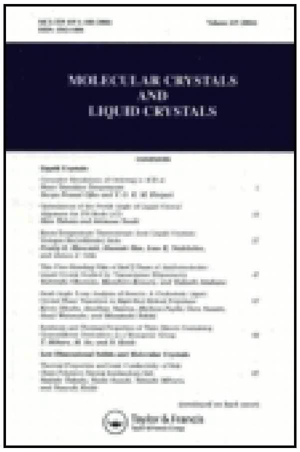

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

Crystal Structure of the 1:1 CT Complex of Biphenylene with 1,2,4,5-Tetracyanobenzene and EPR of Photoexcited Triplet Excitions

G. Agostini [a], C. Corvaja [a], G. Giacometti [a], L. Pasimeni [a], D. A. Clemente [b] & G. Bandoli [c]
[a] Department of Physical Chemistry, University of Padova, 35131, Padova, Italy
[b] Department of General and Inorganic Chemistry, University of Padova, 35131, Padova, Italy
[c] Department of Pharmaceutical Sciences, University of Padova, 35131, Padova, Italy

To cite this article: G. Agostini, C. Corvaja, G. Giacometti, L. Pasimeni, D. A. Clemente & G. Bandoli (1986): Crystal Structure of the 1:1 CT Complex of Biphenylene with 1,2,4,5-Tetracyanobenzene and EPR of Photoexcited Triplet Excitions, Molecular Crystals and Liquid Crystals, 141:1-2, 165-178

To link to this article: http://dx.doi.org/10.1080/00268948608080207

Mol. Cryst. Liq. Cryst., 1986, Vol. 141, pp. 165–178
0026-8941/86/1412-0165/$20.00/0

Printed in the United States of America

Crystal Structure of the 1:1 CT Complex of Biphenylene with 1,2,4,5-Tetracyanobenzene and EPR of Photoexcited Triplet Excitons

G. AGOSTINI, C. CORVAJA, G. GIACOMETTI, L. PASIMENI

Department of Physical Chemistry, University of Padova 35131 Padova, Italy

and

D. A. CLEMENTE

Department of General and Inorganic Chemistry, University of Padova, 35131 Padova, Italy

and

G. BANDOLI

Department of Pharmaceutical Sciences, University of Padova 35131 Padova, Italy

(*Received May 19, 1986*)

The crystal structure of Biphenylene and 1,2,4,5-Tetracyanobenzene (1:1) charge-transfer (CT) complex has been determined at room temperature. The crystals belong to the monoclinic system with space group $P2_1/c$, $a = 7.583(4)$ Å, $b = 7.264(5)$ Å, $c = 15.217(8)$ Å, $\beta = 90.00(8)°$ with two translationally inequivalent complexes per unit cell. EPR spectra of photoexcited triplet excitons have been recorded. They consist of a single pair of lines, the triplet exciton ZFS tensor arising from the average of tensors of the two inequivalent sites because of fast jumping of the exciton between them. ZFS parameters of the excited sites $X = \pm 1306 \pm 5$ MHz, $Y = \pm 1087 \pm 5$ MHz, $Z = \mp 2393 \pm 5$ MHz have been obtained and attributed to local excitation residing mainly on the Biphenylene molecule.

INTRODUCTION

Molecular crystals of weak charge-transfer (CT) complexes have received considerable attention in the last decade. These materials are built up of stacks of alternating donor and acceptor molecules with the molecular planes mutually parallel resulting in quasi one-dimensional structures with very anisotropic interactions. A great deal of efforts is presently devoted to an understanding of their interesting energy and charge transport properties.[1]

Weak CT complexes are characterized by having an almost neutral ground state while in their lowest excited singlet states they contain almost fully ionic contributions. However the lowest excited triplet states in these complexes may have different ionic character depending on the separation of the donor (or acceptor) triplet levels from the CT energy levels.

Triplet states are generated by optical excitation into the singlet manifold followed by intersystem-crossing (ISC). They are mobile excitations (excitons) and the features of their energy migration like anisotropy in the exciton diffusion are strongly dependent on the anisotropy of the intermolecular potential in the crystal.

EPR spectroscopy is a powerful tool for studying exciton dynamics in crystals where motion critically depends on the crystal structure. Frequently EPR spectra (CW and time-resolved) of crystals give direct information about the rate of diffusion of the exciton from one site to another in the crystal.

A precise determination of the position of the molecules in the crystal as obtained by the X-ray structure is the necessary requisite to study quantitatively the exciton motion. In donor-acceptor mixed stack crystals the knowledge of the crystal structure is particularly advisable in that a pair of molecules (donor and acceptor) is allowed to share the triplet excitation.

