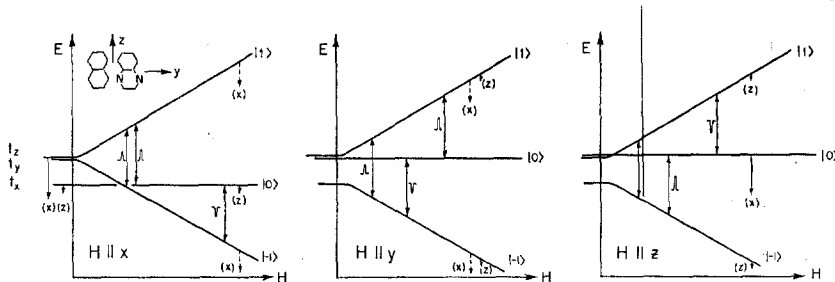


FIG. 1. A schematic representation of the Zeeman levels for the lowest triplet state of either N or Q as a function of  $H$ . The zero-field states appear on the far left; the high-field states on the right. The expected changes in the optical signals for the various ESR transitions are indicated.



spond with the quinoxaline system so that both molecules can be discussed on an equal footing. The  $\Delta m=1$  and  $\Delta m=2$  transitions are shown together with the expected changes in the optical signal assuming the top level to be the major source of emission intensity. Measurements were made on  $N/D$ ,  $dN/D$ ,  $Q/D$ ,  $N/\Phi_2$ , and  $dN/\Phi_2$  for each ESR transition, along each of the three principal axes, and for various polarizer orientations. For  $Q/\Phi_2$  we measured only the  $\Delta m=2$  transition. In every instance, our ODMR results agreed with the predicted changes shown in Fig. 1 regardless of whether the host was durene or biphenyl. As a further check of the emissive properties of N and Q we used the ODMR method to determine the character of the emission from randomly oriented molecules dissolved in rigid glasses.<sup>8</sup> Again, these results are in agreement with our single-crystal results and imply that emission is mainly from the top zero-field level.

Recently Schmidt *et al.*<sup>3</sup> reported their new results, for quinoxaline in durene, obtained by the ODMR method as well as by flash-excitation studies.<sup>6</sup> They also concluded that the emission was mainly from the top zero-field level.

It is important to note at this point that the results of measurements using the "static" optical polarization technique and those using "dynamic" techniques do not depend on the same combination of parameters. The static measurements are a function primarily of the radiative rate constants (or their ratios) whereas ODMR measurements depend upon the nonradiative rate constants as well. Although the nonradiative rate constants are not known, it does not appear possible to choose values for them such that the ODMR results and the static results can be made compatible.

We would like to suggest, therefore, that the emission from the lowest triplet state of naphthalene and quinoxaline originates primarily from the top zero-field level not only in EPA and biphenyl but in durene as well. This would imply that the interpretation of the results obtained by the static method will require re-evaluation, although it is not clear at this point how that should be done.

The foregoing discussion has of necessity been qualitative since the nonradiative rate constants for the individual zero-field states are unknown. However, it should be possible, in principle, to determine both the

radiative and the nonradiative rate constants for each of these states using the ODMR technique. Work toward this end is currently in progress.

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## $T_1/T_2$ and Spin Relaxation in the Benzene Anion\*

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The anomalously broad linewidths of the radical anion of benzene<sup>1,2</sup> ( $B^-$ ) and associated radicals of high symmetry have been the subject of considerable interest. A number of possible explanations have been proposed which are all based on time-dependent interactions between polar solvent (or cation) and  $B^-$  that affect the otherwise vibronic ground-state degeneracy of the molecule.<sup>3-6</sup> There is the crucial question as to which spin-dependent interaction would then be affected, and this can be at least partially answered in terms of comparison with detailed spectral observables. For example, solvent-induced hyperfine fluctuations<sup>3</sup> have been ruled out<sup>7</sup> because of the absence of any significant variation in widths among the hyperfine components. Also, field-dependent contributions were shown not to be important.<sup>8</sup> Spin-orbit (and associated)

interactions<sup>4-6,9,10</sup> which are nuclear-spin independent have also been considered in terms of effects peculiar to the case of vibronic degeneracy.<sup>4-6</sup>

