

# Single Crystal EPR and ODMR Studies of the T<sub>1</sub> States of Indene, Indole, Purine, and Related Molecules<sup>1</sup>

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**Abstract:** We have made single crystal EPR, zero field ODMR, and phosphorescence studies of the lowest excited triplet states of indene, indole, benzofuran, purine, benzimidazole, and indazole using 1,4-dibromobenzene (DBB) host. The magnitudes of ZFS and the directions of the principal axes were determined. The phosphorescence spectra were obtained and compared among each other. It was found that the  $D$  values are very similar ranging from 0.0978 to 0.1133 cm<sup>-1</sup> and  $|E|$  values are relatively large making  $D < 3|E|$ . For indole  $\rho_6 = 0.20$  and  $\rho_5 \leq 0.05$  were estimated. The large  $|E|$  and these spin densities indicate that large spin densities are delocalized into -C=C- groups. It was shown that these systems are adequately described as 1,2-disubstituted benzene (or azabenzene) with a strongly mesomeric substituent. It was found that indazole undergoes isomerization into 2-aminobenzonitrile at liquid helium temperature in DBB host by irradiation.

The lowest excited triplet states of indole, purine, and related molecules have attracted considerable attention in recent years because of their possible involvement in photo-biological processes.<sup>2,3</sup> There have been many spectroscopic,<sup>4-8</sup> EPR,<sup>9-12</sup> and theoretical studies<sup>13-15</sup> of these excited molecular states but details of their electronic wave functions have not been determined experimentally. Molecules such as indene, indole, and benzofuran can be considered as substituted benzenes with very strong mesomeric substituents and comparisons with other substituted benzenes are also interesting. Therefore, it seems desirable to obtain more detailed information about the nature of the T<sub>1</sub> states of these molecules. Magnetic resonance techniques (EPR and ENDOR) are potentially suited to elucidation of the detailed electronic structures of the T<sub>1</sub> state of these systems through hyperfine studies, but previous studies have been limited generally to rigid media EPR studies. No information about hyperfine splittings and spin distributions has been obtained from these studies. Furthermore, erroneous assignments of the axis systems of the zero field tensor and estimates of ZFS (zero field splittings) were sometimes made in such studies.

In the past several years, we have succeeded in making detailed single crystal EPR studies of substituted benzenes<sup>16-18</sup> and aromatic carbonyl molecules using 1,4-dibromobenzene (DBB) host.<sup>19</sup> In several systems we obtained well resolved hyperfine splittings.<sup>18,19</sup> DBB also proved to be a good host system for obtaining ZFS conveniently by ODMR (optically detected magnetic resonance) in numerous substituted benzenes containing no heavy atoms.<sup>20</sup> Accordingly, we have extended our single crystal EPR and ODMR studies to the molecules discussed in this paper. We have made conventional single crystal EPR studies of indole, 6- and 5-fluoroindoles, indene, and benzofuran at 4.2 K and zero field ODMR studies of these molecules as well as benzimidazole, indazole, and purine at 4.2 and 1.5 K. In this paper we discuss the phosphorescence spectra, ZFS, hfs, and some photochemical behavior of indazole. Zero field ODMR studies of indole in different hosts have been reported recently.<sup>21,22</sup>

## Experimental Section

(a) **Sample Preparation.** Mixed single crystals of DBB host and desired guest molecule were grown by the standard Bridgman method. Host DBB was recrystallized twice and zone refined extensively prior to use. Guest materials were purified by recrystallization and vacuum sublimation. About one weight percent of guest molecule was contained in the initial melt, but the actual concentration of the guest molecule is considered to be much lower. The

molecular structures of the guest molecules and the numbering systems used here are given in Figure 1.

(b) **Phosphorescence Spectra.** Phosphorescence spectra of the molecules studied here were obtained with our zero field ODMR setup described elsewhere.<sup>23</sup> These are given in Figure 2.

(c) **ODMR Experiments in Zero Field.** The ODMR method in zero field<sup>24,25</sup> offers a convenient method for obtaining ZFS of triplet state molecules. We have made ODMR determination of ZFS of the T<sub>1</sub> states of the molecules listed in Figure 1 using the rapid passage method.<sup>23,26,27</sup> The experimental setups and the procedures used are essentially the same as those described in a previous paper.<sup>23</sup> The microwave was repeatedly swept through the frequencies corresponding to the  $i \leftrightarrow j$  transitions and the changes obtained in the emissions monitored at the 0-0 band of the phosphorescence were stored and averaged on a Varian C-1024 CAT. Normally, we swept through 0.1-0.5 GHz with sweep times of 0.1-5 sec.