In this paper we present the X-ray structure determination of the Biphenylene (BP)-1,2,4,5-Tetracyanobenzene (TCNB) (1:1) CT crystal along with some EPR results of its photoexcited triplet excitons. We report the ZFS tensor of the CT complex typical of an almost neutral triplet state which has been attributed to a triplet excitation mainly localized on the donor molecule.

As we have shown in other CT complexes of hydrocarbons with TCNB, the latter molecule is responsible for ISC from the CT excited singlet state while the triplet can reside almost completely on the donor.[2] This feature can be conveniently exploited to populate the lowest neutral excited triplet states in cases like that of Biphenylene where optical pumping into the singlet excited states manifold with conversion into the lowest triplet state by ISC is highly inefficient.[3]

EXPERIMENTAL

Biphenylene and TCNB were prepared as described in the literature;[4] they were purified by repeated crystallizations and vacuum sublimed.

The crystals were grown by slow evaporation of spectrophotometric grade acetone (Merck UVASOL) solution. They presented well developed (001) and $(00\bar{1})$ faces.

X-ray diffraction intensities were collected with a Philips PW 1100 diffractometer, graphite-monochromatic Mo-Kα radiation ($\lambda = 0.7107$ Å). The stability of the instrument was monitored by measuring three standard reflections at intervals of 2h. Variations in the intensities were on the average 4%. The cell parameters at room temperature were determined by a least-squares refinement of the setting angle of 25 reflections ($18° \leq \theta \leq 22°$). The intensities were corrected for Lorentz and polarization factors, but no absorption ($\mu = 0.5$ cm^{-1}) neither extinction corrections were applied. Crystallographic and data collection characteristics, data processing and refinement procedure are given in Table 1. The positional and thermal parameters obtained from the refinement are given in Table 2, while bond lengths and angles are listed in Table 3.

The calculations were performed on a CDC/CYBER'76 computer (Centro Calcolo Elettronico Interuniversitario Italia Nord-Orientale, Casalecchio-Bologna).

A list of observed and calculated structure factors may be obtained from the authors.

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). A $CuSO_4 \cdot 5H_2O$ (50 g/l) solution was used as filter with transmission wavelength range $350 < \lambda < 600$ nm.

RESULTS

1. X-ray structure

In the highly coloured (ruby) complex the constituent molecules, which are planar, are stacked alternatively in infinite columns along the *a*-axis, as shown in Figure 1. The interplanar spacing is 3.53 Å. The mixed stacks are familiar in the series of charge-transfer complexes containing TCNB as an electron acceptor.[5] The dimensions of the TCNB molecule are the same as those observed in the uncomplexed molecule[6] and in other electron donor-acceptor complexes.[5] Also the geometry of the Biphenylene[7] is the same as that in the pure biphenylene crystal. The atomic separations of N1 . . . H4 and N2 . . . H4 (2.84 and 2.88 Å) are close to the normal van der Waals separations (Table 4) and parallel to those in similar 1:1 molecular

TABLE I

Data collection, data processing and refinement procedure.

mol formula; mol wt	$C_{12}H_8 \cdot C_{10}H_2N_4$; 330.1
crystal dimensions, mm	0.20 × 0.32 × 0.56
space group; molecules/cell (Z)	$P2_1/c$; 2
cell dimensions	$a = 7.583(4)$ Å $b = 7.264(5)$ $c = 15.217(8)$ $\beta = 90.000(8)^\circ$ $V = 838.2$ Å^3
scanning mode	$\omega/2\theta$
scanning interval in 2θ	$1.4 + 0.3 \tan\theta$
scanning speed in ω	2.4°/min
number of measurements	3409 (up to $\theta = 30^\circ$)
agreement between equivalent reflections $\Sigma\langle\lvert I - I_m\rvert\rangle/\Sigma I_m$	0.058
number of independent reflections	2157
$\sigma(I) = (\sigma^2_{\text{counting}} + p^2I^2)^{1/2}$	$p = 0.04$
intensity requirements	$I > 3\sigma(I)$
number of reflections for structure determination and least-squares input (NO)	1400
phase determination with	MULTAN[a]
refinement, carried on F_{ob}, with	LINEX[b]
weights	$w = \sigma^{-2}(F^2_{\text{obs}})$
temperature factors	anisotropic for non—H, isotropic for H atoms
form factors	refs. *c* and *d*
$R(F) = \Sigma\lvert\lvert F_{\text{obs}}\rvert - k\lvert F_{\text{calc}}\rvert\rvert/\Sigma\lvert F_{\text{obs}}\rvert$	0.056
$R(F)$ for (I) omitting the 011, 202^{-}, 211 reflections suffering for extinction	0.048
$S(F^2) = [\Sigma w(\lvert F_{\text{obs}}\rvert - k\lvert F_{\text{calc}}\rvert)^2/(\text{NO} - \text{NV})]^{1/2}$	2.5 (NV = 138)

[a] G. Germain, P. Main and M. Woolfson, *Acta Cryst.*, **A27**, 368 (1971).