In McConnell's discussion of a spin-orbit pulse (SOP) mechanism<sup>4</sup> he noted "...that the principal effect of the magnetic SOP... is to broaden the PMR lines..." so one might expect  $T_1 > T_2$ . Kivelson's Orbach-type (KO) process<sup>5</sup> and the related rotational spin-orbit (RSO) process<sup>5,6</sup> were expected to involve only nonsecular terms (i.e.,  $S_{\pm}$ ), and this yields a prediction that  $T_1 = \frac{1}{2}T_2$ .<sup>11</sup> Thus, a careful measurement of the *absolute* value of  $T_1/T_2$  for  $B^-$  solutions<sup>12</sup> using progressive saturation techniques<sup>13</sup> was undertaken by us. In order that such results be meaningful, we found that important experimental corrections must be made for (1) variation of microwave field<sup>13</sup> and dc field-modulation amplitude over sample length, (2) geometric distortions of cavity standing-wave patterns<sup>14</sup> due to Dewar insert, etc., and (3) variation of cavity  $Q$  with temperature. Our results are  $T_1/T_2 = 1.1 \pm 0.1$  and are reasonably constant in the region  $-60^\circ$  to  $-120^\circ\text{C}$  (but the ratio increases at higher temperatures) with  $T_2 \approx 1.9 \times 10^{-7}$  sec below  $-90^\circ\text{C}$ .<sup>15</sup> While these results are in disagreement with the mechanisms as initially proposed, it was recognized that the effects of rotational tumbling, which is so important in liquids, had not been included. When a proper analysis is carried out, utilizing in part the generalized spin-relaxation theory,<sup>6</sup> one finds under reasonable assumptions that for the RSO  $T_1^{-1} = T_2^{-1} = (2\Lambda/\tau_R\delta)\Delta g_s \operatorname{sech}(u)$ , where  $\tau_R$  is a rotational correlation time,  $\Lambda$  is the molecular spin-orbit parameter,<sup>4</sup>  $\delta$  the solvent-induced splitting of the degeneracy of the ground vibronic state with  $\Delta g_s$  the average  $g$  shift for the lower energy state, and  $u = \delta/2kT$ ; while for the SOP mechanism  $T_1^{-1} = T_2^{-1} = 2A^2/3\tau_2(1+A^2)$ , where  $A = 2\eta\Lambda\tau_1/\hbar$ ,  $\tau_1$  and  $\tau_2$  are the lifetimes of the symmetrical and distorted radical environments, respectively, and  $\eta$  is a vibronic reduction factor.<sup>4</sup> Both these mechanisms would be simultaneously operable, and they would, in general, be associated with large  $g$  shifts:

$$\Delta g = \Delta g_s \tanh u = (8\Lambda/3\delta)\eta^2 \tanh u$$

which are not observed.<sup>2,5</sup> Kivelson proposed the KO mechanism as a means to avoid this problem which he associated specifically with the SOP mechanism. Our reanalysis shows that the KO mechanism *would* yield *identical* spectral observables as the RSO mechanism, i.e.,  $T_1 = T_2$ , an anomalously large  $g$  shift, and the same dependence on  $\delta$ . Its essential differences are only in the specific source of a nonvanishing spin-orbit matrix element and the use of random solvent-radical vibrational modulation. There is only one remaining way that any of these mechanisms would be expected to be important without being associated with large  $g$  shifts, viz.  $\delta < kT \sim 150 \text{ cm}^{-1}$ , so  $\Delta g \rightarrow 0$ .

