ENDOR Spectra of Pyrene Excited Triplet State in Naphthalene-TCNB Crystals *

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Triplet state traps, observed on optically excited single crystals of Naphthalene-TCNB doped with Pyrene, have been studied by EPR and ENDOR spectroscopy. The magnetic resonance lines recorded at low temperature (20 K) are shown to be due to triplet excitations localized almost completely on a Pyrene molecule. The complete hyperfine tensors of all the protons have been determined. The spin distribution is shown to be distorted in such a way that the triplet Pyrene molecule lacks the in-plane symmetry axes of the ground state molecule. The orientation of the triplet molecule in the crystal lattice and the relative orientation of Pyrene and TCNB are also discussed.

Introduction

Naphthalene forms with 1,2,4,5-tetracyano-benzene charge transfer (CT) complexes, hereafter indicated by N-TCNB, whose crystal structure consists of alternate stacks of Donor (Naphthalene) and Acceptor (TCNB) molecules [1]. The crystal lattice can accommodate several guest molecules which substitute either N or TCNB.

When the N-TCNB crystal is illuminated by visible light in the CT band, mobile triplet excitations (excitons) are formed by inter-system-crossing (ISC) from the lower excited single state. In the presence of guest molecules the triplet excitons become trapped at the impurity sites having a triplet energy level lower than the crystal excitonic triplet band.

Electron spin resonance spectroscopy has been used to investigate the structure and the dynamic behaviour of these triplet traps [2]. The Zero Field Splitting (ZFS) parameters, obtained from the analysis of the EPR spectra, give information on the electronic distribution and on CT character of the triplet state. An information on the possible librational motion of the triplet molecules is provided by the analysis of the spectrum lineshapes and their variation with temperature [3].

N-TCNB undergoes a structural phase transition at $T_c = 62$ K, which is "triggered" by the onset of a large amplitude motion of the Naphthalene molecules [4]. The motion consists in a rotation about the axis perpendicular to the molecular plane, and jumps take place between two sites corresponding to the minima of a double minimum potential well [5].

The orientation of the molecules in the low temperature phase was investigated at 4.2 K by ENDOR spectroscopy of the triplet X-traps [6]. This method cannot apply at higher temperatures because of the thermal detrapping of the swallow X-traps, and therefore deep traps in doped crystals were considered, with the aim to get from them information on the lattice dynamics.

In N-TCNB crystals doped with Pyrene (Py) EPR signals were recorded upon illumination with visible light from liquid helium temperature up to room temperature [7, 8]. Two different excited triplet traps were observed and their ENDOR spectra are discussed in this paper.

Experimental

N (Aldrich) and Py (Ega Chemie) were vacuum sublimed. TCNB was prepared by the method reported in [9] and purified by repeated recrystallizations from ethanol and vacuum sublimation.

The single crystals of N-TCNB with Py were prepared by slow evaporation of the solvent from a spectrophotometric grade acetone (Merck Uvasol) solution containing the dopant at a molar ratio of 1%.

The crystals are monoclinic, space group C2/m, with $a = 9.39$, $b = 12.66$, $c = 6.87$ Å, $\beta = 107.2°$ and $Z = 2$ [1]. In the room temperature structure, the N

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and TCNB molecules are approximately planar and overlap each other with an average interplanar spacing of 3.43 Å.

They are stacked alternately in infinite columns along the *c* axis. While the TCNB molecules in the crystal lattice occupy a fixed position, with their short in-plane symmetry axis along *b*, the orientation of the N molecules is disordered, adopting with equal probability two alternative positions that differ by having their short in-plane axes at ±18° from the crystal symmetry axis *b*.

The EPR and ENDOR spectra were recorded at $T = 20$ K using a conventional Bruker ER 200 D X-band spectrometer equipped with accessories for double resonance spectroscopy and an Oxford ESR-900 helium continuous flow cryostat.

The crystals were mounted on a lucite support in a quartz tube and rotated inside the cavity round the crystallographic axes $a^* b c$.

A cylindrical TE_{011} microwave cavity was substituted for the Bruker ENDOR cavity because the latter lacks an optical access for the illumination of the sample. The ENDOR rf field was produced by four rods inserted in the cavity, parallel to the cylinder axis and forming two one turn coils in a Helmholtz configuraion. The EPR spectrum could be recorded with the usual 100 kHz field modulation provided by two additional rods forming a low impedance coil surrounding the sample. The appropriate low output power amplifier was driven by the 100 kHz oscillator of the Bruker signal channel unit. The ENDOR spectra were recorded with frequency modulation at 6.25 kHz of the rf.