[b] P. Becker and P. Coppens, *Acta Cryst.*, **A31**, 417 (1975).

[c] "International Tables for X-ray Crystallography," Vol. IV, Kynoch Press, Birmingham, England, 1974.

[d] R. F. Stewart, E. R. Davidson and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965).

complexes of TCNB.[5] The component molecules are stacked in linear arrays with the molecular planes being nearly parallel and making an angle of 7.6° with each other and the shortest contact between atoms of different molecules in the stack is C5—C11 (3.37 Å). The relative orientation of the component molecules within the unit cell is shown in Figure 2: the TCNB molecule is symmetrically placed with respect to the two aromatic rings of the donor moiety. The anisotropic thermal motion factors have been analyzed in terms of the vibration of translation (**T**) and libration (**L**), using the approach described by Schomaker and Trueblood[8] and treating each constituent as though

TABLE II

Fractional atomic coordinates with esd's in parentheses and thermal parameters ($\times 10^2$).*

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C1	.4463(2)	.1027(3)	−.0389(1)	3.7	4.8	3.8	−0.5	0.8	−0.1
C2	.4876(2)	−.0861(3)	−.0540(1)	3.7	4.9	3.6	−0.6	0.8	−0.3
C3	.4567(3)	−.1704(3)	−.1326(1)	4.9	6.0	4.3	−0.6	0.9	−0.9
C4	.3817(3)	−.0576(4)	−.1984(1)	5.3	8.3	3.7	−0.9	0.6	−0.5
C5	.3409(3)	.1239(4)	−.1839(1)	4.5	8.0	4.1	−0.4	0.4	1.5
C6	.3727(3)	.2116(4)	−.1020(1)	4.6	5.3	5.3	−0.2	0.9	0.9
C7	.0249(2)	−.1426(3)	−.0605(1)	3.9	4.0	3.8	−0.5	0.5	−0.4
C8	.0746(2)	−.1654(3)	.0265(1)	3.5	3.7	3.9	−0.4	0.3	0.2
C9	.1505(3)	−.3381(3)	.0538(1)	4.9	4.5	4.5	−0.3	−0.4	0.0
C10	.0498(2)	−.0223(3)	.0875(1)	3.6	4.3	3.3	−0.7	0.2	0.2
C11	.0978(3)	−.0465(3)	.1785(1)	4.8	4.9	4.2	−0.1	−0.1	0.0
N1	.2100(3)	−.4753(3)	.0751(1)	7.8	5.1	7.9	0.6	−1.5	0.5
N2	.1332(3)	−.0629(3)	.2510(1)	8.3	7.9	4.3	0.5	−0.9	0.4
H3	.489(3)	−.303(3)	−.146(1)	7.5					
H4	.358(3)	−.118(3)	−.259(2)	8.2					
H5	.286(3)	.195(3)	−.232(1)	6.1					
H6	.342(2)	.340(3)	−.093(1)	5.4					
H7	.046(2)	−.239(3)	−.105(1)	4.5					

*Anisotropic thermal parameters of the form $\exp(-2\pi^2\Sigma_i\Sigma_j U_{ij}h_i a_i^* h_j a_j^*)$.

TABLE III

Bond lengths (Å), before and after libration correction and angles (°) with esd's in parentheses.*

