

**Triplets.** As noted above all of the molecules studied here are ground-state singlets, the triplets being excited states. Energies are given in Table I, and since the geometries presented no unusual features they are not given in the text.

**Cartesian Coordinates.** For all of the molecules studied in this manuscript we are including as supplementary material their cartesian coordinates.

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**Supplementary Material Available:** Listing of Cartesian coordinates for compounds 1-8, 11, and 12 (17 pages). Ordering information is given on any current masthead page.

## Evidence for Triplet State Sublevel Selective Photochemistry in Phthalazine

D. A. Leinwand, S. M. Lefkowitz,<sup>1</sup> and H. C. Brenner\*

Contribution from the Department of Chemistry, New York University, New York, New York 10003. Received February 13, 1985

**Abstract:** The relative sublevel populating rates for the photoexcited triplet-state zero-field sublevels of phthalazine in 2-octanol have been found to be unequal, as determined via ODMR. Hence, the explanation proposed by Basu et al.<sup>2</sup> to rationalize the lack of TM spin polarization in the reaction between photoexcited phthalazine and 2,6-di-*tert*-butylphenol in 2-octanol appears unfounded. We propose a kinetic model where sublevel selective rates for hydrogen abstraction lead to an attenuation of TM polarization. The mechanism for sublevel selectivity is based upon the enhanced reactivity of  $n,\pi^*$  states toward hydrogen abstraction, *vis-à-vis*  $\pi,\pi^*$  states, and the unequal admixture of  $n,\pi^*$  character into each zero-field sublevel of the predominantly  $\pi,\pi^*$  phthalazine  $T_1$  state. Calculations indicate a fivefold decrease in TM polarization for phthalazine (compared to the case of no sublevel selectivity), but only a twofold decrease for quinoxaline, where a TM polarization pattern has been observed.

The photoexcited triplet state of any organic molecule is composed of three nearly degenerate but quite distinct magnetic sublevels. These sublevels arise from the fact that, in the absence of an external magnetic field, the total spin angular momentum of the triplet state may be quantized in one of three mutually perpendicular planes, generally associated with symmetry elements of the molecular framework.<sup>3</sup> The energy splittings of the three sublevels are largely caused by the dipolar interactions of the unpaired electrons' magnetic moments and arise from differences in average interelectron distances in the three zero-field spin states.

A striking variation in behavior between the sublevels concerns the rates of intersystem crossing (isc) to and from each sublevel. Relative rates often vary by factors up to 100 for this spin-forbidden process. These differences can be ascribed to the varying admixtures of singlet character, via spin-orbit coupling, into the sublevels due to their different symmetry properties.<sup>4</sup>

The unequal isc rates of the sublevels may be exploited to determine their individual photophysical parameters via optically detected magnetic resonance spectroscopy (ODMR).<sup>5,6</sup> Here, the populations of the zero-field sublevels of a phosphorescent triplet state are probed by inducing transitions between sublevels via application of resonant microwave radiation (zero-field splittings are typically 0.1 to 10 GHz). The population transfer is observed by detecting changes in the phosphorescent intensity

of the sample, which arise from the differential propensity of each sublevel to radiate to the ground state.

A second consequence of differential intersystem crossing is the phenomenon of triplet mechanism (TM) polarization of the ESR spectra of the free radical products obtained from the reaction of photoexcited triplet states, referred to as TM chemically induced dynamic electron polarization (CIDEP).<sup>7</sup> Sublevel selective isc from the photoexcited  $S_1$  state creates an initial non-Boltzmann population distribution in the  $T_1$  sublevels. This zero-field distribution is "carried over" to the high-field triplet states, which exist in the external ESR magnetic field. The triplet spin polarization may be converted to a doublet spin polarization via chemical reaction of the triplet, often by hydrogen abstraction. Thus, one may observe electron spin resonance signals with either enhanced absorption or emission, relative to the intensity expected for the thermal distribution of radical spin states.

