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Spin-Orbit Coupling in Azines*

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I. INTRODUCTION

A LARGE amount of experimental research in the electronic spectra of polyatomic molecules is devoted to the singlet–triplet transitions in organic systems. These transitions are forbidden by the selection rule $\Delta S = 0$. However, a violation of this multiplicity selection rule is caused by mixing of the singlet and triplet states through spin–orbit perturbation. The probability of a multiplicity forbidden transition $S_0 \leftrightarrow T_1$, between the singlet ground state, S_0, and the lowest triplet state, T_1, is determined by the triplet character in S_0 and the singlet character in T_1.

A complete calculation of $S_0 \leftrightarrow T_1$ transition probability would involve a knowledge of (a) energy eigenvalues for all states that mix with S_0 and T_1 and (b) the transition moments of all the singlet–singlet and triplet–triplet transitions from which $S_0 \leftrightarrow T_1$ transition probability is 'stolen.' The experimental data on many of these energy levels and transition moments are not available. Thus, an accurate prediction of $S_0 \leftrightarrow T_1$ transition intensities is unlikely. Nevertheless, theoretical calculations that predict the polarization of an $S_0 \leftrightarrow T_1$ transition and indicate the major sources of its intensity would be of very significant value to experimental investigations. Indeed, a serious handicap to the interpretation of many results on the multiplicity forbidden transitions is the lack of insight into the various sources of their intensity.

Previous theoretical investigations on aromatic hydrocarbons,[1–4] carbonyl compounds[1,3,5] andazines[6,7] have uniformly assumed that one singlet–singlet transition is the source of singlet–triplet transition intensity. Thus, they give less information than desired.

The importance of singlet–triplet transitions in azines as examples to test spin–orbit coupling theories in molecules was realized before in two previous theoretical articles.[6,7] Taking pyridine as an example, Clementi and Kasha[6] discussed the spin–orbit interaction in azines. The matrix elements were expanded in a cylindrical potential but the numerical evaluation was not carried out. Sidman[7] dealt with the lowest $n \leftarrow \pi^*$ triplet–singlet transition ($^3W \leftrightarrow {}^1A$) in pyrazine. He considered the perturbation of the lowest triplet state by the ^1B_a state only and predicted the polarization of the $S_0 \leftrightarrow T_1$ transition to be along the $N - N$ axis. In both of these investigations the perturbation of the ground state by the excited triplet states was ignored.

In the following investigation we have attempted a more detailed analysis of the sources of $S_0 \leftrightarrow T_1$ transition intensity in azines. Impetus for this study came chiefly from the recent experimental results[8,9] on the polarization of $S_0 \leftrightarrow T_1$ transitions in azines. We have considered, in this article, the mixing of various singlets as well as ground state, S_0, with T_1, and triplets with S_0. We have considered only the matrix elements of the central field spin–orbit Hamiltonian. In view of the fact that we are concerned with the different sources of $S_0 \leftrightarrow T_1$ probabilities and not with their exact numerical value, this approach is well justified.

The molecules selected for investigation are pyridine, pyrazine, pyrimidine, and pyridazine. The lowest triplet state of pyridine is known to be of (π,π^*), but not of (n,π^*) designation.[10] We have included the lowest (n,π^*) triplet state of pyridine in these calculations to serve as a model for other azines.[6] The lowest triplet state in pyrazine[11] and pyrimidine[12] are established to be of (n,π^*) type. A relatively large body of experimental work on the $S_0 \leftrightarrow T_1$ transitions in these molecules commend a theoretical investigation. The lowest (n,π^*) triplet state of pyridazine is considered here to bring forth the importance of the mixing of S_0 and T_1 themselves in singlet–triplet

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[1] D. S. McClure, J. Chem. Phys. **20**, 682 (1952).

[2] M. Mizushima and S. Koide, J. Chem. Phys. **20**, 765 (1952).

[3] H. F. Hameka and L. J. Oosterhoff, Mol. Phys. **1**, 358 (1958).

[4] E. Clementi, J. Mol. Spectroscopy **6**, 497 (1961).

[5] J. W. Sidman, J. Chem. Phys. **29**, 644 (1958).

[6] E. Clementi and M. Kasha, J. Mol. Spectr. **2**, 297 (1958).

[7] J. W. Sidman, J. Mol. Spectr. **2**, 333 (1958).

[8] V. G. Krishna and L. Goodman, Nature **191**, 800 (1961).

[9] V. G. Krishna and L. Goodman, J. Chem. Phys. **36**, 2217 (1962).

[10] D. F. Evans, J. Chem. Soc. **1957**, 3885.

[11] L. Goodman and M. Kasha, J. Mol. Spectr. **2**, 58 (1958).

[12] V. G. Krishna and L. Goodman, J. Am. Chem. Soc. **83**, 2042 (1961).

transition probabilities. However, the $S_0 \leftrightarrow T_1$ transition in pyridazine has not been observed[13] so far.

