.

In molecular crystals of CT complexes whose structure consists of stacks of alternate donor and acceptor molecules the exciton motion occurs preferentially along the stack (quasi linear excitons).^{2,3} However in some cases of monoclinic crystals with two translationally nonequivalent sites a single pair of EPR lines is observed either because of a rapid jumping of the exciton between nonequivalent stacks or because of a fast molecular rearrangement process.⁴⁻⁷

In both cases the linewidth of the exciton EPR signals could change with the orientation of the crystal in the spectrometer magnetic field because of a variation of the splitting of the EPR lines corresponding to the two sites. The linewidth should display a minimum value when the field is directed along the direction where the sites are magnetically equivalent (along the crystal twofold symmetry axis *b* or along the directions perpendicular to it). An analysis of the orientation and the temperature dependence of the linewidth could in principle give important information on the exciton motion in molecular crystals.

Previously¹ we suggested tentatively that in DPA-TCNB crystals the traps could substitute the CT complexes maintaining, as it often happens, the same position and orientation of the host molecules. We inferred the orientation of the latter from the measured ZFS principal directions of the triplet traps. We found that the *z* directions of the two traps sites coincide while the in-plane (*x'*, *x''*) principal directions of the two triplet traps form an angle of 70°; thus for some orientations of the crystal in the magnetic field there is a large splitting of the EPR lines. Under the assumption that the guest molecules are oriented as the host ones, the observation of narrow exciton lines implies a very effective averaging process which could be caused only by a fast two-dimensional motion of the exciton in the (*x*, *y*) molecular plane.

In order to investigate further this interesting DPA-TCNB charge transfer molecular crystal through the properties of its lowest excited triplet state we have first determined its crystal structure by x-ray diffraction analysis which we report in this paper together with the determination of the nature of the trapped triplet and with a thorough

investigation of the spin polarization effects on the traps and exciton EPR spectra.

EXPERIMENTAL

Single crystals of DPA-TCNB 1 : 1 complex were obtained from an acetone solution by slow evaporation. They present well developed (1 $\bar{1}$ 0) and (001) faces. A suitable crystal $0.4 \times 0.4 \times 0.4$ mm³, covered with glue was used for X-ray data collection. Observed systematic absences for hkl data of $h + k = 2n + 1$ indicate a C-centered lattice compatible with three probable monoclinic space groups:⁸ $C2(C_2^3$, No. 5), $Cm(C_s^3$, No. 8), and $C2/m(C_{2h}^3$, No. 12); the centric space group, $C2/m$, was used as subsequently confirmed by the successful solution and refinement of the crystal structure.

The lattice constants for the monoclinic cell at *ca.* 18°C are as follows: $a = 9.632(4)$ Å, $b = 12.403(6)$ Å, $c = 8.131(4)$ Å, $\beta = 101.59(4)^\circ$. The unit cell volume is 951.6 Å³. The X-ray measurements were performed on a Philips PW 1100 diffractometer, graphite-mo-chromated Mo-K α radiation ($\lambda = 0.7107$ Å). The cell parameters were determined by a least-squares analysis of the setting angles of 25 reflections ($13^\circ < \theta < 19^\circ$). The θ - 2θ step scan technique was used to measure intensities. The intensities of three standard reflections showed a little decay at the end of data collection, then all the intensities were corrected accordingly. 3864 Reflections were measured (hkl , $h\bar{k}l$, and some hkl reflections) up to $2\theta = 60^\circ$. Lorentz-polarization corrections and an empirical absorption correction, using the North method,⁹ were made with program RIFLUP.¹⁰ A sorting and merging¹¹ of the data gave 1410 independent reflections, of which 1010 had $I \geq 3\sigma(I)$. The structure was solved by trial and error method taking in mind the already known structure of Biphenyl-TCNB 1 : 1 complex.¹² Positional and thermal parameters were refined by least-squares procedure for all atoms (isotropic parameters only for H atoms) with program LINEX.¹³ The data were corrected for the effects of secondary isotropic extinction ($g = 0.13(3) \cdot 10^4$, mosaic spread: 25''), the reflections most affected by extinction are: 0,2,0 ($y = 0.72$); 1,1, $\bar{1}$ ($y = 0.89$) and 0,4,0 ($y = 0.92$). The usual agreement factors are the following: $R(F) = 0.044$; $R_w(F) = 0.048$; $R_w(F^2) = 0.094$.

