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Crystal Structure of Biphenyl-1,2,4,5-Tetracyanobenzene 1 : 1 CT Complex and EPR Investigation of Photoexcited Triplet Excitons

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The crystal structure of biphenyl and 1,2,4,5-tetracyanobenzene 1 : 1 charge transfer complex has been determined at room temperature. The crystals belong to the triclinic system with space group $C\bar{1}$, $a = 9.592(6)$ Å, $b = 12.359(9)$ Å, $c = 7.335(5)$ Å, $\alpha = 94.17(6)°$, $\beta = 96.50(8)°$ and $\gamma = 89.07(7)°$ with two complexes per unit cell. The increase of the zero-field splitting tensor of photoexcited triplet excitons with increasing temperature has been discussed in terms of two early proposed models. In the former approach a thermal equilibrium between two triplet states was assumed. In the second the variation of the fine structure tensor elements was attributed to changes of the charge transfer character of the triplet state as a consequence of the temperature dependent molecular packing in the crystal. Experimental evidences are in favor of this latter model.

INTRODUCTION

Biphenyl (B) forms with 1,2,4,5-tetracyanobenzene (TCNB) a 1 : 1 charge-transfer (CT) complex which crystallizes with donor biphenyl

and acceptor TCNB molecules alternatively stacked in linear arrays. The molecular arrangement in the solid state is typical of many other CT complexes.[1]

When single crystals of B-TCNB are illuminated inside the microwave cavity of an EPR spectrometer with visible light, strong EPR signals are recorded due to mobile triplet excitations.[2] These are formed from the excited singlet states by an intersystem crossing (ISC) process which selectively populates the low lying triplet sublevels. The lifetime of the triplet state is short enough to prevent the spin lattice relaxation to produce a Boltzmann distribution among the triplet sublevels. As a consequence electron spin polarized (ESP) spectra are obtained with EPR transitions either in enhanced absorption and in emission. The detailed analysis of the ESP effect may give valuable information on the ISC process.[3] The analysis of the orientation dependence of the EPR lines separation gives the zero field splitting (ZFS) parameters of the triplet species and the orientation of the principal directions of the electron dipole–dipole interaction. The values of the ZFS parameters of CT complexes are lower than those of triplet states localized either on the donor or acceptor molecules since the partial delocalization of the electron spins over both molecules of the complex decreases markedly the dipolar interaction. Comparison of the ZFS parameters of the CT complex with those of the localized excitation (on the donor or acceptor) allows derivation of the charge-transfer character. It should be mentioned that the ZFS parameters of triplet excitons may be also used for this purpose instead of those of the single complex provided that the exciton motion takes place among translationally equivalent complexes. If this is not the case the ZFS parameters of the exciton are the averaged values of those of differently oriented complexes in the unit cell and they can be quite different from those of the single complex. The knowledge of the crystal structure is therefore a prerequisite for the study of the charge-transfer properties by ESR.

A spectral feature displayed by the ESR spectra of many CT complexes in single crystals is that the ZFS parameters of the partially charge-transfer triplet state vary with the temperature. Such a change has been reported in CT complexes such as anthracene-TCNB,[4] anthracene-PMDA,[5] naphthalene-TCPA[6] and, more recently, naphthalene-TCNB,[7] but while in the former three cases fine structure constants decrease with increasing temperature the reverse was observed in the naphthalene complex.

Vyas and Ponte Goncalves[4] have interpreted the ZFS variations of anthracene-TCNB in terms of a model in which another thermally accessible triplet state lying above the lowest triplet state is involved.

Contribution to the ZFS parameters from both triplet states that carry different CT characters should lead to their observed dependence on temperature.

Ziegler and Karl[8] suggested that it is likely that the change in values of D and E could originate from a different admixture of CT character into the triplet state when the temperature is raised as a result of the variation of the lattice constraints in the crystal.

In this paper we report the crystal structure of the B-TCNB complex. A detailed analysis of the temperature dependence of the ZFS parameters is also presented and the results are discussed in terms of the two approaches.

