Radiative Triplet Lifetimes in Benzene and Azabenzenes with Particular Reference to Phosphorescence Mechanisms in Benzene

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Calculations of radiative triplet lifetimes of benzene and azabenzenes are carried out by making use of an INDO/S method in which the parametrization of the CNDO/S method is used, retaining the semi-empirical Slater-Condon parameters determined in the INDO/2 method. The calculated excitation energies, oscillator strengths, and radiative lifetimes are in reasonable agreement with experimental values. The possible phosphorescence mechanisms for the $^3B_{1u}$ state of benzene are discussed rather in detail, considering the first-order vibronic as well as the first-order spin-orbit and the second-order spin-vibronic couplings. It is concluded that the strong first-order vibronic coupling between the triplet manifolds, $^3B_{1u}$ and $^3E_{1u}$, is responsible for the almost purely out-of-plane polarized phosphorescence of benzene, borrowing an intensity from the $^3E_{1u}$-$^1A_{1g}$ intercombination, and that the effects of the first-order spin-orbit and the second-order spin-vibronic couplings are small. The conclusion is in accord with the analyses of the Zeeman and MIDP spectra presented by van Egmond and van der Waals.

Theoretical prediction of radiative lifetimes for triplet states of aromatic hydrocarbons not only gives an important information for intersystem crossing mechanisms in luminescence spectroscopy but also serves as a sensitive check for the validity of quantum chemical approximations. The controversy on whether a π-electron model is adequate or states of mixed σ-π electronic character should be included has been almost settled, since the former yields predicted phosphorescence spectra $T_1 \rightarrow S_0$ always to be in-plane polarized whereas observed spectra of many aromatic hydrocarbons are predominantly out-of-plane polarized.[1,2] As for the importance of σ-electrons the earlier paper by Mizushima and Koide[3] was a foresighted one, though the lifetime of the spin-forbidden phosphorescent transition of benzene was only estimated.

As for the phosphorescence mechanisms in benzene, Clementi's scheme[4] for the $^3E_{1u} \rightarrow {}^1A_{1g}$ intercombination and Albrecht's second-order perturbation treatment[5] of the vibronic coupling between the triplet manifolds $^3B_{1u}$ and $^3E_{1u}$ are at present sufficiently convincing. In fact, Veeman and van der Waals[6] calculated the lifetime of the $^3B_{1u} \rightarrow {}^1A_{1g}$ transition to be 23.2 second using those schemes. As for the molecular spin-orbit coupling intergrals, it has been shown by several authors[6—9] that when σ-electron MO's are taken into account together with π-electron MO's the approximation to retain only one-center spin-same orbit coupling integrals is good enough to describe spin-orbit interactions in aromatic hydrocarbons. It is true in general that one-center spin-same-orbit coupling integrals are much larger in their magnitude than two- and three-center ones and also one- and multi-center spin-other-orbit coupling integrals. In the usual π-electron approximation for benzene and other planar aromatic hydrocarbons, all one- and two-center spin-same-orbit integrals vanish and contribution of small three- and four-center integrals to spin-orbit coupling has to be retained to calculate the triplet lifetimes which are therefore too long to compare with the corresponding experimental results.[10]

Though it is clear that the dominant spin-orbit coupling mechanism for radiative $T_1 \rightarrow S_0$ transitions involves $\pi\sigma^*$ and/or $\sigma\pi^*$ rather than $\pi\pi^*$ coupling, what type of approximate method is adequate comes into question. When one uses the CNDO/S method, one meets with a difficulty that energy separations between the singlet and triplet levels of both $\sigma\pi^*$ and $\pi\sigma^*$ states become zero in molecules of high symmetry. It is recognized fairly generally that the original INDO method gives non-zero but too high singlet and triplet states. In order to obtain better wave functions to predict whole lower-lying singlet and triplet levels of molecules, we use in this paper a modified INDO method in which the parametrization of Bene-Jaffé-Ellis-Kuehnlenz's modified CNDO method is adopted without changing the values of the semi-empirical Slater-Condon parameters used in the original INDO/2 method. Another modification is a use of Chojnacki's approximation[13] for two-center electronic repulsion integrals. In this respect, our INDO/S method is somewhat different from those proposed by Chen and Hedges[14] and Ridley and Zerner.[15]

We first check the reliability of the present INDO/S method with regard to singlet and triplet excitation energies and their intensities in benzene and azabenzenes and calculate the radiative lifetimes of lower-lying triplet states. In order to clarify the mechanisms of the phosphorescence in benzene, we investigate the symmetry forbidden lowest triplet radiative lifetime and the phosphorescence polarization in benzene rather in detail.

