ENDOR Spectra of 2-Methyl-Naphthalene-TCNB Triplet Trap in Naphthalene-TCNB Single Crystals

Anna Lisa Maniero, Antonio Toffoletti, and Carlo Corvaja
Department of Physical Chemistry, University of Padova, Padova (Italy)

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Naphthalene-TCNB charge transfer crystals doped with 2-methyl naphthalene illuminated by visible light give rise to triplet traps which have been identified by EPR and ENDOR spectroscopy as 2-methyl naphthalene-TCNB CT complexes in their first excited triplet state. The complete hyperfine tensors of all the 2-methyl naphthalene protons have been obtained by analysis of the variation of the ENDOR frequencies with the crystal orientation in the magnetic field. The structure of the CT complex, the spin distribution and the CT character are discussed.

Introduction

Aromatic hydrocarbons such as Naphthalene (N), when mixed with the electron acceptor 1,2,4,5 tetracyanobenzene (TCNB), form 1:1 charge transfer (CT) complexes in which the hydrocarbon acts as an electron donor. The ground state of such complexes is neutral while the first excited singlet state is ionic because of an almost complete transfer of one electron from the donor molecule to the acceptor one. The excitation to the CT state is responsible for the strong color of the well shaped crystals, of several mm^3 size, which crystallize easily from a solution of the two components. The crystal structure of these CT crystals usually consists of alternate stacks of donor and acceptor molecules with their molecular planes about parallel to each other and, in the case of N-TCNB, perpendicular to the stack axis.

By excitation to the CT band, followed by intersystem crossing, the first excited triplet excitonic band is populated, which has been extensively studied by analyzing its EPR spectrum consisting of narrow lines, being any hyperfine structure averaged out by the fast motion. The nature of this mobile excited triplet state, that is its ionic character depends on several factors as the relative energies of the zero order triplet states localized on the acceptor and on the donor and the CT triplet energy. Another relevant factor is the relative orientation of the partner molecules in the crystal lattice.

Information about the structure and electronic distribution of the complex in the excited triplet state is obtained from the zero field splitting (ZFS) parameters which characterize the electron-electron spin dipolar interaction. The magnitude of these parameters reflects the degree of charge transfer in the triplet state because, when the unpaired electrons are located one in the donor and the other on the acceptor, the magnetic dipolar interaction is much reduced with respect to the case where both unpaired electron spins are localized on the same partner of the CT complex.

Thus in N-TCNB from the ratio of the measured zero field splitting parameter D to the corresponding value of the triplet state of an isolated naphthalene a CT degree of about 30% was determined [1, 2]. In N-TCNB crystals doped with different molecules, substituting the naphthalene in the crystal lattice, the EPR spectrum of trapped excitation is recorded which is characterized by inhomogeneously broadened lines. For the study of these trapped excited triplets, in addition to EPR we have used ENDOR spectroscopy which allows a much deeper insight into the structure and the electronic distribution through the determination of the proton hyperfine tensors [3, 4, 5].

In this paper we report an ENDOR investigation of excited triplet traps in single crystals of N-TCNB doped with 2-methyl naphthalene (2Me-N). These traps have much lower ZFS parameters than the N-TCNB complex, though isolated N and 2Me-N in their excited triplet states have similar ZFS parameters. 2Me-N is interesting in that, a difference with other investigated systems, it is not an alternant hydrocarbon because of the perturbing effect of the methyl group on the π system, and the spin distribu-

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Reprint requests to Carlo Corvaja, Department of Physical Chemistry, University of Padova, via Loredan, 2, I-35131 Padova (Italy).

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tion in the triplet single occupied orbitals should be different. For this reason the transfer of one electron or a fraction of it from the donor HOMO to the acceptor LUMO is expected to produce a redistribution of the total spin density.