Results

The spin hamiltonian of a triplet trap species is

$$H = g\beta \boldsymbol{B}\boldsymbol{S} + XS_x^2 + YS_y^2 + ZS_z^2 + \sum_k \boldsymbol{S}\boldsymbol{A}\boldsymbol{I}_k + \sum_k g_{\mathrm{n}}\,\beta_n \boldsymbol{I}_k, \tag{1}$$

where *X*, *Y*, and *Z* are the ZFS parameters, *x*, *y* and *z* the principal directions of the electron spin dipole interaction, and the sum is over all nuclei interacting with the unpaired electrons. Only spin 1/2 (protons) are considered, and furthermore the small *g* factor anisotropy is neglected.

The EPR spectrum of N-TCNB doped with Py shows broad lines due to trapped excitations. The linewidth changes slightly with the orientation and its typical value is 20 Gauss. The spectrum recorded at high temperature ($T > 100$ K) consists of two lines for any orientation of the magnetic field with respect to the crystal axes. The two lines are due to a triplet trap, hereafter indicated as Trap 1, whose EPR and ENDOR spectra have already been described [7, 8]. By lowering the temperature, two additional pairs of EPR lines appear, whose intensity gradually increases as the temperature is lowered. At the same time the Trap 1 line intensity decreases.

The new lines are due to a second triplet trap (Trap 2) present in the crystal lattice in two magnetically non equivalent sites related by a twofold rotation around the crystallographic *b* axis of the monoclinic crystal. It is worth noting that in a large temperature range including the phase transition temperature of the N-TCNB crystal both Trap 1 and Trap 2 are simultaneously observed, as shown in Fig. 1, by the spectrum recorded at $T = 35$ K.

The ZFS parameters of the two triplet traps, obtained from the analysis of the variation of the EPR line positions with the orientation of the crystal in the Zeeman magnetic field, are reported in the Table 1, together with the principal directions. The ENDOR spectra of Trap 1 have already been described in [8].

ENDOR spectra, recorded at $T = 20$ K by saturating the 0 +1 EPR transitions of one site of Trap 2, consist of five main lines. The variation of the ENDOR frequencies with the orientation of the crystal were fit to the equation [10]

$$\begin{aligned} v = 1/h\{(&\langle S_X\rangle^{+1} A_{XX} + \langle S_Y\rangle^{+1} A_{XY} + \langle S_Z\rangle^{+1} A_{XZ} - l h v_{\mathrm{p}})\}^2 \\ &+ (\langle S_X\rangle^{+1} A_{XY} + \langle S_Y\rangle^{+1} A_{YY} + \langle S_Z\rangle^{+1} A_{YZ} - m h v_{\mathrm{p}})^2 \\ &+ (\langle S_X\rangle^{+1} A_{XZ} + \langle S_Y\rangle^{+1} A_{YZ} + \langle S_Z\rangle^{+1} A_{ZZ} - n h v_{\mathrm{p}})^2\}^{1/2}, \end{aligned} \tag{2}$$

where A_{uv} are the hyperfine tensor elements and $\langle S_{\mathrm{u}}\rangle^i$ are the expectation values of the u component of the total triplet spin in the *i* sublevel. The values of $\langle S_{\mathrm{u}}\rangle^i$

Table 1. ZFS tensors of the triplet traps in the N-TCNB crystal doped with Pyrene.

	Principal values (Gauss)	Direction cosines		
		*a**	*b*	*c*
Trap 1	$X = 403$	1.0000	0.0000	0.0000
	$Y = -110.5$	0.0000	1.0000	0.0000
	$Z = -292.5$	0.0000	0.0000	1.0000
Trap 2	$X = 576$	0.7682	±0.6397	−0.0248
	$Y = -117.5$	−0.6375	±0.7679	0.0627
	$Z = -458.5$	0.0591	∓0.0323	0.9977

