

Temperature Dependence Studies of the Paramagnetic Properties of the Photoexcited Triplet State of Pentacene in *p*-Terphenyl, Benzoic Acid, and Naphthalene Crystals

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Received: March 26, 1993; In Final Form: May 14, 1993

An electron spin echo spectrometer and pulsed nitrogen laser were employed to study the guest deuteration and host effects on the zero-field splittings (ZFS), hyperfine splittings, and the g values of the photoexcited triplet state of pentacene. These studies were performed in a temperature range of 5 K to room temperature in four mixed crystals: pentacene- h_{14} in *p*-terphenyl (PHPT), pentacene- d_{14} in *p*-terphenyl (PDPT), pentacene- h_{14} in benzoic acid (PHBA), and pentacene- h_{14} in naphthalene (PHNA). The ZFS are found to be temperature and host dependent and weakly guest-deuteration dependent: the D values of the PHPT, PDPT, and PHBA systems decrease as the temperature increases in the range 190–300 K and remain unchanged at 5–190 K. The effect is explained in terms of motional modulation arising from jumping among two or more molecular conformations (distortions). The measured g values are independent of guest deuteration, temperature, and host environments.

Introduction

Recently, we reported an electron spin echo (ESE) study of the two-conformation jumping phenomenon in the photoexcited triplet state of the pentacene molecule in *p*-terphenyl crystals at low temperatures.¹ Here we wish to report further ESE studies of the temperature effect on the zero-field splittings (ZFS), hyperfine splittings (HFS), and the g values of the pentacene triplets in three host crystals: *p*-terphenyl (PT), benzoic acid (BA), and naphthalene (NA). Each of these crystals possesses a unique structural feature, i.e., phase transition (order/disorder) in the PT crystal,² dimeric formation through the hydrogen bonding in the BA crystal,^{3–5} and the relatively small volume of the unit cell in the NA crystal.⁶

There have been many temperature dependence studies of the ZFS of organic triplets in mixed crystal environments⁷ and in plastic matrix⁸ by the CW electron paramagnetic resonance (EPR) technique. The range of temperatures reported in these studies was relatively small: 4–77 or 77–200 K. These CW experiments were limited by low signal-to-noise at the high-temperature region due to small steady-state concentration of the photoexcited triplet state. These studies have yielded some useful information: the geometry of the triplet molecule, the relative orientation of the guest molecules with respect to the host molecules in the crystal, and the electronic nature of the triplet state. Here we reported a much wider temperature range study: 5 K to room temperature.

The detection of the photoexcited triplet state of pentacene by either the conventional CW EPR or optical detection of magnetic resonance technique is unsuccessful⁹ due to the spectroscopic characteristics of the pentacene molecule: very fast nonradiative decay to the ground state ($\approx 10^5$ s⁻¹) and low phosphorescence yield. However, the pentacene triplet is highly polarized at birth as reported previously.^{10–14} Here we employ the time-resolved ESE technique to investigate the highly polarized photoexcited triplet state of the pentacene molecules at all temperatures up to room temperature.

In this study we examine the temperature dependence of the motional effect of the host molecules on the guest molecules as reflected in the paramagnetic properties of the triplet guest molecules in several crystal systems. The study further provides better understanding of the nature of guest–host interaction in these systems.

Experimental Section

The determinations of the g values were made in a frequency range of 9.20–10.05 GHz with an interval of 0.20–0.30 GHz between data sets. A digital frequency counter (HP 5245L electronic counter) was employed to measure the microwave frequencies. A Robinson oscillator (proton magnetometer) was used to measure the magnetic field strength. The uncertainty of the field measurement was ± 0.12 G.

The sample temperature was adjusted from 5 K to room temperature by the use of an Oxford ESR10 cryostat system. A thermocouple junction located just below the sample was designed to monitor the cryogenic helium gas stream temperature in the ESR10 system (the setting temperature). Additionally, we placed another thermocouple (chromel *vs* gold) just above the sample to estimate the temperature gradient across the sample and to measure the sample temperature (the reading temperature). In normal operation, it takes about 20 min to reach a stable temperature. The uncertainty of the temperature at the sample is ± 2 for the range 60–300 K and ± 3 for 5–60 K.

We took great effort to align our sample using carefully machined KEL-F wedges so that a maximum separation of the high- and low-field resonance lines for a given canonical orientation was obtained at every temperature of our measurements. Other experimental details and ESE spectrometer setup were given previously.^{1,13} It should be noted that the correct phase shift for the microwave pulse in Figure 1 of ref 1 is 180° instead of 90°.

