

## Short Communication

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### Exciton trapping in dihalonaphthalene crystals

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Recent interest in the optical spectroscopy of dihalonaphthalenes has arisen because crystals of these molecules form excellent models of one-dimensional linear excitons, particularly crystals of 1,4-dibromonaphthalene [1 - 7]. In this communication we present a preliminary study of the phosphorescent triplet states in neat and chemically mixed dihalonaphthalenes of 1,4-dichloronaphthalene (DCN), 1-bromo-4-chloronaphthalene (BCN) and 1,4-dibromonaphthalene (DBN).

Optically detected magnetic resonance (ODMR) techniques were used to identify localized states in single crystals of the dihalonaphthalenes. Initially the triplet states of the dihalonaphthalenes were characterized by the total phosphorescence rate constants, by the triplet state zero field splittings (zfs) and by the vibronic progression in the phosphorescence spectra. In the dihalonaphthalenes these parameters are characteristic of a particular molecule. In the mixed crystal studies the identity of the individual emission peaks in the phosphorescence spectra and hence the zero point energies can be uniquely assigned. In these studies a particular dihalonaphthalene was dissolved in dilute quantities (usually less than 0.5 mol.%) as a guest in another dihalonaphthalene which served as the host matrix. Although the triplet energies of the guest are a sensitive function of the host crystal energies, the triplet state parameters just mentioned fell within a specified narrow range for a particular dihalonaphthalene. Thus the traps which were created in the chemically mixed crystals could be assigned to a particular guest molecule.

DBN was purchased from Pfaltz and Bauer. It was subjected to elution through a neutral alumina column, to recrystallization from ethanol and it was zone refined slowly at a rate of 2 cm h<sup>-1</sup> in a sealed tube for over 200 passes. Both DCN and BCN were synthesized from the respective 1-amino-4-halonaphthalene by the Sandmeyer reaction. The ether extract from the reacted diazotized mixture was washed, was decolorized and was dried over Na<sub>2</sub>SO<sub>4</sub> and the ether was evaporated. Recrystallization of the resulting solid residue from absolute ethanol gave approximately a 20% yield of the desired halonaphthalene. The material was then zone refined for an equiva-

lent of over 200 passes. The middle sections of the material in the zone refining tubes were then sealed under vacuum and single crystals were grown from the melt by the standard Bridgman method. The crystals were carefully annealed at just below the melting temperature.

The kinetic relaxation parameters of the total phosphorescence decay rate constants were obtained by several methods. The decay of the phosphorescence intensity measured subsequent to shuttering of the continuously applied excitation source was repetitively accumulated in a signal averager which was directly interfaced to a minicomputer equipped with a visual display. Using a linear regression program the resulting sum of the three decays was computer fitted to an equation describing the actual phosphorescence decay.

The total phosphorescence decay rate constants from the individual sublevels of the triplet state obtained by the aforementioned shutter method were consistent with those obtained by the microwave-induced delayed phosphorescence technique first described in refs. 7 and 8 and with those obtained by the rapid passage method described by Winscom and Maki [9].

The initial study involved the characterization of the triplet state parameters described earlier. Dilute concentrations of dihalonaphthalene were dissolved in host solvents which formed energetically deep traps. These included DCN, BCN and DBN in naphthalene- $h_8$ , naphthalene- $d_8$  and durene. The data presented in Table 1 show that the total phosphorescence rate constants and the zfs of the individual triplet sublevels are different for the three dihalonaphthalenes.

Once the triplet state parameters were characterized, traps formed in neat single crystals of the dihalonaphthalenes could be examined and the results are presented in Table 2. The zfs and the kinetic behavior of the most prominent trap are given in the table. In the several traps observed for each neat single crystal, the individual traps have slightly different zfs and phosphorescence rate constants, although they are still very similar to those observed in the deep trap systems. DBN and DCN both yielded phosphorescence emission spectra having narrow linewidths (Fig. 1), but the linewidths of the spectrum of BCN were much broader (Fig. 2). Presumably the reduced symmetry of BCN and the small difference in the size of the two substituted halogens would not allow the energetically preferred stacking orientation in the crystal formation. Rearrangements such as rotation about the in-plane long axis would not be easily allowed because of the large energy barrier, even though such a rotation would be the energetically preferred orientation. This was partially confirmed by allowing the BCN crystal to anneal over a period of several days at about  $10^\circ$  below the melting point of the crystal. Noticeable narrowing of the inhomogeneously broadened line was observed subsequent to annealing.