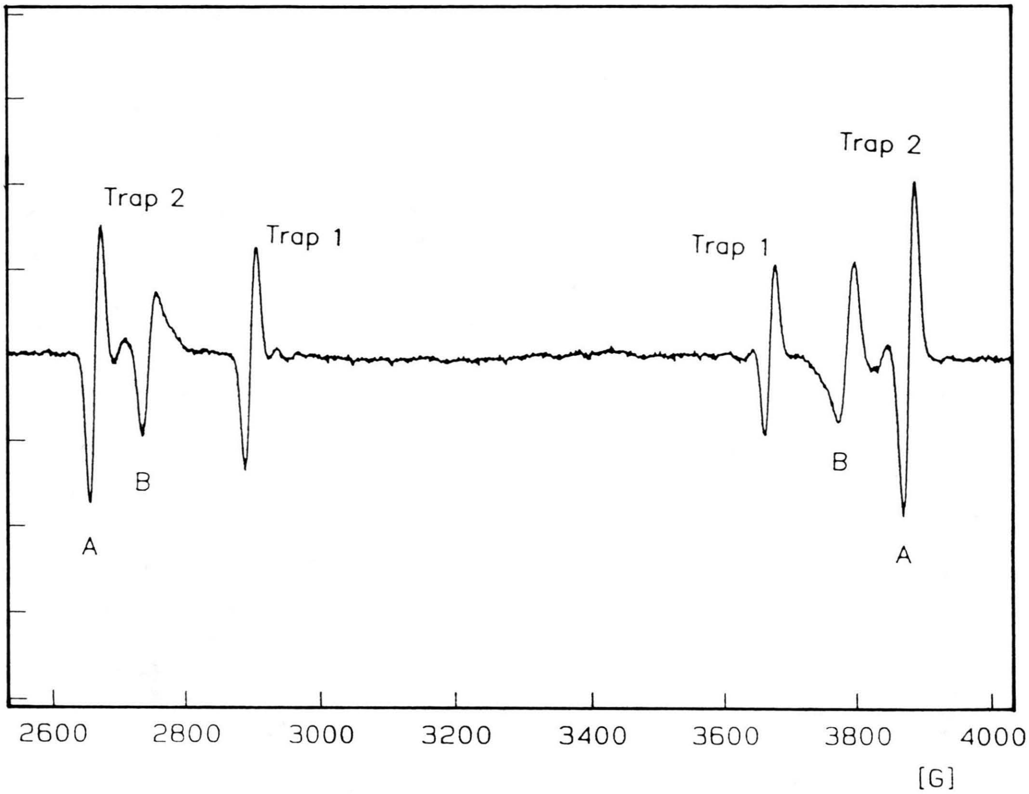


Fig. 1. EPR spectrum of the N-TCNB crystal doped with Pyrene recorded at $T = 35$ K with the magnetic field in the $a^* b$ plane. The lines are due to two different triplet traps (1 and 2) as discussed in the text. Trap 2 is present in two different sites (lines A and B).

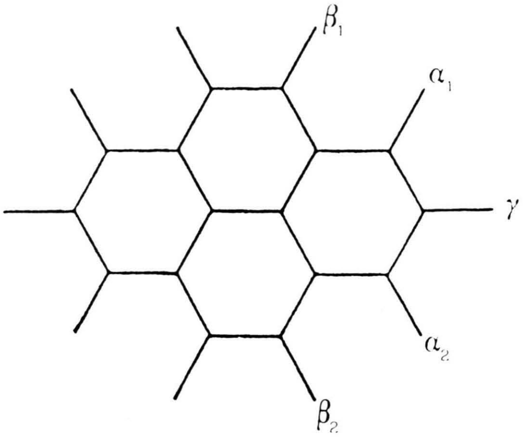
were obtained for each orientation of the magnetic field with respect to the ZFS axes by diagonalization of the hamiltonian matrix of the Zeeman and electron dipolar interaction. The use of the above equation corresponds to substituting the effective spin $\langle S \rangle^i$ to the spin operator $\boldsymbol{S}$ in the third term of the spin hamiltonian (1) or, in other words, to considering the nuclear spin as quantized along the effective field which is the sum of the Zeeman field and the local dipolar field due to the unpaired electrons.

Figure 2 shows a typical ENDOR spectrum and Fig. 3 the ENDOR frequencies with the best fitting to (2), when the magnetic field explores the three crystallographic planes.