Experimental

2-methyl naphthalene is already present as an impurity in naphthalene and it concentrates by zone refining process at one end of the sample tube [6]. The room temperature crystal structure of N-TCNB is monoclinic, space group C2/m with $a = 9.39$ Å, $b = 12.66$ Å, $c = 6.87$ Å, $\beta = 107.2°$, and $Z = 2$ [7]. The TCNB is placed on a symmetry center while the N molecules have their long in plane axes rotated by an angle of $\pm 18°$ with respect to the crystal axis a^*. The N molecules undergo a large amplitude libration about these potential minima positions, and they jump from a minimum to another one at a temperature dependent frequency [2].

At 62 K a phase transition occurs, driven by the freezing of the N motion.

The sample of N-TCNB doped with 2 Me-N consisted of a single crystal of approximate dimensions $(2 \times 3 \times 4)$ mm^3 attached to a quartz rod of a goniometer allowing for a rotation about an axis perpendicular to the Zeeman magnetic field direction.

The sample was illuminated by the light of a 500 W high pressure mercury lamp (OSRAM HBO 500).

The EPR and ENDOR spectra were recorded by a computer controlled Bruker ER 200 D X-band spectrometer whose microwave cavity was substituted by a cylindrical TE_{011} cavity provided with an optical access and a loop for rf irradiation. On Oxford ESR-900 helium flow cryostat was used to control the sample temperature.

Results

The EPR spectra of N-TCNB doped with 2 Me-N consist of two narrow (0.5 Gauss) and spin polarized lines due to triplet excitons together with a number of other lines whose relative intensity changes with the temperature. The spectra recorded at temperatures lower than 40 K are dominated by the presence of four pairs of strong EPR lines due to two triplet traps, each one present in the crystal lattice in two magnetically inequivalent sites, related by a twofold rotation about the symmetry axis of the monoclinic crystal lattice.

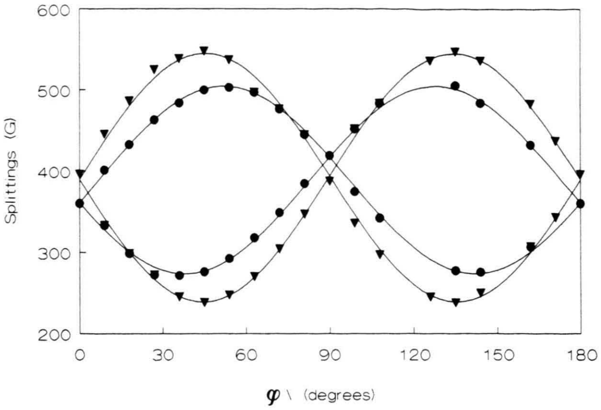

Fig. 1. Splittings of the EPR lines of the two triplet traps in N-TCNB crystal doped with 2 Me-N, measured at $T = 20$ K with the magnetic field in the $a^* b$ plane. Both traps are present in two different sites; triangles refer to the trap I for which the ENDOR spectra have been recorded.

The variation of the line splittings with the crystal orientation is described by the spin hamiltonian

$$\mathscr{H} = g \beta \mathbf{B}_0 \cdot \mathbf{S} + X S_x^2 + Y S_y^2 + Z S_z^2, \qquad (1)$$

the small anisotropy of the g tensor being neglected for our purposes.

The line splittings of the two traps, measured with the Zeeman magnetic field exploring the $a^* b$ $(a^* = b \wedge c)$ crystallographic plane, are shown in Figure 1. The principal values (X, Y, Z) and the principal directions (x, y, z) of the electron spin dipolar tensors with respect to the crystallographic axes are reported in Table 1.

The c direction is perpendicular to the molecular planes of TCNB and naphthalene as determined by the X-rays diffraction analysis [7]. The sign of the tensor components is assigned by taking a negative Z (as z is parallel to c, it is perpendicular to the molecular plane) as it usually occurs for the $\pi\pi^*$ excited triplet states. The above choice agrees with the spin polarization pattern observed in the EPR spectra of several donor-acceptor complexes [8].