II. MIXING OF SINGLET AND TRIPLET STATES

In the absence of external magnetic fields the spin–orbit interaction operator, which mixes singlet and triplet states, can be written, following Kramers[14] and Hameka and Oosterhoff,[3] as

$$H' = H_1' + H_2' + H_3' , \qquad (1)$$

where

$$\begin{aligned} H_1' &= \alpha^2 \sum_i (2mc\mathcal{H}_i + \mathbf{F}_i \times \mathbf{P}_i)\cdot \mathbf{S}_i \\ &= \alpha^2 \sum_\mu \sum_i \frac{Z_\mu}{r_{i\mu}^3} \mathbf{L}_i \cdot \mathbf{S}_i , \qquad (1a) \end{aligned}$$

$$H_2' = -\alpha^2 \sum_{i,j}{}' \frac{\mathbf{P}_i \times \mathbf{r}_{ij}}{r_{ij}^3} \cdot \mathbf{S}_i , \qquad (1b)$$

and

$$H_3' = 2\alpha^2 \sum_{i,j}{}' \frac{\mathbf{P}_j \times \mathbf{r}_{ij}}{r_{ij}^3} \cdot \mathbf{S}_i . \qquad (1c)$$

In the above expressions Z_μ is the effective nuclear charge of the μth nucleus on the ith electron, **L** and **S** are orbital and spin angular momentum operators, α is the fine structure constant defined as $e^2/4\pi\epsilon_0 hc = 1/137$ approximately if **L**, **S**, Z, r are in atomic units, **P** is the linear momentum operator, $\mathcal{H}$ is the external magnetic field which is usually zero, and **F** is the electric field of the nuclei. The first term represents the interaction of the magnetic moment of the moving electron with the Coulomb field of the nucleus and associated spherically symmetric core associated with the same nucleus. The second term comes from the electric field of the other electrons (other than i). The two terms are frequently lumped together[15] by replacing the electric field of the electrons in closed shells (closed shell in both singlet and triplet states) at the ith electron by an effective spherically symmetric electric field (the contribution of the magnetic field of closed shell electrons to spin–orbit coupling is zero) and adding it to the field due to the nucleus:

$$H'(f) = H_1' + H_2' = \alpha^2 \sum_i \sum_\mu \frac{Z_\mu(f)}{r_{i\mu}^3} \mathbf{L}_i \cdot \mathbf{S}_i . \qquad (2)$$

Spin-same and other-orbit interactions involving electrons in open shells given by the second and third terms, are neglected in these calculations. In addition to these terms the complete magnetic Hamiltonian contains higher order terms such as the spin–spin coupling term.[15] These do not contribute any singlet correction to the triplet wave function and hence can be neglected in the calculations of the transition probabilities.

We will now consider the matrix elements of the central field spin–orbit perturbing Hamiltonian, $H'(f)$, given by Eq. (2). It has been noted before that this is only an approximation to the total spin–orbit operator $H_1' + H_2'$. The matrix elements between a singlet state and a triplet state can be expanded as

$$\langle S_k | H'(f) | \mathbf{T}_l \rangle = \langle \Omega_k | \mathbf{H}'(\mathbf{f})_{\text{spin}} | \mathbf{\Omega}_l \rangle \cdot \langle s_k | \mathbf{H}'(\mathbf{f})_{\text{orbital}} | t_l \rangle , \qquad (3)$$

where s_k and t_l are the orbital parts and Ω's are the spin parts of the total electronic wave functions S_k and $\mathbf{T}_l$. $\mathbf{\Omega}_l$ is a column vector formed from the three triplet spin functions. We assume that S_k and $\mathbf{T}_l$ can be expressed as an ASMO product including, if necessary, configuration interaction. Only the orbital part needs to be considered further since the spin part reduces to

$$\langle \Omega_k | \mathbf{H}'(\mathbf{f})_{\text{spin}} | \mathbf{\Omega}_l \rangle = (\tfrac{1}{2}\hbar, -\tfrac{1}{2}\hbar, 0) \qquad (4)$$

for the case of spin functions differing in multiplicity by 2.

$\mathbf{H}'(\mathbf{f})_{\text{orbital}}$ operates on the coordinates of one electron only and hence s_k and t_l should not differ in the occupancy number of more than one orbital. We will represent s_k and t_l by singly excited configurations $\phi_i\phi_j$ and $\phi_h\phi_j$, and respective transitions being $\phi_i \rightarrow \phi_j$ and $\phi_h \rightarrow \phi_j$. The closed shell part is omitted for brevity. The matrix elements can then be further simplified to

$$\begin{aligned} \langle S_k | H'(f) | \mathbf{T}_l \rangle &= (\pm \tfrac{1}{2}\hbar \langle \phi_i | \mathbf{H}'(\mathbf{f})_{\text{orbital}} | \phi_h \rangle, 0) \\ &= (\pm \tfrac{1}{2}\hbar \sum_{\mu,\nu} c_{i\mu} c_{h\nu} \langle \lambda_\mu | \mathbf{H}'(\mathbf{f})_{\text{orbital}} | \lambda_\nu \rangle, 0) , \qquad (5) \end{aligned}$$

where the MO's, ϕ's, are expanded over the atomic orbitals (λ's) in terms of the c's.

We restrict ourselves to the one-center terms ($\mu = \nu$) in the evaluation of the integrals in Eq. (5). In the nitrogen heterocyclics the n orbitals are localized at the nitrogen center and by far the major contribution to the spin–orbit coupling in (n,π^*) states comes, as it will be seen later, from the atomic spin–orbit coupling terms at the N atoms. In addition, we make a reasonable assumption that for azines, which

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[13] In reference 18 this compound was reported to have a *VVW* phosphorescence. Further experiments in this laboratory have shown that an impurity emission was being observed and that no pyridazine luminescence could be observed even under very long exposures.

[14] H. A. Kramers, *Quantum Mechanics* (North-Holland Publishing Company, Amsterdam, 1957).

[15] J. C. Slater, *Quantum Theory and Atomic Structure* (McGraw-Hill Book Company, Inc., New York, 1960), Vol. II.

contain only second row conjugating atoms, the basis set for atomic orbitals, λ_μ, contains $2s$ and $2p$ orbitals only.

