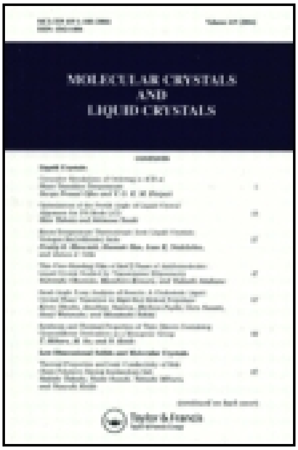

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Coherence in the Phosphorescence Triplet State of Naphthalene in Dihalobenzenes

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Coherence in the Phosphorescence Triplet State of Naphthalene in Dihalobenzenes

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The use of multiple pulse sequence in the lowest phosphorescent triplet state of naphthalene in single crystals of dihalobenzenes, *p*-dichlorobenzene and *p*-dibromobenzene is reported. Spin relaxation times from these experiments indicate that the external perturbations from the halogens overwhelm subtle intramolecular interactions such as deuteration of the guest naphthalene molecule. In addition, the use of a new method of determining the nature of line width broadening is reported. The result of the presaturated pulse optically detected magnetic resonance (ODMR) shows that the zero field ODMR of naphthalene in dihalobenzenes is inhomogeneously broadened for the bulk of the spins.

Recent advances in the use of pulse optically detected magnetic resonance (ODMR) were made by the initial theoretical and experimental work of Harris and co-workers.[1-2] They laid the foundation for the use of the technique based on observing the loss of coherence in the phosphorescent triplet state. More recently, van't Hoff and Schmidt have used multiple pulse sequences to observe spectral diffusion of quinoline in dilute solution of durene at very low temperatures,[3] while Pitts and El-Sayed reported a low power method of obtaining spin diffusional times.[4] We have chosen to study the systems of naphthalene in two dihalogenated benzenes, dichlorobenzene and dibromobenzene. The aim of the study was to observe the effects of deuteration of naphthalene upon the spin relaxation time and the line width, and to

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use multiple pulse sequences to observe spin diffusion within the spectral line width. In addition, a new method of identifying the nature of the line width is presented. By this method, the zero field resonance of naphthalene in dihalobenzenes has been found to be inhomogeneously broadened for the bulk of the spins.

EXPERIMENTAL

Commercially available naphthalene and dihalobenzenes were subjected to multiple crystallizations. The dihalobenzenes were extensively zone refined and doped with naphthalenes using concentration of less than 1% mole/mole. Single crystals were grown by the standard Bridgeman technique.

Conventional ODMR was accomplished by an experimental apparatus described previously.[5] In addition, calibrated microwave attenuators were used for the low power ODMR, along with a PAR Model 124 lock-in amplifier after prefiltration with a Keithly Model 427 current amplifier at the output of the photomultiplier tube. By pumping on the vapor above the liquid helium, temperatures of 1.3 K were routinely obtained. That spin-lattice relaxation was frozen at 1.3 K, relative to the phosphorescence decay processes, was ascertained by noting that the onset of the non-exponential decay occurred at roughly 5 K, below which temperature, all three components of the decay rates could be determined and did not vary by more than the experimental error of about 5–10%.

The coherence data were obtained by an apparatus described in detail in previous articles.[6] A microprocessor controlled both the multiregister photon counter and the pulse sequence generator. Briefly, the photon counter takes a base-line count of the cw phosphorescence intensity prior to the application of the pulse sequence. Then a preprogrammed pulse sequence is applied to the sample via TTL pulses to appropriate microwave switches which control the pulse width of the phase shifted microwave power. Then immediately after the pulse are applied, the photon counter is reactivated to count over a specified time interval, and normalization is accomplished by using the base line count. With spin-locking pulse sequence, the photon counts during the time the spin-locking field is applied, such that the intensity difference is examined between the time the spin-locking field is lifted and the application of the probe pulse. A maximum of 4 registers may be used for counting, with the dead time between the cessation of one register and initiation of the next register being continuously adjustable via the computer. Results are accumulated and averaged over a pre-determined number of experiments before parameters are changed in incremental steps.

In some cases, a chopper was used to extinguish the excitation light, thereby generating coherence signals from microwave induced delayed phosphorescence. In these experiments IR emitter-detector diodes were placed in the path of the chopper blades to generate TTL pulses used as interrupt controls for the computer.