The ENDOR spectra of the triplet trap indicated by I in Table 1 were recorded by saturating the $|0\rangle \rightarrow |1\rangle$ EPR transition of a single crystal site. They consist of seven lines at frequencies higher than the free proton frequency ν_0. By saturating the $|-1\rangle \rightarrow |0\rangle$ EPR transition, these lines appear at frequencies $\nu < \nu_0$, and an eighth line is recorded at $\nu > \nu_0$. This be-

Table 1. Principal values and principal directions of the electron dipolar tensor of the triplet traps in N-TCNB doped with 2 Me-N.

		Principal values (Gauss)	Direction cosines		
			a^*	b	c
Trap I	X	181.5	0.7010	−0.7132	−0.0002
	Y	80.0	−0.7117	−0.7017	−0.0345
	Z	−261.5	0.0325	0.0254	−0.9992
Trap II	X	168.2	0.6148	−0.7887	−0.0041
	Y	91.7	−0.7881	−0.6142	−0.0399
	Z	−259.9	0.0290	0.0278	−0.9992

haviour is what one expects for seven protons with a negative hyperfine coupling and a eight one having a positive coupling. Typical spectra are shown in Figure 2. Very similar spectra were obtained for the other trap but they were not analyzed in detail. Trap II is therefore to be assigned to the same species giving rise to Trap I, however present in a slightly different crystal site The ENDOR spectra were recorded by rotating the crystal in the Zeeman magnetic field exploring two perpendicular crystallographic planes, namely the $a^* b$ and the $a^* c$ planes. The ENDOR frequencies were fitted to the spin hamiltonian [9]

$$\mathscr{H}_{\mathrm{hf}} = \langle \mathbf{S} \rangle \cdot \sum_k \mathbf{A}_k \cdot \mathbf{I}_k - g_n \beta_n \mathbf{B}_0 \cdot \sum_k \mathbf{I}_k, \qquad (2)$$

where the sum is over all the protons. In (2) $\langle \mathbf{S} \rangle$ is the expectation value of the electron spin operator in the electron spin states diagonalizing the spin hamiltonian (1):

$$\mathscr{H} = \mathscr{H}_{\mathrm{Zeeman}} + \mathscr{H}_{\mathrm{ZFS}}. \qquad (3)$$

The best fit curves to the experimental data obtained with $\mathbf{B}_0$ in the $a^* b$ plane are reported in Figure 3. Similar fits are obtained when the Zeeman magnetic field explores the plane $a^* c$. The proton hyperfine tensors giving the best fit are reported in Table 2. The are referred to the x, y, z principal axes of the ZFS tensor.

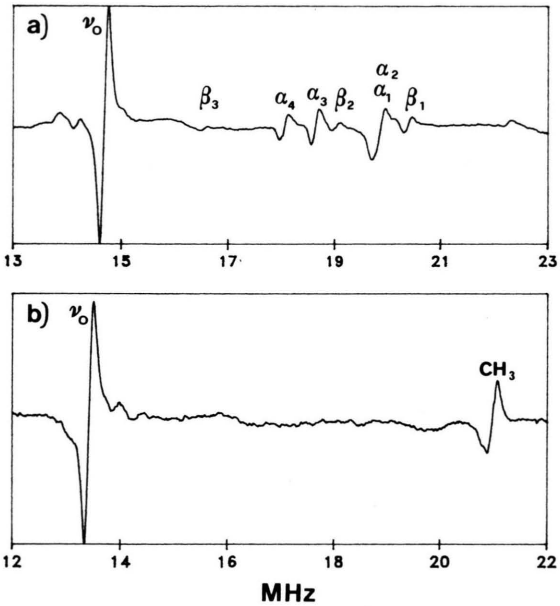

Fig. 2. ENDOR spectra of the triplet trap I recorded at $T = 20$ K with the magnetic field in the $a^* b$ plane at about 20° from b crystallographic axis. Spectra a) and b) have been recorded by saturating, respectively, the $|0\rangle \rightarrow |1\rangle$ and the $|-1\rangle \rightarrow |0\rangle$ EPR transitions. The assignment of the ENDOR lines to the 2 Me-N protons is shown. ν_0 is the free proton frequency.