For EPR investigation single crystals of approximate dimensions $3 \times 3 \times 2$ mm³ were used. Experimental details of the EPR measurements have been already reported.¹ The crystals were mounted on a

goniometer rod and the magnetic field was rotated in the three perpendicular planes defined by the crystal axes a , b , c^* ($c^* = a \times b$).

RESULTS

1. X-ray

The constituent molecules of DPA-TCNB 1:1 complex are planar and overlap each other with an average interplanar spacing of 3.44 Å. They are stacked alternatively in infinite columns along the c -axis as shown in Figure 1 and 2. A situation quite similar to biphenyl-TCNB 1:1 complex, the major difference is that now the molecules lie in the (102) plane instead of (10 $\bar{2}$) plane, and that the pseudomirror is here a true crystallographic mirror plane.

The atomic coordinates of the complex are reported in Table I and bond lengths and angles in the component molecules are listed in Table II. Figure 3, that is a drawing of the molecules in the (102) plane, shows that the packing is dominated by the short-contacts N(1)—H(5)^{IV} and N(1)^{II}—H(5)^{IV} (2.77 Å) as was found in B-TCNB 1:1 complex (for Roman numerals see Table II). These short-contacts, that lie in the (102) plane, are responsible of the sheet-structure in this adduct. A short contact exists also between sheets and is

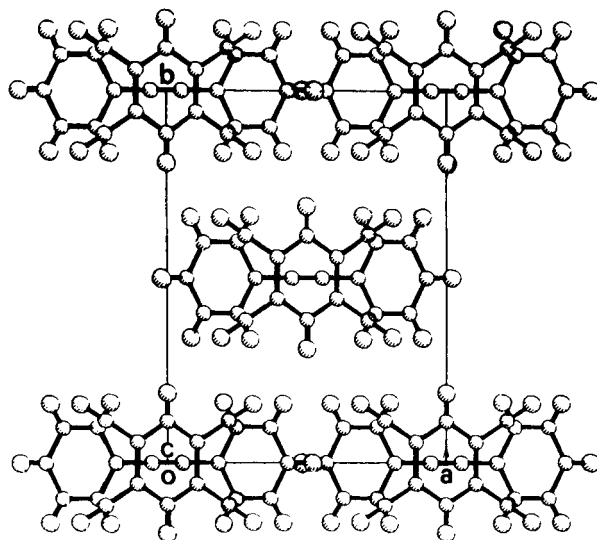


FIGURE 1 The model of overlapping of the component molecules in the DPA-TCNB crystal viewed along [001].

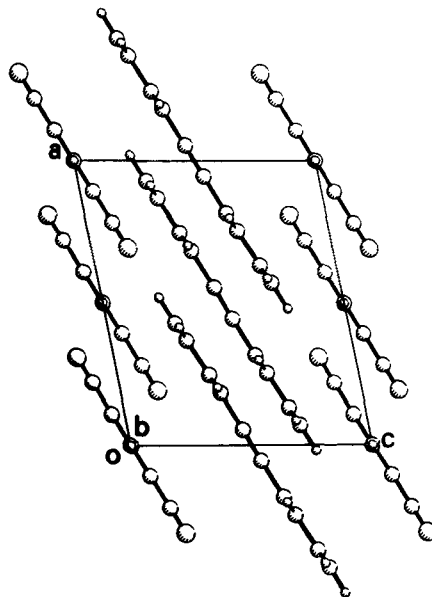


FIGURE 2 Perspective view of DPA-TCNB complex along [010].

TABLE I

Fractional atomic coordinates with estimated standard deviations in parentheses and thermal parameters ($\times 10^3$)