The proton isotropic hyperfine couplings, the eigenvalues and the eigenvectors of the dipolar hyperfine tensors are reported in the Table 2. The latter are referred to the axes system which diagonalizes the ZFS tensor of the Trap 2 in one site. Several other lines at frequencies close to the free proton fre-

Table 2. Isotropic coupling constants, principal values and directions of the dipolar tensors of Pyrene protons in the Trap 2.

Proton	Isotropic value (MHz)	Anisotropic principal values (MHz)	Direction cosines		
			x	y	z
α_1	−13.67	7.20	0.5162	−0.8545	0.0583
		−7.05	0.8542	0.5185	0.0374
		−0.15	−0.0622	0.0305	0.9976
α_2	−14.66	7.63	0.5208	0.8534	0.0219
		−7.68	0.8534	−0.5211	0.0137
		−0.06	−0.0231	−0.0116	0.9997
β_1	−5.83	3.30	0.4924	−0.8701	0.0197
		−2.18	0.8689	0.4928	0.0464
		−1.12	−0.0500	−0.0057	0.9987
β_2	−6.27	3.68	0.4901	0.8709	0.0361
		−2.53	0.8680	−0.4914	0.0712
		−1.15	−0.0797	0.0036	0.9968
γ	2.63	0.56	−0.9903	0.1387	0.0000
		1.28	0.1387	0.9903	0.0000
		−1.84	0.0000	0.0000	1.0000



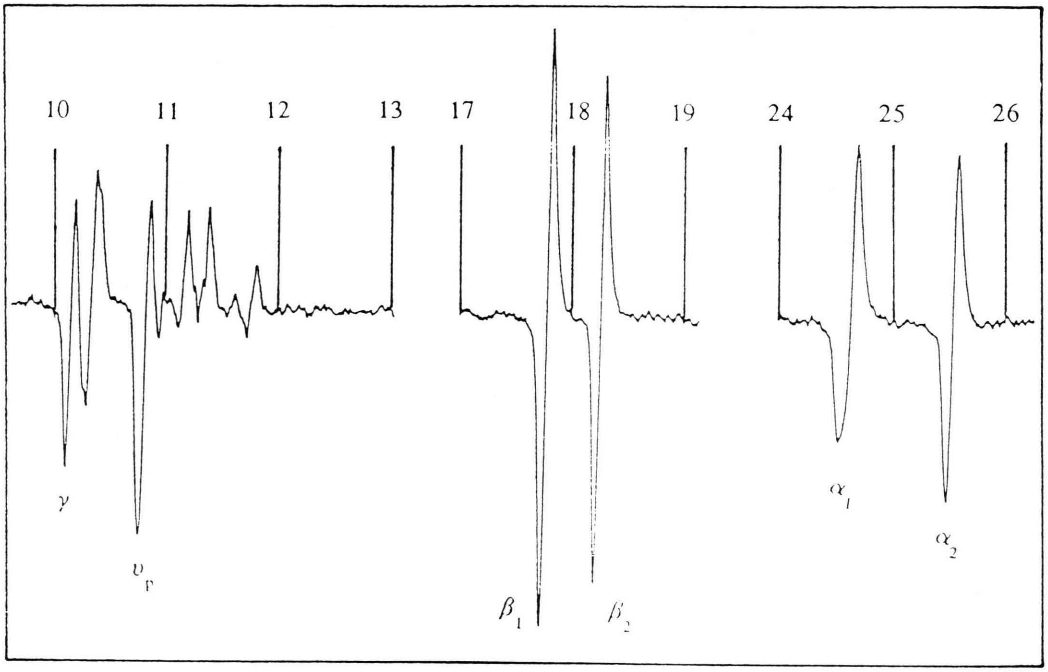


Fig. 2. ENDOR spectrum of the triplet Trap 2 in N-TCNB doped with Pyrene. The spectrum is recorded at $T = 20$ K with the magnetic field parallel to the crystallographic axis c by saturating the $0 +$ EPR transition. The assignment of the ENDOR lines to the Py protons is shown (marks in MHz).

quency ν_p were also present in the spectra. They are due to weakly coupled protons of the host lattice and to ENDOR transitions within the $m_s = 0$ triplet sublevel [11, 12]. These ENDOR lines were not analyzed.