Discussion

Proton Hyperfine Coupling Constants and Charge Transfer Character

N-TCNB crystals doped with different hydrocarbons give, by illumination in the CT band, the EPR spectra of the triplet state of the dopant molecule complexed with TCNB [10, 11]. The triplet states are characterized by ZFS parameters which are those of the isolated donor molecule triplet, reduced by an extent depending on the CT degree. In fact, in a triplet state with CT from the donor to the acceptor the magnetic dipolar interaction is reduced, the averaged distance between the two unpaired electrons localized each one on a different partner of the CT complex being increased.

A peculiar feature of the triplet traps present at low temperature in the illuminated 2 Me-N doped N-TCNB crystals is the low value of the zero field splitting parameters, indicating triplet species with a large CT character [10].

Table 3 shows for comparison the ZFS parameters of N [12] and 2 Me-N [13] in their first excited triplet state, and those of the triplet state of the CT complex N-TCNB [1]. The latter are reduced with respect to those of an isolated naphthalene molecule because of about 30% CT transfer to the TCNB acceptor. 2 Me-N has almost the same ZFS parameters of N; the dramatic decrease in the ZFS parameters of the CT complex by substitution of N with 2 Me-N is quite unex-

Table 2. Experimental hyperfine tensors of the 2 Me-N protons in the 2 Me-N-TCNB triplet state.

Proton	Isotropic value (MHz)	Anisotropic principal values (MHz)	Direction cosines x	y	z
α_1	−11.67	6.47	0.4061	0.9139	0.0000
		−6.46	0.9139	−0.4061	0.0000
		−0.01	0.0000	0.0000	1.0000
α_2	−11.47	6.27	0.3728	0.9279	0.0000
		−6.04	0.9279	−0.3728	0.0000
		−0.23	0.0000	0.0000	1.0000
α_3	−8.27	4.33	0.3700	0.9286	0.0269
		−4.11	0.9257	−0.3710	0.0737
		−0.22	−0.0784	0.0024	0.9969
α_4	−7.63	4.41	0.3587	0.9334	0.0000
		−3.94	0.9334	−0.3587	0.0000
		−0.47	0.0000	0.0000	1.0000
β_1	−3.77	3.12	0.7303	−0.6667	−0.1488
		−2.39	0.6725	0.7400	−0.0154
		−0.73	−0.1204	0.0888	−0.9888
β_2	−3.18	2.78	0.9997	0.0145	−0.0191
		−1.96	0.0156	−0.9980	0.0619
		−0.82	−0.0182	−0.0622	−0.9979
β_3	−1.30	1.70	0.9993	−0.0363	−0.0005
		−1.06	0.0362	0.9966	−0.0738
		−0.64	−0.0027	−0.0736	−0.9973
methyl	8.33	1.27	0.7227	−0.6906	−0.0263
		−0.93	0.6908	0.7230	−0.0016
		−0.34	−0.0201	0.0170	−0.9997

Table 3. ZFS parameters (Gauss).

Triplet species	X	Y	Z	Ref.
N	504	211	−715	[12]
2 Me-N	501	192	−693	[13]
N-TCNB	339	146	−485	[1]
Trap I	182	80	−262	