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
in DPA:									
C(1)	.0546(2)	.0000	.4753(2)	5.03	6.98	4.04	0.00	0.91	0.00
C(2)	.1839(2)	.0000	.4126(2)	4.11	6.69	3.65	0.00	0.70	0.00
C(3)	.2468(2)	.0969(1)	.3801(2)	5.20	6.48	5.38	0.01	0.91	0.12
C(4)	.3692(2)	.0956(2)	.3157(2)	5.04	8.24	6.08	-1.11	0.95	1.03
C(5)	.4296(2)	.0000	.2836(3)	4.32	9.92	5.74	0.00	1.15	0.00
H(3)	.2021(17)	.1651(14)	.4027(19)	6.62					
H(4)	.4144(20)	.1617(15)	.2968(22)	8.26					
H(5)	.5195(26)	.0000	.2385(27)	8.11					
in TCNB:									
C(6)	.0000	.1127(2)	.0000	3.89	3.27	5.29	0.00	1.49	0.00
C(7)	.1070(1)	.0565(1)	-.0538(1)	3.27	3.69	4.02	-.22	0.87	1.11
C(8)	.2193(1)	.1146(1)	-.1093(2)	4.42	3.89	5.83	-.06	1.85	-.09
N(1)	.3078(1)	.1606(1)	-.1525(2)	6.09	5.29	9.34	-.83	3.93	0.11
H(6)	.0000	.1910(17)	.0000	4.90					

Anisotropic thermal parameters of the form $\exp[-2\pi^2(U_{11}a^{*2}h^2 + \dots + 2U_{12}a^*b^*hk + \dots)]$.

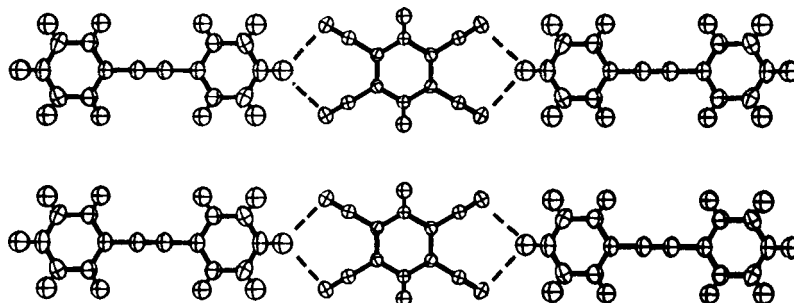


FIGURE 3 Arrangement of molecules in one sheet coincident with the crystallographic plane (102), for clarity also the molecules translated of $+b$ are shown. The drawings were obtained with ORTEP, and the thermal vibration ellipsoids are scaled to enclose 50% probability.

$N(1)-H(6)^V$ (2.73 Å). The molecular overlap of the DPA-TCNB complex is shown in Figure 4.

The dimensions of DPA and TCNB molecules are the same as those observed in the crystal structure of uncomplexed molecule,^{14,15} in particular the $C(1)-C(1)^I$ triple bond distance of 1.199 Å is same of that found in DPA. A little difference is that the shortening of C—C benzene bond due to thermal motion¹⁴ found in DPA is here less pronounced, probably for the presence of the short N—H contacts.

TABLE II

Bond lengths (Å) and angles (°) with estimated standard deviations in parentheses^b

in DPA		in TCNB	
$C(1)-C(1)^{Ia}$	1.199(3)	$C(6)-C(7)$	1.386(2)
$C(1)-C(2)$	1.437(3)	$C(7)-C(8)$	1.445(2)
$C(2)-C(3)$	1.395(2)	$C(7)-C(7)^{II}$	1.402(2)
$C(3)-C(4)$	1.383(3)	$C(8)-N(1)$	1.138(2)
$C(4)-C(5)$	1.369(3)	$C(6)-H(6)$	0.97(2)
$C(3)-H(3)$	0.98(2)	$C(7)-C(6)-C(7)^{III}$	119.6(2)
$C(4)-H(4)$	0.95(2)	$C(6)-C(7)-C(8)$	119.9(1)
$C(5)-H(5)$	1.01(3)	$C(7)-C(8)-N(1)$	179.7(2)
		$H(6)-C(6)-C(7)$	120.2(1)
$C(2)-C(1)-C(1)^I$	178.8(2)		
$C(1)-C(2)-C(3)$	120.5(1)		
$C(2)-C(3)-C(4)$	119.8(2)		
$C(4)-C(5)-C(4)^{II}$	120.1(2)		
$C(3)-C(2)-C(3)^{II}$	119.0(2)		

^aRoman numerals refer to the symmetry-related positions: (I) $-x, -y, 1-z$; (II) $x, -y, z$; (III) $-x, y, -z$; (IV) $1-x, -y, -z$; (V) $1/2+x, 1/2-y, z$;

^bTaking into account the accuracy of cell dimensions.