The height of the signal produced by a single rapid passage is easily obtained by solving the rate equation with appropriate initial conditions under the assumption of slow spin lattice relaxation rate.<sup>22</sup>

$$\frac{dn_i}{dt} = K_i - k_i n_i \quad (1)$$

$K_i$  and  $k_i$  are the populating and decay rates of the sublevel  $i$ . The height of the signal at time  $t$  after microwave sweep is given by

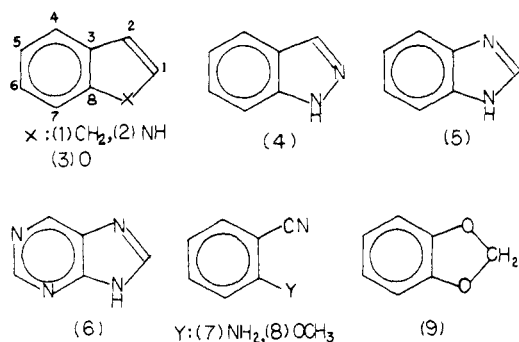
$$\Delta I_{ij}(t) = A(n_j - n_i)(k_i^r e^{-k_i^r t} - k_j^r e^{-k_j^r t}) \quad (2)$$

where  $k_i^r$  and  $n_i$  are the relative decay rate and the steady state population of the sublevel  $i$ .  $A$  is a proportionality constant which depends on the extent of the population transfer by the microwave transition. At time  $t = 0$ , or immediately after the microwave sweep,

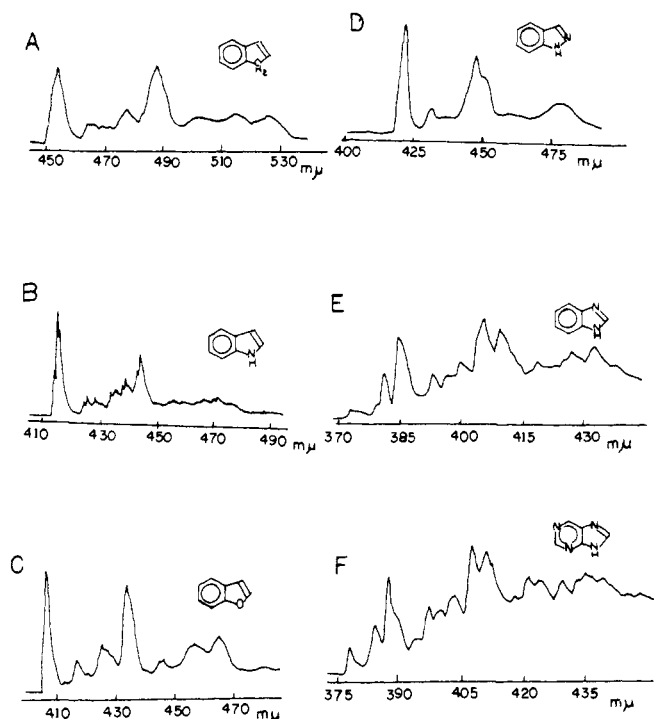
$$\Delta I_{ij}(0) = A(n_j - n_i)(k_i^r - k_j^r) \quad (3)$$

Thus the intensity of the signal depends on  $k_i^r - k_j^r$ ,  $n_j - n_i$ , and  $A$ .

In the present ODMR experiments, we have used DBB, a heavy atom containing host. There are several advantages to the use of this host for the present study, since our primary interest is the magnetic properties of the T<sub>1</sub> state. First, the lifetimes of the guest molecules are shortened (10-100 msec) because of external heavy-atom effect. Thus it is easy to establish the condition that the spin-lattice relaxation time is longer than the lifetime of each spin sublevel. Second, we can use the rapid passage technique very effectively because the lifetimes are short. In these experiments all sublevel decay rates are shorter than 1 sec and a 1 sec microwave sweep rate is sufficient. Normally an accumulated average signal of several hundred repetitive sweeps can be achieved within a few minutes. This is a particular advantage when contrasted with the situation in which many of the same guests in nonheavy atom environment have lifetimes of several seconds.<sup>21</sup> Third, we could obtain large  $k_i^r - k_j^r$  for many of the systems studied here because, al-



**Figure 1.** Molecular structures and the numbering systems: (1) indene, (2) indole, (3) benzofuran, (4) indazole, (5) benzimidazole, (6) purine, (7) 2-aminobenzonitrile, (8) 2-methoxybenzonitrile, (9) 1,2-methylenedioxybenzene.



**Figure 2.** Phosphorescence spectra in DBB host at 4.2 K: (A) indene, (B) indole, (C) benzofuran, (D) indazole, (E) benzimidazole, (F) purine.