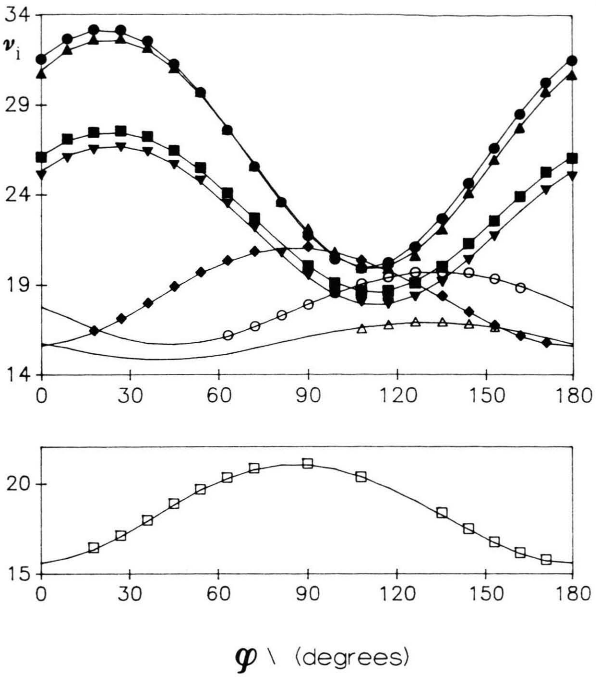

Fig. 3. ENDOR frequencies (MHz) of the 2 Me-N protons in the 2 Me-N-TCNB triplet trap with the magnetic field exploring the $a^* b$ crystallographic plane. The best-fit curves are calculated by (2) using the tensor elements reported in Table 2. Symbols refer to the α_1 (●), α_2 (▲), α_3 (■), α_4 (▼), β_1 (◆), β_2 (○), β_3 (△), and methyl (□) 2 Me-N protons.

pected. We note that another possible source of the reduction of ZFS parameters is a large amplitude molecular motion, which is allowed in this crystal in some cases [1].

The observed ENDOR spectra and the hyperfine tensors obtained from the angular variation of the ENDOR frequencies (see Table 2) are fully accounted for by the hyperfine coupling of the triplet unpaired electron spin with seven aromatic ring protons, having a negative isotropic hyperfine coupling, and with the methyl protons with a positive isotropic coupling, as it occurs in 2 Me-N. The methyl protons are magnetically equivalent due to the fast rotation of the methyl group about the single bond. It should be noted that the sign of the hyperfine coupling constant can be assigned once the signs of the ZFS tensor elements are known [9]. These considerations indicate that in the observed trap the triplet excitation resides to a large part on the 2 Me-N molecule.

Apart from the ZFS parameters, the CT character of the 2 Me-N-TCNB complex in its triplet state can be inferred also from the reduction of the hyperfine coupling of the donor protons due to the reduced spin density, and in particular from the isotropic hyperfine component. In fact, the isotropic coupling constant gives directly the spin density on the bonded carbon atom, and its value is not affected by the molecular motion while the anisotropic components of both ZFS and hyperfine tensors could be partially averaged out [3].

The assignment of the measured hyperfine tensors to the protons in the α positions, 1, 4, 5, and 8, can be made by considering that they have parallel principal directions; however an assignment to the individual α protons based only on the experimental data is not possible. With regard to the β protons, 3, 6, and 7, we note that two of them, 3 and 7, are expected to have hyperfine tensors with almost parallel principal directions. The principal directions of the remaining one, 6, should coincide with those of the methyl protons tensor, as it occurs indeed for the tensor we have indicated as β_1 in Table 2. It should be noted that the proton 6, whose tensor assignment is unique, has the largest isotropic hyperfine coupling among the β protons. For the assignment of other two tensors to protons, 3 and 7, the same considerations made above for the α protons hold.

The assignment could be done by comparing the measured isotropic couplings with those (a_i^{loc}) expected for a triplet state localized on the 2 Me-N, reduced according to the degree of charge transfer b^2 [10]:

$$a_i = a_i^{\mathrm{loc}}(1 - b^2/2)\,. \tag{4}$$

This procedure is correct only if the donor molecule is an alternant hydrocarbon. In fact, for these systems the pairing theorem applies, stating that the triplet spin density of the two monooccupied MOs is the same; therefore the transfer of the electron from the donor highest bonding orbital (HOMO) to the acceptor will decrease the spin density on the different carbon atoms in the same way, which corresponds to having a fraction of two triplet electrons on the donor molecule. Moreover, if the hyperfine couplings of the uncomplexed donor triplet state are not known, one can resort to the data more easily available regarding the radical anion or the radical cation, which are expected to have the same spin distribution as the triplet.