Theoretical Background

With the first-order perturbation theory, the spin-contaminated wave functions for the ground state, $|S_0{}^c\rangle$, and ith excited triplet state, $|T_i{}^c\rangle$, produced by spin-orbit coupling are written down as

$$|S_0{}^c\rangle = |S_0\rangle + \sum_m \gamma_m |T_m\rangle \text{ with } \gamma_m = \frac{\langle T_m|H_{so}|S_0\rangle}{E(S_0)-E(T_m)} \tag{1}$$

$$|T_i{}^c\rangle = |T_i\rangle + \sum_n \delta_n |S_n\rangle \text{ with } \delta_n = \frac{\langle S_n|H_{so}|T_i\rangle}{E(T_i)-E(S_n)}. \tag{2}$$

Here the spin-orbit Hamiltonian has the following form in the notation of our previous paper:[16]

$$H_{\mathrm{so}} = \alpha^2\{\sum_{i}\sum_{\mathrm{N}} Z_{\mathrm{N}}(\vec{l}_{\mathrm{N}i}/r_{\mathrm{N}i}{}^3)\cdot\vec{S}_i + \sum_{i}\sum_{j\neq i}(2\vec{\mathrm{p}}_i-\vec{\mathrm{p}}_i)$$
$$\times\ (\vec{r}_{ij}/r_{ij}{}^3)\cdot\vec{S}_i\} \tag{3}$$

The transition moment between the states $|\mathrm{S_0}^{\mathrm{c}}\rangle$ and $|\mathrm{T}_i{}^{\mathrm{c}}\rangle$ is then given by

$$\langle \mathrm{S_0}^{\mathrm{c}}|\vec{M}|\mathrm{T}_i{}^{\mathrm{c}}\rangle = \sum_{n}\delta_n\langle \mathrm{S_0}|\vec{M}|\mathrm{S}_n\rangle + \sum_{m}\gamma_{m^*}\langle \mathrm{T}_m|\vec{M}|\mathrm{T}_i\rangle \tag{4}$$

where $\vec{M}$ is the electric dipole operator. The corresponding oscillator strength and lifetime are derived from

$$f(\mathrm{S_0}-\mathrm{T}_i) = 1.085\times 10^{-5}\,\nu(\mathrm{S_0}-\mathrm{T}_i)\,|\langle \mathrm{S_0}^{\mathrm{c}}|\vec{M}|\mathrm{T}_i{}^{\mathrm{c}}\rangle|^2 \tag{5}$$

$$\tau(\mathrm{T}_i-\mathrm{S_0}) = 1.5(g_{\mathrm{T}}/g_{\mathrm{s}})/[\nu^2(\mathrm{S_0}-\mathrm{T}_i)f(\mathrm{S_0}-\mathrm{T}_i)] \tag{6}$$

where $\nu(\mathrm{S_0}-\mathrm{T}_i)$, the frequency of the emission from the lowest triplet state, is measured in units of cm^{-1} and the transition moment in units of Å. g_{s} and g_{T} represent the degeneracies in the ground singlet and excited triplet states, respectively, being put to be $g_{\mathrm{s}}=1$, $g_{\mathrm{T}}=3$ for temperature higher than 4.2 K and $g_{\mathrm{T}}=1$ for temperature lower than 1.34 K according to experimental evidence.[17,18] $g_{\mathrm{T}}/g_{\mathrm{s}}=3$ is used throughout our computation.