in biphenylene[a]			in TCNB[b]		
C1—C2	1.425(6)	1.431	C8—C9	1.441(6)	1.446
C1—C2′	1.505(5)	1.509	C8—C10	1.406(6)	1.413
C2—C3	1.364(5)	1.369	C9—N1	1.141(6)	1.145
C3—C4	1.413(6)	1.417	C8—C7	1.386(5)	1.391
C4—C5	1.372(8)	1.378	C7—C10′	1.387(6)	1.391
C5—C6	1.420(6)	1.425	C10—C11	1.442(5)	1.447
C6—C1	1.364(6)	1.368	C11—N2	1.142(5)	1.145
C3—H3	1.01(4)		C7—H7	0.99(4)	
C4—H4	1.04(5)				
C5—H5	0.99(4)		C7—C8—C10	120.4(4)	
C6—H6	0.97(4)		C8—C7—C10′	119.8(4)	
			C8—C10—C7′	119.8(3)	
C2′—C1—C2	90.1(3)		C9—C8—C10	120.4(3)	
C1—C2—C1′	89.9(3)		C7—C8—C9	119.2(3)	
C6—C1—C2	122.3(3)		C8—C9—N1	179.6(4)	
C1—C2—C3	122.4(3)		C11—C10—C7′	119.5(3)	
C2—C3—C4	115.5(4)		C8—C10—C11	120.6(4)	
C3—C4—C5	122.3(3)		C10—C11—N2	178.5(5)	
C4—C5—C6	122.3(4)		C8—C7—H7	122(2)	
C5—C6—C1	115.3(5)		H7—C7—C10	118(2)	
C—C—H mean	121(2)				

[a] Apostrophe denotes at $1-x, -y, -z$ [b] Apostrophe denotes at $-x, -y, -z$

*Taking into account the accuracy of cell dimensions.

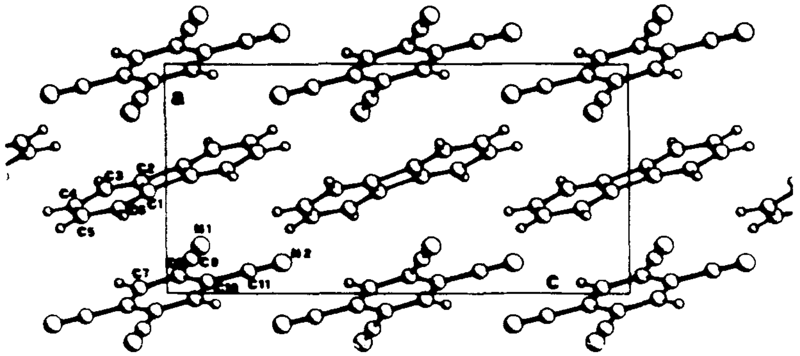

FIGURE 1 Perspective view of the complex along *b*-axis.

it were a separate rigid body (Table 5). The values of $\{\Sigma_{ij}[U_{ij}(\text{obs}) - U_{ij}(\text{calc})]^2/(n-s)\}^{1/2}$ (n is the number of U_{ij} terms and s the number of rigid-body parameters) were 0.0017 for the Biphenylene and 0.0030 for TCNB, compared with the corresponding $\sigma(U_{ij})$ (mean) values of 0.0020 and 0.0035. The rigid-body approximation therefore gives a reasonable fit to the data. The most significant libration for TCNB 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 (0.007 Å) for libration has to

TABLE IV

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

N1————H4^{I} 2.84;	C9—N1———H4^{I} 102°;	C4—H4———N1^{I} 139°
N2————H4^{I} 2.88;	C11—N2———H4^{I} 100°;	C4—H4———N2^{I} 113°
	N1—H4^{I}———N2 90°	
N2————H7^{I} 2.70;		
N1————H7^{II} 2.88		

Atomic parameters obtained from those in Table 2 by following transformation:
I) $x, -1/2-y, 1/2+z$ II) $-x, -1-y, -z$

Plane	*P*	*Q*	*R*	*S*
(1) benzene: (C7, C8, C10)	6.896	2.588	−3.264	0.000
[C9 −.01;C11 −.03;N1 −.03;N2 −.06; H4 0.04]				
(2) biphenylene: (C1, C2, C3, C4, C5, C6)	6.933	1.904	−4.698	3.466
[H3 0.03;H4 0.01;H5 −.02;H6 −.01				