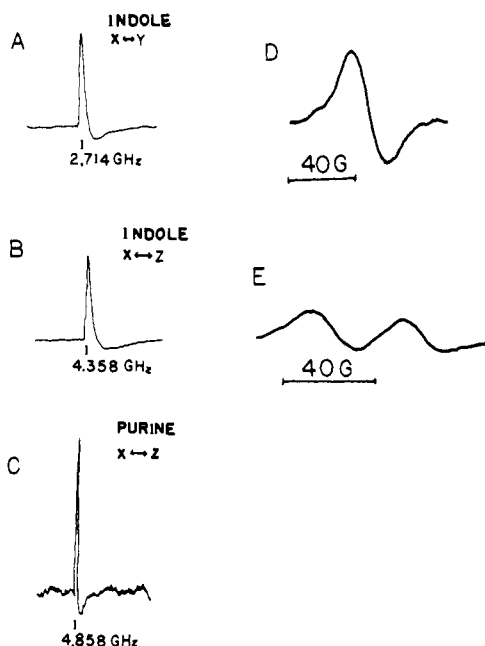
though the external heavy atom effect enhances all the radiative decay rates, one of them was usually enhanced tremendously giving very large  $k_i^r - k_j^r$ . Fourth, population of triplet states via host  $S_0 \rightarrow T_1$  transition followed by triplet state energy transfer often brings favorable population differences and large  $n_i - n_j$ . In Table I  $k_i$ ,  $k_i^r$ , and  $n_i$  of indole in DBB are given to illustrate these points. It is clear that large  $k_i^r - k_j^r$  and  $n_i - n_j$  are obtained here. Although we did not determine these quantities for other systems, we feel that judging from the strong signal intensities obtained large  $k_i^r - k_j^r$  and  $n_i - n_j$  are obtained in many of the systems studied here. Fifth, the guest molecules studied here dissolve in DBB host reasonably well and give relatively narrow well defined ODMR signals.

There is one disadvantage of using heavy atom containing host. The decay rates obtained here are not an intrinsic molecular property. However, the use of heavy atom containing host has proved to be useful in studying the magnetic properties of the many molecules in the  $T_1$  state. Typical ODMR signals are shown in Figure 3.

(d) **EPR Measurements in High Field.** Although zero field ODMR experiments conveniently give information about the energies of spin sublevels, they do not yield information about the di-

**Table I.** Dynamic Properties of Indole in DBB Host

	$i$	$k_i$ , sec <sup>-1</sup>	$k_i^r$ relative	$K_i$	$n_i$	$(k_i^r - k_j^r)(n_j - n_i)$ relative
Indole	$x$	127	1	1	1	$xy$ 2.18
(DBB)	$y$	12.3	0.16	0.35	3.6	$yz$ 0.072
	$z$	11	0.10	0.21	2.4	$zx$ 1.26



**Figure 3.** Typical ODMR and EPR signals. A to C, rapid passage ODMR signals obtained in DBB host at 4.2 K. (A) Indole:  $x \leftrightarrow y$  transition; 0.5 sec sweep over 170 MHz; average over 300 scans. (B) Indole:  $x \leftrightarrow z$  transition; 0.5 sec sweep over 340 MHz; average over 300 scans. (C) Purine:  $x \leftrightarrow z$  transition; 0.5 sec sweep over 1140 MHz; average over 70 scans. (D and E) EPR signals of the z axis peaks of 5- and 6-fluoroindole: (D) 5-fluoroindole, (E) 6-fluoroindole.

rections of the principal axes of fine structure tensors. Accordingly we made high-field EPR measurements of some of the present systems. All EPR measurements were made at 4.2 K with a Varian V-4502 spectrometer. A Varian V-4531 multipurpose cavity was widened with two silver spacers in order to accommodate a homemade fingertip (13 mm OD) helium dewar. The cold shield for the fingertip section of the dewar was supplied by the cavity itself which was cooled down by liquid nitrogen contained in a brass can directly connected to the cavity. The brass can and the cavity were thermally insulated from the outside by styrofoam and an evacuated quartz window. The sample crystal was mounted on a plexiglass holder connected to a stainless steel rod whose rotation angle was read at the top of the Dewar. Excitation light was supplied by a Hanovia 1000 W mercury-xenon lamp. The exciting light was filtered through a saturated solution of NiSO<sub>4</sub> and a Corning UV transmitting filter. The EPR measurements and determination of ZFS were made in a similar manner as that described by Hutchison and Mangum.<sup>28</sup>

The monoclinic DBB crystal has two molecules per unit cell and cleaves in the  $bc$  plane.<sup>29</sup> The crystal was cut to  $\sim 5 \times 8 \times 1$  mm with the cleavage plane as the largest plane. In order to orient the crystal in a desired orientation the direction of the crystallographic  $c$  axis was identified with the aid of a polarizing microscope. Since we did not know the exact orientation of the guest molecules in DBB host, we first assumed that the guest molecules replace host molecule as shown by either Figure 4a or Figure 4b with their molecular planes parallel to each other. We next aligned the crystal so that the direction of the applied field ( $H$ ) rotated within the  $N-\alpha$  or  $L-M$  plane of one type of DBB molecule. This is done in the following way. The flat surface ( $bc$  plane) of the crystal was placed on the flat surface of the mounting rod as shown in Figure 4e. When we wished to rotate  $H$  within the  $N-\alpha$  plane of one type of