EXPERIMENTAL

Single crystals of B-TCNB 1 : 1 complex grew as prisms from an acetone solution by slow evaporation, elongated in the [001] direction. They present well developed (110) and ($1\bar{1}0$) faces (sometimes also the small face (010)) that are truncated by the ($10\bar{2}$) or (001) pinacoids.

According to our structure determination the 1 : 1 CT complex of biphenyl with TCNB crystallizes in the triclinic space group $C\bar{1}$ with two complexes in each unit cell. The space group $C\bar{1}$ was chosen to take into account the pseudo-mirror plane nearly perpendicular to *b*. The cell parameters are $a = 9.592(6)$ Å, $b = 12.359(9)$ Å, $c = 7.335(5)$ Å and $\alpha = 94.17(6)°$, $\beta = 96.50(8)°$, $\gamma = 89.07(7)°$ with a cell volume of

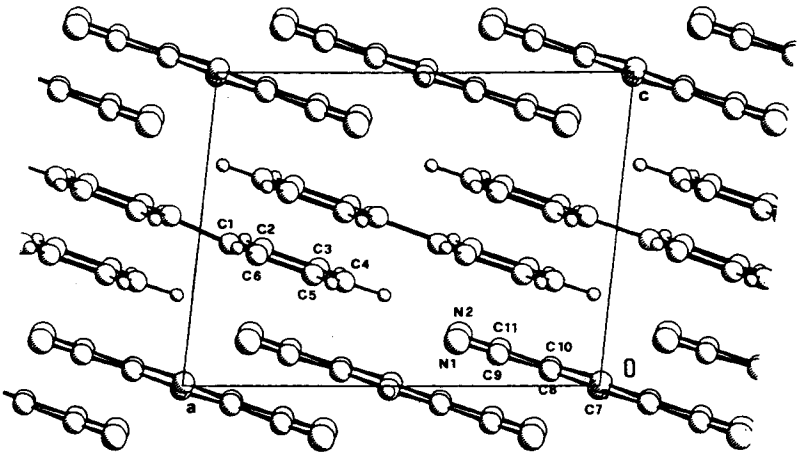

FIGURE 1 Perspective view of the B-TCNB complex along [010].

861.6 Å.^{3} X-ray diffraction intensities were collected with a Philips PW1100 diffractometer, graphite-monochromated Mo-Kα radiation ($\lambda = 0.7107$ Å). The cell parameters at room temperature were determined by a least-squares refinement of the setting angles of 25 reflections ($18 \leqslant \vartheta \leqslant 22°$). The intensities were corrected for Lorentz and polarization factors, but not for absorption ($\mu = 0.5\,cm^{-1}$). 3517 reflections were measured and averaged to 2285 independent reflections. The structure was solved by direct methods. Positional and thermal parameters were refined by least squares procedure for all atoms (isotropic parameters only for H atoms). Final usual R factor was 0.063. By inspection of these values and from Figure 1 one deduces that the biphenyl and the TCNB molecules lie in the $(10\bar{2})$ plane with their short axis in the [010] direction. By attaching the crystal on a goniometer rod by the $(10\bar{2})$ face, the magnetic field could be rotated in the molecular plane *xy* of Figure 2.