The method used to obtain the full width at half maximum (FWHM) of the zero field transition was an ODMR technique somewhat similar to that reported by van der Velden and Veeman, but modified with the simultaneous application of a pre-saturation and pulse microwave sources. This technique is discussed in detail elsewhere.[7] Briefly, the technique involves the use of short microwave pulses which frequency is slowly swept in time. The pulse width is set to correspond to an inversion, or a π pulse (usually between 50–100 ns), as determined by a transient nutation experiment. Simultaneously, the *entire* zero field resonance transition is continously saturated by a very low power white noise. Depending upon the line shape, the resulting resonance signals can be classified into three distinct cases: (1) If the entire conventional ODMR line width is homogeneously broadened, no pre-saturated pulse ODMR signal is observed. However, the conventional slow passage ODMR signal will confirm that the zero field transition is present. (2) If the entire line width is inhomogeneously broadened, then the resultant signal will be identical in shape to a conventional ODMR signal. (3) If the zero field resonance is a combination of homogeneously and inhomogeneously broadened lines, then a dip will occur which shape will be the homogeneous low power conventional ODMR signal, except inverted. The wings of the line shape are caused by the inhomogeneous components. Noteworthy is that the inhomogeneously broadened wings are not generally observed by conventional slow-passage ODMR even with microwave power of about 1 W; some broadening is observed but this is due to power broadening or unresolved hyperfines. If the zero field resonance is a combination of inhomogeneously broadened lines of differing saturabilities, then a dip may also be observed. These two possibilities under 3 can clearly be distinguished, however, by comparing the homogeneous relaxation times from pulse ODMR experiments with the FWHM measurements (cf. Figure 1).

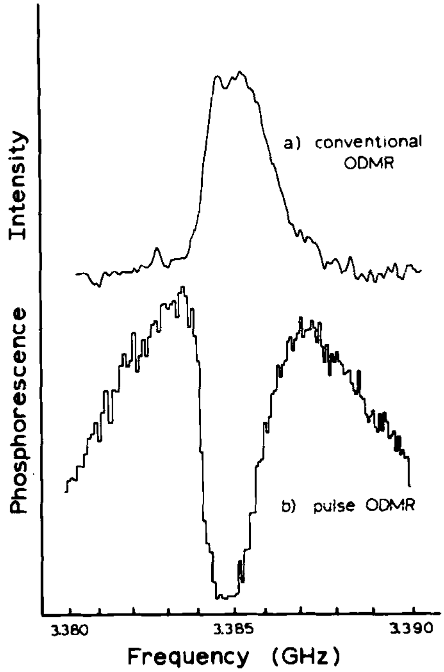

FIGURE 1 A comparison of the conventional low-power slow passage ODMR signal in a, and the pre-saturated pulse ODMR shown in b for one of the zero field transitions of naphthalene in dichlorobenzene host crystal.

RESULTS AND DISCUSSION

In Table I, tentative vibronic assignments of naphthalene in dihalobenzene host single crystals are shown, consistent with previous work on naphthalene single crystals by Hanson.[9] As indicated in this table, the phosphorescence spectra of these systems exhibits intense 0,0 phosphorescence origin band with relatively weak vibronic band intensities.

In Table II, a cumulative summary of triplet state data on naphthalene in dihalobenzene is given. As expected, the phosphorescence 0,0 band is red shifted by about 100 cm^{-1} upon deuteration of the naphthalene molecule. Host effects are not as pronounced, as reflected in the much smaller (ca. 4–12 cm^{-1}) shift in the 0,0 energies compared to chlorinated and brominated hosts, and even smaller (2–4 cm^{-1}) effect is observed upon host deuteration; in addition, no definitive trends in the shift can be ascertained. That intramolecular perturbation are manifest to a larger degree than intermolecular interaction is consistent with previous work on quinoline in heavy atom solvents.[4]

TABLE I

Tentative vibronic assignments from the phosphorescence spectra of naphthalene in *p*-dichlorobenzene (DCB) and *p*-dibromobenzene (DBB) single crystals at 1.4 K.