Dihedral angle between (1) and (2): 7.6°

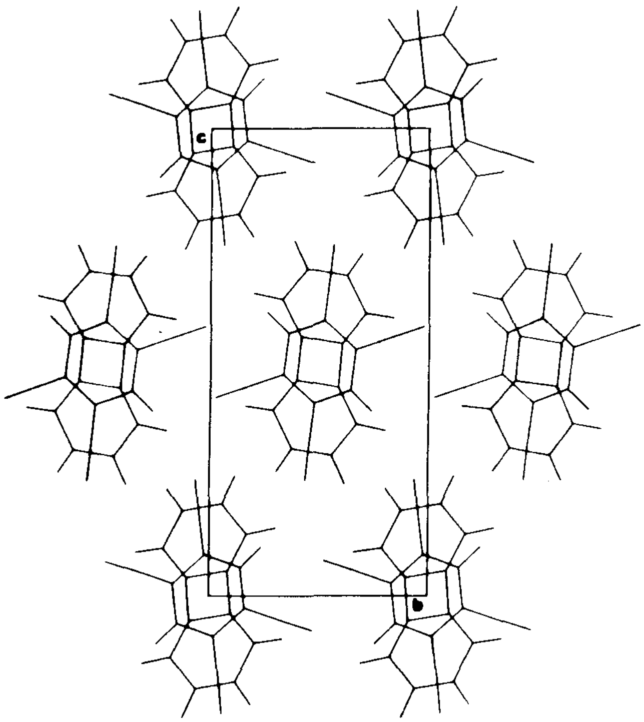

FIGURE 2 The mode of overlapping of the component molecules in the crystal viewed along *a*-axis.

be applied to the C8—C10 distance, while the other corrections are almost uniform and average 0.004 Å, or about 0.5 esd. As it appears from Table 5, for Biphenylene the translation motion is rather isotropic, being slightly smaller normal to the molecular plane than in the plane; the ω_1 and ω_2 librations are comparable and the corrections for rigid-body libration are uniform and average 0.005 Å. Moreover, the dominant motion present in the uncomplexed unities[6,7] retains also in the molecular complex.

2. EPR spectra

Illumination with visible light of the BP-TCNB crystal gives rise to two EPR signals typical of triplet excitons described by the spin Hamiltonian

$$H = g\beta\overline{B}_0\cdot\overline{S} - X_e S_x^2 - Y_e S_y^2 - Z_e S_z^2 \qquad (1)$$

TABLE V

Analysis of rigid-body thermal motion. Eigenvalues and eigenvectors of L (deg^2) and T matrix (Å^2 × 10^4) relative to the inertial axes.*

Principal axes		Direction cosines		
(i) TCNB				
(a) *L*				
	26.6	0.1593	−.0039	−.9872
	9.1	0.4406	−.8946	0.0746
	6.0	−.8835	−.4468	−.1407
(b) *T*				
	429	0.1311	0.4662	−.8749
	367	0.0695	−.8847	−.4609
	200	−.9889	−.0004	−.1484
(ii) biphenylene				
(a) *L*				
	15.2	0.5418	0.1461	−.8277
	12.2	0.8388	−.0310	0.5435
	4.4	0.0537	−.9888	−.1393
(b) *T*				
	485	0.1995	0.6914	−.6945
	414	0.3315	−.7145	−.6162
	250	−.9222	−.1073	−.3717

*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 centres of libration necessarily coinciding with the inversion centres.

written in the principal axes system of the fine structure tensor. X_e, Y_e, Z_e are the principal components of the traceless electron dipolar tensor.

The two EPR lines appear with opposite phases because one corresponds to absorption of microwave radiation while the other corresponds to emission. This is a consequence of the optical spin polarization (OEP)[9] that is generated at the birth of the triplet by intersystem-crossing from the excited singlet states manifold. 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 information on the ISC process and on the energy migration from the exciton to a trap is described elsewhere.[10]

EPR measurements have been performed by rotating the magnetic field B_0 in the *bc* and *ca* crystallographic planes and they are reported in Figure 3. In the *ab* plane signals are too weak to be detected. The

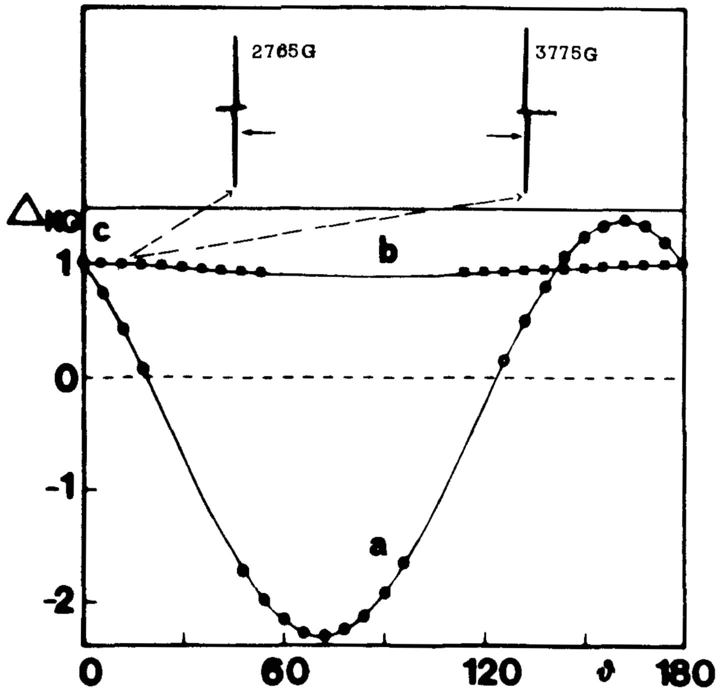

FIGURE 3 EPR spectrum of triplet exciton in the BP-TCNB crystal detected at 250K with B_0 that lies in the bc plane and angular dependence of the fine structure splitting when B_0 is rotated in the bc and ca crystallographic planes.