In the neat DCN, the appearance of the band origin at 4943 Å was very dependent on the past history of the crystal, particularly on impurity concentration and on the manner in which the crystal was grown (see Fig. 1). The lifetime of this band is much shorter than the lifetime of any of the

TABLE 1

Zfs, rate constants and the 0,0 band of the phosphorescence of DCN, BCN and DBN in naphthalene-h<sub>8</sub>, naphthalene-d<sub>8</sub> and durene

<i>Guest</i>	<i>Host</i>	<i>0,0 band (cm<sup>-1</sup>)</i>	<i>Transitions (MHz)</i>	<i>k<sub>1</sub> (s<sup>-1</sup>)</i>	<i>k<sub>2</sub> (s<sup>-1</sup>)</i>	<i>k<sub>3</sub> (s<sup>-1</sup>)</i>
DCN	Naphthalene-h <sub>8</sub>	20202	3328	19	16	0.71
			2485			
	Naphthalene-d <sub>8</sub>	20109	3370	25	14	0.51
			2497			
	Durene	19877	3283	72	21	0.52
			2491			
19798			3275			
BCN	Naphthalene-h <sub>8</sub>	20218	3157	180	75	2.2
			2647			
	Durene	20222	3164	160	60	2.0
DBN	Naphthalene-h <sub>8</sub>	20175 <sup>a</sup>	2926	267	164	11.1
			2829			
	Naphthalene-d <sub>8</sub>	20036	3182	120	12	0.60
	Durene	19908	2532	270	120	8.4

<sup>a</sup>Data taken from ref. 4.

TABLE 2

Zfs, 0,0 bands and rate constants of the first prominent localized state in neat single crystals of the dihalonaphthalenes

<i>Dihalonaphthalene</i>	<i>0,0 band (cm<sup>-1</sup>)</i>	<i>Transitions (MHz)</i>	<i>k<sub>1</sub> (s<sup>-1</sup>)</i>	<i>k<sub>2</sub> (s<sup>-1</sup>)</i>	<i>k<sub>3</sub> (s<sup>-1</sup>)</i>
DCN <sup>a</sup>	(20231)		(200)	(59)	—
	20198	3360	15	7.5	0.75
BCN	20214	3165	170	110	6.9
		2675			
DBN <sup>b</sup>	20164	2958	251	180	10.2
		2827			

<sup>a</sup>The parameters in parentheses are assigned to the exciton origin.

<sup>b</sup>Data taken from ref. 4.

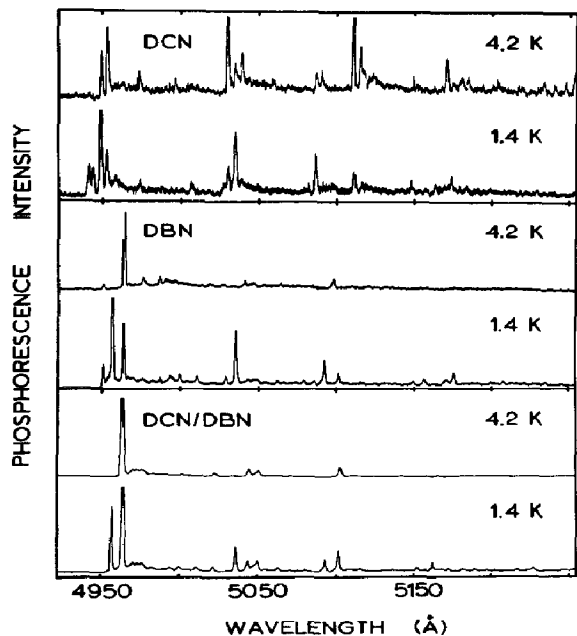


Fig. 1. Phosphorescence spectra of neat single crystals of DCN and of DBN at 4.2 and 1.4 K. Spectra for chemically mixed DCN in a DBN single crystal at the two temperatures are also shown.

traps found either in neat DCN or in crystals in which DCN is the guest. We have tentatively assigned this peak to the exciton origin and are attempting to observe the exciton magnetic resonance at zero field.