Host	DCB-h_4		DBB-h_4		DBB-d_4[a]			
Guest	$\Delta\nu$[b]	I[c]	$\Delta\nu$[b]	I[c]	$\Delta\nu$[b]	I[c]	Assignment[d]	
Naphthalene-h_8	(4829 Å)[e]	vs	(4827 Å)	vs	(4827 Å)	vs	0,0 origin	
	510	m	509	m	504	m	ν_1 (and ν_{17})[e]	a_{1g} (b_{3g})
	1018	vw	1017	vw	—	—	$2x\nu_1$	a_{1g}
	1163	vw	1160	vw	1165	vw	ν_4	a_{1g}
	1381	m	1381	m	1379	m	ν_5	a_{1g}
	1576	w	1575	w	1572	w	ν_7	a_{1g}
	1890	vw	1889	w	1886	w	$\nu_1 + \nu_5$	a_{1g}
	2084	vw	2082	vw	2078	vw	$\nu_1 + \nu_7$	a_{1g}
Naphthalene-d_4	(4807 Å)	vs	(4806 Å)	vs	(4805 Å)	vs	0,0 origin	
	492.2	m	487	m	488		ν_1 (and ν_{17})	a_{1g} (b_{3g})
	835	vw	829	vw	—		?	—
	981	vw	976	vw	—		$2x\nu_1$	a_{1g}
	1326	vw	1319	vw	—		ν_1 + ?	—
	1386	m	1383	m	1388	m	ν_5	a_{1g}
	1552	w	1547	w	1557	m	ν_7	a_{1g}
	1875	vw	1870	vw	1881	w	$\nu_1 + \nu_5$	a_{1g}
	2041	vw	2034	vw	2049	w	$\nu_1 + \nu_7$	a_{1g}

[a] Subspectra appear in systems with DBB-d_4 host with 0,0 at 4714 Å for naphthalene-h_8 and at 4735 Å for naphthalene-d_8.

[b] In cm^{-1}, ±5 cm^{-1}.

[c] Relative intensity with respect to 0,0 band. 100–80% vs; 80–50% s; 50–30% m; 30–10% w; 10–1% vw.

[d] Assignment with respect to reference 9.

[e] Normally superimposed, symmetry in parenthesis.

TABLE II

Triplet state parameters for naphthalene in dihalobenzene single crystals at 1.4 K.

Guest	Host	0,0 origin (cm^{-1})		Total Decay Contents k_i (sec^{-1})	Relative Radiation Rates k_i' (sec^{-1})	Zero Field Transitions[a] (MHz)
Naphthalene	DBB[b]	20,718	x	20.0	1.4	3372
			y	14.6	1.0	2401
			z	64.1	3.8	(910)
Naphthalene	DCB[b]	20,706	x	1.7	—	3385
			y	1.7	—	2474
			z	1.7	—	(911)
Naphthalene-d$_8$	DBB[c]	20,807	x	16	1.0	3376
			y	16	1.0	2407
			z	55	2.2	(909)
Naphthalene	DBB-d$_4$	20,710	x	12	1.0	3374
			y	15	1.2	2463
			z	66	6.3	(911)
Naphthalene-d$_8$	DCB[b]	20,803	x	0.59	0.10	3389
			y	0.32	0.07	2479
			z	1.85	0.84	(910)
Naphthalene-d$_8$	DBB-d$_4$	20,810	x	18	—	3377
			y	12	—	2467
			z	61	—	(910)

[a] Transitions listed in order: $\tau_x - \tau_z$, $\tau_y - \tau_z$, $\tau_x - \tau_y$. Values in parenthesis are from the difference of the other two resonances.

[b] Values of k_i and k_i' from Ref. 10.

[c] Values of k_i and k_i' from Ref. 12.

The decay constants from the sublevels of the phosphorescent triplet state are also given in Table II. The axis system used here is shown in Figure 2 with the zero field splittings for naphthalene-h$_8$ in dibromobenzene-h$_4$ as an example. Novosad and Hochstrasser have attributed the large increase in all of the rate constants and in particular, k_z, to external spin-orbit coupling via an electron-transfer mechanism between the guest and host along the *c*-axis of the host crystal.[10] The argument is based on the possible electron transfer between the lowest triplet of naphthalene and the singlet state of the N$^-$DCB$^+$ complex which results in the enhancement of radiative processes from all the triplet sub-levels of the guest molecule. Some preliminary T_2 experiments with molecular complexes involving naphthalene and perhalogenated benzenes indicate that homogeneous relaxation time of the magnitude observed here correspond closely to those observed in the molecular complexes.[11]

Zero field splittings for these systems are shown in Table II. The per-

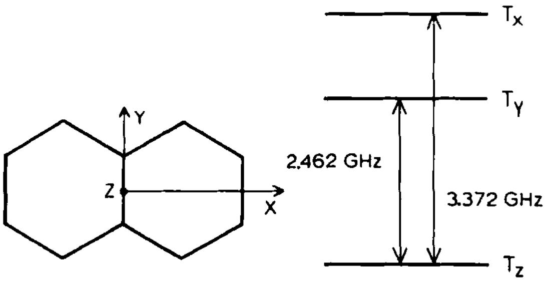

FIGURE 2 Axis system used in the text, along with the relative ordering of the zero field triplet state sublevels and resonances for naphthalene in dibromobenzene.