The important point is that a large spin–orbit interaction is possible between two p orbitals at the same atomic center with different m_l eigenvalues. The mixing of different orbitals through spin–orbit perturbation depends upon the symmetry of $\mathbf{H}'(\mathbf{f})_{\text{orbital}}$ which is governed by the orbital angular momentum operator, $\mathbf{L}$. The components of $\mathbf{L}$ — L_x, L_y and L_z—have the property of rotation operators R_x, R_y, and R_z. Thus $L_xp_z = -ihp_y$ and $L_zp_z = 0$, for example. Because of this local symmetry condition, the matrix elements of the form $\langle p_y|H_x'(f)_{\text{orbital}}|p_z\rangle$, arising from the LCAO expansion as in Eq. (5) reduce to the expectation value for the r^{-3} potential [Eq. (2)] of the effective central field at the atom μ:

$$\langle\phi_i|H_x'(f)_{\text{orbital}}|\phi_h\rangle > \sum_\mu c_{i\mu}c_{h\mu}\langle p_{y\mu}|H_x'(f)_{\text{orbital}}|p_{Z\mu}\rangle \cdot$$

$$= \sum_\mu c_{i\mu}c_{h\mu}\alpha^2 Z_\mu(f)\langle p_{y\mu}\left|\frac{1}{r_\mu^3}\right|p_{y\mu}\rangle = \sum_\mu c_{i\mu}c_{h\mu}\zeta_\mu\ , \tag{6}$$

where

$$\zeta_\mu = \alpha^2 Z_\mu(f)\left(\frac{\bar{1}}{r_\mu^3}\right).$$

From the purely imaginary Hermitian property of angular momentum operators, it follows that $H'(f)$ is also imaginary Hermitian. Hence,

$$\langle S_k|H'(f)|\mathbf{T}_l\rangle = -\langle\mathbf{T}_l|H'(f)|S_k\rangle = \langle\mathbf{T}_l|H\ (f)^*|S_k\rangle\ .$$

By the same token the matrix elements of the form $\langle p_x|H'(f)_{\text{orbital}}|p_x\rangle$ vanish. Thus, we see that the rotational property of $H'(f)_{\text{orbital}}$ allows mixing between two p orbitals of different symmetry at the same atomic center. The result is the one-center analog of the selection rules given by McClure[16] and Weissman.[17]

The singlet–triplet matrix elements encountered in azines are very similar to the ones discussed above. Thus, the interaction of an (n,π^*) and a (π,π^*) configuration in a monoazine leads to an integral

$$\langle n,\pi^*|H'(f)_{\text{orbital}}|\pi,\pi^*\rangle = \tfrac{1}{2}\ (2/3)^{\frac{1}{2}}c_{iN}S_{nn'}\xi_N\ , \tag{7}$$

where sp^2 hybridization is assumed for the nitrogen atom in the ground state. $S_{\text{nn}'}$ is the overlap integral between the nonbonding nitrogen orbitals in the ground state (n) and in the (n,π^*) state (n'). Any rehybridization of the n orbitals upon $n \rightarrow \pi^*$ promotion will be taken into account by this factor. Evidences from singlet–triplet intervals[18] and the splitting of diazine levels[19] indicate that the n' orbital may have very little s character. An appropriate value for $S_{\text{nn}'}$ is 0.7 to 0.8. Choosing Slater functions with effective nuclear charge of Z_N one obtains

$$\xi_N = \alpha^2 Z_N(f)Z_N^3/48 \quad \text{(a.u.)}\ .$$

If $Z_N(f)$ is assumed equal to $Z_N = 3.75$, then $\xi_N = 48$ cm^{-1} and $S_{\text{nn}'}\xi_N = \xi_N'$ is calculated to be between 30 and 40 cm^{-1}. [Note that the equality $Z_N(f) = Z_N$ is not basically justified, and hence this calculation is somewhat arbitrary.] Despite the crudeness of these estimates, the central field matrix elements can be seen to be large.

For azines, neglecting the many small multicenter integrals is probably a valid assumption because of the large magnitude of the one-center term. The other possible sources of $S_0 \leftrightarrow T_1$ probability are through spin–orbit interaction with Rydberg states of the correct molecular and local symmetry, and through radiation inducement.[20] However, these perturbations must be regarded as of little importance—in the former case because of the low density near the nuclei for Rydberg states, and in the latter case because of the large internal spin–orbital matrix elements.

Having indicated the method of evaluating the matrix elements for spin-orbit coupling we will turn to the transition probabilities. According to first-order perturbation theory the wave functions for the ground state, S_0, and the triplet state, T_1, will be modified as

$$S_0^1 = S_0^0 + \sum_k \frac{\mathbf{H}_{0k}}{\Delta E_{0k}}\mathbf{T}_k^0 \tag{8}$$

and

$$\mathbf{T}_1^1 = \mathbf{T}_1^0 + \sum_j \frac{\mathbf{H}_{1j}}{\Delta E_{1j}}S_j^0\ , \tag{9}$$

where $\mathbf{H}_{0k}$ and $\mathbf{H}_{lj}$ are the abbreviations for the matrix elements $\langle S_0^0|H'(f)|\mathbf{T}_k^0\rangle$ and $\langle\mathbf{T}_1^0|H'(f)|S_j^0\rangle$. ΔE is the energy difference between the two interacting states. From Eqs. (8) and (9) the transition moments of $T_1 \leftrightarrow S_0$ can be seen to be

$$\mathbf{M}(\mathbf{T}_1,S_0) = \sum_k \frac{\mathbf{H}_{0k}}{\Delta E_{0k}}\mathbf{M}(\mathbf{T}_1,\mathbf{T}_k) + \sum_j \frac{\mathbf{H}_{1j}}{\Delta E_{1j}}\mathbf{M}(S_0,S_j)\ , \tag{10}$$

where $\mathbf{M}$'s are the transition moment integrals defined, e.g., as

$$\mathbf{M}(S_0,S_k) = \langle S_0|\textstyle\sum_i \mathbf{r}_i e|S_k\rangle\ . \tag{11}$$

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[16] D. S. McClure, J. Chem. Phys. **17**, 665 (1949).