angular variation of the fine structure splitting of the EPR lines have been fitted by the equation

$$\Delta(\vartheta) = D_{ii} \cos^2\vartheta + D_{jj} \sin^2\vartheta - 2\, D_{ij} \sin\vartheta\cos\vartheta \qquad (2)$$

where $D_{ij}/3$ are the elements of the fine structure tensor. The indices i and j refer to the particular plane (*ab*, *bc*, *ca*) in which the magnetic field is rotated. Diagonalization of the tensor gives the principal values and the principal direction of the electron-electron dipolar interaction which are reported in Table 6.

DISCUSSION

There are two translationally unequivalent sites A and B in the unit cell where both donor and acceptor molecules are differently ori-

TABLE VI

ZFS tensor of the triplet exciton in the BP-TCNB CT crystal

Tensor			Eigenvalues	Eigenvectors		
				a	*b*	*c*
−1796	0	1051	$X = 1303$	0.3210	0	0.9471
	849	0	$Y = 849$	0	1	0
		947	$Z = -2152$	0.9471	0	−0.3210

a) The values are given in MHz.
b) The eigenvectors refer to the crystallographic axes a, b, c.

ented. The direction cosines of the molecular symmetry axes of the donor and acceptor molecules with respect to the *a*, *b*, *c* frame are reported in Table 7. The angles formed by the corresponding molecular axes of the Biphenylene and TCNB molecules at one site are: $(z_{\mathrm{BP}}, z_{\mathrm{TCNB}}) = 8.07°$, $(x_{\mathrm{BP}}, x_{\mathrm{TCNB}}) = 31.33°$, $(y_{\mathrm{BP}}, y_{\mathrm{TCNB}}) = 32.01°$. The molecular planes of BP and TCNB are nearly parallel while their long in-plane axes of the molecules are rotated one to other by an angle of about 30°. This fact gives rise to important features in the angular dependence of spin polarization of the exciton and it will be discussed in detail elsewhere.[10] The angles formed by the BP symmetry axes of the two A and B unequivalent crystal sites are

$$(z_{\mathrm{BP}}^{\mathrm{A}}, z_{\mathrm{BP}}^{\mathrm{B}}) = 149.6°, \ (x_{\mathrm{BP}}^{\mathrm{A}}, x_{\mathrm{BP}}^{\mathrm{B}}) = 8.94°, \ (y_{\mathrm{BP}}^{\mathrm{A}}, y_{\mathrm{BP}}^{\mathrm{B}}) = 148.27°.$$

According to the crystal structure one expects that the EPR spectrum of triplet excitons in the BP-TCNB crystal consists either of two

TABLE VII

Direction cosines of the molecular symmetry axes of Biphenylene and TCNB in the two crystal sites with respect the crystallographic axes.

Molecular	Axis	*a*	*b*	*c*
Biphenylene	x	0.33894	∓0.07797	0.93757
	y	0.22061	∓0.96192	−0.16137
	z	±0.91431	0.26216	∓0.30872
TCNB	x	0.38702	∓0.57144	0.72365
	y	0.13463	∓0.74011	−0.65887
	z	±0.91270	0.35477	∓0.20275

The x axis is along the long in-plane molecular axis, z is normal to the molecular plane and the third is perpendicular to these. The upper and lower choice of signs refers to sites A and B, respectively.

pairs of lines or of a single one, the latter occurring if the interaction between the two complexes in the unit cell is larger than the difference of their electron dipolar splittings $\Delta_A(\vartheta) - \Delta_B(\vartheta)$. We have detected EPR spectra composed by a single pair of lines at any orientation of the magnetic field B_0 with respect to the crystal indicating that the exciton diffuses very rapidly from A to B sites whatsoever the value of $\Delta_A(\vartheta) - \Delta_B(\vartheta)$.