Results and Discussion

For the convenience of our discussion, we briefly summarize the structural parameters of the host crystals used in our study as follows:

(1) *p*-Terphenyl: It has two molecules in a monoclinic unit cell ($Z = 2$) of the dimensions $a_0 = 8.08$ Å, $b_0 = 5.60$ Å, $c_0 = 13.59$ Å, and $\beta = 91.9^\circ$. The space group is $C_{2h}^5(P2_1/a)$. The space group changes to $P\bar{1}$ with $Z = 4$ (triclinic) at and below the phase transition temperature ($T_c = 193$ K).^{2,15,16}

(2) Benzoic acid: It forms monoclinic crystals with a tetramolecular unit of the dimensions⁶ $a_0 = 5.52$ Å, $b_0 = 5.14$ Å, $c_0 = 21.90$ Å, and $\beta = 97^\circ$. All atoms are in general positions of $C_{2h}^5(P2_1/c)$.

(3) Naphthalene: The crystals are monoclinic with two molecules per unit cell of the dimensions $a_0 = 8.235$ Å, $b_0 = 6.003$ Å, $c_0 = 8.658$ Å, and $\beta = 122.9^\circ$. The space group is $C_{2h}^5(P2_1/a)$.¹⁵

TABLE I: g Values and ZFS of Pentacene Triplet in p -Terphenyl, Benzoic Acid, and Naphthalene Crystals at Room Temperature^a

	g_{xx}	g_{yy}	g_{zz}	D, cm^{-1}	E, cm^{-1}
PHPT	2.0026(4)	2.0023(5)	2.0020(5)	0.046 48(2)	-0.001 77(2)
PDPT	2.0025	2.0021	2.0020	0.046 46	-0.001 78
PHBA	2.0025	2.0022	2.0018	0.046 46	-0.001 83
PHNA	2.0025	2.0022	2.0020	0.046 30	-0.001 52
average	2.0025(4)	2.0022(5)	2.0020(5)	0.046 42(2)	-0.001 73(2)

^a PHPT = pentacene- h_{14} in p -terphenyl, PDPT = pentacene- d_{14} in p -terphenyl, PHBA = pentacene- h_{14} in benzoic acid, and PHNA = pentacene- h_{14} in naphthalene.

The spin Hamiltonian including the Zeeman, the dipolar interaction, and the hyperfine interaction is given as

$$H_S = \beta \mathbf{H} \cdot \mathbf{g} \cdot \mathbf{S} + D(S_z^2 - 1/3 S^2) + E(S_x^2 - S_y^2) + \mathbf{S} \cdot \mathbf{T} \cdot \mathbf{I} \quad (1)$$

where $S^2 = S_x^2 + S_y^2 + S_z^2$, D and E are the ZFS parameters, and \mathbf{T} is the hyperfine tensor. We designate the molecular axes of pentacene as follows: the long in-plane axis as the x axis, the short axis as the y axis, and the out-of-plane axis as the z axis. We shall discuss the g values, the hyperfine structure, and the fine structure-ZFS parameters in the following sections.

1. The g Values. The g values are calculated from two sets of ESE spectra measured at different microwave frequencies using the following equation:¹³

$$g_{ii}^2 = 2(\omega_1^2 - \omega_2^2) / \beta^2(H_{i1}^2 - H_{i2}^2 + L_{i1}^2 - L_{i2}^2) \quad (2)$$

where i index refers to the principal axis (x , y , and z), ω_1 and ω_2 are two different microwave frequencies, and H_{i1} and L_{i1} are the resonance magnetic fields of the high- and low-field transitions along the i axis at ω_1 , with similar meanings for H_{i2} and L_{i2} at ω_2 . β is the Bohr magneton. We have assumed that the principal axes of the g tensor coincide with those of the ZFS tensor in our calculation. The calculated g values and the D and E values at room temperature are summarized in Table I. Our experiments show that the g values are independent of temperature while the ZFS are highly temperature dependent in the range 190–300 K (see below).

As shown in Table I, the average g values are $g_{xx} = 2.0025$ (0.0004), $g_{yy} = 2.0022$ (0.0005), and $g_{zz} = 2.0020$ (0.0005). The anisotropy of the g values is comparable to previously reported values for other aromatic organic triplet species within experimental uncertainties. For example, the g values of the anthracene triplet in diphenyl crystals¹⁷ are $g_{xx} = 2.0029$ (0.0002), $g_{yy} = 2.0032$ (0.0003), and $g_{zz} = 2.0024$ (0.0006), and those of naphthalene in durene crystals¹⁸ are $g_{xx} = 2.0030$ (0.0004), $g_{yy} = 2.0031$ (0.0003), and $g_{zz} = 2.0023$ (0.0006).