[17] S. I. Weissman, J. Chem. Phys. **18**, 232 (1950).

[18] L. Goodman, J. Mol. Spectr. **6**, 109 (1961).

[19] M. A. El-Sayed and G. W. Robinson, J. Chem. Phys. **34**, 1840 (1961).

[20] H. F. Hameka, J. Chem. Phys. **37**, 328 (1962).

The two terms on the right-hand side of Eq. (11) give the intensity 'stolen' from the triplet–triplet and the singlet–singlet transitions, respectively. It will be convenient to consider these terms separately.

III. PERTURBATION BY THE SINGLETS

The perturbing singlet configurations are listed in the second and fourth columns of Table I. Their transition moments and their configurational energies are needed to evaluate the contribution to $\mathbf{M}(T_1,S_0)$. The orbital designation can be understood by reference to Fig. 1.

TABLE I. Perturbation of the lowest (n,π^*) triplet state by the (π,π^*) singlet configurations.[c]

Configuration[a]	M[b]
Pyridine: $^3B_2[A_1]$; (n,π_4)	
(π_2,π_4) ; L_a (z)	0.218
(π_2,π_4) ; B_a (z)	0.177
(π_1,π_4) (z)	0.009
$(\pi_1^2,\pi_2^2,\pi_3^2)$ (z)	0.098
Pyrazine: $^3B_{2u}[B_{3g}]$; (n_-,π_4)	
(π_2,π_4) ; L_a (z)	0.294
(π_2,π_4) ; B_a (z)	0.226
Pyrimidine: $^3B_2[B_1]$; $[0.95\,(n_-,\pi_5)+0.30\,(n_+,\pi_4)]$	
(π_2,π_5) ; L_b (x)	−0.189
(π_2,π_5) ; B_b (x)	0.084
(π_1,π_5) (x)	−0.001
(π_3,π_4) ; L_b (x)	0.182
(π_3,π_4) ; B_b (x)	0.082
Pyrimidine: $^3B_2[A_1]$; $[0.95\,(n_-,\pi_5)+0.30\,(n_+,\pi_5)]$	
$(\pi_1^2,\pi_2^2,\pi_3^2)$ (z)	0.057
(π_3,π_5) ; L_a (z)	0.143
(π_3,π_5) ; B_a (z)	−0.105
(π_2,π_4) ; L_a (z)	−0.021
(π_2,π_4) ; B_a (z)	−0.014
(π_1,π_4) ; (z)	0.005
Pyridazine: $^3B_2[A_1]$; (n_-,π_5)	
(π_2,π_5) ; L_b (x)	−0.200
(π_2,π_5) ; B_b (x)	0.102
$(\pi_1^2,\pi_2^2,\pi_3^2)$ (x)	0.289
Pyridazine: $^3B_2[B_1]$; (n_-,π_5)	
(π_1,π_5) ; (z)	−0.015
(π_3,π_5) ; L_a (z)	−0.097
(π_3,π_5) ; B_a (z)	0.073

[a] The configuration is followed by the state through which it enters with the resulting polarization indicated in the brackets. The symmetry notation is $^3\Gamma$ orbital [Γ total].

[b] Contribution by the configuration to the singlet–triplet transition moment $\mathbf{M}(\mathbf{T}_1,S_0)$. $\mathbf{M}$ is in atomic units if $\xi_N' = S_{nn'}\,\xi_N$ is in eV.

[c] In the above calculations SCF–MO's of Matago and Nishimoto (reference 23) were used for pyridine and pyrazine. Pyrimidine and pyridazine orbitals were obtained by perturbing the benzene $2p(\tau)$ AO's with a value of $0.6\,\beta$ for the difference of the Coulomb integrals on nitrogen and carbon in a Hückel scheme. [L. Goodman and R. W. Harrell, J. Chem. Phys. **30**, 1131 (1959).] The singlet state energies were obtained from the experimental values quoted by McWeeny and Peacock (reference 24).

The configurations (π_2,π_4), (π_3,π_4), (π_2,π_5), and (π_3,π_5) enter into the L_a, L_b, B_a, and B_b states whose zeroth-order functions are [21]

$$\begin{aligned}
(^1L_b) &= (1/\sqrt{2})(\pi_3\pi_4 - \pi_2\pi_5)\,,\\
(^1L_a) &= (1/\sqrt{2})(\pi_2\pi_4 + \pi_3\pi_5)\,,\\
(^1B_a) &= (1/\sqrt{2})(\pi_2\pi_4 - \pi_3\pi_5)\,,\\
(^1B_b) &= (1/\sqrt{2})(\pi_3\pi_4 + \pi_2\pi_5)\,.
\end{aligned}\tag{12}$$

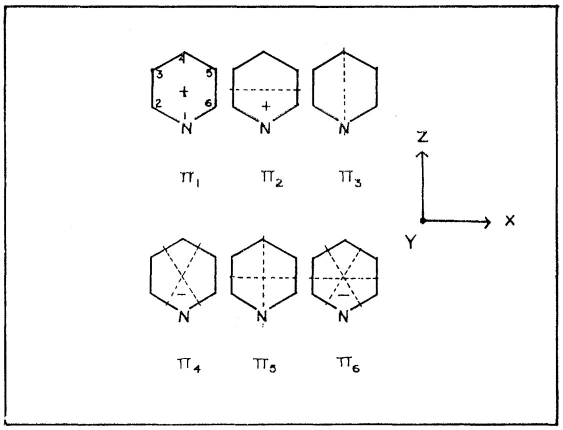

FIG. 1. The nodal properties of the π orbitals illustrated with pyridine as an example. The nitrogen atoms are at the 2 and 6 positions for pyrimidine, the 2 and 3 positions for pyridazine, and 1 and 4 positions for pyrazine.