These considerations are not applicable to the 2 Me-N, where the methyl group perturbation removes the alternation and therefore the electron distribution in the HOMO and LUMO (the first antibonding orbital) becomes different. In this case the measured isotropic hyperfine couplings should be compared with those of a triplet state having one unpaired electron localized on the HOMO of 2 Me-N and the second one on a molecular orbital which is a linear combination of the LUMO of 2 Me-N and of the LUMO of TCNB. Equation (4) should be modified in the following way:

$$a_i = (1/2)\,a_i^{+} + (1/2)\,a_i^{-}\,(1 - b^2)\,, \tag{5}$$

where $a_i^{\pm}$ are the proton hyperfine couplings of the 2 Me-N anion and cation radical. Table 4 shows the proton hyperfine coupling constants of the 2 Me-N radical anion and cation. They were obtained from the calculated spin densities on the carbon atoms using the McConnell equation with $Q(H) = 72.2$ MHz [14]. For the methyl protons we used a $Q(\mathrm{CH_3}) = 110$ MHz [15, 16]. The MO calculations for the case of the anion radical give a rather good agreement with the experimental data [17, 18]. For the cation the latter are not available [2], although several other substituted methyl naphthalene radical cations have been prepared and studied by EPR [19, 20]. We note that in the cation radical, unlike the anion case, the β proton having the largest isotropic hyperfine coupling is that in the position opposite to the $\mathrm{CH_3}$ group, as we found for the excited triplet. For that reason we made the reasonable choice to assign also the other experimental tensors to the individual protons in such a way as to reflect a distribution similar to that found for the cation radical. In this way we have related the experimental isotropic couplings to the individual protons as shown in Table 4. Moreover, Table 5 shows the triplet proton hyperfine tensor elements as calculated from the spin densities obtained from the experimental isotropic couplings and the above assignment (details on the calculation will be reported later). The agreement with the experimental tensors is quite satisfactory.

Table 4. Calculated hyperfine coupling constants (MHz) of the anion and cation 2 Me-N radical protons and experimental h.c.c. of 2 Me-N-TCNB triplet trap protons.

Position	2 Me-N anion a_{iso}	2 Me-N cation a_{iso}	2 Me-N-TCNB triplet a_{iso}
1	−10.03	−17.27	−11.67
2 ($-\mathrm{CH_3}$)	4.91	10.90	8.33
3	−8.44	−1.63	−1.30
4	−13.47	−11.63	−8.27
5	−14.17	−10.88	−7.63
6	−3.60	−6.72	−3.77
7	−6.44	−3.27	−3.18
8	−12.51	−13.16	−11.47

By considering that in the CT complexes the charge transfer from the donor to the acceptor should take place from the donor HOMO, the experimental result

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[2] Some tentative experiments were performed without success with the aim to prepare the 2 Me-N radical cation and to measure its proton hyperfine coupling constants. 2 Me-N was allowed to react with $\mathrm{AlCl_3}$ in nitromethane; a broad EPR signal was obtained consisting of a single line without any hyperfine structure.

Table 5. Calculated dipolar hyperfine tensors of the 2 Me-N protons in the 2 Me-N-TCNB triplet state.

Proton	Anisotropic principal values (MHz)	Direction cosines		
		x	y	z
α_1	6.21	0.3553	0.9347	0.0000
	−5.81	0.9347	−0.3553	0.0000
	−0.40	0.0000	0.0000	1.0000
α_2	5.99	0.3980	0.9174	0.0000
	−5.67	0.9174	−0.3980	0.0000
	−0.32	0.0000	0.0000	1.0000
α_3	4.65	0.4077	0.9313	0.0000
	−4.29	0.9131	−0.4077	0.0000
	−0.36	0.0000	0.0000	1.0000
α_4	4.45	0.3465	0.9380	0.0000
	−3.90	0.9380	−0.3465	0.0000
	−0.55	0.0000	0.0000	1.0000
β_1	3.58	0.6737	−0.7390	0.0000
	−2.54	0.7390	0.6737	0.0000
	−1.04	0.0000	0.0000	1.0000
β_2	3.63	0.9998	0.0204	0.0000
	−2.30	0.0204	−0.9998	0.0000
	−1.33	0.0000	0.0000	1.0000
β_3	2.62	0.9951	−0.0965	0.0000
	−1.18	0.0965	0.9951	0.0000
	−1.44	0.0000	0.0000	1.0000
methyl	1.64	0.7224	−0.6914	0.0000
	−0.89	0.6914	0.7224	0.0000
	−0.75	0.0000	0.0000	1.0000

that the 2 Me-N triplet spin distribution is similar to the spin distribution of the cation radical is a clear indication of the occurrence of a relatively large charge transfer.