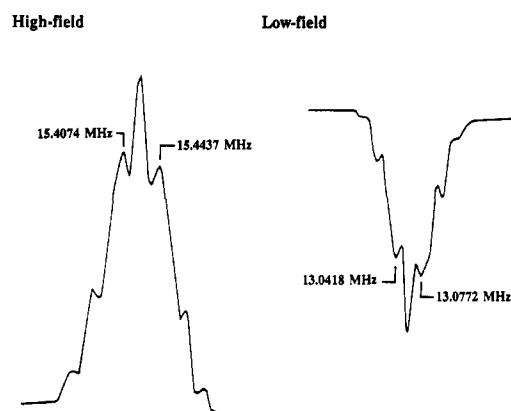
Also from Table I, we note the g values of the protonated and deuterated pentacene in the PT host crystal are the same within our experimental uncertainty. A similar result was reported for the protonated and deuterated naphthalene triplet in the durene crystal.¹⁸ Moreover, we note the g values of the pentacene triplet are not affected by the different host environments. This agrees with previous studies; e.g., the g values of the anthracene triplet in the diphenyl crystal are identical to those in phenazine within experimental uncertainty.¹⁹

Our studies indicate that guest deuteration and host crystals do not induce additional spin-orbit coupling in the pentacene triplet, thus introducing negligibly small corrections to the g values.

2. Field Scan ESE Spectra and Hyperfine Structure. (a) *Pentacene- h_{14} in p -Terphenyl (PHPT).* We observed four resonance lines: two at the low fields (below free electron resonant field) and two at the high fields for $H_0 \parallel y$ and z . This indicates there are two magnetically inequivalent pentacene molecules in a PT unit cell.²⁰ Two of the resonance lines correspond to a canonical pair which is the subject of our discussion.

On the other hand, we observed only two resonance lines for

(a) Room Temperature



(b) 180 K

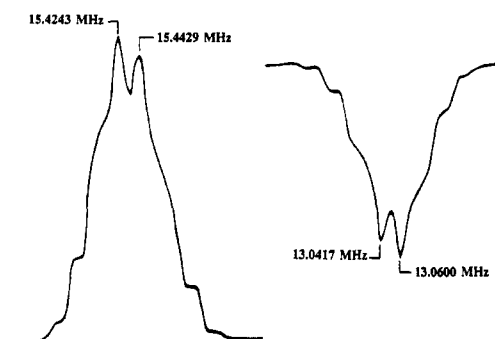


Figure 1. Hyperfine structure of PHPT for $H_0 \parallel x$. The indicated frequencies are proton frequencies for field calibration: (a) high- and low-field resonance lines at room temperature and (b) high- and low-field resonance lines at 180 K.

$H_0 \parallel x$. This indicates that x axis of the translationally inequivalent sites is coincidental.

The 70-G field scan spectra for $H_0 \parallel x$ are given in Figure 1. The observed splittings are due to HFS. The spectral pattern is slightly asymmetric, which could arise from the spectral superposition of inequivalent sites. The spectra become very asymmetric at and below T_c . The well-resolved spectral lines observed at room temperature are askew in the range 70–180 K. The resolved and more symmetric pattern, similar to the one observed at room temperature, reappears at 6 K. The spectral changes in the low-temperature region are described in terms of a two-conformation jumping phenomenon in a previous publication.¹ We did not observe HFS in either y or z orientation.

In the temperature dependence studies, we found that the magnetic field separation between the low- and high-field resonance lines increases with decreasing temperature for $H_0 \parallel y$ and z (190–300 K) but is almost independent of temperature for $H_0 \parallel x$.

(b) *Pentacene- d_{14} in p -Terphenyl (PDPT).* The spectral behavior of the PDPT system as a function of temperature is almost the same as those of PHPT except we observed no HFS in all orientations. This can be explained by two factors: (1) the HFS is reduced by a factor of 6.51 upon deuteration (the ratio of g_H/g_D), and (2) the spectral overlapping is more in the deuterated compound ($I_D = 1$ vs $I_H = 1/2$). We further notice that the single spectral line ($H_0 \parallel x$) at room temperature is split into two components at 150 K. The intensity ratio and the magnitude of the splitting of these two components are a function of temperature. We have described the spectral behavior in terms of a two-conformation jumping phenomenon.¹

(c) *Pentacene- h_{14} in Benzoic Acid (PHBA).* We observed four resonance lines in all three canonical orientations. This indicates there are two magnetically inequivalent pentacene molecules in