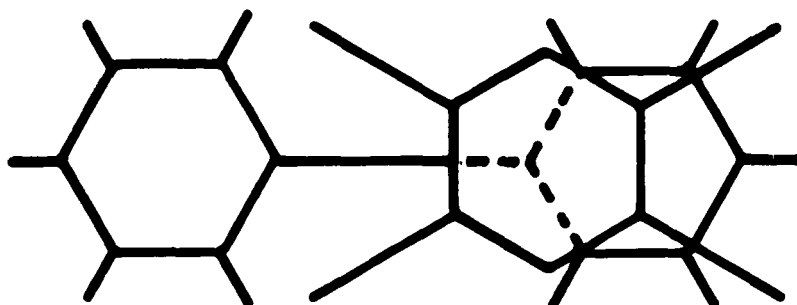


FIGURE 4 Molecular overlap in the columnar stacking of DPA-TCNB complex. The view direction is normal to the least-squares molecular plane.

TABLE III

Least-squares Planes and deviations (Å). The equations of the planes are of the form $Px + Qy + Rz = S$, where x, y, z are the fractional coordinates.

	<i>P</i>	<i>Q</i>	<i>R</i>	<i>S</i>
(a) DPA molecular plane C(1) 0.02; C(2) 0.03 C(3) 0.02; C(4) -0.01 C(5) -0.02; H(3) 0.02 H(4) 0.02; H(5) -0.02	3.410	0.000	6.871	3.435
(b) TCNB molecular plane C(6) 0.000; C(7) -0.004 C(8) -0.002; N(1) 0.003 H(6) 0.000	3.413	0.000	6.869	0.000

Dihedral angle between planes (a)-(b) is 0.0000.

2. EPR

The EPR spectra of irradiated single crystals consist of a pair of narrow lines (~ 1 G) due to triplet exciton and of two pairs of broader lines (~ 15 G) due to triplet traps in two unequivalent sites in the crystal lattice. They were described in ref. 1.

The analysis of the variation of the trap EPR line position with the orientation of the crystal gave ZFS parameters of the triplet trap $X = 645$; $Y = -94$; $Z = -551$ G and $X = 26$; $Y = 293$; $Z = -320$ G for the exciton. Moreover, we noted that the trap signal intensity, relative to that of the exciton, decreases with increasing the purity of DPA used in the preparation of the crystals.

Another important feature presented by the EPR spectra is the large amount of spin polarization carried by both the exciton and the trap species. The presence of polarization is manifested by the fact that

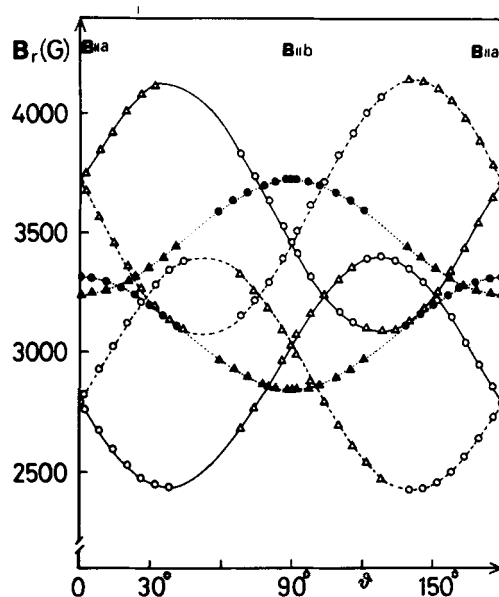


FIGURE 5 Plots of the resonant magnetic fields at which EPR lines of the exciton (full symbols) and of the trap (empty) species were observed. Circles represent lines in emission whereas triangles refer to those in enhanced absorption. Resonant fields of the traps are indicated by pairs of solid and dashed lines.

each pair of lines separated by the fine tensor splitting appears with opposite phases indicating that one line is in emission and the other in enhanced absorption as shown in Figure 5.

It is known that impurities in the crystal lattice can originate the onset of an efficient mechanism of quenching of the triplet excitons through the trapping of the excitation at the impurity centers.

An inspection of the angular dependence of the phases of the EPR signals due to the exciton and to the trap reveals that they follow the same trend. It means that the EPR lines of the mobile and localized triplet excitation corresponding to the same microwave transition (e.g. $|0\rangle \rightarrow |+\rangle$) are both in emission or absorption at any orientation of the crystal with respect to the magnetic field. This fact can give valuable information on the energy transfer process from the exciton to the trap and it will be considered in more detail in the next section.