In the triplet trap the measured total spin density on the α and β 2 Me-N carbon atoms obtained from the above mentioned values of $Q(\mathrm{H})$ and $Q(\mathrm{CH_3})$ amounts to 0.73. The contribution of the spin density on the carbon atoms 9 and 10 is expected to be negligible.

By considering that the triplet total spin density should decrease from 1 to 1/2 by a complete transfer of one electron from the donor to the acceptor, the total spin density of 0.73 indicates a CT degree of 54%.

This value compares well with the value obtained using the ZFS tensor elements which are related to the CT degree by the equation

$$D_{ij}^{\mathrm{complex}} = (1 - b^2)\, D_{ij}^{\mathrm{loc}} + b^2\, D_{ij}^{\mathrm{ion}}, \quad i = x, y, z, \qquad (6)$$

where the superscripts refer to the CT complex, to a triplet state fully localized on the donor 2 Me-N, and to a triplet state completely ionic. While the local values were obtained experimentally from the EPR spectra of 2 Me-N in naphthalene crystals [13], the D_{ij}^{ionic} cannot be measured and have to be calculated by assuming a proper distribution of one electron spin on the donor (cation) and one on the acceptor (anion) and a proper geometry of the complex.

By using (6), we obtain a mean value of the CT degree of 50%.

Therefore the CT degree of the 2 Me-N-TCNB triplet trap is much higher than in the case of unsubstituted naphthalene, and this fact needs some comments which will be discussed in a following section.

Proton Dipolar Tensors and Structure of the 2 Me-N-TCNB Triplet Trap

The orientation relative to the crystal axes of the 2 Me-N molecule in the triplet state of the CT complex can be obtained from the directions of the principal axes of the proton hyperfine tensors.

The dipolar hyperfine interaction of an aromatic ring proton has local and non-local contributions. The first one is due to the spin density on the π-orbital of the carbon atom directly bonded to the proton. In the case of those protons having a large isotropic coupling for which the local spin density is large, the dipolar tensor components are mainly determined by the local contribution, and the principal directions reflect the local geometry. In particular the direction relative to the lowest eigenvalue corresponds to the C–H bond direction. This situation is verified for the α protons and this fact allows for a rough indication on the orientation of the excited molecule with respect to the crystal frame.

However, a more reliable determination is obtained from the experimental dipolar tensors of all the protons, by comparing them with those which can be calculated by using a well known theoretical procedure [21] which can be applied because we know the spin distribution in the 2 Me-N-TCNB triplet state.

The results of the calculations are reported in Table 5. They refer to a frame of orthogonal axes fixed in the molecule, while the experimental tensors refer to the frame which diagonalizes the ZFS tensor; however the orientation of the latter frame with respect to the crystal axes has been already determined.

The best agreement of calculated and experimental proton dipolar tensors is obtained assuming ZFS and