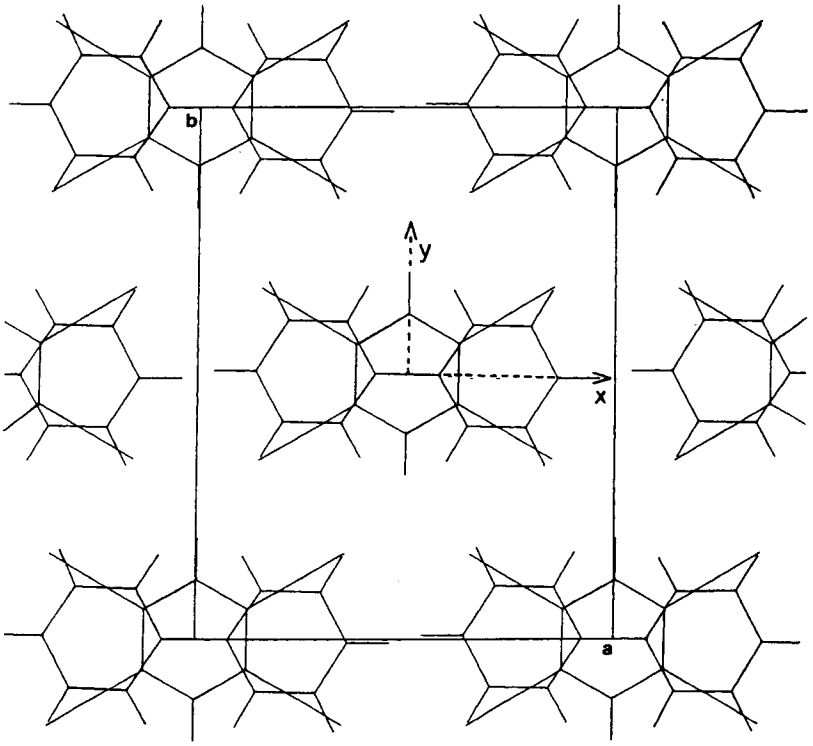

FIGURE 2 The model of overlapping of the component molecules in the B-TCNB crystal viewed along [001].

RESULTS

1. X-ray structure

The constituent molecules of the B-TCNB complex are planar and overlap each other with an average interplanar spacing of 3.62 Å. They are stacked alternately in infinite columns along the *c*-axis as shown in Figure 1. The dimensions of the TCNB molecule are the same as those observed in the crystal structure of uncomplexed molecule[9] and in other electron donor–acceptor complexes.[10] The geometry of biphenyl is the same as in the biphenyl crystal.[11] 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. The atomic separations of N1-H4 and N2-H4 (2.79 and 2.81 Å) are close to the normal Van der Waals separations. The component molecules are stacked in linear arrays with the molecular planes being nearly parallel and making an angle of 1.3° with each other. The shortest contact between atoms of different molecules in the stack is C6-C10 (3.55 Å) (see Tables III and IV).

TABLE I

Fractional atomic coordinates with estimated standard deviations in parentheses and thermal parameters ($\times 10^2$)[Δ]

Atom	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
in Biphenyl									
C1	.9244 (3)	.0013 (2)	.4659 (3)	6.0	5.5	4.6	−0.4	1.1	0.3
C2	.8429 (4)	−.0913 (3)	.4413 (5)	7.2	6.8	9.4	−1.3	−0.5	2.0
C3	.7032 (4)	−.0885 (4)	.3778 (5)	6.7	9.3	11.1	−2.7	−0.5	2.1
C4	.6380 (4)	.0070 (4)	.3355 (5)	5.6	10.7	8.2	−0.4	0.6	1.0
C5	.7148 (4)	.0999 (3)	.3571 (5)	7.0	7.9	9.9	1.5	0.3	0.5
C6	.8556 (4)	.0971 (3)	.4208 (5)	7.1	5.7	9.0	0.1	0.8	0.3
H2	.889 (4)	−.156 (4)	.470 (5)	12.2					
H3	.651 (4)	−.155 (3)	.360 (5)	11.3					
H4	.538 (4)	.007 (3)	.292 (4)	10.1					
H5	.668 (4)	.173 (3)	.330 (5)	11.4					
H6	.905 (3)	.164 (3)	.443 (4)	10.3					
in TCNB									
C7	.0022 (3)	.1115 (2)	−.0108 (4)	4.8	3.8	7.2	−0.5	0.7	0.9
C8	.1234 (2)	.0571 (2)	.0473 (3)	4.1	4.3	5.7	−0.6	0.8	0.5
C9	.2518 (3)	.1149 (2)	.0991 (4)	4.7	4.7	7.5	−0.5	0.1	1.3
C10	.1217 (2)	−.0561 (2)	.0588 (3)	4.0	4.4	5.5	0.0	0.7	0.8
C11	.2484 (3)	−.1132 (2)	.1180 (4)	4.7	4.6	7.4	−0.7	0.3	0.5
N1	.3531 (3)	.1617 (2)	.1415 (4)	5.7	5.5	11.1	−1.3	−0.8	1.7
N2	.3490 (3)	−.1599 (2)	.1634 (4)	5.6	6.1	10.9	0.4	−0.6	1.1
H7	.003 (3)	.190 (2)	−.017 (3)	6.7					