Table II. Spectroscopic and Magnetic Properties

	$V_{00}, \text{cm}^{-1}$	$D, \text{cm}^{-1}$	$E, \text{cm}^{-1}$	$X, \text{GHz}$	$Y, \text{GHz}$	$Z, \text{GHz}$	Main vibrational bands, $\text{cm}^{-1}$
1. Indene	22,075	0.1079	-0.0472	2.493	-0.336	-2.156	570, 1125, 1580.
2. Indole	24,155	0.0978	-0.0453	2.335	-0.381	-1.995	600, 766, 1050, 1313, 1569
3. Benzofuran	24,570	0.1076	-0.0530	2.664	-0.514	-2.150	548, 1063, 1544
4. Indazole	23,753	0.1003	-0.0382	2.147	-0.134	-2.004	550, 1370, 1555
5. Benzimidazole	26,810	0.1133	-0.0409	2.358	-0.094	-2.264	457, 570, 825, 1364, 1600, 1782, 2154, 2369
6. Purine	26,434	0.1009	-0.0584	2.759	-0.742	-2.016	456, 695, 1110, 1330, 1476, 1663, 1932, 2162
7. 2-Aminobenzonitrile	24,552	0.1019	-0.0277	1.849	0.189	-2.037	
8. 2-Methoxybenzonitrile <sup>a</sup>	26,371	0.0995	-0.0781	3.334	-0.1348	-1.999	
9. 1,2-Methylenedioxybenzene	27,189	0.0845	-0.0407	2.065	-0.376	-1.689	

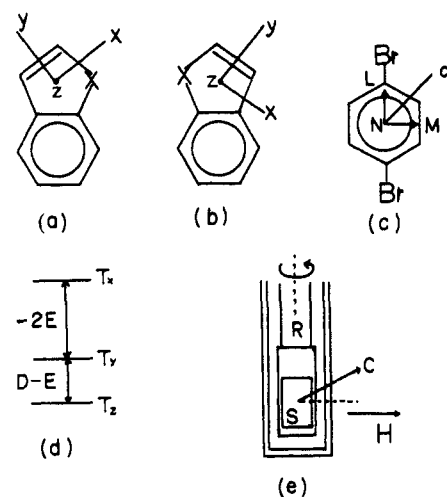
<sup>a</sup>The assignment of ZFS is tentative.

DBB molecule, the crystal was mounted so that the  $c$  axis is rotated counterclockwise by  $30^\circ$  from the direction of  $\mathbf{H}$  (Figure 4e). The rotation of the sample holder then rotates  $\mathbf{H}$  approximately within the  $N-\alpha$  plane and within the  $z-x$  or  $z-y$  plane of the guest molecules if the guest molecule replaces a host molecule as shown in Figure 4. Similarly we can rotate  $\mathbf{H}$  within the molecular plane of one DBB molecule by mounting the crystal with the  $c$  axis  $60^\circ$  clockwise from the  $\mathbf{H}$  direction. Since the guest molecule can occupy either the (a) or (b) orientations shown in Figure 4, we may expect signals from four differently oriented guest molecules. In practice we normally observed two sets of strong signals coming from the guest molecules occupying two translationally inequivalent sites. Presumably one orientation is favored in most systems. Examples of EPR signals are given in Figure 3.

## Results

**(a) Phosphorescence Spectra.** The phosphorescence spectra of indene, indole, and benzofuran are very similar to each other (Figure 2). The spectra are characterized by a strong 0-0 band and a band corresponding to  $\sim 1550 \text{ cm}^{-1}$   $-\text{C}=\text{C}-$  stretching mode. The phosphorescence spectra of indole and benzofuran are similar to those reported by previous workers,<sup>4,6,7,30</sup> although the energies of the 0-0 bands are somewhat different. On the other hand, the phosphorescence spectrum of indene is entirely different from those reported previously<sup>7,31</sup> with the 0-0 band located about  $3000 \text{ cm}^{-1}$  lower than those reported previously. The vibrational structures are also very different. In view of the similarity of ZFS and the vibronic structures of the emission spectra between indene, indole, and benzofuran and the strong phosphorescence emission obtained in DBB host in all cases, we feel that our phosphorescence spectrum of indene is genuine. The phosphorescence of indene in glass at 77 K is extremely weak and we think that the previously reported indene spectra might have been due to impurities. The spectrum of indazole has strong bands at 0-0, 0-1370 and 0-1550  $\text{cm}^{-1}$ . Our spectrum is similar to that reported previously.<sup>4</sup>

On the other hand, the phosphorescence spectra of benzimidazole and purine are very different from those of the above systems but are remarkably similar to each other. Both spectra have weak 0-0 bands and are rich in vibronic bands, although the vibrational frequencies are considerably different. Hence, the main features of the phosphorescence spectra of purine and benzimidazole seem to be determined by the  $-\text{N}=\text{C}-$  group. Although our purine spectrum is more structured, the general aspect of the spectrum is rather similar to that reported by Cohen and Goodman.<sup>5</sup> The detailed radiative and nonradiative properties of these molecules will be investigated in the future.