turbation to the zero field splittings arise from second order terms involving the spin-orbit coupling of singlet and triplet π, π^* with σ, π^* or π, σ^* states.[12,13] As seen in Table III, relative to isotopically mixed naphthalene single crystal, the depression in the triplet state zero field energies for τ_x, τ_y and τ_z are −0.4%, −12% and −3.9% respectively for DBB and 0, −11, and −3.4% for DCB host. The crystallographic data reveal little difference in the crystal structures for the two hosts, with the intermolecular distances between the stacked molecules along the c-axis found to be about 4.1 Å for both crystals.[14,15] The substitution of naphthalene in the host crystals occurs with the halogen–halogen axis collinear to the naphthalene long axis.[10] Thus the components of the orbital angular momentum which affect the τ_y and τ_z sublevels will be l_y and l_z, with l_y having the larger effect because of the projection axis of the perturbing dihalobenzene molecule.

An advantage of the pulse method in ODMR is the ability to directly observe effects of nuclear interactions. An example of this is the Carr–Purcell pulse train which detects the loss of phase coherence via randomly fluctuating local fields due to spin flips of nuclei in the vicinity of the Triplet electrons. The pulse sequence used was the Meiboom–Gill modification of the Carr–Purcell sequence and the results are shown in Table III. For sake of comparison the echo intensities were made to fit a first order exponential, and reflected in the large uncertainty. The difference in T_{2_p} between protonated and deuterated naphthalene in the host dihalobenzenes can be attributed to the smaller magnetic moment of the heavier hydrogen.

The T_2 times were determined by analysis of the decay of the intensity maximum of the echo shape as a function of the time allowed for the bulk magnetization vector to dephase and rephase (cf. Figure 3). The dephasing times are reflected in the T_2^* times and can be analyzed

TABLE III

Coherence times from multiple pulse sequence experiments for naphthalene in dihalobenzenes.

Guest[a]	Host[a]	Zero Field Resonance (MHz)	FWHM[b] (μs)	T_2[c] (μs)	T_2^*[c] (μs)	T_{2p}[d] (ms) $2\tau = 0.5$	T_{2p}[d] (ms) $2\tau = 1.0$	T_{2p}[d] (ms) $2\tau = 1.5$
Naphthalene	DBB	3372	0.60	4.8	1.4	0.63	0.28	0.042
		2462	0.43	3.8	0.30	0.24	0.15	0.036
Naphthalene	DCB	3385	0.50	3.4	0.30	0.31	0.32	0.10
		2474	0.29	2.6	0.080	2.0	1.1	0.20
Naphthalene-d_8	DBB	3376	1.1	3.8	0.23	0.10	0.072	0.016
		2467	0.70	2.6	0.34	5.6	0.14	0.052
Naphthalene-d_8	DCB	3389	0.65	3.6	0.42	4.0	2.6	0.062
		2479	0.44	2.0	0.12	8.9	4.3	0.044

[a] —d_8 indicates perdeuterated naphthalene; no suffix indicates protonated guest.

[b] FWHM as determined from pre-saturated pulse ODMR (see text).

[c] ±20%.

[d] 2τ in μsec (±30%).

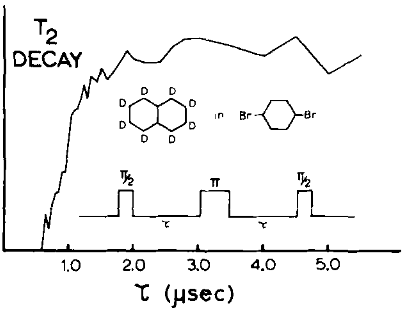

FIGURE 3 An example of an echo maximum decay signal for naphthalene-d_8 in dibromobenzene. The pulse sequence with microwave frequency at 3376 MHz is shown also, in which the two τ's are varied simultaneously.

by the spin echo shape (cf. Figure 4). The shape of the spin echo can be described by the average over a collection of Lorentzian line shapes and is given by

$$r_3 = r_3^0 \exp[-(\tau + \tau')/T_2] \exp[\,|\tau - \tau'|/T_2^*] \cos \overline{\Delta\omega}(\tau - \tau')$$

for a $\pi/2$, τ, π, τ', $\pi/2$ pulse sequence.[1] Here, r_3 is one of the three parameters in the geometrical model and is equal to the difference in the two vectors of the density matrix along $+z$ and $-z$. The factor in $\overline{\Delta\omega}$ must be included for off resonance cases. The variable T_2 used in the equation is from the analysis of the echo maximum decay. The T_2^* is then varied until a best fit to the experimental data is found, and this T_2^* is reported in Table III. An example of a computer fit is shown in Figure 5 for naphthalene in dibromobenzene.