DISCUSSION

1. The nature of the triplet trap

On the basis of the assignment of the principal directions of the ZFS tensor, it was inferred¹ that the crystal structure of the DPA-TCNB

complex consists of alternate stacks of TCNB and DPA molecules with the direction z normal to the molecular planes making an angle of 31.7° with the stacking direction.

The molecular arrangement proposed is nicely confirmed by the present x-ray diffraction investigation (see Figure 2). Moreover, the crystal structure of the DPA-TCNB complex presents some characteristics that are quite relevant for the discussion of the EPR spectra of the excited triplet species.

First of all, the two molecular units that are present in the monoclinic cell, are translationally equivalent. Therefore, the ZFS parameters which were determined from the spectra of the triplet exciton correspond to those one would measure for an isolated excited molecule. No motional averaging of the fine structure tensor is in fact occurring. The principal values $X = 26$, $Y = 293$ and $Z = -320$ G are similar to those of the corresponding CT complex of TCNB with Biphenyl¹² (38; 361 and -399 G respectively) indicating a quite similar structure of the two complexes with a larger CT character in the DPA-TCNB triplet state. If we indicate with Z_{loc} and Z_{ion} the local and the ionic contributions to the Z principal component, application of the relationship

$$\chi_{\text{CT}} = \frac{Z_{\text{complex}} - Z_{\text{loc}}}{Z_{\text{ion}} - Z_{\text{loc}}} \quad (1)$$

gave the value of $\chi_{\text{CT}} = 0.54$ for the CT character. The reason why two different sites are observed for the trapped signal depends on the nature of the trap itself as it will be clear in the following.

The ZFS parameters of the trap are quite different from those measured for the exciton and thus the trap should originate from impurities having a lower energy triplet state, the assignment of the signal to simple crystal defects being excluded.

A possible impurity is *t*-Stilbene and in fact the ZFS values of the triplet trap in DPA-TCNB are very similar to those we measured for triplets in single crystals of *t*-Stilbene (tS)-TCNB 1 : 2 CT complex,¹⁶ i.e. $X = 675$, $Y = -92$, $Z = -583$ G. In addition, single crystals of DPA-TCNB obtained with highly purified DPA and then doped with small amount ($\sim 1\%$) of *t*-Stilbene gave EPR spectra showing the same triplet trap. The presence of tS molecules as impurities in DPA is not surprising since the latter is usually contaminated with stilbene.¹⁷ As this forms a 1 : 2 CT complex with TCNB, one tS guest molecule is expected to substitute two DPA host molecules. A close examination of the crystal structure (see Figure 1) really shows that there are two

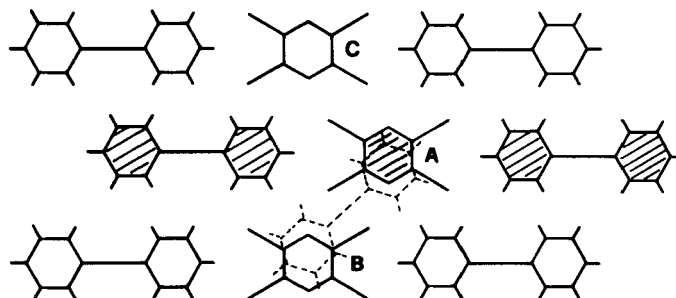


FIGURE 6 Molecular sheets in the crystallographic plane (102). Sheet of shaded molecules is shifted out of plane by 1.72 Å. TCNB molecule pairs AB and AC are shown. They participate to the formation of $tS-(TCNB)_2$ complex in the two possible arrangements.

possible arrangements of a tS molecule in the DPA-TCNB crystal lattice by forming a 1 : 2 complex. Of them one is shown in Figure 6 and the other is obtained by a twofold rotation of the donor molecule around the binary axis b .

A further evidence was gained that t -Stilbene is indeed involved in the trapped CT complex. When the magnetic field is directed along the z principal axis of the exciton fine structure tensor, the EPR lines of the localized triplet species display an hyperfine structure that was previously attributed to hyperfine coupling with the nitrogen nuclei of the TCNB molecule.¹ But when crystals of DPA-TCNB grown with highly purified starting materials, were doped with fully deuterated t -stilbene, the hyperfine structure for B parallel to z disappeared and a marked reduction of the linewidth of the trap spectra was observed at any orientation. In Figure 7 the high field EPR lines of the tSh_{12} -TCNB and tSd_{12} -TCNB complexes are reported when the magnetic field is directed along the z principal axis.