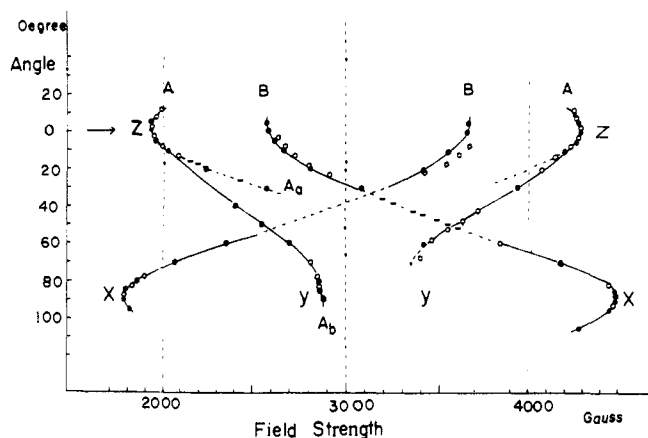
**Figure 4.** Axis system and possible orientations of guest molecules. (a) and (b) are two possible orientations of the guest molecule with respect to the host molecule DBB (c). (d) Triplet state sublevel energy scheme. (e) shows the mounting of crystal on the sample holder. S, sample crystal; R, holder rod. H and C indicate the directions of the applied field and the  $c$  axis of the sample crystal, respectively.

**(b) ODMR Results.** The zero field parameters of the molecules shown in Figure 1 were determined from zero field ODMR results using the spin Hamiltonian

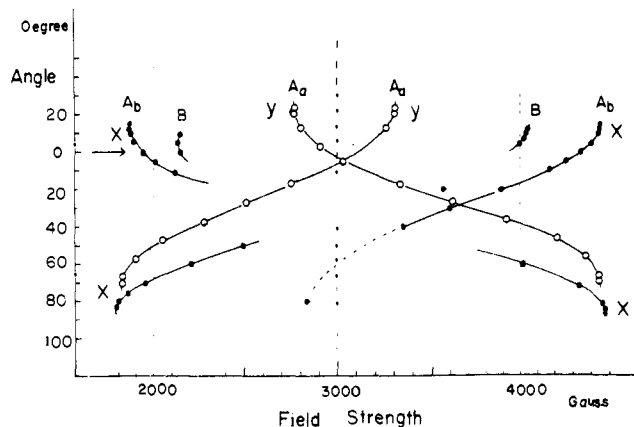
$$\begin{aligned} \mathcal{H} &= D(S_z^2 - \frac{1}{3}S^2) + E(S_x^2 - S_y^2) \\ &= -XS_x^2 - YS_y^2 - ZS_z^2 \end{aligned} \quad (4)$$

where  $X = \frac{1}{3}D - E$ ,  $Y = \frac{1}{3}D + E$ , and  $Z = -\frac{2}{3}D$ . Here we assumed the energy level scheme shown in Figure 4d. In analogy with the other  $^3\pi\pi^*$  aromatic molecule<sup>1</sup> the  $T_z$  sublevel is considered to be the bottom sublevel. As discussed in the next section our high-field EPR results show that  $D < 3|E|$  in indole, indene, and benzofuran indicating  $|T_x - T_y| > |T_y - T_z|$ . Although no high-field EPR experiments were made for indazole, benzimidazole, and purine, we tentatively assign  $3|E| > D$  for these systems in analogy with the cases of indene, indole, and benzofuran. The ZFS determined by the ODMR method are given in Table II. The  $D$  values are similar ranging from  $0.0978 \text{ cm}^{-1}$  for indole to  $0.1133 \text{ cm}^{-1}$  for benzimidazole. The  $|E|$  values are relatively large for all the systems and range from  $0.0382 \text{ cm}^{-1}$  in indazole to  $0.0584 \text{ cm}^{-1}$  for benzofuran.

Maki et al. recently made ODMR experiments with indole in various environments including indole crystal and



**Figure 5.** Angular dependence of the EPR signals of indene in DBB at 4.2 K. Crystals were oriented so that **H** rotates within the  $N-\alpha$  plane of one type of DBB molecule. A and B indicate the signals for the molecules occupying two translationally inequivalent molecules. a and b indicate two different orientations indicated in Figure 4. (●) and (○) indicate two different measurements with different crystals. → indicates the angle at which the cleavage plane of the crystal faces to the exciting light.



**Figure 6.** Angular dependence of the EPR signals of indene and 6-fluoroindole in DBB. Crystal was oriented so that **H** rotates within the molecular plane of one type of DBB. A, B, a, b, and → are the same as those used in Figure 5: (●) indene, (○) 6-fluoroindole.

indane.<sup>21,22</sup> They found that the signals are broad even in indole and indane crystal and are accompanied by satellites, which may arise from multiple sites of guest molecules. On the other hand, we have found strong ODMR peaks with relatively narrow line widths (typically less than 10 MHz) and few satellites for all the molecules studied here. Therefore, all the guest molecules studied here seem to fit reasonably well into DBB host in one preferred orientation.

(c) **EPR Spectra, Directions of Principal Axes, and Hfs.** EPR signals from indole, benzofuran, and indene at 4.2 K are fairly strong at stationary points. However, they quickly weaken when the crystal is turned away from the stationary points. Accordingly, we made complete angular dependence studies only in indene and 6-fluoroindole. In other systems signals were studied only near the stationary points (Figures 5 and 6).