The singlet and triplet state functions are expressed in terms of the Slater determinantal wavefunctions ${}^{2S+1}\psi_{i\to j}(SM)$ where S and M denote the total spin angular momentum and its z-projection, as follows:

$$|S(00)\rangle = \sum_{l} C_{i\to j}^{(l)}\,{}^1\psi_{i\to j}(00) \tag{7}$$

$$|T(1M)\rangle = \sum_{l} C_{i\to j}^{(l)}\,{}^3\psi_{i\to j}(1M),\quad M=0,\ \pm 1 \tag{8}$$

After obtaining CI coefficients, it is convenient for practical applications to transform the triplet state functions $|\mathrm{T(1\ M)}\rangle$ into $|\mathrm{T^x}\rangle$, $|\mathrm{T^y}\rangle$ and $|\mathrm{T^z}\rangle$ so as to belong to the same representation of the appropriate point group as the cartesian components of the spin angular momentum.[10] Namely,

$$\begin{aligned}
|\mathrm{T^x}\rangle &= \frac{1}{\sqrt{2}}\{|\mathrm{T}(1-1)\rangle-|\mathrm{T}(11)\rangle\} = \sum_{l} C_{i\to j}^{(l)}\,{}^3\psi_{i\to j}^{\mathrm{x}}\\
|\mathrm{T^y}\rangle &= \frac{i}{\sqrt{2}}\{|\mathrm{T}(1-1)\rangle+|\mathrm{T}(11)\rangle\} = \sum_{l} C_{i\to j}^{(l)}\,{}^3\psi_{i\to j}^{\mathrm{y}}\\
|\mathrm{T^z}\rangle &= |\mathrm{T}(10)\rangle \qquad\qquad\qquad\qquad = \sum_{l} C_{i\to j}^{(l)}\,{}^3\psi_{i\to j}^{\mathrm{z}}
\end{aligned} \tag{9}$$

where

$$\begin{aligned}
{}^3\psi_{i\to j}^{\mathrm{x}} &= \frac{1}{\sqrt{2}}\{{}^3\psi_{i\to j}(1-1)-{}^3\psi_{i\to j}(11)\}\\
{}^3\psi_{i\to j}^{\mathrm{y}} &= \frac{i}{\sqrt{2}}\{{}^3\psi_{i\to j}(1-1)+{}^3\psi_{i\to j}(11)\}\\
{}^3\psi_{i\to j}^{\mathrm{z}} &= {}^3\psi_{i\to j}(10)
\end{aligned} \tag{10}$$

The matrix elements over MO's for the one-electron part of H_{so} are given by [19,20]

$$\sum_{\mu=\mathrm{x,y,z}}\langle {}^1\psi_0|H_{\mathrm{so}}^{\mu}|{}^3\psi_{i\to j}^{\mu}\rangle = \frac{1}{\sqrt{2}}\langle i|H_{\mathrm{so}}^{\mathrm{x}}-H_{\mathrm{so}}^{\mathrm{y}}-H_{\mathrm{so}}^{\mathrm{z}}|j\rangle \tag{11}$$

$$\sum_{\mu=\mathrm{x,y,z}}\langle {}^1\psi_{i\to j}|H_{\mathrm{so}}^{\mu}|{}^3\psi_{k\to l}^{\mu}\rangle = \frac{1}{2}\delta_{jl}\langle i|H_{\mathrm{so}}^{\mathrm{x}}-H_{\mathrm{so}}^{\mathrm{y}}-H_{\mathrm{so}}^{\mathrm{z}}|k\rangle$$
$$-\frac{1}{2}\delta_{ik}\langle j|H_{\mathrm{so}}^{\mathrm{x}}-H_{\mathrm{so}}^{\mathrm{y}}-H_{\mathrm{so}}^{\mathrm{z}}|l\rangle \tag{12}$$

which are reduced to the spin-same-orbit coupling integrals over AO's. The one-center spin-same-orbit integrals over 2p AO's are analytically given as

$$\begin{aligned}
\langle 2\mathrm{p_y}|H_{\mathrm{so}}^{\mathrm{z}}|2\mathrm{p_x}\rangle &= -\langle 2\mathrm{p_x}|H_{\mathrm{so}}^{\mathrm{z}}|2\mathrm{p_y}\rangle = -\langle 2\mathrm{p_y}|H_{\mathrm{so}}^{\mathrm{x}}|2\mathrm{p_z}\rangle\\
&= \langle 2\mathrm{p_z}|H_{\mathrm{so}}^{\mathrm{x}}|2\mathrm{p_y}\rangle = \langle 2\mathrm{p_x}|H_{\mathrm{so}}^{\mathrm{y}}|2\mathrm{p_z}\rangle = -\langle 2\mathrm{p_z}|H_{\mathrm{so}}^{\mathrm{y}}|2\mathrm{p_x}\rangle\\
&= i\alpha^2(Z_{\mathrm{N}}{}^4/24)\ (\mathrm{Rydberg}) = 5.8437\,i\ (Z_{\mathrm{N}}{}^4/28)\ (\mathrm{cm^{-1}})
\end{aligned} \tag{13}$$