Since the inductive perturbation of the nitrogen does not change the coefficients appreciably,[21–24] the above zeroth-order functions are used for azines. The qualitative conclusions given below, however, are not based on this assumption. A model calculation performed with first-order functions[22] gave essentially the same results as the calculations with the zeroth-order functions. The transition moment between the ground state and each of these configurations is the same in the above approximation, and was obtained from the experimental value of the benzene $^1A_{1g} \rightarrow {}^1E_{1u}$ transition intensity.

The configurations (π_1,π_4) and (π_1,π_5) enter into the benzene $^1E_{2g}$ state. With the introduction of the nitrogen perturbation a transition to this state becomes weakly allowed, the transition moment being calculated as $\sim 10^{-1}$ a.u. for the (π_1,π_4) configuration and 10^{-3} for the (π_1,π_5) configuration. The energy of the $^1E_{2g}$ state is calculated to be 3.3 eV above the $^1B_{2u}$ state.[25] The contribution to $\mathbf{M}(T_1,S_0)$ by (π_1,π_4) and (π_1,π_5) configurations can be seen from Table I

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[21] R. Pariser and R. G. Parr, J. Chem. Phys. **21**, 767 (1953).

[22] L. Goodman and H. Shull, J. Chem. Phys. **27**, 1388 (1957).

[23] N. Mataga and K. Nishimoto, Z. Physik Chem. **13**, 140 (1957).

[24] R. McWeeny and T. E. Peacock, Proc. Phys. Soc. (London) **A70**, 41 (1957).

[25] R. G. Parr, D. P. Craig, and I. G. Ross, J. Chem. Phys. **18**, 1561 (1950).

to be less than 0.01 ξ'_N, the small value resulting mainly from the smallness of the ${}^1A_{1g} \rightarrow {}^1E_{2g}$ transition moment and not from the questionable assumption utilized above for the energy.

In Table I the ground state is included in the perturbing singlets. The perturbation by the ground state is allowed by symmetry for pyridine, pyrimidine, and pyridazine and there is no reason for ignoring it. In these cases the transition moment, $\mathbf{M}(S_0,S_0)$, will be equal to the dipole moment of the molecule in the ground state. It is 2.15 D for pyridine,[26] 2.19 D for pyrimidine,[27] and 3.94 D for pyridazine.[28]

Table I shows that for the lowest triplet state of pyridine and pyrazine the important perturbation comes from the (π_2,π_4) singlet configuration. This configuration enters in phase into both the ${}^1L_a$ and ${}^1B_a$ states. Besides the ${}^1L_a$ and ${}^1B_a$ states, the ground state also provides an important perturbation to the lowest triplet state in pyridine. The perturbation by the ground state of the lowest triplet state will be significant in singlet–triplet transition probabilities, as can be seen in this example, in polar molecules (cf., pyridazine).

The lowest triplet state of pyrazine is perturbed by both ${}^1L_a$ and ${}^1B_a$ states. In phase addition of the contributions from these two states result in a large spin–orbit coupling.

In considering the spin–orbit coupling scheme in pyrimidine, cognizance needs to be taken of the inadequate description of the lowest (n,π^*) triplet state by a single configuration. However, the lowest triplet states of pyridine, pyrazine, and pyridazine seem to be accurately described by single configurations. In the description of the lowest triplet state of pyrimidine the major contribution comes from the (n_-,π_5)[29] configuration but there is probably considerable (n_+,π_4) character. A more accurate description of the lowest triplet state of pyrimidine has been estimated[18] to be in the proximity of $0.95\,(n_-,\pi_5) + 0.30\,(n_+,\pi_4)$. Hence, the perturbation of both these configurations is taken into account in Table I.

Major perturbation for the B_1 component of the lowest triplet state of pyrimidine comes from the (π_2,π_5) and (π_3,π_4) configurations. For the A_1 component the important perturbation arises from the (π_3,π_5) configuration. A relatively higher probability for the transition between the B_1 component and the ground state is caused by an in-phase addition of the contributions from the (π_3,π_4) configuration through the ${}^1L_b$ and ${}^1B_b$ states. Both the (π_2,π_5) and (π_3,π_5) configurations enter out-of-phase through ${}^1L_{a,b}$ and ${}^1B_{a,b}$ states, and consequently their contribution to $S_0 \leftrightarrow T_1$ probability diminished. The transitions between the ground state and A_1 and B_1 components of the triplet state are polarized along the x and z axes, respectively, referred to in Fig. 1. A higher probability for the transition between the ground state and the B_1 component will lead to an x polarization for the triplet–singlet transition. The perturbation of the triplet state by the ground state is fairly small in pyrimidine and it effects only the transition involving the A_1 component. (The importance of this perturbation is shown by the example of pyridazine, where the principle contribution to $S_0 \leftrightarrow T_1$ probability comes from the dipole moment in ground state.)

IV. PERTURBATION OF THE GROUND STATE BY THE TRIPLETS

The perturbing triplet configurations are listed in Table II. In order to evaluate their contribution to $\mathbf{M}(\mathbf{T}_1,S_0)$ we need to know (1) their configurational energy above the ground state and (2) the transition moments between these configurations and the lowest triplet state, $\mathbf{M}(\mathbf{T}_j,\mathbf{T}_1)$. The experimental energies

TABLE II. Perturbation of the ground state by the (n,π^*) triplet configurations.