The photochemistry<sup>8</sup> and photophysics<sup>9</sup> of "mixed" excited states have been the subject of much recent investigation. In such molecules, typically with carbonyl or azine chromophores, the lowest excited state is not purely  $n,\pi^*$  in nature but exhibits properties consistent with varying admixtures of both states. The consequences of excited-state mixing in triplets have become manifest in such phenomena as the rate of hydrogen abstraction,<sup>10</sup> variations in the zero-field splitting parameters,<sup>11</sup> and ESR TM polarization.<sup>12</sup>

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Recently Basu et al.<sup>2</sup> measured an anomalous lack of TM polarization in the time-resolved ESR spectrum observed in the hydrogen abstraction reaction between phthalazine, an azine with a mixed  $T_1$  state, and 2,6-di-*tert*-butylphenol (DTBP). Their explanation, that this might be due to equal  $T_1$  sublevel populating rates, was somewhat unsatisfying due to the known symmetry properties of the phthalazine phosphorescent triplet state. We therefore undertook an experimental investigation of the relative populating rates for the phthalazine  $T_1$  sublevels and finding them *not* equal formulated a model involving sublevel selective hydrogen abstraction rates due to selective degrees of  $n, \pi^* - \pi, \pi^*$  mixing to account for the lack of observed polarization.

During the course of this work Yamauchi et al.<sup>13</sup> published results where emissive TM polarization was observed under more sensitive conditions (i.e., higher laser power and lower temperature) than those reported by Basu.<sup>2</sup> Since the aim of the present work is to show that sublevel selective hydrogen abstraction rates attenuate but do not eliminate the expected TM polarization, these new results do not affect the validity of our arguments to any great extent.

The notion of sublevel selective photochemistry is intriguing and has been previously investigated. Dellinger et al. have demonstrated that, in the unimolecular photodecomposition of dimethyl-*s*-tetrazine, the sublevel with the greatest admixture of singlet character reacts most rapidly to yield singlet products.<sup>14</sup> The biphotonic decomposition of pyrimidine in benzene was also shown to be sublevel selective, though no mechanism for this was given.<sup>15</sup> Shaik has suggested that sublevel selectivity might be involved in concerted (2 + 2) cycloadditions due to the different sublevel propensities for accelerated isc, though this hypothesis has not been tested.<sup>16</sup> Indeed, both Wan<sup>17</sup> and McLauchlan<sup>18</sup> have suggested that sublevel selective reactions could influence the observed TM polarization but no one has yet proposed a detailed mechanism for this effect. Our model is then most novel in predicting selectivity where spin is expected to be conserved during the chemical reaction and in its susceptibility to experimental testing.

### Experimental Section

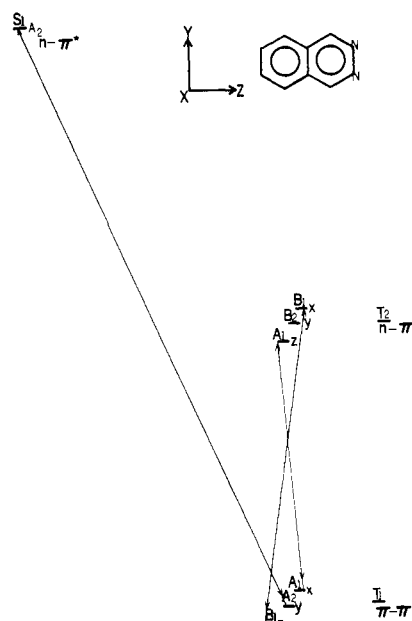
Phthalazine (98% Aldrich) was purified by vacuum sublimation. 2-Octanol (Aldrich) was purified by fractional distillation with a 10-cm Vigreux column. Samples of 0.2 M phthalazine in octanol were quick frozen by immersion in liquid  $N_2$ , resulting in a glassy sample. This solvent is the same as used in the time-resolved ESR experiments of Basu et al., which is significant since solvent effects on mixed excited states are quite important.<sup>11</sup>