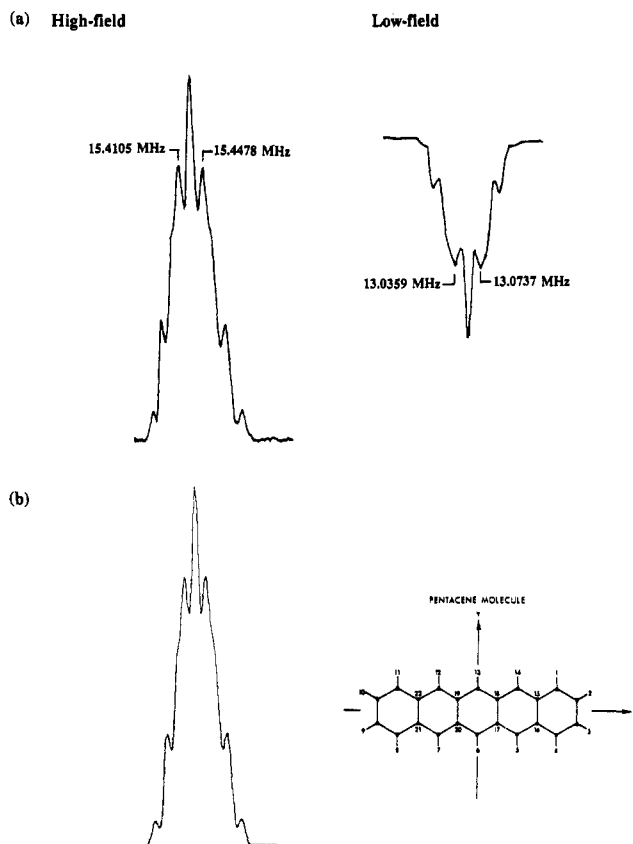


Figure 2. Hyperfine structure of PHBA for $H_0 \parallel x$ at room temperature: (a) high- and low-field resonance lines and (b) computer-simulated spectra fitted with the following proton HFS: $a_{13} = 7.25$, $a_{12} = 4.60$, $a_{11} = 0.95$, and $a_{10} = 0.40$ G and a line width of 1.4 G.

the unit cell even though there are four molecules per cell. Each pentacene molecule must occupy a benzoic acid dimeric site.

The hyperfine structure of PHBA for $H_0 \parallel x$ is displayed in Figure 2. It shows a symmetric structure with respect to the central peak. The hyperfine pattern remains the same over the entire temperature range. A computer-simulated spectrum and the assignment are also given in Figure 2. The spin density distribution of the pentacene triplet will be published elsewhere.²¹

The field separation between the high- and low-field resonance lines for a canonical pair increases with decreasing temperature (from 190 to 300 K) for the y and z orientations, but it is almost independent of temperature along the x axis over the entire temperature range. The overall temperature dependence of PHBA is similar to that of PHPT and PDPT systems.

(d) *Pentacene- h_{14} in Naphthalene (PHNA).* The ESE spectra for the PHNA system at 1.2 K have been reported previously.¹⁴ There are four resonance lines for $H_0 \parallel y$ and z and two for $H_0 \parallel x$. This shows that the long axes of the two translationally inequivalent pentacene molecules are accidentally parallel to each other in the naphthalene unit cell.

The study further shows that one pentacene molecule occupies two naphthalene sites in the mixed crystal system. The dipolar principal axes of the pentacene triplet state deviate from those of the naphthalene molecule by about 10° . This is in contrast to the systems of PHPT, PDPT, and PHBA where the dipolar principal axes of the pentacene are parallel to those of the host molecules. This difference in spectral behavior may arise from the unique structural nature of the NA crystal, namely, the relatively small unit cell volume: 361 \AA^3 for NA vs 615 \AA^3 for PT and 617 \AA^3 for BA.⁶

The hyperfine structure of PHNA system for $H_0 \parallel x$ is symmetric with respect to the central peak and remains the same throughout the entire temperature range. The magnitude and the pattern of HFS and its temperature dependence are the same

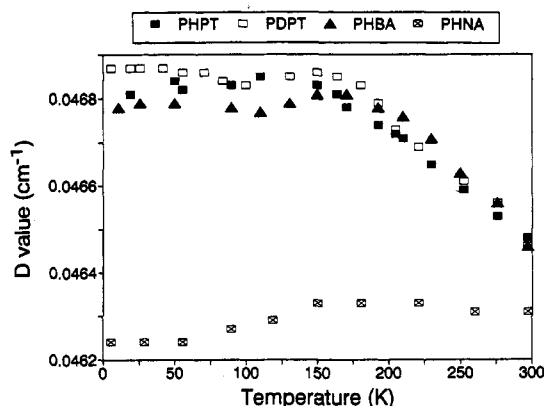


Figure 3. Plot of D value vs temperature for the pentacene triplet in three different host crystals.

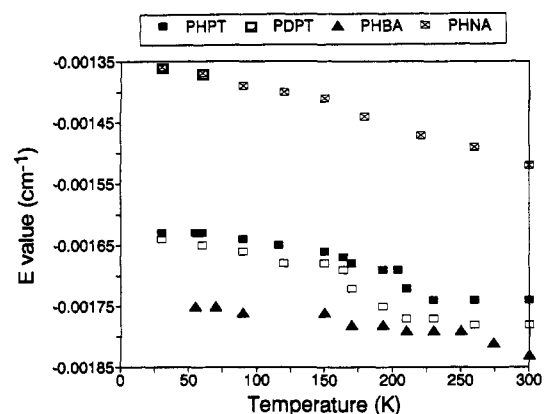


Figure 4. Plot of E value vs temperature for the pentacene triplet in three different host crystals.

as in the PHBA system. However, we note new shoulders emerge on both sites of the seven-line spectrum of the PHBA system at low temperatures.