Stilbene could simply substitute for a single diphenylacetylene since the ethylene bond takes two possible orientations about 50° apart. However, we have excluded this possibility since a description of stilbene electronic levels¹⁸ has shown that its lowest excited states must consist of excitations mainly localized on the benzene rings. This result is confirmed by the presence of more than four hyperfine lines in the EPR spectrum, indicating that spin density is surely spread over the benzene fragments. These facts indicate that the triplet trap observed in DPA-TCNB crystals have to be attributed to an excitation residing on the $tS-(TCNB)_2$ complex with a local contribution of the donor molecule.

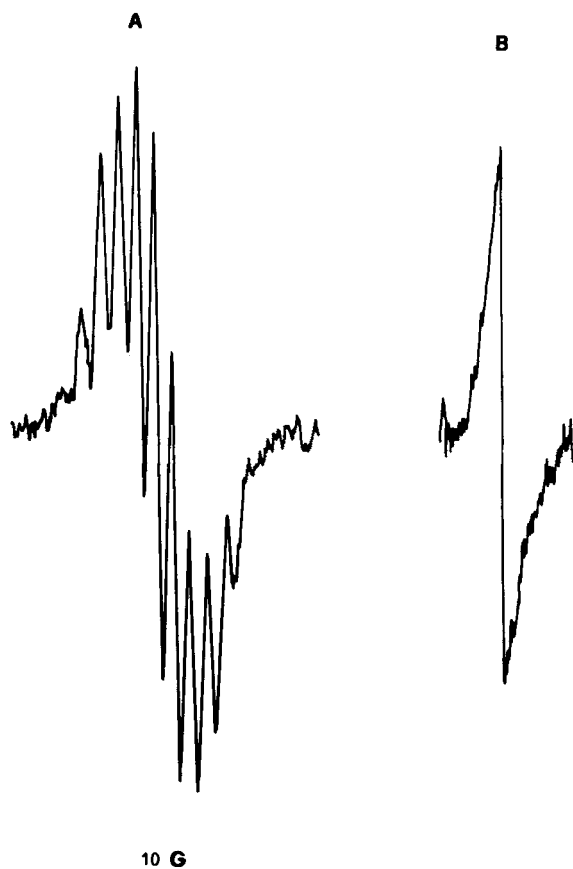


FIGURE 7 High field EPR lines of traps in $tSh_{12}-(TCNB)_2$ (A) and $tSd_{12}-(TCNB)_2$ (B) with magnetic field parallel to z .

The proposed structures of the $tS-(TCNB)_2$ complex as shown in Figure 6 agree nicely with the results obtained from the analysis of the ZFS principal directions of exciton and trap.¹ In fact, if we assume that in the latter the triplet wavefunction extends mainly over the benzene rings of tS , these are rotated to that of $TCNB$ by approximately the same angle found by the ZFS principal directions.¹⁸

It is worth noting that the two $TCNB$ molecules that participate to the $tS-(TCNB)_2$ complex do not lie on the same plane (see Figure 6). A conformation of the tS molecule in which the two phenyl rings are nearly parallel to the $2p_z$ atomic orbitals of the ethylenic fragment fulfills nicely the packing requirements of the host lattice.

Finally, the presence of two translationally unequivalent sites of the traps does not reflect the symmetry of the crystal lattice which is composed of the equivalent sites, but it is due to the fact that the guest molecules can take two different arrangements in the lattice.

2. Spin polarization

When the magnetic field is rotated with respect to a reference frame centered on the crystal the intensity of the EPR lines changes and certain orientations are attained at which a change of the signal phase is observed. The appearance of the polarized spectra is primarily a consequence of the selectivity in the populating process of the three triplet sublevels which are differently mixed with the excited singlet states through the spin-orbit interaction. If the spin-lattice relaxation time between the triplet levels is not too fast with respect to their decay rates, in a continuous triplet generation experiment the steady state populations of the sublevels may even largely deviate from the Boltzmann distribution.