The ODMR spectrometer used in this work has been previously described.<sup>19</sup> The samples were excited with a 100-W mercury lamp, whose output was passed through a saturated 1-cm  $NiSO_4$  solution filter and a Corning 7-54 glass filter. Sublevel kinetic measurements and steady-state ODMR spectra were obtained at 2 K. As a source for microwaves we used a Hewlett-Packard HP8690 sweep oscillator with a HP8699B Plug-in module. For a typical kinetic experiment the sample was excited at right angles to the direction of observation. A home-built pulse generator was used to drive a pair of synchronously linked mechanical shutters and, after a preset delay time, a General Microwave DM864 PIN diode switch opened to allow a microwave pulse. Multiple decay curves were accumulated on a signal averager to enhance the signal-to-noise ratio.

Sublevel kinetic parameters were determined with use of ODMR techniques as reported by Chan and Nelson.<sup>20</sup> In this approach a microwave-induced delayed phosphorescence (MIDP)<sup>21</sup> signal is recorded for the sample with use of the same duty cycle and system gain as an instantaneous fast passage microwave sweep under steady-state illumina-

**Table I.** Triplet State Sublevel Kinetic Parameters for Phthalazine in 2-Octanol

Total Sublevel Decay Constants ( $s^{-1}$ )	
$k_x$	$0.62 \pm 0.16$
$k_y$	$12.00 \pm 1.72$
$k_z$	$4.20 \pm 1.29$
Relative Steady-State Populations	
$N_x$	$0.11 \pm 0.07$
$N_y$	1.00
$N_z$	$0.08 \pm 0.02$
Relative Populating Rates	
$P_x$	$0.006 \pm 0.004$
$P_y$	1.000
$P_z$	$0.029 \pm 0.006$



**Figure 1.** Orbital symmetry and spin-orbital coupling scheme for phthalazine. The  $T_1$ - $T_2$  energy gap is  $2150 \text{ cm}^{-1}$ . The  $S_1$ - $T_1$  energy gap is  $4400 \text{ cm}^{-1}$ .<sup>22,27</sup> The actual energy ordering of the sublevels in  $T_1$  is  $z$ ,  $y$ ,  $x$  (highest to lowest).

tion. The ratio of the preexponential of the MIDP decay to the initial change in phosphorescence observed in the steady-state experiment can be used to obtain the ratio of the steady-state populations of the sublevels coupled by the microwaves. These relative steady-state populations, when combined with determinations of the total decay rates for each sublevel determined by MIDP,<sup>21</sup> give the relative sublevel populating rates, which are the quantities needed for a prediction of the TM ESR polarization pattern.

### Results

The kinetic parameters for the  $T_1$  state of phthalazine in 2-octanol are reported in Table I. The  $x$ ,  $y$ , and  $z$  designations refer to the zero-field states which are defined with respect to the molecular symmetry axes depicted in Figure 1.

The relative populating rate is substantially larger for the  $y$  sublevel (30 and 200 times  $z$  and  $x$ , respectively), which is expected from symmetry considerations assuming isc is promoted via spin-orbit (SO) coupling. Specifically, since  $S_1$  has a total symmetry of an  $A_2$  state,<sup>22</sup> spin-orbit coupling with the  $y$  sublevel of  $T_1$  is allowed. Yamauchi et al.<sup>22</sup> suggest that spin-vibronic mixing of  $T_1$  and  $T_2$  is not important in the nonradiative decay of phthalazine. Our data also suggest that spin-vibronic coupling is not the controlling promoter of isc and will therefore be neglected in the balance of the paper.

Given the large differences in relative populating rates, one would expect that the hydrogen-abstraction reaction between the phthalazine  $T_1$  state and DTBP should yield TM polarized radical

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products. Basu et al.<sup>2</sup> have not observed this, and we now examine some rationalizations for the lack of observed polarization.