where the leading sign is plus when the sequence of the sub- and super-scripts μ=x, y, z on $2\mathrm{p}_{\mu}$ AO's and H_{so}^{μ} is cyclic and it is minus when the sequence is uncyclic, and Z_{N} is the effective nuclear charge.

Method of Calculation and Results

We use an INDO-type method based on the parametrization of the CNDO/S method which was first presented by Del Bene and Jaffé[11] and later somewhat reparametrized by Ellis, Kuehnlenz and Jaffé[12], retaining the semi-empirical Slater-Condon parameters determined in the INDO/2 method. The method is therefore called the INDO/S method hereafter. Like the CNDO/S method, the calculation of the off-diagonal matrix elements of the Fock operator $F_{\mu\nu}$, after the notation of Pople and Beveridge,[21] is carried out through the equation

$$F_{\mu\nu} = \beta_{\mathrm{AB}}^{0}S_{\mu\nu} - \frac{1}{2}P_{\mu\nu}\gamma_{\mathrm{AB}}\quad (\mu\in\mathrm{A},\ \nu\in\mathrm{B}) \tag{14}$$

where

$$S_{\mu\nu} = K_{\sigma}G_{\sigma}S_{\mu\nu}^{\sigma} + K_{\pi}G_{\pi}S_{\mu\nu}^{\pi} \tag{15}$$

for a pair of $2\mathrm{p_i}$ and $2\mathrm{p_j}$ (i, j ∈ x, y, z). G_{σ} and G_{π} are geometrical factors needed to project an arbitrary pair of 2p AO's in the cartesian coordinates suitably chosen onto the local bond axis. We adopted $K_{\sigma}=1$ and $K_{\pi}=0.585$ which are the values fixed by Del Bene and Jaffé[11] in their CNDO/S method. Other authors use a little different values for parameters K_{σ} and K_{π}. We found however that these parametrization does not produce an important effect in the final result, compared with the choice of an approximation for two-center electronic repulsion integrals which will be mentioned below. The zero differential overlap approximation is relaxed by retaining one-center integrals of the type $\langle 2\mathrm{s}|e\vec{r}|2\mathrm{p_i}\rangle$ and $\langle 2\mathrm{p_i}|e\vec{r}|2\mathrm{p_i}\rangle$ in the computation of transition moments.[12]

We have prepared a program for the present INDO/S method by modifying the computer program QCPE 91 for the CNDO/2 method written by Segal.[22] Throughout our computation, we solve 30×30 CI matrices made up of all the excitations which are unconditionally produced from *five* MO's below the highest occupied orbital to *six* MO's above the lowest unoccupied orbital. Reduction of the matrix elements over molecular integrals into those over atomic integrals in the INDO type method is prescribed by Ho *et al.*[23]

and Ridley and Zerner.[15)]

With our INDO/S method, we carried out a pilot calculation of the excitation energies and oscillator strengths of benzene using the Nishimoto-Mataga (NM)[24)] and the Ohno[25)] approximations for two-center electronic repulsion integrals. The NM approximation was found to produce singlet levels tolerably well but lower triplet levels too low. On the other side, when Ohno's approximation is used the low-lying triplet levels are well reproduced but the singlet levels are not, in particular the $^1B_{2u}$ and $^1B_{2u}$ levels turn out to be reversed. These features are not typical of our INDO/S method but are also the cases whenever a Pariser-Parr-Pople type scheme is adopted for a π-electron model benzene (and other aromatic hydrocarbons) with the NM and Ohno approximations.