The line intensity is proportional to the population difference ΔN of the Zeeman levels connected by the microwave field and to the EPR transition probability b according to the relation

$$I = cb \Delta N \quad (2)$$

where the parameter c accounts for the experimental conditions. The line intensity $I_+ = c(N_+ - N_0)b_+$ and $I_- = c(N_0 - N_-)b_-$ for the two $\Delta m = \pm 1$ transitions are obtained by solving for N_0 , N_+ and N_- under stationary conditions ($\dot{N}_i = 0$) the set of kinetic equations

$$\begin{aligned} \frac{dN_+}{dt} &= (-K_+ - W_1 - W_3)N_+ + W_1e_1N_0 + W_3e_3N_- + P_+N_s \\ \frac{dN_0}{dt} &= W_1N_+ + (-K_0 - W_1e_1 - W_2)N_0 + W_2e_2N_- + P_0N_s \\ \frac{dN_-}{dt} &= W_3N_+ + W_2N_0 + (-K_- - W_3e_3 - W_2e_2)N_- + P_-N_s \end{aligned} \quad (3)$$

P_i and K_i are the populating and depopulating rate constants of the Zeeman levels $+$, 0 , $-$ while W_i and e_i are the relaxation rate constants and the Boltzmann factors of the level pairs $(+, 0)$, $(0, -)$ and $(+, -)$, respectively. N_s indicates the population of the excited singlet state precursor of the triplet.

In general the steady-state N_i of eqs. (3) depend on a set of nine parameters. However, under suitable approximations that number can

be considerably reduced. In fact, for triplet excitons that deactivate by triplet-triplet annihilation or by trapping processes, the decay rate constants are almost independent of the orientation of the magnetic field.^{19,20} Thus the quantities K_i can be replaced by just one single parameter K . The same can be done for the relaxation frequencies W_i although it does not seem to be an essential assumption in the calculation of the signal intensities I_{\pm} .²¹

With these simplifications the only step producing spin polarization consists of the triplet populating process. In a magnetic field the rate constants P_i ($i = 0, +, -$) of the Zeeman levels are related to the corresponding quantities P_u ($u = x, y, z$) at zero field by the relation

$$P_i = \sum_u |C_{iu}|^2 P_u \quad (u = x, y, z) \quad (4)$$

The coefficients C_{iu} express the eigenvectors of the total hamiltonian $H = H_{\text{Zeeman}} + H_{\text{ZFS}}$ in terms of the eigenfunctions of the ZFS hamiltonian and depend on the strength and direction of the magnetic field with respect to the ZFS principal axes. If the quantities P_u are different among themselves, the same occurs for the P_i ones. According to eqs. (3) the stationary populations N_i which are a function of P_i , have their values largely deviating from the Boltzmann distribution provided that the spin-lattice relaxation is not too fast with respect to the decay from the spin sublevels. On account of the spin polarization carried by the population difference ($N_+ - N_0$) the line intensity I_+ may change its sign by varying the orientation of the magnetic field.

A recent investigation²² concerning the quantum efficiency of intersystem crossing (ISC) in CT complexes of aromatic hydrocarbons with TCNB indicated that in these complexes the ISC process involves only the acceptor molecule because of the larger spin-orbit coupling constant on the nitrogen. These expectations have been confirmed in our recent studies of the spin polarization of triplet excitons in Anthracene-TCNB,²¹ Naphthalene-TCNB²³ and Biphenyl-TCNB.²⁴ Even when the ZFS parameters clearly show that the triplet excitation is almost completely localized on the donor molecules the P_u values that fit the angular dependence of the polarized signal intensity are typical of the TCNB triplet.^{21,23}

In view of these results we have applied the same procedure to reproduce the angular dependence of the EPR line intensity I_+ of the triplet exciton in the DPA-TCNB crystals. The same behaviour is obtained for I_- since at high fields I_- has the same value of I_+ but opposite sign. The plots of I_+ reported in Figure 8 were calculated by

allowing rotation of the magnetic field in the crystallographic frame a, b, c^* to have a comparison with the experimental points. The orientations at which an inversion in the sign of I_+ take place, do not set symmetrically with respect to the crystallographic axes since the latter do not coincide with the ZFS tensor principal axes. Calculations were carried out by employing the set of populating rate constants $P_x : P_y : P_z = 1 : 0.32 : 0.16$ measured by the MIDP method for the TCNB triplet.²⁵ The good agreement between the experimental and the calculated relative values of I_+ in all the three crystallographic planes confirms that also in the DPA-TCNB complex the latter molecule is responsible of its selective population in the triplet state.