### Theory and Discussion

**Polarization Attenuation via SLR.** In TM CIDEP, free radical products exhibiting a polarized spectrum must originate from a triplet precursor with a nonthermal population distribution among the sublevels.<sup>7</sup> Kinetically, this means that the rate of chemical reaction from  $T_1$  must be competitive with spin-lattice relaxation (SLR) in the  $T_1$  sublevels. It is then conceivable that, in phthalazine, this competition is skewed too far in favor of SLR, leading to reaction from a thermalized triplet. The rate of photoreaction between phthalazine and DTBP is expected to be very near that measured for the reaction of quinoxaline with the same substrate,<sup>2</sup> which does show a predictable TM polarization pattern. We also expect little significant difference between the rate of triplet SLR in phthalazine vs. quinoxaline, since this relaxation depends only on the rate of rotational diffusion and the zfs.<sup>23</sup>

Hence, while we cannot rule out rapid SLR relative to hydrogen abstraction as the cause for the lack of a TM pattern in phthalazine, this seems unlikely by comparison to quinoxaline which has a similar molecular shape and a closely analogous  $T_1$  state. We note that Basu et al. also believe it unlikely that sublevel SLR is unusually rapid in the phthalazine  $T_1$  state.<sup>2</sup>

A second possible mechanism for attenuation of TM polarization is thermal promotion of molecules residing in  $T_1$  to  $T_2$ , followed by demotion to  $T_1$ , which has been implicated as a source of efficient SLR in molecules with closely spaced excited triplet states.<sup>24</sup> While phthalazine does possess closely spaced triplets, calculation of the characteristic time of SLR via this mechanism, assuming an upper state lifetime of  $10^{-12}$  s and a  $10^\circ$  rotation of spin axes, yields  $4 \times 10^{-3}$  s, which is substantially slower than the microsecond time scale of the experiment.

**Calculation of Sublevel Selective Rates for Hydrogen Abstraction.** As mentioned above, ideas concerning sublevel selective reactivity have previously concentrated on the differing admixture of singlet character into each sublevel, giving differing rates of reaction to form singlet products.<sup>14</sup> However, in a hydrogen abstraction reaction, one would not a priori expect any dependence of the reaction rate on the multiplicity of the excited state, and it has been extensively demonstrated that, all else being equal, excited singlet and triplet states abstract hydrogen with equal facility.<sup>25,26</sup>

The large variations in hydrogen abstraction rates noted for various aromatic ketones and azines have been ascribed to the varying amounts of  $n, \pi^*$  admixture into their  $T_1$  states.<sup>26</sup> In relatively pure states, rate constants for hydrogen abstraction of  $n, \pi^*$  states exceed those of  $\pi, \pi^*$  states by ca. 3 orders of magnitude.<sup>25</sup> We then postulate that  $\pi, \pi^*$  states are not reactive toward hydrogen abstraction and furthermore that the rate constant for reactivity is directly proportional to the "amount" of  $n, \pi^*$  character in the reactive state.

In order to quantify this, we assume that a first-order perturbation treatment for state mixing will suffice, i.e., that  $T_1$  is mainly  $\pi, \pi^*$  with a small fraction of  $n, \pi^*$  character admixed. We thus write the sublevel selective rate as

$$K_m \propto \left| \frac{\langle T_{1,m} | H_{so} | n, \pi^* \rangle}{\Delta E} \right|^2 \quad (1)$$

where  $K_m$  = the sublevel selective rate for hydrogen abstraction ( $m = x, y, \text{ or } z$ ),  $T_{1,m}$  = the sublevels of  $T_1$ ,  $H_{so}$  = the spin-orbit coupling operator,  $n, \pi^*$  = the  $n, \pi^*$  state being coupled to the particular sublevel of  $T_1$ , and  $\Delta E$  is the energy separation of the relevant states.