[Δ] Anisotropic thermal parameters of the form $\exp\left(-2\pi^2 \sum_i \sum_j U_{ij} h_i a_i^* h_j a_j^*\right)$.

TABLE II

Bond lengths (Å), before and after libration correction, and angles (°) with estimated standard deviations in parentheses.[Δ]

	in biphenyl			in TCNB	
C1-C2	1.386 (9)	1.407	C8-C9	1.433 (7)	1.438
C1-C1′[b]	1.480 (8)	1.486	C8-C10	1.408 (7)	1.420
C1-C6	1.389 (9)	1.408	C9-N1	1.140 (8)	1.143
C2-C3	1.369 (10)	1.374	C8-C7	1.375 (7)	1.378
C3-C4	1.366 (12)	1.385	C7-C10′[a]	1.379 (7)	1.383
C4-C5	1.364 (12)	1.385	C10-C11	1.436 (7)	1.440
C5-C6	1.379 (10)	1.384	C11-N2	1.145 (8)	1.149
C2-H2	0.93 (7)		C7-H7	0.97 (5)	
C3-H3	0.96 (6)				
C4-H4	0.98 (6)		C7-C8-C10	120.0 (4)	
C5-H5	1.02 (7)		C8-C7-C10′	120.5 (5)	
C6-H6	0.95 (6)		C8-C10-C7′	119.4 (4)	
C1′-C1-C2	122.4 (5)		C9-C8-C10	119.5 (4)	
C1′-C1-C6	121.8 (5)		C7-C8-C9	120.5 (5)	
C2-C1-C6	115.8 (5)		C8-C9-N1	179.2 (6)	
C1-C2-C3	122.1 (7)		C11-C10-C7′	120.4 (5)	
C2-C3-C4	120.8 (8)		C8-C10-C11	120.1 (4)	
C3-C4-C5	118.8 (7)		C10-C11-N2	179.0 (6)	
C4-C5-C6	120.4 (7)		C8-C7-H7	120 (3)	
C5-C6-C1	122.0 (7)		H7-C7-C10′	119 (3)	
C-C-H	mean 120 (3)				

[a] Apostrophe denotes atom at $-x, -y, -z$
[b] Apostrophe denotes atom at $2 - x, -y, 1 - z$
[Δ] Taking into account the accuracy of cell dimensions

The relative orientations of the component molecules within the unit cells are shown in Figure 2; the TCNB molecules are placed symmetrically with respect to the two aromatic rings of the donor moieties.

The anisotropic thermal motion factors have been analyzed in terms of the translational (T) and librational (L) motion, using the approach described by Schomaker and Trueblood[12] and treating each constituent

TABLE III

Some relevant contacts (Å)

N1----H4	2.79;	C9-N1---H4	104°;	C4-H4---N1	134°
N2----H4	2.81;	C11-N2---H4	103°;	C4-H4---N2	133°
		N1---H4---N2	91°		
N2----H7[I a]	2.71;				
N1-H7[II a]	2.59				

[a] Atomic parameters obtained from those in Table I by the following transformations:
[I] $1/2 + x, -1/2 + y, z$
[II] $1/2 - x, 1/2 - y, -z$

TABLE IV

Equations of least-squares planes in the form $Px + Qy + Rz = S$, where x, y, z are fractional coordinates; displacements (Å) of relevant atoms are in square brackets.