The magnetic field separation between the high- and low-field EPR resonances of the canonical pair is slightly temperature dependent: decreases for $H_0 \parallel x$ but increases for $H_0 \parallel y$ when the temperature decreases. It remains almost unchanged for $H_0 \parallel z$ throughout the entire temperature range. This differs from what we have observed in PHPT, PDPT, and PHBA systems. We shall discuss the guest deuteration, host, and temperature effects on the ZFS in the following section.

3. The Fine Structure: Zero-Field Splittings. The spin dipolar interaction of a triplet state gives rise to the zero-field splitting parameters: D and E values. The D and E values were calculated from the field separations of the high- and low-field resonance lines using the equations given in ref 22. The calculated D and E values of the pentacene triplet in these host crystals as a function of temperature are given in Figures 3 and 4. We shall discuss the following three effects on the ZFS parameters:

(a) *Guest-Deuteration Effect.* We observe that the D and E values of PHPT differ slightly from those of PDPT: $D_D - D_H \approx |E_D - E_H| \approx 3 \times 10^{-5} \text{ cm}^{-1}$ at all temperatures. These differences are only slightly greater than our experimental uncertainty of $2 \times 10^{-5} \text{ cm}^{-1}$. Therefore, we shall not elaborate on the significance of the guest-deuteration effect on the ZFS.

(b) *Host Effect.* We observe that the D and E values of the pentacene triplet in PT and BA crystals differ from those in NA system. This may arise from a unique steric interaction between the pentacene and the host naphthalene which could perturb the electronic wave function of the guest triplet and change the ZFS parameters. Also, some differences in the polarizability of the host and the guest molecules could further influence the ZFS. Local polarization would tend to reduce the ZFS due to an increase in the delocalization of the unpaired electrons. We further note

that the dipolar principal axes of the pentacene are parallel to the symmetry axes of PT and BA molecules, but they deviate by about 10° from the naphthalene symmetry axes.¹⁴ The host effect also shows a remarkable influence on the ZFS in the following temperature dependence studies.

(c) *Temperature Effect.* We note that the D values of PHPT, PDPT, and PHBA increase with decreasing temperature with a temperature coefficient of $2.6 \times 10^{-6} \text{ cm}^{-1}/\text{deg}$ in the range 190–300 K, and they remain almost constant with an average value of $4.68 \times 10^{-2} \text{ cm}^{-1}$ in the range 5–190 K within experimental uncertainty. On the other hand, the D value of PHNA remains almost the same, $4.628(\pm 0.005) \times 10^{-2} \text{ cm}^{-1}$, throughout the entire temperature range. We further note that the E values of all systems increase almost linearly as the temperature decreases with a temperature coefficient of $5.0 \times 10^{-7} \text{ cm}^{-1}/\text{deg}$ in all temperature ranges. The temperature coefficient of the D value is a factor of 5 greater than that of the E value.

The temperature effect on ZFS parameters might arise from the following two factors: (1) thermal population of higher vibrational or phonon modes and/or (2) motional effects of guest and host molecules.

(1) *Thermal Population of Higher Vibrational or Phonon Modes.* A study of temperature dependence of ZFS of many organic triplets in plastic was reported previously.⁸ The study was concerned with the $\Delta m = 2$ transition, which gives a combined ZFS parameter D^* ($D^* = (D^2 + 3E^2)^{1/2}$). The study showed that D^* increases by about 5% with decreasing temperature from room temperature to 77 K. The temperature dependence of D^* values was explained in terms of the redistribution of triplet population to higher vibrational levels at elevated temperatures.

If this mechanism is plausible by invoking the C–H or C–D vibrational modes, we would expect the population of the higher vibrational state of PDPT to be greater than that of PHPT (deuteration effect) at a given temperature, and the effect of temperature on the ZFS of PDPT would be greater than that of PHPT. Experimentally, we did not observe such a deuteration effect; thus, we can rule out the involvement of C–H or C–D vibrational modes. However, it has been indicated that the C–C bending modes (out-of-plane) could play an important role in the intersystem crossing processes.²³ Thus, we could not rule out this possibility.

Another mechanism along the same line of argument is the population of a low-lying local phonon mode which is on the order of 10 cm^{-1} above the zero-phonon line (ZPL).²⁴ It has been shown that a rotation of principal axes by as much as 10° could take place upon thermal excitation from the ZPL to the local phonon state. Thus, the observed ZFS will decrease if this process occurs. However, the change may not be noticeable in the moderate temperature range ($> 50 \text{ K}$).