Discussion

The EPR spectra of the triplet traps in Py doped N-TCNB crystal were already investigated by Möhwald and Erdle [7]. They observed a variation of the spectrum as the temperature was changed from above to below the phase transition temperature T_c. The EPR lines were attributed to triplet excitations trapped on a Py-TCNB complex having 20% CT character, where the Py molecules of the complex experience a lattice variation due to the phase transition and change accordingly their orientation. At the same time there is a change in the ZFS parameters of the trap. This conclusion was based on the following arguments:

For $T > T_c$ the EPR spectrum due to Py host molecules consisted of two lines indicating either that Py occupies a symmetrical position in the monoclinic crystal lattice or that it undergoes a fast librational

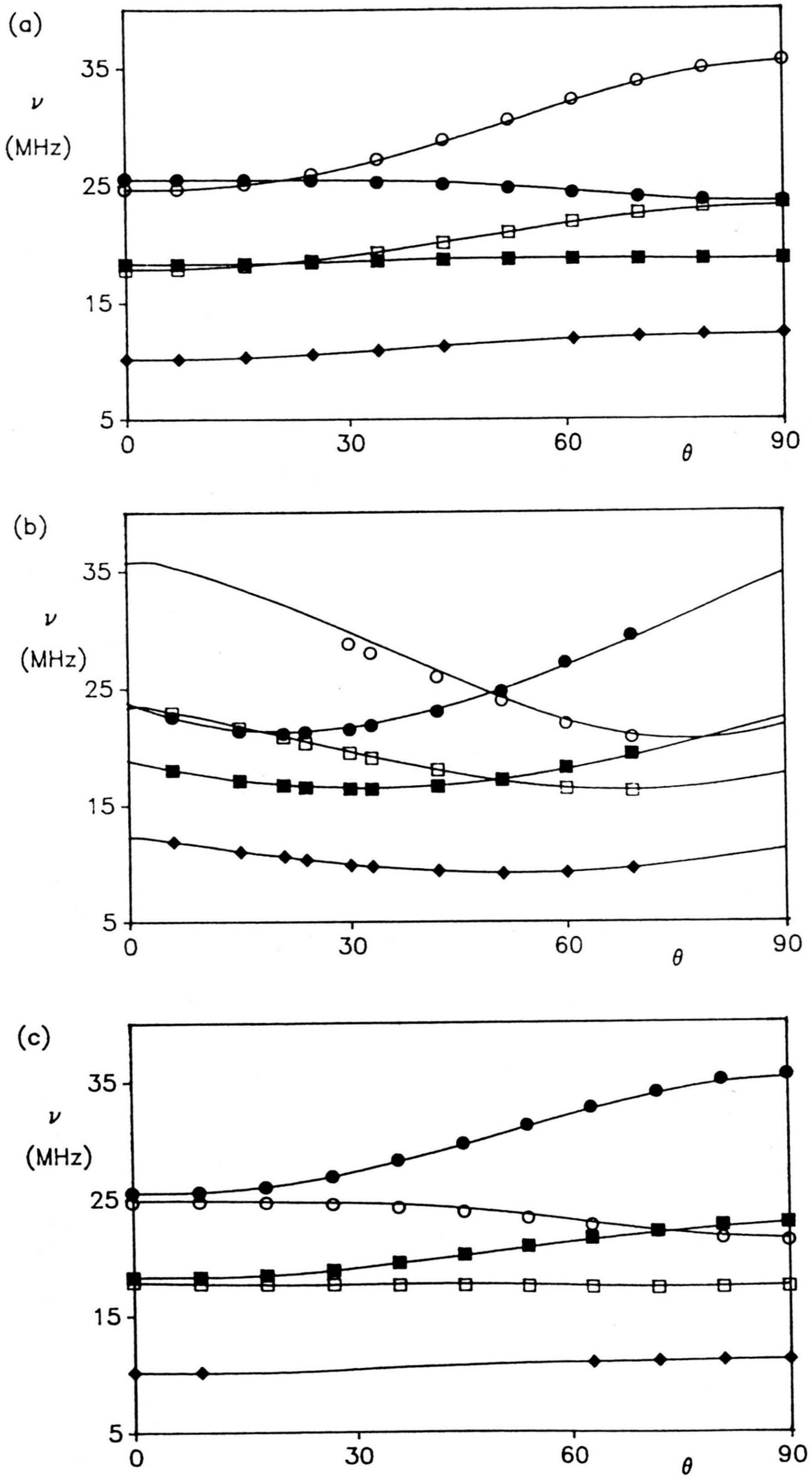


Fig. 3. Experimental frequencies of the ENDOR lines of the α_1 (○), α_2 (●), β_1 (□), β_2 (■), and γ (◆) Pyrene protons when the magnetic field explores respectively the ca^* (a), a^*b (b), and cb (c) crystallographic planes. The best-fit curves are calculated by (2) (angles in degrees).

motion which exchanges the orientation between two symmetry related positions.