The relaxation times derived from pre-saturated pulse ODMR are

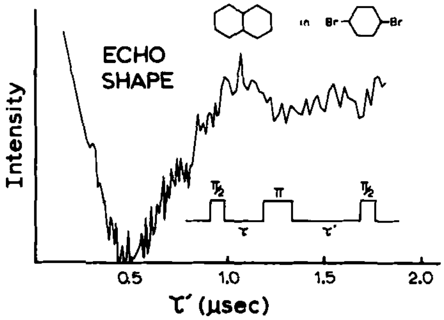

FIGURE 4 An on-resonance echo shape for naphthalene in dibromobenzene at 3372.0 MHz with the pulse sequence in which τ' is varied. Since τ is fixed at 0.5 μs, the echo minimum occurs at precisely the same τ' value.

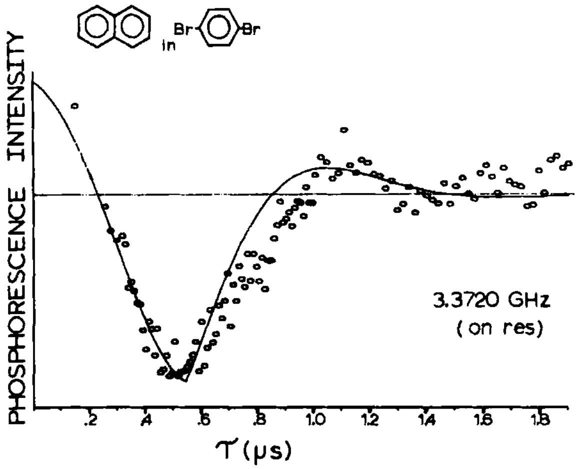

FIGURE 5 An echo shape analysis of the data shown in Figure 4 for naphthalene in dibromobenzene. The circled points are the original data and the solid line is the plot of the theoretical equation describing the echo shape. The solid horizontal line is the base line.

about a factor of two faster than those from coherence experiments for protonated naphthalene and indicate that the protons contribute to the line broadening in the zero field resonance. However, the fact that the T_2 and ODMR relaxation times are different indicates that the interaction occurs roughly in the time region of 10^{-6} sec or longer. This is consistent with proton interaction energies. Such contribution to line width broadening is not present in the perdeuterated naphthalenes as seen from the agreement found with the T_2 and relaxation times from pulse ODMR. Comparing T_2 and T_2^*, the large differences can be attributed to contribution to the spin relaxation times from inhomogeneously broadened components as identified from the pre-saturated pulse ODMR. In fact, the contribution to the total line width from the distribution of spin environments is roughly an order of magnitude more effective than any homogeneous processes (cf. Table III).

The analytical form of the Lorentzian echo line shape fits well for the $\tau_y - \tau_z$ transition, but the echo line shape for the $\tau_x - \tau_z$ resonance is extremely Gaussian. In addition, the pre-saturated ODMR shows greater contribution from the inhomogeneous components for the $\tau_y - \tau_z$ transition. Finally, the differences in the two transitions are reflected in the line widths of the pulse ODMR. The line width is narrower by roughly 50% for the $\tau_x - \tau_z$ transition when compared to that for $\tau_y - \tau_z$ resonance. The anisotropy in the T_2 and therefore in the line width, is reflected in the direction of the halogens which most influence the decrease in the zero field energies as discussed above. Additionally, the pulse ODMR experiments show consistently that $\tau_y - \tau_z$ resonance is admixed with larger amounts of inhomogeneously broadened species than the $\tau_x - \tau_z$ resonance. The spin-diffusional effects reflect the line width measurements when comparing the two resonances. This fact would allow one to conclude that the spin diffusion occurs within 10^{-3} seconds, but is slower than the multiple pulse duration used in T_2 measurements. This is consistent with rate constant estimates by van't Hoff and Schmidt of about 10-250 × 10^{-3} s^{-1}.[3]

For all the systems under study, spin-locking experiments yielded $T_{1\rho}$ times which corresponded well with the average of the phosphorescent lifetimes of the sublevels to which the microwave field coupled. This confirmed that the spin relaxation did not involve any geometrical rearrangements within the time the spin-locking field was applied.

In summary, spin coherence properties of the phosphorescent triplet state of naphthalene appear to be a sensitive function of intramolecular effects. External intermolecular interactions cause a large change in data as obtained by conventional ODMR. The pre-saturation pulse ODMR technique indicates that the single crystals containing naphthalene as a guest have substantial amount of spins in inhomogeneous environments. The characterization of the nature of these species is currently being undertaken.

Acknowledgments

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