When the crystal is mounted so that **H** rotates within the  $N-\alpha$  plane of one type (A type orientation) of DBB molecule, **H** becomes parallel to **N** when the cleavage (*bc*) plane nearly faces the exciting light. At this orientation we obtained stationary point peaks from indene at 4282 and 1947 G. These peaks are identified as the **Z** axis peaks (Figure

5). We obtain another set of signals coming from the molecules occupying translationally inequivalent sites (B type molecule) at ~2650 and 3600 G. The rotation of the sample holder by 90° brings two sets of stationary points, one at 4470 and 1795 G (we call these *x* axis peaks) and another at 2880 G, and with this rotation **H** becomes approximately parallel to the ethylenic  $-C=C-$  or perpendicular to it depending on whether indene replaces DBB in the (a) or (b) orientation. The experimental results on indene show that the 2880 peaks are main ones although both types of signals are observable. The crystal rotation described above also brings **H** nearly parallel or perpendicular to  $-C=C-$  in the B type molecule at this orientation. The B type molecules give the 4470 and 1800 G signals. Similar angular dependences were obtained in the case of other guest molecules.

When the crystal was oriented so that **H** rotates within the LM plane of the (A) type molecule we obtained the angular dependence of the signals given in Figure 6. In the case of indene the *x* axis peak was obtained when **H** is about 10° away from the *bc* plane. On the other hand, in 6-fluoroindole we obtained the *x* axis signals when **H** is about 70° away from the *bc* plane. These differences are presumably due to the difference in the dominant orientations of the guest molecules.

The complete angular dependence of the signal of 6-fluoroindole in the L-M plane is shown in Figure 5. In the case of indene a rotation of about 90° also produces the 4400 and 1850 G signals of the (B) type molecules.

In the above EPR studies we have oriented crystals assuming that the guest molecules replace the host molecules substitutionally as shown in Figure 4. In order to confirm the validity of this assumption we have calculated the field strengths of the stationary points in the high-field EPR experiments using ZFS obtained by zero field experiments. The field strengths of the stationary points are given by<sup>2a</sup>

$$H_z = \frac{1}{g\beta} \{ (h\nu \pm D)^2 - E^2 \}^{1/2}$$

$$H_{x,y} = \frac{1}{g\beta} \left\{ \left( h\nu \pm \frac{D \pm 3E}{2} \right)^2 - \frac{(D \pm E)^2}{4} \right\}^{1/2}$$

The values calculated using  $g = 2.0023$  are compared with the high-field experimental results in Table III. Considering the errors inherent in orienting the crystal and the deviations of the  $g$  values from the free-electron value the agreement is considered as very satisfactory.

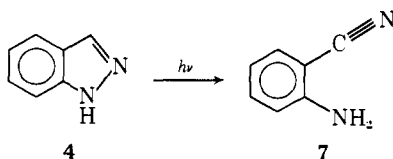
The angular dependence of the signals of indene, indole, and benzofuran indicate that: (1) the differences ( $\Delta H_x$ ) between the high- and low-field *x* axis signals (in-plane stationary points) are larger than that ( $\Delta H_z$ ) for the *z* axis signals (out-of-plane stationary points) showing  $D < 3|E|$  when we take the *z* axis normal to the plane of the molecule. This result is in agreement with the conclusion obtained for indole from the magnetophotoselection experiment by Zuclich.<sup>11</sup> (2) The *x* axis is nearly parallel or perpendicular to the  $-C=C-$  direction if the guest molecule replaces the host molecules as shown by Figure 4.

However, the experimental results cannot determine the direction of the *x* axis unambiguously, since the *x* direction of the (a) orientation and the *y* direction of the (b) orientation are close to each other. If the large spin density on the  $-C=C-$  group is the cause of the large  $|E|$ , it is likely that the direction of the *x* axis is parallel to  $-C=C-$  and the orientation (b) is the preferred one for indene. The calculation of ZFS for indole by Zuclich also predicts that the *x* axis is along the  $-C=C-$  direction.<sup>15</sup> Accordingly, we make the axis assignment given in Figure 4 tentatively.

In our high-field EPR experiments no proton hfsc's were obtained. Therefore, we investigated 5- and 6-fluoroindole

in order to study spin distributions. The  $z$  axis peak of 6-fluoroindole gave well resolved hfsc's with 38 G separation, while that of 5-fluoroindole was a single peak with a line width of 18 G (Figure 3, D and E). Using  $A_z = 193$  G for the  $z$  axis fluorine hfsc,<sup>32</sup> we obtain  $\rho_6 = 0.20$ . Since the extra broadening of the  $z$  axis peak of 5-fluoroindole due to fluorine substitution is estimated to be less than 5 G,  $\rho_5$  is estimated to be less than 0.05. Since the fluorine substitution is not expected to alter spin distributions significantly, these spin densities approximate those of indole.