Configuration[a]	M[b]
Pyridine: ${}^1A_1$–${}^3B_2[A_1]$; (n,π_4)	
(n,π_4) (z)	−0.039
(n,π_6) (z)	0.091
Pyrazine: ${}^1A_a$–${}^3B_{2u}[B_{3g}]$; (n_-,π_4)	
(n_+,π_4) (z)	0.575
(n_-,π_6) (z)	0.123
Pyrimidine: ${}^1A_1$–${}^3B_2[B_1]$; $0.95\,(n_-,\pi_5) + 0.30\,(n_+,\pi_4)$	
(n_-,π_6) (x)	0.103
(n_+,π_5) (x)	0.323
(n_-,π_4) (x)	0.062
Pyrimidine: ${}^1A_1$–${}^3B_2[A_1]$; $0.95\,(n_-,\pi_5) + 0.30\,(n_+,\pi_4)$	
(n_-,π_5) (z)	−0.047
(n_+,π_4) (z)	0.008
(n_+,π_6) (z)	0.010
Pyridazine: ${}^1A_1$–${}^3B_2[A_1]$; (n_-,π_5)	
(n_-,π_5) (x)	0.018
(n_-,π_6) (x)	0.063
Pyridazine: ${}^1A_1$–${}^3B_2[B_1]$; (n_-,π_5)	
(n_-,π_4) (z)	−0.024
(n_+,π_5) (z)	−0.160

[a] The perturbing configuration is followed by the polarization it gives to the singlet–triplet transition.
[b] See footnote b to Table I.

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[26] B. B. de More, W. S. Wilcox, and J. H. Goldstein, J. Chem. Phys. **22**, 876 (1954).

[27] W. Hückel and C. M. Salinger, Ber. Deut. Chem. Ges. **77**, 810 (1944). The value in this article is used for reasons given in reference 31.

[28] W. C. Schneider, J. Am. Chem. Soc. **70**, 627 (1948).

[29] Defined by $n_\pm = (1/\sqrt{2})\,(\sigma_\mu \pm \sigma_\nu)$ where σ_μ and σ_ν are lone pair orbitals, directed *similarly*, on nitrogens μ and ν in a diazine.

of the higher perturbing triplet configurations are not available. Reasonable values can be assumed from the knowledge of the singlet–triplet intervals. The values[18] used (the energy of the ground state is taken as zero) are 6.0 eV for the (n_-,π_6) configurations, 4.0 eV for the (n,π_4) configuration of pyridine, and 3.5 eV for the rest of the configurations in Table II.

The transition moments are estimated by considering only the one-center terms. That this approximation is valid can be seen from the nature of the integrals involved. The different types of transition moment integrals arising from the perturbation of the ground state can be illustrated by the following three examples:

(1) The transition moment which results between the (n,π_6) perturbing triplet configuration of pyridine and the lowest triplet state [of (n,π_4) configuration]. This transition moment integral is a pure π-electron moment and can be expanded as $\langle\pi_4|\mathbf{r}e|\pi_6\rangle = \sum_{\mu=1}^{6} \times c_{4\mu}c_{6\mu}\mathbf{r}_\mu e$, the theoretical computation of which is straight forward.

(2) The transition moment between the (n_+,π_4) perturbing triplet configuration of pyrazine and the observed triplet state [of (n_-,π_4) configuration]. The transition moment integral takes the form,

$$\langle n_+|\mathbf{r}e|n_-\rangle = \mathbf{r}_{NN}e/2 + \boldsymbol{\mu}_n' , \qquad (13)$$

where $\mathbf{r}_{NN}e$ is the moment along the N—N axis with magnitude in atomic units equal to the N—N distance and $\boldsymbol{\mu}_n'$ is the moment of the single nitrogen nonbonding electron in the (n,π^*) state.

(3) The third type of the integral is illustrated by the perturbation of the ground state by the (n_-,π_5) configuration arising from the B_1 component of the lowest triplet state of pyrimidine. In this case the transition moment integral, $\mathbf{M}(\mathbf{T}_1^0,\mathbf{T}_1^0)$, will be equal to the dipole moment of pyrimidine in the lowest triplet state.

$$\langle n_-,\pi_5|\mathbf{r}e|n_-,\pi_5\rangle = \boldsymbol{\mu} - \boldsymbol{\mu}_l + \boldsymbol{\mu}_n' + \boldsymbol{\mu}(\pi_5) . \qquad (14)$$

The last term on the right-hand side is the dipole moment due to an electron in the π_5 orbital. It can be estimated by $\langle\pi_5|\mathbf{r}e|\pi_5\rangle = \sum_{\mu=1}^{6} c_{5\mu}\mathbf{r}_\mu e$. The quantities $\boldsymbol{\mu}$ and $\boldsymbol{\mu}_l$ refer, respectively, to the molecular dipole moment in the ground state and the nitrogen lone-pair moment.

It is clear that the type (2) dipole matrix elements given by Eq. (13) are very large for diazines. This is because the transition moment integral involves an $N \rightarrow V$ type transition between excitons with different phase and thus essentially reduces to the $N^{+1/2e}$—$N^{-1/2e}$ moment. This term, the first on the right of Eq. (13), is about 6 D. For pyridine, or for any other azine with only one nitrogen atom, no such term is possible, so that the unobserved pyridine $n \rightarrow \pi^* S - T$ transition should remain considerably more forbidden (and thus weaker) than corresponding transitions in the diazines.