In order to obtain better wave functions which can predict both excitation energies and oscillator strengths, we tried to find out a parameter θ in the Chojnacki-type approximation[13)]

$$\gamma_{AB} = \theta\gamma_{AB}^{NM} + (1-\theta)\gamma_{AB}^{Ohno} \qquad (\theta<1) \tag{16}$$

where γ_{AB} is the two-center Coulomb repulsion integral. Chojnacki obtained $\theta=0.4$ in his P-P-P type π-electron calculations,[13)] the value producing both first singlet and triplet levels which are in good agreement with experimental values. In our INDO/S calculations, however, a suitable value for θ was not obtained so as to reproduce the singlet and triplet levels of benzene simultaneously well. We adopted the Chojnacki's value $\theta=0.4$ because this was found to give a best compromise in simultaneous singlet and triplet level setting in benzene.

The results of our INDO/S calculation are listed in Table 1 for benzene and in Table 2 for azabenzenes. For comparison, we calculated the lower three $\pi\pi^*$ singlet and triplet state energies with the same procedure as our INDO/S but with the NM and Ohno approximations; these are 4.84, 6.06, 6.98 eV (NM) and 4.62, 4.93, 7.41 eV (Ohno) for the singlets, and 2.41, 3.93, 4.84 eV (NM) and 3.39, 4.45, 4.94 eV (Ohno) for the triplets. In so far as these lower excitation energies are concerned, it can be safely said therefore that the Chojnacki-type approximation produces better overall agreement with observed values than the NM and Ohno approximations. The oscillator strength and the lifetime of the transition $^3E_{1u}\rightarrow{}^1A_{1g}$ in benzene are calculated from Eqs. 5 and 6 and are listed at the bottom of Table 1.

The calculated excitation energies and oscillator strengths of the lower triplet states of some azabenzenes listed in Table 2 are fairly in good agreement with experimental values. As for 1, 3, 5-triazine, though the calculated lowest triplet state $^3E''$ comes rather high, the radiative lifetime from the state is computed to be 0.323 second which compares well with the

TABLE 1. CALCULATED EXCITATION ENERGIES (ΔE), OSCILLATOR STRENGTHS (f), AND PHOSPHORESCENCE LIFETIME (τ) OF BENZENE[a)]

State No.	States	ΔE(eV)	$f(S_0\rightarrow S_i)$	State No.	States	ΔE	$f(T_1\rightarrow T_i)$	$f(T_2\rightarrow T_i)$
1	$^1B_{2u}(\pi\pi^*)$	4.90	0	1	$^3B_{1u}(\pi\pi^*)$	3.04	Ref.	
		⟪4.93⟫	⟪0.001⟫			⟪3.95⟫		
2	$^1B_{1u}(\pi\pi^*)$	5.21	0	2A, B	$^3E_{1u}(\pi\pi^*)$	4.26		Ref.
		⟪6.21⟫	⟪0.1⟫			⟪4.75⟫		
3A, B	$^1E_{1u}(\pi\pi^*)$	7.23	2.070 (x, y)	3	$^3B_{2u}(\pi\pi^*)$	4.90		
		⟪6.96⟫	⟪0.690⟫			⟪5.60⟫		
4	$^1A_{2u}(\sigma\pi^*)$	7.82	0.003 (z)	4A, B	$^3E_{2g}(\pi\pi^*)$	6.11	0.022 (x, y)	0.052 (x, y)
5A, B	$^1E_{2u}(\pi\sigma^*)$	7.88	0			⟪6.75⟫		
6A, B	$^1E_{2u}(\pi\sigma^*)$	7.94	0	5A, B	$^3E_{2u}(\pi\sigma^*)$	7.16		
7	$^1A_{1u}(\sigma\pi^*)$	8.02	0	6	$^3B_{2g}(\pi\sigma^*)$	7.65	0.052 (z)	
8A, B	$^1E_{2g}(\pi\pi^*)$	8.15	0	7	$^3A_{2u}(\sigma\pi^*)$	7.70		
		⟪7.48⟫		8A, B	$^3E_{2u}(\sigma\pi^*)$	7.79		
9	$^1B_{2g}(\pi\sigma^*)$	8.99	0	9	$^3A_{1u}(\sigma\pi^*)$	7.89		
10	$^1B_{1g}(\pi\sigma^*)$	9.00	0	10A, B	$^3E_{1g}(\pi\sigma^*)$	8.61		0.097 (z)
11A, B	$^1E_{1g}(\sigma\pi^*)$	9.12	0	11	$^3B_{1g}(\pi\sigma^*)$	8.93		
12A, B	$^1E_{2g}(\pi\pi^*)$	10.32	0	12A, B	$^3E_{2g}(\pi\pi^*)$	9.22	0.412 (x, y)	1.983 (x, y)
13A, B	$^1E_{1g}(\sigma\pi^*)$	10.64	0	13A, B	$^3E_{1g}(\sigma\pi^*)$	10.50		4×10^{-5} (z)
14A, B	$^1E_{1u}(\sigma\sigma^*)$	11.76	0.992 (x, y)	14A, B	$^3E_{1u}(\sigma\sigma^*)$	10.60		
15	$^1A_{2g}(\sigma\pi^*)$	12.37	0	15	$^3A_{1g}(\sigma\pi^*)$	11.75		
16	$^1A_{1g}(\sigma\pi^*)$	12.52	0	16A, B	$^3E_{2g}(\sigma\sigma^*)$	11.84	2×10^{-5} (x, y)	3×10^{-4} (x, y)
17A, B	$^1E_{2g}(\sigma\sigma^*)$	12.71	0	17	$^3A_{2g}(\sigma\pi^*)$	11.93		2×10^{-5} (x, y)
18	$^1B_{2u}(\pi\pi^*)$	12.79	0	18	$^3B_{2u}(\pi\pi^*)$	12.36		
19A, B	$^1E_{2u}(\pi\sigma^*)$	14.00	0	19	$^3B_{2g}(\pi\sigma^*)$	12.85	0.001 (z)	
				20A, B	$^3E_{2u}(\pi\sigma^*)$	13.65		