(2) *Motional Effects of Guest and Host Molecules.* One may further invoke a structural distortion of the guest molecule influenced by the motion of the host molecules as another factor affecting the ZFS in the high-temperature region. One expects the ZFS to decrease as the triplet state subjected to motional modulation, such as periodic structural distortion away from molecular planarity or other orientational distortion as the host molecules undergo large-amplitude librational motion. The dipolar interaction will be averaged to zero in the ultrafast motion regime (much faster than the reciprocal of the frequency of ZFS) such as in liquid solution at high temperature. In the slow motion regime such as in rigid lattice or at low temperatures, the ZFS will be modulated and progressively become larger until the motional effect could be “frozen” out at low temperatures.

Since the effect of molecular motion seems to occur only in the PHPT, PDPT, and PHBA systems, the field separation of the resonance lines for $H_0 \parallel y$ and z increases with decreasing temperature (190–300 K), and it is almost independent of temperature for $H_0 \parallel x$. We shall discuss the temperature

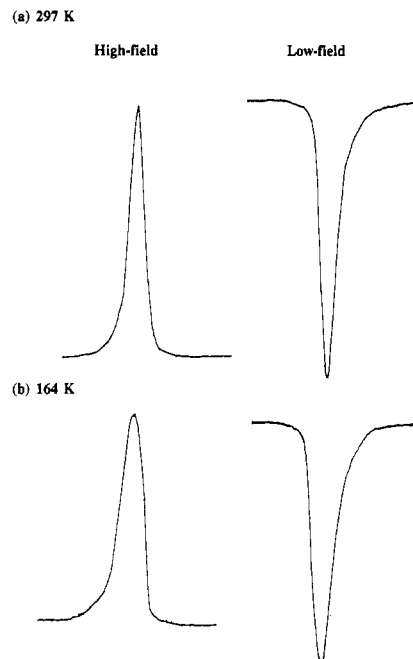


Figure 5. Resonance spectra of PDPT system for $H_0 \parallel z$ at two temperatures: (a) 297 K (fwhh = $3.1 \pm 0.2 \text{ G}$) and (b) 164 K (fwhh = $4.5 \pm 0.2 \text{ G}$).

dependence of the ZFS of the pentacene triplet in both PT and BA host crystals.

The X-ray and neutron studies of PT crystals indicated that the thermal motion of the center ring with respect to the outer rings is substantial and temperature dependent.^{2,16,25} The root-mean-square libration amplitude of the center ring along the long axis is 16.1° , and that of the outer rings is 8.3° at room temperature. The PT molecule is planar in its mean conformation at room temperature. However, at and below T_c , the rings are locked into the frozen positions and the molecule becomes nonplanar: the center ring is $\approx 23^\circ$ out of plane with respect to the outer rings: -7° , -16° , and -7° .² The librational motion of the rings follows a double-well potential with an activation energy of 200 cm^{-1} . The libration amplitude of the center ring diminishes further in the frozen state: 4° at 113 K. Thus, the motional effect should be minimal below T_c . This is further demonstrated in the NMR study of PT crystals: The proton T_1 diminishes drastically and becomes practically temperature independent below T_c .²⁶ Thus, the motional effect on the D value in PHPT and PDPT should occur only above T_c . The effect may be described in terms of multiple sites jumping of the pentacene triplet in the PT crystal.

The multiple sites structure of the PHPT system at liquid helium temperatures have been reported previously.^{23,27} The most recent fluorescence and intersystem crossing study of the pentacene triplet in PT crystals showed that pentacene could assume as many as four different distorted conformations as local structures. The energies of these four sites measured from the lowest $S_0 \rightarrow S_1$ transition origin O_1 are 4 cm^{-1} (O_2), 123 cm^{-1} (O_3), and 182 cm^{-1} (O_4). The conformations of O_1 and O_2 are nearly planar, while O_3 and O_4 are nonplanar. The distortion of pentacene in PT crystals could arise from the difference of molecular length between pentacene and PT along the long molecular axis.²³

The motional modulation effect is further supported by the line width measurements of the corresponding systems. The ESE field scan spectra of PDPT at two temperatures are displayed in Figure 5. The full width at the half-height (fwhh) is $3.1 \pm 0.2 \text{ G}$ at room temperature and $4.5 \pm 0.2 \text{ G}$ at 164 K, and it remains the same within our experimental uncertainty down to 5 K. We have not observed such a drastic change of the line width in the PHNA system, so the modulational narrowing at high temperature is manifested in the line width measurements.