For $T < T_c$ each line of the triplet trap spectrum was found to split into two lines supporting the second hypothesis. However, the field positions of the new lines where not found to be symmetric with respect to the position of the single line observed at $T > T_c$. The latter situation is what one would expect for triplet traps when a fast motion between two non equivalent sites is slowed down. The experimental observation was explained by the freezing of the librational motion together with a variation of the ZFS parameters of the trap due to a different geometry of the CT complex.

The EPR signals we assign to Trap 1 and Trap 2 correspond to those observed respectively above and below the phase transition temperature in [7].

In our crystals we observe both Trap 1 and Trap 2 simultaneously present in a broad temperature range from 20 K to 100 K, that is well below and above the transition temperature T_c. This observation rules out the idea that we are facing with a single triplet trap species which experiences a different dynamic situation due to a change in the lattice structure. On the contrary, it indicates that two different triplet traps can be simultaneously populated. The fact that, at elevated temperatures, only Trap 1 is observed, is explaned by an efficient thermal detrapping of Trap 2 whose energy should be close enough to the triplet exciton band. At low temperature, the thermal detrapping process does not occur and both traps are observed in relative concentrations which depend on the populating rates and the triplet lifetimes.

The nature of the traps is discussed in the following section in relation to the measured ENDOR spectra.

ENDOR Spectra

The ENDOR spectra of Trap 1 are fully consistent with a triplet excitation localized on Py in a CT complex [8]. For an arbitrary orientation of the crystal in the magnetic field, the ENDOR spectra consist of five lines due to the α_1, α_2, β_1, β_2 and γ protons of Py and two lines due to the TCNB protons. At particular orientations (in particular when the magnetic field direction is along the twofold *b* axis or perpendicular to it) the ENDOR lines reduce to three because the α_1 and α_2 as the β_1 and β_2 protons become magnetically equivalent. From the variation of the ENDOR line frequencies with the orientation of the magnetic field, the complete hyperfine tensors were measured.

The four α and the four β proton tensors were found to be related in pairs by twofold rotation axes indicating that in Trap 1 the Py molecule maintains its twofold symmetry axes in the triplet state of the CT complex.

From the isotropic hyperfine interaction of the Py and TCNB protons a CT character of 16% was estimated.

Also the ENDOR spectra of Trap 2 consist of five lines. The angular variation of their frequencies is very similar to that of the protons of Trap 1, provided it is represented in the principal axes which diagonalize the ZFS interaction. This behaviour is what one expects if the principal axes of the proton hyperfine tensors of the two traps are oriented in a similar way with respect to their ZFS axes. We recall that the ZFS interaction principal axes *z* of the two triplet traps coincide; however, while the axis *y* of Trap 1 is directed along the crystal axis *b*, for Trap 2 the *y* axes of the two sites make angles of ±40 degrees with *b*.

Moreover the values of the isotropic coupling constants of Trap 1 protons are simply those of Trap 2 scaled by a factor of 0.8–0.9, and, furthermore, the ZFS parameters agree with those of the triplet state of Py diluted in fluorene or biphenyl crystals [13, 14]. These facts lead us to conclude that also the second trap consists of excitations localized on Pyrene in a Py-TCNB complex with a very little CT character and to assign the hyperfine tensors to the α_1, α_2, β_1, β_2, and γ protons of this molecule. The assignment is further supported by the similarity of the proton isotropic coupling constants with those of the pyrene anion radical [15, 16] and by the good agreement with the experimental values of the dipolar hyperfine tensor elements calculated, as explaned later, with a spin distribution on a pyrene molecule.

However, at variance with the case of Trap 1, the ENDOR lines of Trap 2, attributed to the α_1, α_2, and β_1, β_2 protons do not coincide when the magnetic field is along the symmetry axis *b* or perpendicular to it, and different tensors are measured. This fact indicates that the Py molecule in the triplet state in Trap 2 has only the inversion centre and looses its twofold symmetry axes in the molecular plane.