Since $\Delta_A(\vartheta) - \Delta_B(\vartheta)$ is comparable with the absolute values of the ZFS parameters we can safely assume that the exciton moves in the regime of strong intersite coupling, i.e., the lattice interaction between the two nearest neighbours A and B sites is larger than the triplet ZFS parameters. According to the Sternlicht and McConnell theory,[11] in this limit the exciton Hamiltonian is the average of the two sites molecular Hamiltonians

$$H = 1/2\,(H_A + H_B) \tag{3}$$

The EPR spectrum is composed by a single pair of lines. The ZFS parameters of the exciton that appear in eq. (1) can be expressed in terms of those of the sites[12]

$$\begin{aligned} X_e &= l_x^2 X + l_y^2 Y + l_z^2 Z \\ Y_e &= m_x^2 X + m_y^2 Y + m_z^2 Z \\ Z_e &= n_x^2 X + n_y^2 Y + n_z^2 Z \end{aligned} \tag{4}$$

where X, Y and Z are the ZFS parameters of triplet excitation when it is frozen at a site of the lattice and $l_i^2 = l_{iA}^2 = l_{iB}^2$, $m_i^2 = m_{iA}^2 = m_{iB}^2$,$n_i^2 = n_{iA}^2 = n_{iB}^2$. The l_{iA}, l_{iB}, m_{iA}, m_{iB}, n_{iA}, n_{iB} are the direction cosines of the angles between the principal magnetic axes of the individual sites and those of the exciton.

Application of eq. (4) allows one to extract the ZFS principal values of either the localized triplet or the exciton once the relative orientation of the two ZFS principal axes frames is known. In the case of the BP-TCNB crystal we have assumed that in the locally excited site the triplet excitation resides on the Biphenylene molecule. This assumption relies on the support of two facts: i) The large values of the ZFS parameters point to a triplet excitation almost neutral in character although recently it has been claimed that also triplets with practically complete charge separation could have large ZFS parameters;[13] ii) In the description of the triplet state of the BP-TCNB complex by the triplet wavefunction

$$ {}^3\psi_{\text{complex}} = a\ {}^3\psi(D^*A) + b\ {}^3\psi(DA^*) + c\ {}^3\psi(D^+A^-) $$

the local contribution ${}^3\psi(DA^*)$ from the TCNB molecule has been discarded since its level is higher in energy than the others.[15] The neglect of the acceptor contribution in ${}^3\psi_{\text{complex}}$ is indirectly supported by the fact that application of eq. (4) with the whole local contribution attributed to the TCNB molecule has given ZFS parameters inconsistent with those of TCNB in its lowest excited triplet state.[16]

Under the above assumption we have determined the ZFS parameters of the Biphenylene triplet by applying eq. (4). The squared direction cosines of eq. (4) can be cast in the matrix form with elements having values

$$ \begin{pmatrix} 0.9936 & 0.0062 & 0.0000 \\ 0.0058 & 0.9254 & 0.0687 \\ 0.0004 & 0.0683 & 0.9313 \end{pmatrix} $$

The values of the ZFIS parameters of the excited crystal site are: $X = \pm 1306 \pm 5$ MHz, $Y = \pm 1087 \pm 5$ MHz and $Z \mp 2393 \pm 5$ MHz, the x direction being along the long molecular axis, the z one is perpendicular to the molecular plane of Biphenylene and the y axis is perpendicular to these.

As a final remark, we emphasize that optical pumping into the singlet CT band of the BP-TCNB crystal followed by ISC conversion has produced a lower lying triplet state probably without CT character in very much the same manner as in the Anthracene-TCNB[17] and t-Stilbene-TCNB_2[18] crystals. This method of irradiating by light weak CT molecular crystals can be applied to populate neutral triplet states that cannot be generated directly, as result of the optical cycle inside their neutral states manifold.[19]

CONCLUSION

We have shown that the crystal structure of the BP-TCNB crystal consists of two inequivalent lattice sites per unit cell. In the BP-TCNB complex of each site the molecular in-plane symmetry axes of the donor are rotated by about 30 with respect to those of TCNB. We have found that triplet exciton moves rapidly from one site to another in the unit cell giving rise to a single averaged ZFS tensor. The ZFS parameters of the triplet species on the lattice site have been extracted under the assumption that triplet excitation resides mainly on the Biphenylene molecules.