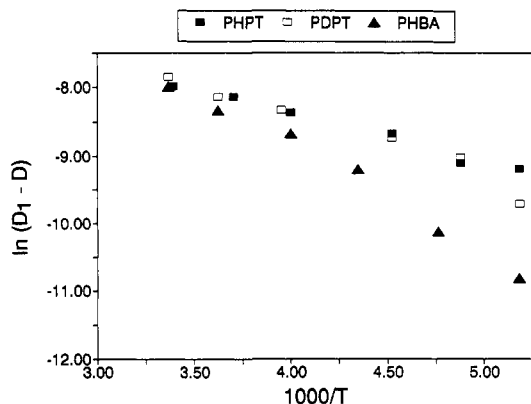


Figure 6. Plot of $\ln(D_1 - D)$ vs $1/T$ for the pentacene triplet in *p*-terphenyl and benzoic acid host crystals.

We would like to point out that the motional narrowing observed at high temperature in the ESE spectra is caused by a set of molecules undergoing multiple sites jumping, a dynamic effect, while the multiple sites observed at liquid helium temperatures in the optical spectra are a statistical distribution of molecules in multiple configurations, a static effect. Unfortunately, the multiple transition origins due to multiple sites observed in the optical studies were not observed in our low-temperature ESE experiments. Our low-temperature ESE signals may correspond to the most stable conformation.

We also would like to point out that the spin jumping reported in ref 1 is between two conformations of the same molecule (*intramolecular* jumping) and becomes measurable by spin echo techniques at low temperatures ($T < T_c$). The spin jumping described here is among multiple sites of different molecules (*intermolecular* jumping) which becomes important at high temperatures ($T > T_c$).

Since the rocking motion of the phenyl rings in PT at high temperatures ($T > T_c$) is the precursor of the multiple site formation at low temperatures, we may take these low-temperature conformations as the transient species involved at high temperatures in the motional modulation. If the multiple sites structure of the triplet manifold is similar to that of the singlet state, we may then consider the multiple site jumping in a pseudo-two-site model by taking O_1 and O_2 as one site and the distorted O_3 and O_4 sites as the second site. Then the observed D values can be evaluated from the following equation:

$$D = N_1 D_1 + N_2 D_2 \quad (3)$$

where N_1 and N_2 are the population fractions: $N_1 + N_2 = 1$ and $N_2/N_1 = \exp(-\Delta E/kT)$ with ΔE being the activation energy, D_1 is the limiting D value of the frozen state (0.04682 cm^{-1} for PHPT and 0.04685 cm^{-1} for PDPT), and D_2 is the average D value of the other multiple sites in the upper energy levels. If $N_1 \gg N_2$ (i.e., in the limit of $\Delta E > kT$), then eq 3 can be rewritten as follows

$$D_1 - D = (D_1 - D_2) \exp(-\Delta E/kT) \quad (4)$$

Thus, a plot of $\ln(D_1 - D)$ vs $1/T$ yields $\Delta E = 500 \pm 20 \text{ cm}^{-1}$ and $D_2 = 0.04241 \text{ cm}^{-1}$ for both PHPT and PDPT systems (Figure 6). The activation energy of 500 cm^{-1} is about 2.5 times greater than the reported activation energy for the librational motion of the rings in the neat PT crystal. This may be understood by considering that pentacene is a rigid molecule, and the distortion energy would be greater than the energy of the ring motion of PT molecules in the crystal.

We would like to point out the activation energy reported here refers to the jumping between two pentacene molecules at two different crystal sites, an *intermolecular* jumping as mentioned earlier. Note that the activation energy of the *intermolecular* jumping is almost 1 order of magnitude greater than that of the

intramolecular jumping (two conformations of the same site) reported in ref 1. Naturally, we would expect that the activation energy of the *intermolecular* jumping to be greater than that of the *intramolecular* jumping. Spectroscopically, the *intermolecular* jumping can cause motional narrowing effect and tends to reduce the ZFS at higher temperatures as we observed here, while the *intramolecular* jumping gives rise to spectral doubling and the intensity ratio of the doublets are governed by the Boltzmann distribution as described in ref 1.

Similar temperature effects may also occur in BA crystals. It is known that BA molecules form dimers in the crystal via hydrogen bonding between the carboxylic groups.³⁻⁵ These two configurations are interconvertible by simultaneous proton transfer along the two hydrogen bonds of the dimer (along the x axis). At high temperature both tautomers are equally populated, and the acid protons occupy the two positions corresponding to the energy minima of the double-well potential. The barrier heights were determined to be in the range $400\text{--}500 \text{ cm}^{-1}$. The interconversion between two tautomers was found to occur by thermally activated barrier crossing at a rate of $5 \times 10^9\text{--}9 \times 10^{10} \text{ s}^{-1}$ at room temperature.