**(d) Low-Temperature Photochemistry of Indazole.** In the course of our ODMR experiments on indazole we noted that a new phosphorescence spectrum appears upon the irradiation of indazole in DBB at 4.2–1.5 K (Figure 7). The intensity of the new spectrum increases with time as the sample is irradiated. ODMR signals monitored at the 407  $m\mu$  band (the peak due to the irradiation product) were obtained at 1.664, 2.221, and 3.884 GHz. When we monitor the ODMR signals at 421  $m\mu$  we have signals at 4.358 and 1.879 GHz in addition to those obtained at the 407  $m\mu$  peak. We felt that the most probable photochemical process for indazole is the isomerization shown by,



To test this hypothesis we studied the phosphorescence spectrum and ODMR signal of 2-aminobenzonitrile. As shown in Figure 7, the 0–0 band of **7** agrees with the 0–0 of the indazole photoproduct. The microwave transition frequencies of **7** agree exactly with those obtained at the 407  $m\mu$  band of the photoproduct. Accordingly, we conclude that the above photochemical process is taking place effectively in DBB host at 1.5 K. After this work was completed, a report was published on the room-temperature photochemical conversion of **4** into **7**.<sup>33</sup> Our results show that the same reaction can take place through the  $T_1$  state even at 1.5 K in solid state.

## Discussion

**(a) Triplet State Energies.** The energies of the  $T_1$  states of indole and benzofuran are about 24,500  $\text{cm}^{-1}$  and similar to those reported by the previous workers. The energy of indene is considerably lower than those of indole and benzofuran and indicates that the interaction between the phenyl ring and the  $-\text{C}=\text{C}-$  group is stronger in indene than in indole and benzofuran. The  $-\text{C}=\text{C}-$  group in indole and benzofuran may deviate slightly from the plane of the phenyl ring reducing the interaction between  $-\text{C}=\text{C}-$  and the phenyl ring. It is interesting to note that the energy of the  $T_1$  state of indene determined here is close to that of styrene determined by Evans from  $S_0 \rightarrow T_1$  absorption.<sup>34</sup>

Among the molecules we have investigated, the  $T_1$  states of benzimidazole and purine are considerably higher than those of the other systems. The interaction between the ring and the  $-\text{N}=\text{C}-$  group seems to be considerably weaker than the interaction between the phenyl ring and the  $-\text{C}=\text{C}-$  group. The location of the 0–0 band of purine determined in DBB host is very close to that obtained by Cohen and Goodman in ethanol.<sup>5</sup>

**(b) EPR Parameters and Electronic Structures.** The zero field splittings of indole and purine have been determined previously. Our  $D = 0.0978$   $\text{cm}^{-1}$  and  $E = -0.0453$   $\text{cm}^{-1}$  for indole are similar to those determined by Maki et al. using indane crystal.<sup>22</sup>  $D^*$  of purine has been reported to be 0.154  $\text{cm}^{-1}$ .<sup>10</sup> Our  $D$  and  $E$  values give  $D^* = 0.1428$   $\text{cm}^{-1}$ ,

Table III. Comparisons between the Observed and Calculated Field Strengths (G) for the Stationary Points

		Indene		Indole		Benzofuran	
		Obsd	Calcd	Obsd	Calcd	Obsd	Calcd
$H_x$	High	4470	4481	4398	4400	4565	4575
	Low	1795	1797	1895	1889	1715	1709
$H_y$	High	<i>a</i>	3235	<i>a</i>	3275	3315	3308
	Low	2860	2861	2865	2855	2750	2743
$H_z$	High	4282	4283	4165	4177	4250	4272
	Low	1947	1941	2055	2058	1932	1948

<sup>a</sup> Difficult to observe this peak because of the overlapping with strong free-radical signal.

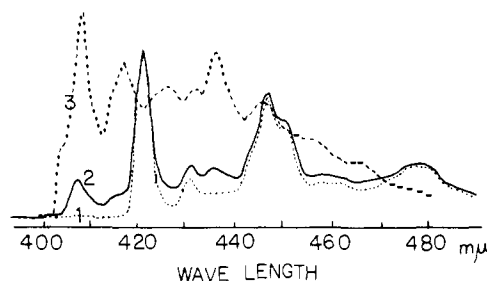


Figure 7. Phosphorescence spectra of indazole and 2-aminobenzonitrile in DBB host at 4.2 K: (---) initial phosphorescence spectrum of indazole; (—) phosphorescence spectrum of indazole after irradiation of 2 hr; (- - -) phosphorescence spectrum of 2-aminobenzonitrile.

which is considerably lower than the value given by Helene.<sup>10</sup> However, solvent effect may be large in this type of system.