$f(^3E_{1u}\rightarrow{}^1A_{1g}) = 0.92247\times10^{-9}$

$\tau(^3E_{1u}\rightarrow{}^1A_{1g}) = 4.13$ s

a) Geometry: C–C 1.40 Å; C–H 1.10 Å.

⟪ ⟫ Obsd, J. Karwowski, *Acta Phys. Polon.*, **A37**, 417 (1970).

Table 2. Calculated triplet excitation energies (ΔE), oscillator strengths (f), and phosphorescence lifetimes (τ) of some azabenzenes[a)]

States	ΔE (eV) Calcd	ΔE (eV) Obsd[b)]	$f(T_i \rightarrow S)$	τ (s) Calcd	τ (s) Obsd
Pyridine (x-axis: out-of-plane)					
$^2B_1(n\pi^*)$	3.62	3.68	0.109×10^{-7} (z)	0.485	—
$^3A_1(\pi\pi^*)$	3.84		0.341×10^{-8} (x)	1.378	
$^3B_2(\pi\pi^*)$	3.93		0.602×10^{-10} (x)	73.451	
$^3A_1(\pi\pi^*)$	4.64		0.464×10^{-7} (x)	0.069	
Pyrazine (x-axis: out-of-plane)					
$^3B_{3u}(n\pi^*)$	2.52	3.32	0.199×10^{-6} (z)	0.055	0.02[c)]
$^3B_{2u}(\pi\pi^*)$	3.12		0.182×10^{-11} (z)	1.759×10^{3}	
$^3B_{1u}(\pi\pi^*)$	3.86		0.873×10^{-8} (x)	0.532	
$^3B_{2g}(n\pi^*)$	3.90		0		
Pyrimidine (x-axis: out-of-plane)					
$^3B_1(n\pi^*)$	3.68	3.63	0.462×10^{-7} (y)	0.090	0.01—0.02[c)]
			0.105×10^{-7} (z)		
$^3A_2(n\pi^*)$	4.13		0.174×10^{-6} (x)	0.016	
			0.675×10^{-7} (z)		
$^3B_2(\pi\pi^*)$	4.20		0.219×10^{-6} (x)	0.018	
$^3A_1(\pi\pi^*)$	4.40		0.268×10^{-8} (x)	1.335	
Pyridazine (x-axis: out-of-plane)					
$^3B_1(n\pi^*)$	2.89	3.01	0.135×10^{-7} (y)	0.380	0.05[d)]
			0.826×10^{-8} (z)		
$^3B_2(\pi\pi^*)$	3.50		0.667×10^{-7} (x)	0.084	
$^3A_2(n\pi^*)$	3.51		0.138×10^{-4} (x)	0.388×10^{-3}	
$^3A_1(\pi\pi^*)$	4.02		0.188×10^{-6} (x)	0.023	
1,3,5-Triazine (z-axis: out-of-plane)					
$^3E''(n\pi^*)$	4.48	3.08	0.776×10^{-8} (x)	0.323	0.4[e)]
			0.291×10^{-8} (y)		
$^3A_2''(n\pi^*)$	4.63		0.163×10^{-6} (x)	0.631×10^{-2}	
			0.162×10^{-6} (y)		
			0.187×10^{-6} (z)		
$^3A_2''(n\pi^*)$	4.70		0.110×10^{-6} (x)	0.014	
			0.110×10^{-6} (y)		
1,2,4,5-Tetrazine (x-axis: out-of-plane)					
$^3B_{3u}(n\pi^*)$	1.18	1.69	0.195×10^{-6} (y)	0.222	72×10^{-6} [f)] 10×10^{-9} [a)]
			0.291×10^{-7} (z)		
$^3B_{1g}(n\pi^*)$	2.95		0		
$^3B_{1u}(\pi\pi^*)$	3.21		0.375×10^{-7} (x)	0.179	
$^3A_u(n\pi^*)$	3.25		0.152×10^{-7} (x)	0.039	
			0.987×10^{-7} (y)		
			0.523×10^{-7} (z)		