Plane	P	Q	R	S
(1) benzene in TCNB	−3.077	0.755	7.100	0.000
[C7, C8, C10 0.00; C9 0.02; C11 −0.01; N1 0.04; N2 −0.03; H7 0.01]				
(2) biphenyl	−3.191	0.978	7.060	0.338
[C1, C2, C3, C4, C5, C6 0.00; H2 −0.01; H3 −0.03; H4 0.01; H5 0.03; H6 0.06]				

Dihedral angle between (1) and (2): 1.3°

as though it were a separate rigid body (Table V). The values of $\Sigma[U_{ij}(\text{obs}) - U_{ij}(\text{cal})]^2/(n-s)^{1/2}$ (n is the number of U_{ij} terms and s the number of rigid-body parameters) were 0.0026 for the biphenyl and 0.0027 for the TCNB moiety, compared with the corresponding $\sigma(U_{ij})$ (mean) values of 0.0031 and 0.0030, respectively. The rigid-body approximation therefore gives a reasonable fit to the data. The most sig-

TABLE V

Analysis of rigid-body thermal motion for B-TCNB. Eigenvalues and eigenvectors of L(deg^2) and T matrix (Å$^2 \times 10^4$) relative to the inertial axes.[a]

Principal axes	Direction cosines		
(i) TCNB			
(a) L			
53.5	−.0647	−.0136	0.9978
4.4	0.6996	0.7124	0.0551
3.2	−.7116	0.7017	−.0366
(b) T			
450	−.5669	−.0616	0.8215
434	0.5083	−.8109	0.2899
368	0.6483	0.5819	0.4910
(ii) biphenyl			
(a) L			
112.2	−.1432	−.0647	0.9876
12.9	0.8510	0.5014	0.1563
7.9	−.5053	0.8628	−.0168
(b) T			
646	−.1773	−.3156	0.9322
518	−.0915	0.9484	0.3036
441	−.9799	−.0314	−.1971

[a] The first principal axis is perpendicular to the molecular plane, the third is along the long molecular axis and the second is perpendicular to these, the center of libration necessarily coinciding with the inversion centers.

nificant libration for the TCNB moiety is about an axis roughly parallel to the inertial axis bisecting the C8-C10 bond, i.e. along the long molecular axis. As a consequence the major correction (0.012 Å) for libration has to be applied to the C8-C10 bonded distance, while the other corrections are almost uniform and average to 0.004 Å, or about 0.5 esd. As it appears from Table V the librational tensor has an unusually large value of 112.2 for the libration nearly around the long axis of the molecule (C1-C4). Thus the major corrections (ca. 0.020 Å) concern the bond distances normal to this axis.

2. EPR spectra and temperature dependence of the ZFS parameters

Upon illumination with visible light in the wavelength range 320 nm $<$ λ $<$ 600 nm, B-TCNB gives rise to two strong EPR signals characteristic of triplet excitons described by the spin Hamiltonian

$$H_t = H_z + XS_x^2 + YS_y^2 + ZS_z^2 \qquad (1)$$

written in the principal axes system of the fine structure tensor. H_z is the Zeeman Hamiltonian and X, Y, Z are the principal components of the traceless electron dipolar tensor. The linewidth changes with the temperature and this variation was already studied.[2] The two EPR lines appear with opposite phases because one corresponds to absorption of microwave radiation while the other corresponds to emission. The polarization changes with the crystal orientation with respect to the direction of the spectrometer static magnetic field. The analysis of the orientation dependence which gives important informations on the intersystem crossing process by which the triplet state is populated, is described elsewhere.[3] The electron-electron dipolar interaction tensor of the triplet exciton has principal components $X = +0.0037 \pm 0.0005$ cm^{-1}, $Y = +0.0327 \pm 0.0005$ cm^{-1}, $Z = -0.0367 \pm 0.0005$ cm^{-1}. These values agree with those previously measured[2] and the principal directions were found to coincide with the molecular axes x, y and z, where x is the long axis of TCNB (and biphenyl), y the short axis and z that perpendicular to the molecular plane.