In order to estimate the magnitude of the nonbonding moment in the (n,π^*) excited state [the second term in Eq. (13)] a knowledge of the n orbital hybridization is necessary, in as much as the integral $\langle s_N|\mathbf{r}e|p_N\rangle = 5Z_N/\sqrt{3}$ has an appreciable numerical value. Hameka and Liquori[30] have considered the contribution of the nitrogen lone-pair moment to the dipole moments of azines and they estimated from an *a priori* consideration of the hybridization moment integral that the lone-pair nitrogen moment for sp^2 hybridization is about 3.6 D. More recent calculations by Amos and Hall[31] on the dipole moment of azines indirectly suggest that the lone-pair moment may be slightly larger than this, but not larger than 4.0 D. If the hybridization remained unchanged in going to the excited state then the magnitude of $\boldsymbol{\mu}_n' = 1/2\boldsymbol{\mu}_l$ will be about 1.8 to 2.0 D. If the nonbonding orbitals in the excited state were pure p orbitals then $\mu_n^1 = 0$. In any case the matrix elements of the form (2) are large because of the first term on the right-hand side of Eq. (13).

A comparison of the different perturbations in Table II reveal that the major contribution to $\mathbf{M}(\mathbf{T}_1,S_0)$ comes from the (n_+,π_4) configuration for pyrazine and the (n_+,π_5) configuration in pyrimidine and pyridazine. The transition moment integrals between these two configurations and the lowest triplet state have the form given in Eq. (13). Because of the large type (2) transition moments and the favorable energy differences of 3.5 to 4.0 eV from the ground state, the contribution to $\mathbf{M}(\mathbf{T}_1,S_0)$ due to these configurations is high. The relatively small perturbation of the ground state by the triplet configurations in pyridine can be attributed to the lack of such perturbing configurations.

It is not easy to discuss the matrix elements of type (3). They are clearly much smaller than the ones of type (2) inasmuch as the lone-pair moment is out-of-phase with other moments. For sp^2 hybridization in the excited state, $M(\mathbf{T}_1,\mathbf{T}_1)$ in Eq. (14) becomes 2.13–3.90 + 1.95 + 0.30 = 0.50 D. For smaller s character, this increases reaching a maximum of 1.6 D for zero s character. For the computation of the matrix elements in Table II we have assumed an s character of 0.1 in the excited state.[18] The nonbonding moment, μ_n', is computed to be sizable

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[30] H. F. Hameka and A. M. Liquori, Mol. Phys. **1**, 9 (1958).

[31] A. T. Amos and G. G. Hall, Mol. Phys. **4**, 25 (1961).

for this hybridization. The value for μ_n' utilized in Table II is 1.1 D. The contribution to $\mathbf{M}(\mathrm{T}_1,S_0)$ from the triplet configurations which give transition moment integrals of the form (3) [as in Eq. (14)] are considerably smaller than μ_n'. The transition moment in these cases, as noted before, reduces to the dipole moment in the lowest triplet state which is small because of the subtraction of the large lone-pair moment with an addition of only a small π moment. The (n,π) configuration of pyridine and the (n_-,π_5) configuration for the A_1 triplet component of pyrimidine and pyridazine belong to this class.

The rest of the triplet configurations listed in Table II have their n orbitals in common with the lowest triplet state. The transition moment integral, therefore, takes the form of type (1). Their magnitudes vary from 2 to 5 Debyes except in the case of matrix elements between the (n_-,π_4) perturbing configuration of pyrimidine and the (n_-,π_5) configuration for the B_1 component of the lowest triplet, where the transition moment is about 0.03 D. Their contributions to $\mathbf{M}(\mathrm{T}_1,S_0)$, however, are reduced because of the unfavorable energy difference.

As in the previous section, we describe the lowest triplet state of pyrimidine by 0.95 (n_-,π_5) + 0.30 (n_+,π_4). Of the triplet configurations listed under pyrimidine in Table II, the first four can radiatively combine with the (n_-,π_5) configuration and the last two with the (n_+,π_4) configuration. Since the contribution of the (n_+,π_4) configuration to the lowest triplet state in pyrimidine is relatively minor and only type (1) or (3) moments are encountered, the contribution of the last two configurations to $\mathbf{M}(\mathrm{T}_1,S_0)$ is small.

V. CONCLUSIONS

The polarization of $T_1 \rightarrow S_0$ emissions in pyrazine and pyrimidine have been experimentally determined to be along the N–N and short (x in Fig. 1) axes, respectively.[9]

The present theoretical treatment predicts, in agreement with the experiment, an N–N axis polarization for the $T_1 \rightarrow S_0$ transition in pyrazine. Of the three components of the lowest triplet state of pyrazine only the ${}^3B_{2u}(B_{3g})$ component[32] can radiatively combine with the ground state. Inasmuch as this result can be derived from the symmetries of the electronic states,[9] no novel prediction on the polarization of pyrazine $T_1 \leftrightarrow S_0$ can be said to be obtained.

In the lowest triplet state of pyrimidine two components can radiatively combine with the ground state. The theoretical results predict a much higher probability for the ${}^3B_2(B_1) \leftrightarrow {}^1A_1$ transition over that of the ${}^3B_2(A_1) \leftrightarrow {}^1A_1$ transition. Due to the large spin–orbit interaction the degeneracy of the three components of the triplet state will be removed. It is clear that the predominant observed x-axis polarization requires that the pyrimidine phosphorescence is mainly the ${}^3B_2(B_1) \rightarrow {}^1A_1$ transition. Thus, the experimentally observed x polarization for pyrimidine $T_1 \rightarrow S_0$ emission seems to be justified by these theoretical results.