Choice of the appropriate matrix elements in eq 1 is made via symmetry arguments. In phthalazine, using a "zero"-order approximation,  $T_1$  is  $\pi, \pi^*$  and could be mixed with either the  $n, \pi^*$   $T_2$  or  $S_1$  states. In Figure 1, we show the total symmetries (orbital  $\times$  spin) of the phthalazine  $T_1$  and  $T_2$  sublevels and  $S_1$  state.<sup>22</sup> From this we see that mixing is SO allowed between the  $x$  and  $z$  sublevels of  $T_1$  and the  $z$  and  $x$  sublevels of  $T_2$ , respectively, while the  $y$  sublevel of  $T_1$  couples with the  $S_1$  state. Hence the matrix elements that need to be evaluated are

$$\langle T_{1,x} | H_{so} | T_2 \rangle \quad \langle T_{1,z} | H_{so} | T_2 \rangle \quad (2)$$

$$\langle T_{1,y} | H_{so} | S_1 \rangle \quad (3)$$

Yamauchi<sup>22</sup> estimated the value of matrix element 2 using Hückel MO coefficients for the nitrogen atoms and the spin-orbit coupling parameter of the nitrogen atom ( $\zeta = 48 \text{ cm}^{-1}$  ( $Z = 3.25$ )) to be  $9.4 \text{ cm}^{-1}$ . Scott et al.<sup>27</sup> have calculated matrix element 3 using an INDO all-valence calculation. The method of Pople and Beveridge was used to calculate the required orbital coefficients. This gave a value of  $6.8 \text{ cm}^{-1}$ .

Values for the relative sublevel selective H abstraction rate constants in phthalazine are calculated from eq 1 with use of these matrix elements and the values measured for  $T_1-T_2$  and  $S_1-T_1$  energy gaps ( $2150$  and  $4400 \text{ cm}^{-1}$ , respectively),<sup>22,27</sup> yielding

$$K_x = K_z = 10K_y \quad (4)$$

Hence, we see that, in zero field, the  $x$  and  $z$  sublevels are expected to be ten times more reactive than  $y$ , as a consequence of the sublevel selectivity in state mixing.

**TM Polarization Implications of Sublevel Selective Reactivity.** We now examine the effects of the sublevel selective reaction rate constants calculated above on the TM polarization expected in the free radical species obtained from the reaction of phthalazine  $T_1$  with a suitable H donor. The kinetic model used is based on Atkins' approach,<sup>7</sup> where the total magnetization along the external magnetic field ( $S_{Z,D}$ ), after sufficient time has elapsed for all triplets to react, is given by

$$S_{Z,D} = \frac{1}{2} K_T \int_0^\infty dt \{ N_{+1}^T(t) - N_{-1}^T(t) \} \quad (5)$$

where  $N_n^T$  is the population of the  $n$  ( $H||Z$ ) high-field triplet state, and  $K_T$  is the nonselective rate constant for triplet reaction. Note that  $Z$  here refers to the direction of the external magnetic field and is not the  $z$  molecular based axis direction.  $S_{Z,D}$  is directly proportional to the observed polarization  $\gamma$  since

$$\gamma = (S_Z - S_{Z,e}) / S_{Z,e} = (S_Z / S_{Z,e}) - 1 \quad (6)$$

where  $S_{Z,e}$  is the equilibrium bulk magnetization.

In order to observe an effect on the TM polarization from sublevel selective reactivity, the magnetization must be sampled before a large preponderance of excited triplets have reacted. This condition is apparent, since the effect of sublevel selectivity will only alter the time dependence of the TM polarization; at  $t = \infty$  all sublevels will have reacted to yield a polarization value dependent only on the initial relative sublevel populations (neglecting competitive processes such as SLR or physical decay of  $T_1$ , see above). Therefore, the first modification of eq 5 is to consider the reaction in some short time interval  $\tau$ .