Note added in the Proof: During printing of this work we became aware that the crystal and molecular structure of BP-TCNB was already determined by J. J. Stezowski, R. D. Stigler and N. Karl in J. Chem. Phys., **86**, 5162 (1986). They have described the structure as $P2_1/a$, while our atomic parameters are given in $P2_1/c$, but after the necessary changes one can see that the differences between atomic coordinates are always within the esd's, only the x of C(9) and y of C(5) differ by near two times the esd's. Although bond distances are more affected than bond angles, the agreement is excellent and always within one time the standard deviation, only our C1—C2 distance of Biphenylene 1.425(6) becomes 1.414 Å in the work of Stezowski et al. Then we conclude that the two structure determinations are exactly the same within the esd's.

Acknowledgment

This work was supported in part by the Italian National Research Council (CNR) through its "Centro di Studio sugli Stati Molecolari Radicalici ed Eccitati" and in part by the Ministero della Pubblica Istruzione.

References

1. D. Haarer and M. R., Philpott, in "Modern Problems in Condensed Matter Science, V. M. Agranovich and A. A. Maradudin Eds., North-Holland, Amsterdam, 1983, Vol. 4.
2. (a) L. Pasimeni, G. Guella and C. Corvaja, *Chem. Phys. Letters*, **84**, 466 (1981); (b) C. Corvaja and L. Pasimeni, *Chem. Phys. Letters*, **88**, 367 (1982).
3. R. M. Hochstrasser and R. D. McAlpine, *J. Chem. Phys.*, **44**, 3325 (1966).
4. F. M. Logullo, A. H. Seitz and L. Friedman, *Org. Syntheses*, **48**, 12 (1968).
5. (a) J. D. Wright, K. Yakuski and H. Kuroda, *Acta Cryst.*, **B34**, 1934 (1978); (b) M. C. Couldwell and K. Prout, J. C. S. Perkin II, 160 (1978); (c) C. K. Prout, T. Morley, I. J. Tickle and J. D. Wright, J. C. S. Perkin II, 523 (1973); (d) H. Tsuchiya, F. Marumo and Y. Saito, *Bull. Chem. Soc. Japan*, **40**, 1826 (1967); (e) Y. Ohashi, *Acta Cryst.*, **B29**, 2863 (1973); (f) H. Tsuchiya, F. Marumo and Y. Saito, *Acta Cryst.*, **B28**, 1935 (1972); (g) N. Miimura, Y. Ohashi and Y. Saito, *Bull. Chem. Soc. Japan*, **41**, 1815 (1968); (h) Y. Ohashi, H. Iwasaki and Y. Saito, *Bull. Chem. Soc. Japan*, **40**, 1789 (1967); (i) S. Kumakura, F. Iwasaki and Y. Saito, *Bull. Chem. Soc. Japan*, **40**, 1826 (1967); (l) L. Pasimeni, G. Guella, C. Corvaja, D. A. Clemente and M. Vicentini, *Mol. Cryst. Liquid Cryst.*, **91**, 25 (1983); (m) L. Pasimeni, C. Corvaja and D. A. Clemente, *Mol. Cryst. and Liquid Cryst.*, **104**, 231 (1984).
6. C. K. Prout and I. J. Tickle, J. C. S., Perkin II, 520 (1973).

7. T. C. W. Mak and J. Trotter, *J. Chem. Soc.* (1962). 1; J. K. Fawcett and J. Trotter, *Acta Cryst.*, **20**, 87 (1966).
8. V. Schömaker and K. N. Trueblood, *Acta Cryst.*, **B24**, 63 (1968).
9. K. H. Hausser and H. C. Wolf, *Advan. Magn. Reson.*, **8**, 85 (1976).
10. G. Agostini, C. Corvaja, G. Giacometti and L. Pasimeni, to be published.
11. H. Sternlicht and H. M. McConnell, *J. Chem. Phys.*, **35**, 1793 (1961).
12. R. H. Clarke, R. E. Connors, H. A. Frank and J. C. Hoch, *Chem. Phys. Letters*, **45**, 523 (1977).
13. F. C. Bos and J. Schmidt, *J. Chem. Phys.*, **84**, 584 (1986).
14. S. Iwata, J. Tanaka and S. Nagakura, *J. Chem. Phys.*, **47**, 2203 (1967).
15. D. F. Evans, *Opt. Anregung Org. Syst.* 586 (1966).
16. M. Yagi, N. Nishi, M. Kinoshita and S. Nagakura, *Mol. Phys.*, **35**, 1369 (1978).
17. A. M. Ponte Goncalves, *Chem. Phys.*, **19**, 397 (1977).
18. G. Agostini, C. Corvaja, G. Giacometti and L. Pasimeni, *Chem. Phys.*, **85**, 421 (1984).
19. M. Yagi, *Chem. Phys. Letters* **124**, 459 (1986).