Since such a small value of  $\delta$  might be unreasonable<sup>2-5</sup> for ionic interactions between  $B^-$  and cation (or polar solvent), it appears necessary to look to some other mechanism. However, a more careful analysis suggests that the inherent symmetry of this interaction was not fully exploited in the above mechanisms. That is, the potential function for solvent- $B^-$  interactions is of sixfold symmetry, e.g., if attack of a positive ion between two adjacent carbon atoms is the most stable configuration,<sup>3</sup> there must be six such potential minima corresponding to interaction with each of the six C-C bonds, and there is a potential maximum for the positive ion displaced symmetrically with respect to the ring. But this description is nothing more than that for the lower potential sheet of a Jahn-Teller situation, wherein now the relative motions of cation and  $B^-$  split the ground-state  $B^-$  degeneracy and lead also to equivalent nonsymmetric locations of the cation in the lower sheet. Thus  $\delta$  in the above mechanisms corresponds nearly to the Jahn-Teller distortion energy. Suppose now,  $\delta$  is large enough to render the spectral contributions of the above expressions (and equivalent ones for the KO mechanism) insignificant. There can still be a rotation or tunneling of the solvent distortion or cation around the edge of the ring<sup>16a</sup> with a consequent orbital following:  $\psi = (1/\sqrt{2})[e^{i\theta}F_0^{(2)} - e^{-i\theta}F^{(-2)}]$ , where  $F_0^{(\pm 2)}$  are degenerate vibronic<sup>16</sup> functions<sup>3</sup> and  $\theta$  gives the orientation of cation. Thus, stationary states of the combined system may be classified according to sixfold-symmetry yielding ground and low-lying rovibronic tunneling states which are either doubly degenerate ( $E$ -type symmetry) or nondegenerate ( $A$ -type symmetry). When a simple limiting model of harmonic oscillations (at frequency  $\omega_a$ ) of the cation within each potential well is considered and allowance is made for the small overlap integral  $\gamma_0$ ,<sup>16b</sup> there is a nonvanishing diagonal spin-orbit contribution which splits the stationary-state  $E$  levels into energies:  $\pm \hbar\epsilon = \pm 2\eta\Lambda S_z [3\gamma_0/(2+\gamma_0)]$  when McConnell's spin-orbit term is used.<sup>4</sup> The additional reduction factor of order  $\gamma_0$  is a Franck-Condon-type factor, the analogue of which should also appear in the earlier mechanisms since the equilibrium position of cation in the upper potential sheet is different from those of the lower sheet. The effect of thermal fluctuations is to induce transitions between the tunneling levels (combined with other rotational transitions), yielding lifetimes of  $\tau_v$ . An analysis for liquids yields, for this spin-orbit tunneling (SOT) mechanism,

$$T_1^{-1} = T_2^{-1} = (4/3) | \epsilon |^2 \tau_v (2+e^v)^{-1} \quad (\text{when } T_e \omega_0 \ll 1),$$

where

$$\tau_v^{-1} = (2+e^v)\tau_i^{-1} + \tau_R^{-1}$$

and  $v$  is the tunneling splitting of  $A$  and  $E$  levels divided by  $kT$ .

Thus, the suggested SOT mechanism is independent of  $\delta$ ; it allows for tunneling through relatively low barriers, as opposed to a SOP mechanism which involves classical activation to a relatively high barrier (of energy  $\delta$ ); it has no associated large  $g$  shifts. Further details will be discussed elsewhere.<sup>17</sup>

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‡ National Institutes of Health Predoctoral Fellow 1967-1968.

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<sup>15</sup> A similar measurement made on tropenyl radical in the liquid phase by W. V. Volland in these laboratories yielded  $T_1/T_2 = 1.0 \pm 0.1$  and  $T_2 = 4.2 \times 10^{-7}$  sec at  $+165^\circ\text{C}$ .

<sup>16</sup> (a) Typical values of  $\Delta$ , the height of the saddle points, are usually an order of magnitude less than  $\delta$ . U. Öpik and M. H. L. Pryce, *Proc. Roy. Soc. (London)* **A238**, 425 (1957); W. D. Hobey and A. D. McLachlan, *J. Chem. Phys.* **33**, 1695 (1960); L. C. Snyder, *ibid.* **66**, 2299 (1962). (b) One can estimate  $\tau_{\text{vib}} \cong \exp(-3\Delta/2h\nu_{\text{vib}})$ . I. B. Bersuker, *Soviet Phys.-JETP* **16**, 933 (1963).