Orientation of the Trap 2 in the Crystal Lattice

The orientation of the triplet molecule with respect to the crystal axes can be inferred from the orientation of the ZFS tensor principal axes. The latter should coincide, in principle, with the symmetry axes of the molecule. However, in several cases of a guest triplet molecule, a substantial deviation has been measured [17], due to the interaction with the surrounding host molecules. Therefore the naive assumption that the ZFS axes of Py coincide with the symmetry axes should be taken with caution.

A test for the orientation can be obtained from the proton hyperfine dipolar tensors by comparing their calculated and experimental principel directions, expressed in the same reference frame.

The experimental tensor principal directions are referred to the x, y, z frame which diagonalizes the ZFS tensor of Trap 2 in one of the two inequivalent sites (Table 2). For the calculations we have used a reference frame coincident with the symmetry axes system of the Py molecule (with x' along the in-plane long axis, z' perpendicular to the molecular plane and y' completing the right-handed orthogonal system). Furthermore:

- The Py molecule was assumed planar with bond angles and bond lengths as determined by X-ray diffraction studies of Py in pure crystals [18].
- The triplet unpaired electrons were considered to occupy carbon 2p Slater orbitals [19] with a spin density as obtained by the McConnell equation [20] from the experimental values of isotropic coupling (Table 2) and a Q value of 72.4 MHz [6].
- For carbon atoms not bonded to protons, we assumed the spin densities used for the Py anion to fit NMR results [16].
- The contribution to the dipolar tensor elements due to a unity spin density on the carbon atom bonded to the considered proton (local contribution) was taken as 41.36, −0.18, −41,18 MHz for the components along the C−H bond, the p orbital and the direction perpendicular to the first two [21]. These values were scaled according to the carbon spin density.

The results of the calculations are shown in Table 3, along with the angles between the respective experimental and calculated principal directions.

The dipolar tensors of α_1, α_2, β_1, and β_2 protons are in good agreement with the calculated ones, while for the γ proton which is bonded to a carbon atom bearing a negative spin density, the agreement is worse. A similar behaviour was observed in other cases for protons bonded to negative spin density positions in triplet [8, 12, 22] as well as in doublet [23] state molecules, and it has been already discussed [22].

The satisfactory agreement between the experimental and calculated principal directions allow us to conclude that in Trap 2 the ZFS tensor principal axes concide within few degrees with the symmetry axes of the Py molecule.

Table 3. Calculated principal values and directions of the dipolar tensors of Pyrene triplet protons.

Proton	Anisotropic principal values (MHz)	Direction cosines			
		x'	y'	z'	ϑ
α_1	7.84	0.5204	−0.8539	0.0000	2.2
	−7.27	0.8539	0.5204	0.0000	3.3
	−0.57	0.0000	0.0000	1.0000	3.9
α_2	8.38	0.5222	0.8528	0.0000	1.0
	−7.83	0.8528	−0.5222	0.0000	1.3
	−0.55	0.0000	0.0000	1.0000	1.4
β_1	3.87	0.5340	−0.8455	0.0000	3.7
	−2.55	0.8455	0.5340	0.0000	3.0
	−1.32	0.0000	0.0000	1.0000	2.9
β_2	4.22	0.5326	0.8463	0.0000	4.9
	−2.91	0.8463	−0.5326	0.0000	3.6
	−1.31	0.0000	0.0000	1.0000	4.5
γ	1.38	−0.9198	0.3925	0.0000	15.0
	1.05	0.3925	0.9198	0.0000	15.0
	−2.43	0.0000	0.0000	1.0000	0.0

ϑ: Angles (degrees) between the experimental and calculated principal directions.