It is then important to estimate the reaction time of phthalazine with DTBP, to ascertain if the above condition is fulfilled. A literature search revealed no published value for the rate constant of this reaction, though we may estimate a value based on the following set of data. The reaction of *tert*-butoxy radicals with DTBP in benzene has a rate constant of  $4.3 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$  as reported by Scaiano.<sup>28</sup> The reaction of *tert*-butoxy radicals with 2-propanol<sup>29</sup> has a rate constant of ca.  $9 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$  whereas the rate constant for reaction of triplet phthalazine with 2-

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propanol<sup>30</sup> is ca.  $2.0 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ . Thus, we estimate that the *tert*-butoxy radical is 450 times more reactive than phthalazine toward hydrogen abstraction (this makes sense since the *tert*-butoxy radical is assumed to be analogous to a pure,  $n, \pi^*$  state, and phthalazine is believed to have a largely  $\pi, \pi^*$   $T_1$  state as mentioned above).

Dividing the rate constant for the reaction of *tert*-butoxy radical with DTBP by 450 to correct for the different relative reactivities, we estimate the rate constant for the reaction of phthalazine with DTBP to be  $9.6 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ . For the concentration of quencher used in Basu's<sup>2</sup> work (2.5 M) we calculate a reaction time of 4.2  $\mu\text{s}$  which is about 3 times the sampling time (1.3  $\mu\text{s}$ ) of the spectrometer used in the Basu<sup>2</sup> study and within the regime described above for this effect to be observed. Hence, the condition that a large preponderance of triplets be unreacted is satisfied.

Solvent effects are important in hydrogen abstraction reactions,<sup>28</sup> and we note that the value quoted for the reaction of *tert*-butoxy radicals with DTBP applied to benzene, a nonpolar solvent, whereas the reaction studied by Basu<sup>2</sup> was in 2-octanol. However, it is reported that hydrogen bonding solvents tend to decrease the reactivity of the phenol.<sup>28</sup> This would only serve to increase the reaction time and thus enhance the effect we are about to describe.

The second modification of eq 5 is the substitution of individual rate constants,  $K_{+1}$  and  $K_{-1}$  (for reaction from  $m_s = +1$  and  $-1$  states of  $T_1$ , respectively), for the overall rate constant ( $K_T$ ). Under the conditions given above and neglecting second-order terms in  $\tau$ , we then obtain

$$S_{Z,D} = \frac{1}{2} N^T(0) \tau \{K_{+1} q_{+1} - K_{-1} q_{-1}\} \quad (7)$$

where  $N^T(0)$  is the initial population of  $T_1$ ,  $\tau$  is the sampling time interval discussed above, and  $q_n$  is the fraction of  $T_1$  population residing in the ( $n = +1, -1$ ) high-field triplet sublevel at  $t = 0$ .

We now transform the relative zero-field sublevel populations ( $q_m$ ) and reaction rates ( $K_m$ ) into their respective high-field counterparts ( $q_n$  and  $K_n$ ) by calculating the mixing coefficients ( $C_m$ ) for each zero-field state in the high-field states, when the external field ( $H_0$ ) is along each of the zero-field axes (canonical orientations). For illustration, we assume  $H_0$  is along the  $z$  axis. The wave function for the  $m_s = +1$  state is then given by<sup>31</sup>

$$|\psi_{+1}\rangle = C_{1,z} |\phi_x\rangle + C_{2,z} |\phi_y\rangle \quad (8)$$

where  $\psi$  and  $\phi$  are the high-field and zero-field states, respectively. We may then write

$$q_{+1} = |C_{1,z}|^2 q_x + |C_{2,z}|^2 q_y \quad (9)$$

$$K_{+1} = |C_{1,z}|^2 K_x + |C_{2,z}|^2 K_y \quad (10)$$

with analogous equations for  $q_{-1}$  and  $K_{-1}$ .