The most logical way to look at the electronic structures of the  $T_1$  states of the present systems is to view them as 1,2-disubstituted benzene with one very strong mesomeric group. Accordingly, we have studied ZFS of several 1,2-disubstituted benzenes. The  $D$  values of the present systems are considerably smaller than those of monosubstituted benzenes such as benzonitrile ( $D = 0.1430$   $\text{cm}^{-1}$ ) and phenylacetylene ( $D = 0.1339$   $\text{cm}^{-1}$ ),<sup>17,18</sup> but substantially larger than those of some 1,2-disubstituted benzenes such as 1,2-methylenedioxybenzene ( $D = 0.0845$   $\text{cm}^{-1}$ ). They are indeed similar to those of 2-aminobenzonitrile ( $D = 0.1019$   $\text{cm}^{-1}$ ) and 2-methoxybenzonitrile ( $D = 0.0995$   $\text{cm}^{-1}$ ), which have one strongly mesomeric group. The  $D$  values of the present systems thus are consistent with those of other 1,2-disubstituted benzenes with one strong mesomeric group. In this type of system the spin density at the position para to the strongly mesomeric substituent is large. The large  $\rho_6$  and very small  $\rho_5$  observed in indoles are similar to known cases of  $T_1$  states of substituted benzenes with a strong mesomeric group and further support our view of them as substituted benzenes with a strong mesomeric substituent.

Although a complete analysis of ZFS requires much detailed calculation, we can discuss them qualitatively based on the theoretical work<sup>35–37</sup> on ZFS of benzene, naphthalene, and their substituted molecules. Generally speaking, the two most important factors which determine the magnitude of  $D$  are considered to be the extent of configuration mixing and the extent of delocalization of unpaired electrons. The former tends to increase  $D$  while the latter tends to decrease  $D$ . The extent of delocalization in the present systems is larger than in other substituted benzenes but smaller than in naphthalene. In a previous paper<sup>18</sup> we have shown that the extent of configuration mixing is rather small (under 10%) in phenylacetylene and benzonitrile. The observation that  $D$  is similar to that of naphthalene but

Table IV. Estimated Degree of Spin Delocalization into Substituents

System	0-0, cm <sup>-1</sup>	$\rho_p^a$	In substituents
Indole (-C=C-)	24155	0.20	0.40
Acetophenone (-C=O)	25324	0.29	0.30
Phenylacetylene (-C≡C-)	25120	0.31	0.25
Benzonitrile (-C≡N-)	26780	0.34	0.20

<sup>a</sup>  $\rho_p$  is the spin density at the carbon para to the substituent.

much smaller than those of benzonitrile and phenylacetylene indicates that the lowest excited triplet state of the present systems is also approximately described by the one-electron excitation from the highest occupied  $\pi$  electron MO ( $\pi_{-1}$ ) to the lowest unoccupied MO ( $\pi_{+1}$ ) and that the extent of configuration mixing is very small. However,  $D$  calculated for benzene with a single excited configuration is less than 0.1 cm<sup>-1</sup>.<sup>35</sup> In fact,  $D$  for 1,2-methylenedioxybenzene was found to be rather small showing that it is possible to have a small  $D$  for substituted benzenes with little delocalization. This indicates that some configuration mixing is necessary to explain the observed magnitude of the ZFS.

The observation that the in-plane principal axes of the zero field tensor are nearly parallel and perpendicular to the C=C direction indicates that  $E$  is likely to be determined by the spin density on the C=C group and that there is a large delocalization of spins into the C=C group. This is in agreement with the results of simple  $\pi$ -electron MO calculations, although the results of MO calculations strongly depend on the choice of parameters.

The large delocalization of spins into the -C=C- group is shown clearly, if we compare the observed  $\rho_6$  of indole with those of other substituted benzenes with strong mesomeric groups. In these systems the spin distribution so far known experimentally and the results of UHF calculation indicate that  $\rho_4 \approx \rho_8 \approx 0.5\rho_6$ ,  $\rho_3 < \rho_6$ , and that  $\rho_5 \approx \rho_7$  are small.<sup>18</sup> If we apply this to 6-fluoroindole, it is estimated that about 40% of spins are delocalized into the -C=C- group. In Table IV the estimated values of the spin densities delocalized into the -C≡N, -C≡CH, -C=O, and -C=C- groups are compared. It is clear that the order of the extent of delocalization is -C=C- > C=O  $\approx$  -C≡CH > -C≡N.

The spin distributions in the present systems should resemble those of the corresponding radical anions, since the configuration  $\pi_{-1} \rightarrow \pi_{+1}$  dominates. Although the spin densities of the negative ions of indole are not known, styrene negative ion may well be chosen as a system for comparison, because the -C=C- group is the dominant perturbing substituent which determines the spin distribution. Indeed  $\rho_6 = 0.20$  and  $\rho_5 \leq 0.05$  estimated for the T<sub>1</sub> state of 6-fluoroindole is in good agreement with  $\rho_6 = 0.205$  and  $\rho_5 = 0.032$  in styrene negative ion.<sup>38</sup> Combined with our previous results<sup>17,18</sup> on the T<sub>1</sub> states of substituted benzenes and <sup>3</sup> $\pi\pi^*$  aromatic carbonyls, there seems little doubt that the

spin distributions of the triplet state of substituted benzenes with a strong mesomeric group are very similar to those of the corresponding radical anions. Indeed, the spin distributions in the T<sub>1</sub> states seem to be similar to those in doublet states in a large number of systems.<sup>17-19,39-41</sup>

**Acknowledgment.** The present work was supported in part by an institutional NSF grant.

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