It is interesting to note that, different from what occurs for other systems,[13,14] the principal values of the dipolar tensor of the triplet exciton are the same as one expects for the isolated triplet since we have found that in the crystal all the complex molecules are magnetically equivalent. In this case the exciton motion has no effect on the ZFS parameters.

The EPR spectra of the B-TCNB triplet exciton display a marked change of the ZFS parameters with temperature: the splitting increases with temperature. This variation cannot be due to a tilting of the principal axes of the ZFS interaction, as shown in Figure 3 where the orien-

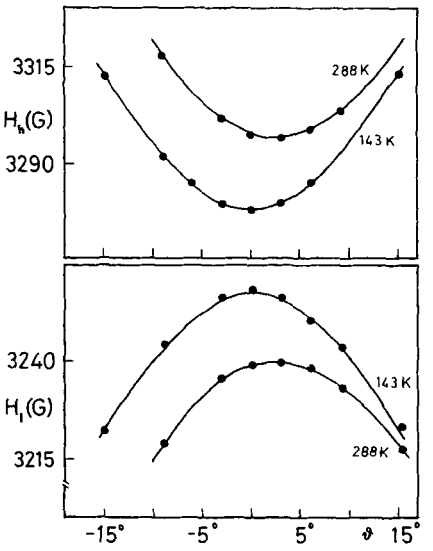

FIGURE 3 Angular dependence of the line splitting of B-TCNB when H is rotated in the xy principal plane. At $\vartheta = 0°$ H lies along the x principal axis.

tational dependence of the resonance field at different temperatures is reported with the magnetic field rotated in the xy plane in the neighborhood of the x axis. In fact, the principal direction x changes quite slightly ($\approx 2°$) in the temperature range 143 ÷ 288 K in which measurements were performed.

An analogous observation has been made with the magnetic field in the neighborhood of the z axis. When H was set parallel to the y axis, signals were too weak to be detected. However, since in the range 143 ÷ 288 K we observed changes of the fine structure splitting by the same amount when H was along the x and z principal axes, a small variation of the principal dipolar component Y is expected because the dipolar interaction tensor has zero trace. In Figure 4 we report measurements of the fine structure splitting with the magnetic field parallel to the x axis.

DISCUSSION

The low lying triplet state of B-TCNB may be described by the following wave function

$$^3\psi(1,2) = (1 - \chi_{CT})^{1/2}\, {}^3\psi_{loc}(1,2) + \chi_{CT}^{1/2}\, {}^3\psi_{ion}(1,2) \qquad (2)$$

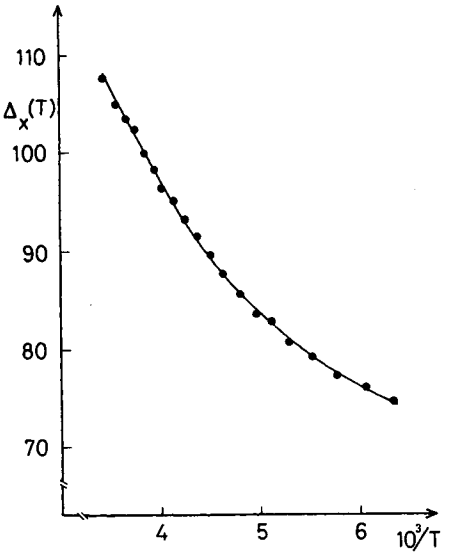

FIGURE 4 Temperature dependence of the line separation with the magnetic field along the x principal axis. Points indicate the experimental values while solid line represent the least squares fitting curve obtained by applying Eq. (5) (see later in the text).

where χ_{CT} is the degree of charge transfer character while $^3\psi_{loc}$ represents a triplet localized on the TCNB molecule and $^3\psi_{ion}$ a triplet state where one electron is transferred from the donor B to the acceptor TCNB. The contribution to the wave function of a triplet localized on the donor is negligible since this state is at higher energy according to optical investigations.[15]

The use of Eq. (2) for $^3\psi(1,2)$ gives the following expression for the Z principal component of the fine structure tensor of the complex