The mixing coefficients ( $C_{m,z}$ ) are obtained by the standard treatment,<sup>31</sup> using our measured zero-field-splitting parameters for phthalazine in 2-octanol ( $D = 3.39 \text{ GHz}$ ,  $|E| = 0.472 \text{ GHz}$ ) and  $H_0 = 3000 \text{ G}$ , yielding

$$C_1 = -0.9105 / (2)^{1/2}$$

$$C_2 = -i(1.0821) / (2)^{1/2}$$

High-field relative populations ( $q_m$ ) and reaction rate constants ( $K_m$ ) for  $H_0 \parallel z$  may now be calculated by using eq 9 and 10, respectively. For no sublevel selectivity  $K_{+1} = K_0 = K_{-1} = 1/3$ . Substituting the appropriate values (see Table II) into eq 7, we calculate the magnetization for the case of equal sublevel reactivities as

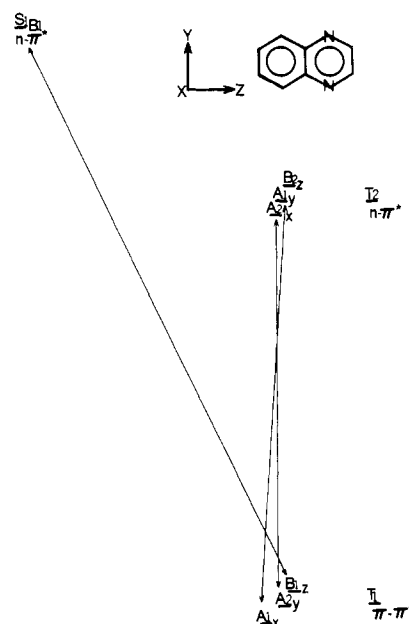
$$S_Z = \frac{1}{2} N(0) \tau (0.055)$$

and for sublevel selective reaction

$$S_Z = \frac{1}{2} N(0) \tau (0.007)$$

**Table II.** Calculated Bulk Magnetizations for Phthalazine Photoproducts (see Text, Equation 7)

Normalized Initial Sublevel Populations		
	$q_x = 0.006$	
	$q_y = 0.966$	
	$q_z = 0.028$	
Normalized Sublevel Reaction Rate Constants		
sublevel selective	nonselective	
$K_x = 0.476$	$K_x = 0.333$	
$K_y = 0.048$	$K_y = 0.333$	
$K_z = 0.476$	$K_z = 0.333$	
Bulk Magnetization (at 3000 G and 298 K)		
orientation	sublevel selective	nonselective
H  x	-0.0017 [ $N^T(0)\tau$ ]	-0.0173 [ $N^T(0)\tau$ ]
H  y	0.0024 [ $N^T(0)\tau$ ]	0.0017 [ $N^T(0)\tau$ ]
H  z	0.0074 [ $N^T(0)\tau$ ]	0.0547 [ $N^T(0)\tau$ ]
average	0.0027 [ $N^T(0)\tau$ ]	0.0130 [ $N^T(0)\tau$ ]



**Figure 2.** Orbital symmetry and spin-orbital coupling scheme for quinoxaline. The  $x$ ,  $y$ , and  $z$  symmetry labels correspond to the symmetry axes shown in the upper right. The  $T_1$ - $T_2$  energy gap is  $2900 \text{ cm}^{-1}$ . The  $S_1$ - $T_1$  energy gap is  $5200 \text{ cm}^{-1}$ .<sup>35</sup> The matrix element for  $S_1$ - $T_1$  mixing is  $10.3 \text{ cm}^{-1}$ .<sup>27</sup> The  $T_1$ - $T_2$  matrix element is taken by analogy to phthalazine to be  $9.4 \text{ cm}^{-1}$ .<sup>22</sup>

Continuing this analysis for the other two canonical orientations, and averaging the results (see Table II), the model predicts that the magnetization, and hence the polarization, will be attenuated 5 times by including the effects of the predicted sublevel selective reactivities.

We may also calculate the effects of sublevel selective H abstraction for the case of quinoxaline, which also possesses a mixed (but predominantly  $\pi, \pi^*$ )  $T_1$ , but has yielded a TM polarization pattern in its photoreaction with DTBP.<sup>2</sup> The excited-state coupling scheme is depicted in Figure 2. Performing a similar analysis to that done for phthalazine, using the  $q_m$ 's determined by van der Waals et al.,<sup>21,32</sup> we find that sublevel selectivity does attenuate the predicted polarization, but only by a factor of 2, as opposed to the factor of 5 attenuation predicted for phthalazine. Hence, the results of these calculations are in qualitative agreement with the CIDEP results of Basu et al.,<sup>2</sup> showing an attenuation of the TM pattern in phthalazine but not in quinoxaline run under similar experimental conditions.