From the matrix elements in Table I and II the lifetimes are calculated to be 3×10^{-3} sec for the ${}^3B_2(A_1) \rightarrow {}^1A_1$ intercombination of pyridine, 1×10^{-3} sec for the ${}^3B_{2u}(B_{2u}) \rightarrow {}^1A_g$ emission of pyrazine, 5×10^{-3} and about 0.3 sec for the ${}^3B_2(B_1) \rightarrow {}^1A_1$ and ${}^3B_2(A_1) \rightarrow {}^1A_1$ emissions, respectively, of pyrimidine, and about 0.5 and 3×10^{-2} sec for the A_1 and B_1 components, respectively, of the ${}^3B_2 \rightarrow {}^1A_1$ pyridazine intercombination. An experimental value of 2×10^{-2} sec is reported for the $T_1 \rightarrow S_0$ emission of pyrazine.[11,33] The order of magnitude discrepancy between this and the theoretical result clearly represents a significant failure of the theory in this case since the actual pyrazine triplet-state lifetime is very likely longer than the observed (radiative) lifetime due to competing radiationless processes. Further, in discussing sources of transition probability between T_1 and S_0 we have neglected vibronic coupling of T_1 with other triplet states. Inclusion of this effect [which is significant for (π,π^*) triplet states[34]] and inclusion of the high-lying perturbing states such as Rydberg are expected to decrease the predicted lifetime still further.

Innes and Giddings,[35] on the basis of rotational analysis of the pyrazine $S_0 \rightarrow T_1$ $0-0$ band absorption, have concluded that the band is parallel type and hence has a transition moment ⊥ to the molecular plane, in contradiction to the emission polarization experiment[8] involving the same band. To reconcile these apparently contradictory observations, Innes and Giddings suggested that $T_1 \leftrightarrow S_0$ is a magnetic dipolar transition. An assignment which is consistent with this is $T_1 : {}^3B_{3g}(n_+\pi_4)$[36] rather than our assumed assignment of ${}^3B_{2u}(n_-\pi_4)$. On energetic grounds this assignment appears plausible since El-

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[32] See footnote a of Table I for the notation.

[33] D. S. McClure, J. Chem. Phys. **17**, 905 (1949).

[34] A. C. Albrecht, J. Chem. Phys. **33**, 169, 937 (1960); **38**, 354 (1963).

[35] K. K. Innes and L. E. Giddings, Trans. Faraday Soc. (to be published).

[36] See footnote 29.

Sayed and Robinson[37] have assigned the lowest singlet state in pyrazine as forbidden and thus presumably as ${}^1B_{3g}(n_+\pi_4)$. Spin-orbit interactions can couple $(\pi_1\pi_4)$, $(\pi_2\pi_6)$ singlet (A_g) configurations with ${}^3B_{3g}(A_g)$. These configurations on the basis of the D_{2h} molecular symmetry can combine with the ground state by magnetic dipolar radiation, but not by electric dipolar radiation. (Magnetic dipolar radiation is forbidden directly between a triplet and singlet.) They are locally forbidden however, because of the vanishing atomic magnetic dipolar transition moment at each atomic center for (π,π^*) states. Hence the only nonvanishing terms are the weak multicenter magnetic moments involving no change in m_l. An estimation of the pyrazine T_1 lifetime on the basis of this assignment is ~1 sec. In order to rationalize the short radiative lifetime (on the basis of ~1 sec natural lifetime) it is necessary to suppose a very low quantum yield for the pyrazine $T_1 \to S_0$ emission, contrary to experiment. Further the radiative lifetime of the pyrimidine $T_1 \to S_0$ emission ($1\text{–}2 \times 10^{-2}$ sec),[38] where only electric dipole transitions are possible, is not very different from the pyrazine lifetime. Hence, the above reassignment of the pyrazine triplet does not seem to rationalize the lifetime. Its extension to *s*-triazine may however lead to the essential explanation of the long lifetime of the triplet state—$\frac{1}{2}$ sec[39] in that molecule.

Another cause for the failure of the theory resides in the replacement of $Z(f)$ by Z. This may be especially critical for (n,π^*) states, since in this case H_2 in Eq. (1b) produces a nonvanishing one-center contribution to the spin-orbit matrix elements. Further calculations using the noncentral forms of the spin-orbit operator are clearly needed.

These calculations bring forth the importance of the perturbation of the ground state by the triplet states. Further, the ground state itself provides a perturbation—which cannot be neglected— on the lowest triplet state in polar molecules.

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We wish to express our thanks to Professor H. F. Hameka for critically reading the manuscript and for several suggestions.

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Importance of Core Polarization on the Calculation of Nuclear Moments from Hyperfine Structure Data. Nuclear Moments of C^{11}

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I. INTRODUCTION

THE value of the nuclear magnetic moment of an atom is generally known from direct measurement. But, as in the case of the nuclear electric quadrupole moment, if the nuclear magnetic moment is not available, then one should be able to deduce it from the experimental hyperfine constant.

In this paper we deduce the values of the magnetic moments for B^{11}, O^{17}, and F^{19} using the average values of the magnetic field of the electron which we have previously calculated[1] from (a) the Hartree–Fock functions, (b) the spin-polarized Hartree–Fock functions, and (c) the projection of the spin-polarized functions. From a comparison of the magnetic moments deduced from these three types of functions with the experimental values, we should be able to see how important core polarization is in the "calculation" of the nuclear magnetic moment.[2]

Recently, Haberstroh *et al.*[3] have measured the hyperfine constants for the ${}^3P_2$ atomic state of C^{11}. The magnetic dipole moment is not known from a direct experiment and, as far as we know, no value for the electric quadrupole moment has been proposed. In

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[1] N. Bessis, H. Lefebvre-Brion, and C. M. Moser, Phys. Rev. **128**, 213 (1962); N. Bessis, Cahiers Phys. **15**, 345 (1962).

[2] For a discussion of this effect for atoms in ${}^2S$ state see, W. W. Holloway, Z. Naturforsch. **17a**, 89 (1962).

[3] R. A. Haberstroh, W. J. Kossler, O. Ames, and D. R. Hamilton, Bull. Am. Phys. Soc. **8**, 8 (1963).