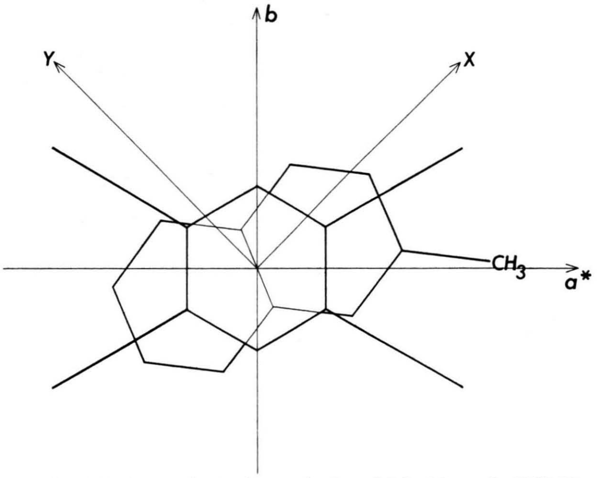

Fig. 4. Relative orientation of the 2 Me-N and TCNB molecules in the trap I. The TCNB is supposed to lie with the short symmetry axis along the crystal *b* axis as in the host N-TCNB lattic. The 2 Me-N molecule is placed in the crystal frame according to the relative orientation of the ZFS tensor principal axes *x* and *y* with respect to the 2 Me-N molecular axes and to the *a** and *b* crystallographic axes.

molecular axes rotated, for one of the crystal sites, as shown in Fig. 5, where the crystallographic axes are also shown.

The *X* principal axis of the ZFS turns out to be located close to the C_3-C_7 bond, and it makes an angle of about 21° with the long in plane molecular axis of 2 Me-N. Nothing can be said about the TCNB partner of the CT complex, however we can safely assume that it maintains the same position on a symmetry center of the N-TCNB host crystal lattice. In this way we obtain a structure very similar to that of N-TCNB complexes in their minimum energy conformation where the N molecules are rotated by an angle of $\pm 18°$ with respect to the long symmetry axis of the TCNB, that is parallel to the *a** axis.

In this structure the methyl substituent is placed in an optimum position to minimize the steric hindrance with the acceptor cyano groups.

CT Character of N-TCNB and 2 Me-N-TCNB Complexes

The TCNB CT complexes of aromatic hydrocarbons have an almost completely neutral ground state, while the first excited singlet state is ionic.

The CT character of the first excited triplet state T_0 changes from one donor to another and depends on two main factors. The first one is the energy difference ΔE between the zero order triplet state energy of the donor and the energy of the ionic triplet state. The second important factor is the transfer integral t which measures the electron interaction between the donor and acceptor π molecular orbitals. t is therefore affected by the relative donor-acceptor orientation. A first order calculation [22] gives

$$b^2 = \left(\frac{t}{\Delta E}\right)^2.$$

The transfer integral is expected to change very little on passing from N to 2 Me-N donors. In fact, the electron distribution in the relevant molecular orbitals are quite similar and we have shown that the two CT complexes with TCNB have similar geometrical structures. Therefore the ratio between the CT degrees of the two complexes in their first excited triplet states should depend mainly on the ratio between their respective ΔE values.

The triplet state energy of N is known from several studies [12, 23, 24], while that of 2 Me-N triplet traps in $N-h_8$ has been found to lie 313 cm^{-1} below the host triplet exciton band [12].

The ionic CT triplet energy is expected to lie close to the CT singlet state because of the small exchange interaction when two electrons are distributed on different molecules. For N-TCNB the CT state energy is 23 500 cm^{-1} [25] while for 2 Me-N-TCNB no data are available. However we can resort to the use of a well known linear relation between CT singlet excitation energy and donor ionization potential [26, 27]:

$$h\nu = 0.85\, I_{\text{donor}} - e,$$

where e is the acceptor electron affinity.

From the difference between the ionization potential of N [28] and 2 Me-N [29] 0.17 eV, one obtains 22 330 cm^{-1} for the energy of the 2 Me-N-TCNB CT singlet state and from these data the ratio between the CT degree of N-TCNB and 2 Me-N-TCNB first excited triplet states turns out to be about 0.4 while the experiments give about 0.5.

Conclusions

We have shown that the triplet traps with small ZFS parameters observed in single crystals of N-TCNB doped with 2 Me-N are due to a CT complex of the acceptor TCNB with the dopant molecule. The spin distribution on the donor is similar to that of the

2 Me-N radical cation, which is explained by the electron transfer to the acceptor from the highest monooccupied molecular orbital of the donor. The larger CT degree of the 2 Me-N-TCNB triplet state compared with that of N-TCNB is accounted for by the lowering of the CT state due to a smaller ionization potential of the 2 Me-N donor.

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