In the hole burning and antihole production experiments at liquid helium temperatures, as many as five photopopulated sites were reported for the $S_0\text{--}S_1$ transition of the PHBA system.²⁸ The multiple-site formation in PHBA was attributed to a molecular motion (or lattice heating) induced in the excitation process due to the strong interaction between the hydrogen bond tautomerism of BA dimers and the photoexcited pentacene. The proton tunneling in the tautomerization of the BA crystal could further induce a slight rotation of the principal axes of the ZFS tensor as indicated in a recent spin-lattice relaxation measurement of the triplet state of pentacene-6,13-quinone in the BA crystal hosts.²⁹ We also found the spin dynamics of the pentacene triplet was affected dramatically by a deuteration at the carboxylic group.¹²

Thus, it is likely that the local BA tautomer states could influence the electronic structure of the guest molecule resulting in multiple conformations of the photoexcited pentacene molecule, planar and nonplanar or other orientational distortion, and therefore affect the ZFS parameters. Again, in a pseudo-two-site model, we obtain an activation energy of $950 \pm 50 \text{ cm}^{-1}$ from a plot of $\ln(D_1 - D)$ vs $1/T$ (Figure 6). The end-to-end length of BA is comparable to PT. Thus, a steric distortion of pentacene could be induced by the interconversion of the hydrogen bonding. Consequently, the motion of protons could introduce additional H...H repulsion between BA and pentacene. The proton T_1 of BA have been measured from room temperature down to 50 K. The T_1 decreases by about a factor of 50 from room temperature to 120 K, and it remains nearly constant from 120 to 50 K.⁵ This implies that molecular motion may become negligibly small below a critical temperature in BA crystals.

Thus, the molecular motion along the x axis of pentacene following the long-axis librational motion of PT and BA molecules will modulate the Z and Y principal values and therefore reduce the D value accordingly as we observed in the temperature dependence studies. We expect the molecular motion and/or distortion of pentacene to take place relatively more easily along the x axis, which could induce the H...H repulsion between the host and guest molecules.

On the other hand, we observed different temperature dependence in the PHNA system: the resonance field separation is strongly temperature dependent in the x and the y orientations and affects the E values, but it is only slightly temperature dependent in the z -axis orientation. We explain the effect arising from the small unit cell volume of the naphthalene host crystal ($\approx 60\%$ of PT and BA), where a pentacene molecule occupies two naphthalene sites in the crystal. This not only causes the misalignment of the principal axes of the guest molecule with

respect to those of the host by about 10° but also imposes some constraints on the motion of the guest molecule. Thus, a steric effect between the pentacene protons and the naphthalene protons could hinder the librational motion of the pentacene molecule along the x axis and in the yz plane. The molecular motion of pentacene in the naphthalene system may therefore be forced to take place more in the xy plane where the least steric effect is attained. Furthermore, there is no physical "disorder" (such as phase transition) associated with the NA crystals in the low-temperature region.

Finally, we would like to mention that the T_1 and T_m (phase memory time) and other kinetic parameters measured in our ESE studies show a remarkable temperature dependence for the PHPT, PDPT, and PHBA systems, but not for PHNA.¹³ We shall report these results to lend further support to the motional modulation effect in a forthcoming paper.²¹

Conclusion

Our detailed field scan ESE studies of the photoexcited triplet state of the pentacene molecule as a function of guest deuteration, host environment, and temperature yield the following results:

(1) The g values are independent of temperature, deuteration, and host, but they are anisotropic: $g_{xx} = 2.0025$, $g_{yy} = 2.0022$, and $g_{zz} = 2.0020$.

(2) The ZFS parameters are almost independent of the guest deuteration, but they show host and temperature dependence. The behavior of PHNA differs from that of the other systems which is attributed to the relatively small volume of the NA crystal (60% of PT and BA) and causes a misalignment of the principal axes of pentacene with respect to the host NA by about 10° .

(3) The D values of PHPT, PDPT, and PHBA increase with decreasing temperature in the range 190–300 K, and they remain almost constant in the range 5–190 K within experimental uncertainty. On the contrary, the D value of PHNA remains almost the same throughout the entire temperature range. The E value of all systems increase slightly and almost linearly with decreasing temperature throughout the entire range. We explain the temperature dependence of ZFS in terms of the following factors: (a) thermal population to higher vibrational or phonon modes and/or (b) motional modulation of the pentacene molecule due to the librational motion along the long-axis of p -terphenyl molecules in the PHPT and PDPT systems and the proton-transfer motion along the two hydrogen bonds of benzoic acid dimers in the PHBA system. Thus, we believe that the motional effect via

the modulation or steric distortion may play an important role in the temperature dependence of the ZFS, especially in the high-temperature region.

Acknowledgment. We thank Professor S. I. Weissman for his valuable comments. Acknowledgment is made to the National Science Foundation (CHE-9106499) and to the donors of the Petroleum Research Fund, administered by the ACS, for support of this research.

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