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## Heat of Formation and the Structure of Pyrene-*N,N*-Dimethylaniline Heteroexcimer

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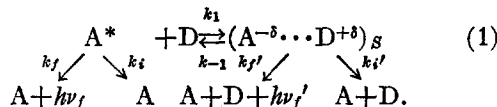
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In order to elucidate the electronic structure of the pyrene-*N,N*-dimethylaniline (DMA) heteroexcimer (h.e.),<sup>1</sup> we previously studied the effect of solvent polarity on the frequency of the h.e. fluorescence; we also pointed out the strongly polar nature of the h.e.<sup>2</sup> Later, Weller and co-workers<sup>3</sup> extended similar studies to several other systems.

From studies concerning the solvent effects upon the

quantum yield and the decay time of the pyrene-DMA h.e. fluorescence, we have concluded that solvent molecules affect not only the molecular geometric configurations of the h.e., but also its electronic structure,<sup>4</sup> namely, the h.e. becomes more ionic and accordingly,  $k_f'$  decreases and  $k_i'$  increases as the solvent polarity is increased. Therefore, the extent of the decrease of the quantum yield of the h.e. fluorescence with increase of solvent polarity is much larger than that of the fluorescence decay time. The direct participation of solvent molecules in the formation of the h.e., even in slightly polar solvents such as toluene and monochlorobenzene, seems to be essential. This solute-solvent interaction may finally lead to the formation of the ion pair or to the dissociation of the h.e. into the ion-radicals in the moderately or strongly polar solvent causing the complete quenching of the fluorescence:



On the other hand, Weller and co-workers<sup>5</sup> have interpreted similar results in the case of anthracene-*N,N*-diethylaniline h.e. as due to the competition of the two processes,  $\text{A}^* + \text{D} \rightarrow (\text{A}^{\cdot-\cdots}\text{D}^{\cdot+})^*$  and  $\text{A}^* + \text{D} \rightarrow (\text{A}_S^{\cdot-\cdots}\text{D}_S^{\cdot+})$ , where  $(\text{A}^{\cdot-\cdots}\text{D}^{\cdot+})^*$  is the fluorescent h.e. and  $(\text{A}_S^{\cdot-\cdots}\text{D}_S^{\cdot+})$  represents the solvent shared ion pair which is nonfluorescent. It is assumed that the latter process depends on the solvent polarity whereas the former process is independent of it.

In order to clarify further the fluorescence behavior of the h.e., we have made some detailed studies on the formation and decomposition processes and the heat of formation of the pyrene-DMA h.e. in several solvents.

$$\frac{\eta_f}{\eta_f'} = \frac{k_f}{k_f'[\text{D}]} \left[ \frac{k_i' + k_i}{k_1^0} \exp\left(\frac{E_1}{kT}\right) + \frac{k_{-1}^0}{k_1^0} \exp\left(-\frac{B}{kT}\right) \right], \quad (2)$$

$$[\text{D}] = \frac{1}{\tau k_1^0} \exp\left(\frac{E_1}{kT}\right) + \frac{\tau' k_{-1}^0}{\tau k_1^0} \exp\left(-\frac{B}{kT}\right),$$

where  $k_1 = k_1^0 \exp(-E_1/kT)$ ,  $k_{-1} = k_{-1}^0 \exp(-E_{-1}/kT)$ ,  $B = (E_{-1} - E_1)$ ,  $\eta_f$  and  $\eta_f'$  are fluorescence quantum yields of  $\text{A}^*$  and the h.e., respectively, and  $[\text{D}]_h$  is the half-value concentration of Reaction (1). From the plots of  $\log(\eta_f/\eta_f')$  or  $[\text{D}]_h$  against  $1/T$ , the heat of formation  $B$  can be evaluated using the linear relation at the high-temperature region and the activation energy  $E_1$  can be estimated from the linear relation at the low-temperature region. By using the  $B$  value and the observed values of  $\nu_f$  and  $\nu_f'$ , the ground-state destabilization energy  $U$  can be obtained. The results are given in Table I, where  $\epsilon$  is the static dielectric constant of the solvent. In the case of pyridine solution, because it was difficult to observe clearly the straight line corresponding to the second term in Eq. (2), the values given in the table are only approximate ones.