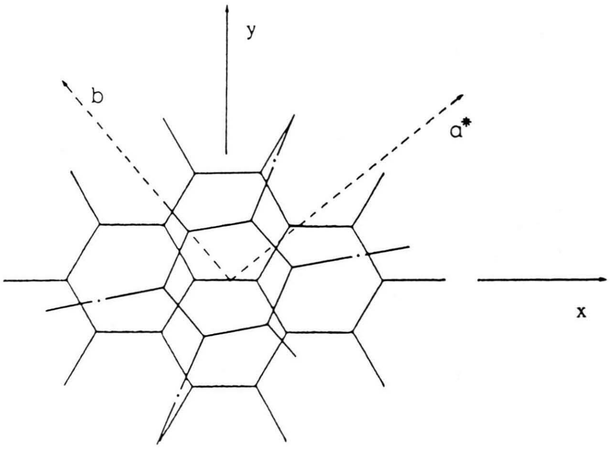


Fig. 4. Relative orientation of the Pyrene and TCNB molecules in Trap 2. The TCNB molecule is supposed to lie with the short symmetry axis along the crystal axis b as in the host N-TCNB lattice. The Pyrene molecule is oriented according to the principal directions of the ZFS tensor.

If we assume that the TCNB molecule in the traps maintains its orientation as in the crystal lattice of N-TCNB, the structure of Trap 2 becomes as shown in Figure 4.

It is interesting to note that the relative orientation of TCNB and Py are very similar to that found in the crystal lattice of the Py-TCNB CT complex [24]. This fact could suggest that in Py doped N-TCNB crystals there are clusters of Py-TCNB complexes, and that Trap 2 could be localized on them. Finally, we note that the asymmetric orientation of TCNB with respect to Py is the probable cause of a polarization of the spin distribution, which lacks the two in-plane symmetry axes present in the Py ground state, and of the lower CT character of Trap 2 with respect to Trap 1 owing to a smaller overlap between donor and acceptor π orbitals.

[1] S. Kumakura, F. Iwasaki, and Y. Saito, Bull. Chem. Soc. Jap. **40,** 1826 (1967).

[2] H. Möhwald and E. Sackmann, Z. Naturforsch. **23a,** 1216 (1974).

[3] H. Möhwald, E. Erdle, and A. Thaer, Chem. Phys. **27,** 79 (1977).

[4] R. M. McFarlane and S. Ushioda, J. Chem. Phys. **67,** 3214 (1977).

[5] J. Ripmeester, A. H. Reddoch, and N. S. Dalal, J. Chem. Phys. **74,** 1526 (1981).

[6] A. Grupp, H. C. Wolf, and D. Schmid, Chem. Phys. Letters **85,** 330 (1982).

[7] H. Möhwald and E. Erdle, Phys. Stat. Sol. (b) **103,** 757 (1981).

[8] C. Corvaja, A. L. Maniero, and L. Pasimeni, Chem. Phys. **100,** 265 (1985).

[9] E. A. Lawton and D. D. McRitchie, J. Org. Chem. **24,** 26 (1956).

[10] M. D. Kemple, in: Multiple Electron Resonance Spectroscopy (M. M. Dorio and J. H. Freed, eds.), Plenum Press, New York 1979, Chapt. 12.

[11] V. Zimmermann, M. Schwoerer, and H. C. Wolf, Chem. Phys. Letters **31,** 401 (1975).

[12] A. L. Maniero, C. Corvaja, and L. Pasimeni, Chem. Phys. **122,** 327 (1988).

[13] S. W. Charles, P. H. H. Fischer, and C. A. McDowell, Mol. Phys. **9,** 517 (1965).

[14] P. H. H. Fischer and A. B. Denison, Mol. Phys. **17,** 297 (1969).

[15] A. H. Reddoch, C. L. Dodson, and D. H. Paskovich, J. Chem. Phys. **52,** 2318 (1970).

[16] B. M. P. Hendriks, Ph.D. Thesis, University of Nijmegen, Netherland 1973.

[17] M. S. de Groot, I. A. M. Hesselmann, F. J. Renders, and J. H. van der Waals, Mol. Phys. **29,** 37 (1975).

[18] A. Camerman and J. Trotter, Acta Cryst. **18,** 636 (1965).

[19] H. M. McConnell and J. Strathdee, Mol. Phys. **2,** 129 (1959).

[20] H. M. McConnell, J. Chem. Phys. **24,** 764 (1956).

[21] R. H. Clarke and C. A. Hutchison Jr., Chem. Phys. **54,** 2962 (1971).

[22] A. L. Maniero and C. Corvaja, Chem. Phys. **135,** 277 (1989).

[23] U. R. Boehme and H. C. Wolf, Chem. Phys. Letters **17,** 58 (1972).

[24] C. K. Prout, T. Morley, I. J. Tickle, and J. D. Wright, J. Chem. Soc. Perkin Trans. II **5,** 523 (1973).