The other feature displayed by the EPR spectra recorded in the DPA-TCNB was that the trap signals too were polarized. When the triplet excitation migrates into the crystal, the excitons sample sites that are translationally equivalent, and eventually become trapped at the impurity centers of $tS\text{-(TCNB)}_2$ complexes. During the random walk the triplet excitation originated at a particular site has the principal directions of the ZFS tensor that are not subjected to any averaging process.

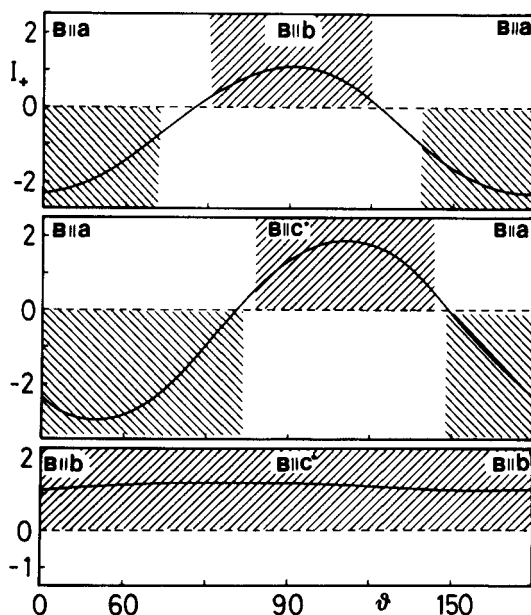


FIGURE 8 Calculated curves of I_+ when the magnetic field is rotated in the crystallographic planes. Experimental points for the $|0\rangle \rightarrow |+\rangle$ EPR transition fall into the shaded areas.

The independent populating directions of the DPA-TCNB complex coincide with the ZFS tensor principal directions throughout the exciton motion and the original alignment of the spin states is preserved.

When the mobile triplet is trapped by the tS-(TCNB)₂ complex the principal directions of the ZFS tensor in the latter do not coincide with those of the preferential spin alignment. Calculation of the angular dependent intensity I_+ for the signal relative to one of the two translationally inequivalent traps is accomplished by taking into account this misalignment. Following the procedure described for the case of the polarized signal intensity I_+ in the exciton, the populating rate constants P_i expressed in the Zeeman reference frame are related to P_u through the relation

$$P_i = \sum_u |C'_{iu}|^2 P_u \quad (5)$$

Here, the coefficients C'_{iu} represent the eigenvectors of the trap Hamiltonian projected to those of the exciton Hamiltonian. In this way the plots of I_+ of the trap follow perfectly those of the exciton and reproduce nicely the experimental behaviour as evidenced by measurements reported in Figure 8.

Since the sites of the lattice in DPA-TCNB are translationally equivalent little can be known about the dimensionality of the exciton motion from the dependence of the EPR linewidth on temperature. Jumps from a site to another belonging to the same stack or to different ones have the same effect on the linewidth. Only averaging of the hyperfine structure occurs and the linewidth is determined by the fastest process. If we indicate by P_{11} the most rapid jumping rate constant the relation applies

$$P_{11} = \Delta\omega_{1/2 \text{ trap}}^2 / 8 \Delta\omega_{1/2 \text{ exc}} \quad (6)$$

where $\Delta\omega_{1/2 \text{ exc}}$ is the linewidth of the exciton at one temperature and $\Delta\omega_{1/2 \text{ trap}}$ represents the value when the mobile excitation become x -trapped. We did not observe x -traps in DPA-TCNB crystals, however we can assume that the value of its linewidth is similar to that of the tS-(TCNB)₂ trap. With the experimental values of $\Delta\omega_{1/2 \text{ trap}} = 2.2 \times 10^8 \text{ s}^{-1}$ and $\Delta\omega_{1/2 \text{ exc}}(100 \text{ K}) = 1.5 \times 10^7 \text{ s}^{-1}$, we find $P_{11}(100 \text{ K}) = 4 \times 10^8 \text{ s}^{-1}$.

CONCLUSION

We have shown that the crystal structure of the DPA-TCNB crystal consists of equivalent lattice sites and only the hyperfine structure is averaged by exciton motion while fine structure principal directions do not change on jumping. The observation of magnetically inequivalent traps is due to the particular nature of the trap whose donor molecule can take two different arrangements in the monoclinic lattice. The observed polarization carried by exciton was provided by ISC in which the TCNB is involved.

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