Although there are six possible guest-host combinations in the chemically mixed crystals, only DCN in DBN formed identifiable localized energy traps involving the guest molecule. This observation is peculiar considering that, in the neat crystals, the energies of the phosphorescence origin are

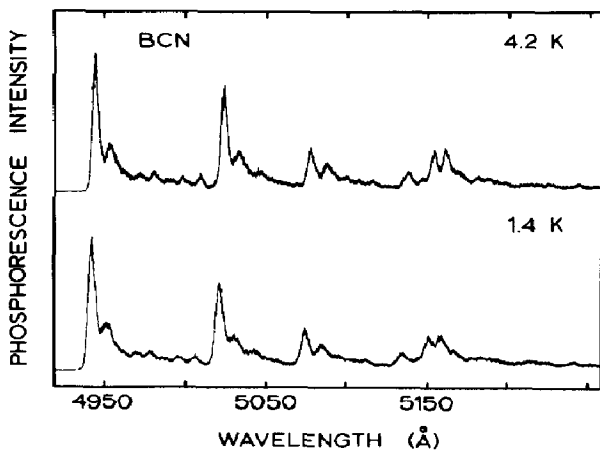


Fig. 2. Phosphorescence spectra of neat BCN at 4.2 and 1.4 K.

20 190, 20 214 and 20 231  $\text{cm}^{-1}$  for DBN, BCN and DCN respectively. The trend is consistent with arguments by Petruska [10] in which the halogen substituents would be predicted to cause a red shift due to first order inductive and second order conjugative and charge transfer effects. Table 3 gives the zfs, the trap depth and the kinetic parameters of the localized excitation of DCN in DBN crystals. The zfs and the rate constants of the origin at 20 164  $\text{cm}^{-1}$  are consistent with the assignment of the origin as arising from a trap found in neat DBN (*cf.* Table 2 and Trap I in ref. 4). The next energetically lower origin, however, has zero field parameters characteristic of DCN (*cf.* Tables 1 and 2) and the trap intensity is dependent on the concentration of DCN in the DBN solvent. We have tentatively assigned this origin to phosphorescent DCN molecules.

Attempts were made to observe BCN phosphorescence in DBN crystals. One of the phosphorescence origins found in neat DBN at 38  $\text{cm}^{-1}$  below the exciton band does vary somewhat in intensity with BCN concentration but a definitive assignment was not made. Because of the shallowness of the suspected BCN phosphorescence origin, the decay kinetics of the phosphorescence may be influenced by the thermal repopulation of the trap to the exciton band.

A preliminary solubility study of the various solid solutions of dihalonaphthalenes showed that, at about 10 mol.% of DCN in DBN, the phosphorescence linewidths became dramatically broadened indicating limited solubility. This is consistent with results of Bellows and Prasad [6] in which the solubility was found to be limited to less than 10%. DCN in BCN showed broadened phosphorescence at a concentration of about 7 mol.%, whereas no noticeable line broadening was observed for BCN in DBN at these concentrations.

Particularly in neat DCN and neat DBN, the presence of multiple trapping sites makes the characterization complex and only a portion of the ODMR results for one of several traps in each system is presented here. Following the crystallographic structural results in DCN, a complete examination of the dynamics of the trapping process using polarization measurements

TABLE 3

Zfs, rate constants and trap depths for the phosphorescent triplet states of DCN in a single crystal of DBN at 1.4 K

<i>0,0 origin</i> ( $\text{cm}^{-1}$ )	<i>Trap depth</i> ( <i>from exciton origin</i> )	<i>Transitions</i> (MHz)	$k_1$ ( $\text{s}^{-1}$ )	$k_2$ ( $\text{s}^{-1}$ )	$k_3$ ( $\text{s}^{-1}$ )
20164	28	≈ 2900	290	90	25
		—			
20145	47	3321	17	6.0	0.71
		—			
		—			

in ODMR, similar to those used by Dennis and Tinti [11] and by Lin and El-Sayed [12], will be presented. Also in progress is the use of pulse ODMR to study spin relaxation in the exciton trapping process.

### *Acknowledgment*

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