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## Conclusion

We have obtained the relative populating rates for the reactive triplet state of phthalazine and have found them unequal. This result excluded the hypothesis given by Basu et al.<sup>2</sup> to explain the somewhat puzzling lack of TM polarization observed in the ESR spectra of the products of the H abstraction reaction of phthalazine with DTBP. We have developed a model for sublevel selective rate constants, which predicts a larger attenuation of the TM polarization in phthalazine than in quinoxaline, where a TM pattern has been observed.

While our model is certainly unsophisticated and is in need of greater rigor, particularly our kinetic treatment, we believe its foundations to be quite rigorous. The much higher reactivity of  $n-\pi^*$  excited states relative to  $\pi-\pi^*$  states toward H abstraction is a well documented and rationalized tenet. Sublevel selectivity in state mixing is also a well-accepted concept. Hence, we consider our most important contribution not to be our actual numerical predictions but to consist of both pointing out the details of this mechanism and showing it might influence TM polarization to a significant extent.

The model for TM polarization via sublevel selective chemistry has other implications which we have not pursued in this paper. It is, of course, directly applicable (and possibly verifiable) in other mixed  $n-\pi^*$ ,  $\pi,\pi^*$  excited states which undergo H abstraction reactions, the most likely being other aromatic azines and aromatic carbonyls, which have already been experimentally investigated.<sup>18</sup> We also expect this effect to be most pronounced in systems where the reaction rates are slowest: i.e., systems where the lowest state is largely  $\pi-\pi^*$  will show the largest relative effects of selective  $n-\pi^*$  mixing.

The kinetic treatment used here is certainly not rigorous, as it does not describe the time dependence of the polarization. It is intuitively clear that the growth and decay of TM polarization via this mechanism is substantially different from that expected for non-sublevel-selective reaction. For example, the added effect of sublevel selectivity should be greatest initially and decrease as the most reactive triplets are consumed, eventually giving the same integrated polarization as the equal reactivity scheme. Also, sublevel selectivity could, depending on the case, yield TM polarization even in the extreme case where SLR is rapid compared to reaction, since the radicals (initially) may be formed unequally from the thermalized +1 and -1  $T_1$  sublevels.

We believe that sublevel selective photochemistry may have ramifications beyond alteration of TM CIDEP polarizations. We first note that no external magnetic field is needed to induce this selectivity and in fact only attenuates the intrinsic zero-field effect (see Discussion). If alternate pathways, either chemical or physical, exist for the reactive triplet states, then we could expect the actual branching ratios for the excited state to be sublevel dependent. Hence, an excited-state perturbation might affect the product yield of a photoreaction not only by changing the total yield of reactive triplets but also by changing the relative populations of the zero-field sublevels in the ensemble.<sup>33</sup> This mechanism for sublevel selective reactivity is not limited to  $n-\pi^*$ ,  $\pi-\pi^*$  states but could also be present in other "bichromophoric" molecules, such as  $\beta-\gamma$  unsaturated carbonyls, which have reactive triplets and where the reactivities are believed to depend largely upon the nature of excited-state mixing.<sup>34</sup>

Most generally, we hope that this paper will stimulate the thinking of photochemists along lines which have been well established by those interested in the photophysics of excited states: that excited triplet states consist of three distinct substates, and these states should possibly be regarded as distinct chemical, as well as physical, species.

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**Registry No.** Hydrogen, 1333-74-0; phthalazine, 253-52-1; 2,6-di-*tert*-butylphenol, 128-39-2.

(33) For example, heavy atoms have been found not only to enhance intersystem crossing but to do this in a sublevel selective fashion. See, e.g.: Szejda, P.; Maki, A. H.; Anderson, R. H. *J. Am. Chem. Soc.* **1978**, *100*, 7138.

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