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

allowing the value of χ_{CT} to be determined if Z_{loc} and Z_{ion} are known. Analogous relationships hold for the X and Y principal components. ZFS parameters of the TCNB triplet have been measured[16] while we rely on calculated values for the dipolar contribution of the ionic state.[17] The quantity Z_{ion} of Eq. (3) was calculated by using the relation

$$Z_{ion} = -\frac{1}{2}(g_e\beta)^2 \sum_{p=1}^{n_A} \sum_{q=1}^{n_D} c_p^2 d_q^2 \frac{r_{pq}^2 - 3z_{pq}^2}{r_{pq}^5} \tag{4}$$

where β is the electron Bohr magneton, g_e the free electron g value and

d_q and c_p are the coefficients of the HOMO π molecular orbital of the donor and of the LUMO π orbital of the acceptor, which are spread over n_D and n_A atomic centers, respectively. The distance vector r_{pq} connects atom p of the acceptor with atom q of the donor and z_{pq} indicates its z component. Application of Eq. (3) gives the value of $\chi_{CT} = 0.46$ for the degree of the CT character. We point out that the other two dipolar components X and Y have values lower and higher, respectively, than those expected according to this value of χ_{CT}. This fact has been already noted in other cases[18] and it was ascribed to the inadequacy of the triplet wavefunction $^3\psi(1,2)$ of Eq. (2) for a thorough description of the CT triplet state.

The most striking feature presented by the X and Z principal components of the dipolar tensor is that they increase in absolute value when the temperature is raised. This behavior is opposite to that reported for most of the other CT complexes.[4,6,8]

Vyas and Ponte Goncalves[4] proposed that the temperature dependence of the resonance fields observed in anthracene-TCNB crystals, may arise from the mixing of the lower lying triplet state $^3\psi_a$ with a thermally accessible triplet state of higher energy $^3\psi_b$ having a different charge-transfer character and hence different ZFS parameters. This model was shown to give the following equation for the change Δ_μ of the resonance field separation at the crystal orientation μ

$$\Delta_\mu(T) = \Delta_\mu^a + \delta_\mu e^{-\epsilon/KT}/(1 + e^{-\epsilon/KT}) \tag{5}$$

where ϵ is the energy separation between the two states, Δ_μ^a the splitting for the state a and $\delta_\mu = \Delta_\mu^b - \Delta_\mu^a$.

By fitting the experimental values of $\Delta_\mu(T)$ with Eq. (5), a value of $\epsilon = 589 \pm 54$ cm^{-1} was obtained for anthracene-TCNB[4] and $\epsilon = 150$ cm^{-1} for the CT complex of naphthalene with tetrachlorophtalic anydride.[6] Moreover, in both cases when H is parallel to z the values of δ that fit the experimental data were found to be negative which implies a lower dipolar interaction and a larger CT character of the upper lying triplet state. It was suggested that the naphthalene-TCPA system is best described as an excitation jumping between a localized state and a thermally accessible higher delocalized state.[6]

If the same arguments are applied to the B-TCNB case, the least squares fit of the experimental values of the splitting reported in Figure 4 by means of Eq. (5) gives $\epsilon = 422 \pm 30$ cm^{-1} and $\delta_x = 390 \pm 40$ (Gauss) which corresponds to having the higher triplet state with a lower charge-transfer character.

As mentioned above, an alternative explanation of the temperature

dependence of the dipolar splitting was provided by Ziegler and Karl[8] who suggested that the change in the values of the zero-field splitting parameters D and E could originate from a temperature dependent admixture of the CT character of the observed triplet $^3\psi_a$ as a result of the variation of the lattice constraints of the crystal without the need of assuming the presence of a second thermally populated triplet state.

The charge transfer character defined through Eq. (3) is determined by the matrix element t of the electronic Hamiltonian between the two wavefunctions $^3\psi_{ion}$ and $^3\psi_{loc}$, and by the energy separation $\Delta = E_{ion} - E_{loc}$ between the fully ionic and the completely localized triplet states.

In terms of the ratio (Δ/t) the charge transfer character χ_{CT} can be expressed as[19]

$$\chi_{CT} = \left\{2 + \frac{1}{2}\left(\frac{\Delta}{t}\right)^2 + \left(\frac{\Delta}{t}\right)\left[\frac{1}{4}\left(\frac{\Delta}{t}\right)^2 + 1\right]^{1/2}\right\}^{-1} \tag{6}$$

The above equation shows that in the limit of a very large value of Δ/t, $\chi_{CT} = 0$ and the low lying triplet state is fully neutral (localized), instead when the ratio Δ/t becomes close to zero, $\chi_{CT} = 0.5$ and there is an equal admixture of neutral and ionic states. The first situation is approached by the triplet state of A-TCNB, where the zero-field splitting parameters reflect those of the pure anthracene triplet, while the second limit is attained by B-TCNB whose triplet state has ZFS parameters much smaller than those of the neutral state (localized on TCNB) and the calculated CT character is about 0.5.

Eq. (6) shows that the temperature dependence of χ_{CT} is determined by the variation of the ratio Δ/t. Both Δ and t are expected to change with temperature because both depend on the relative position and distance between donor and acceptor molecules. It has been observed that in CT complexes with alternate stacks there is a general increase of the donor-acceptor interplanar distance as the temperature is raised.

This produces two effects: first, the energy of the ionic state shifts upwards since the stabilization due to the Coulomb attraction of the two opposite charges is reduced; second, the integral t which depends on the overlap of the two wavefunctions, decreases. Both effects cause a decrease of the CT character χ_{CT} with increasing temperature as it occurs for B-TCNB.

A quantitative analysis of the ZFS parameters in terms of the variation of χ_{CT} with temperature according to Eq. (6) cannot be performed because we do not know the analytical function of Δ/t over T.

Nevertheless, in the limit of $\Delta/t \ll 1$ and χ_{CT} close to 0.5, which is

the case for B-TCNB, we can write Eq. (6) in a simpler form by expanding in power series the square root term and we obtain

$$\chi_{CT} = \left\{2 + \frac{\Delta}{t} + \frac{1}{2}\left(\frac{\Delta}{t}\right)^2\right\}^{-1} \tag{7}$$

by considering terms up to the second order.

In this approximation Eq. (7) can be considered as a power expansion truncated at the second term of the function

$$\chi_{CT} \approx (1 + e^{\Delta/t})^{-1}$$

A comparison of this relation with Eq. (5) would suggest Δ/t proportional to T^{-1} for values of Δ/t close to zero if the model of Ref. 4 were appropriate.

In the case of A-TCNB, where the opposite trend is observed, we know that there is a librational motion of the anthracene molecules that changes their orientation with respect to the TCNB molecules.[20,21] Since the librational amplitude depends on the temperature, there may be an increase of the overlap and consequently of t if the anthracene resides longer at an orientation corresponding to the perfect alignment of its long axis with the long axis of TCNB.

The donor-acceptor orientation in CT crystals is determined by a compromise between the tendency to maximize the CT interaction, and the crystal packing requirements. Therefore a different behavior is expected if the A-TCNB complex is placed in a different lattice.

We have prepared a sample of B-TCNB doped with anthracene. Since the anthracene-TCNB triplet has an energy lower than that of the B-TCNB complex, the triplet exciton becomes trapped on a A-TCNB complex. As expected by the above model we observed an opposite trend of the temperature dependence of the zero field splitting of the A-TCNB triplet which increases with a rise of temperature, similar to the behavior of the B-TCNB host triplet. We should stress that this behavior is not expected on the basis of the other model.[4]

Another system where the donor molecule is known to undergo a large amplitude libration is naphthalene-TCNB. Here, however, the librational motion takes place inside a double minimum potential well and the π overlap decreases with increasing temperature.[7] Thus the temperature coefficient of the CT character is negative like the one observed in the B-TCNB system.

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