a) Molecular geometries are taken from K. K. Innes, J. P. Byrne and I. G. Ross, *J. Mol. Spectrosc.*, **22**, 125 (1967). b) J. Karwowski, *Acta Phys. Polon.*, **A37**, 417 (1970). c) Ref. 17, p. 217. d) R. M. Hochstrasser and C. Marzzacco, *J. Chem. Phys.*, **46**, 4155 (1967). e) J. Paris, R. Hirt, and R. Schmitt, *J. Chem. Phys.*, **34**, 1851 (1961). f) J. R. McDonald and L. E. Brus, *J. Chem. Phys.*, **59**, 4966 (1973).

observed value 0.4 second and the assignment of the excited triplet states is in reasonable agreement with the experimentally fixed order. We do not list calculated results for lower singlet states of these azabenzenes since the results are quite similar to those obtained by Ridley and Zerner.[15)] These authors used a modified NM approximation in their INDO type calculations of lower excited singlet states of azabenzenes but did not refer to their excited triplet states. The choice of CI's in the present paper is rather different from that of Ridley and Zerner. Nevertheless, this does not yield much discrepancies in the final results for the low-lying singlet states. Chen and Hedges[14)] used a rather different parametrization in their INDO type calculation and obtained fairly good results for both low-lying singlet and triplet levels. Their assignment for higher energy levels is, however, much different from those obtained in the present paper and by Ridley and Zerner.

In the next section, we use the present results as a theoretical foundation to explain the phosphorescence mechanisms in benzene.

Phosphorescence Mechanisms in Benzene

${}^3E_{1u}\rightarrow{}^1A_{1g}$ Intercombination. In the range of our choice of CI's, the ${}^{1,3}\mathrm{B}_{2u}$ and ${}^{1,3}\mathrm{B}_{1u}$ states of benzene are found to be almost pure $\pi\pi^*$ states, so that the matrix element $\langle{}^1\mathrm{B}_{2u}|H^z_{so}|{}^3\mathrm{B}_{1u}\rangle$ vanishes provided that only the one-center spin-same-orbit coupling integrals are retained. It should be noted therefore that the ${}^{1,3}\mathrm{E}_{1u}$ states having considerable amount of $\sigma\sigma^*$ characters play an important role in the spin-orbit mechanism.

Our starting wave functions for the degenerate E_{1u} states are, for example, of the forms (the state numbers 3A and 3B follow after Table 1)

$$\begin{aligned}|{}^{1,3}\mathrm{E}_{1u}\begin{Bmatrix}3\mathrm{A}\\2\mathrm{A}\end{Bmatrix}\rangle = &\begin{Bmatrix}0.6829\\-0.4011\end{Bmatrix}({}^{1,3}\phi_{14\to16}-{}^{1,3}\phi_{15\to17})\\ &-\begin{Bmatrix}0.0983\\0.5824\end{Bmatrix}({}^{1,3}\phi_{14\to17}+{}^{1,3}\phi_{15\to16})\\ &+\begin{Bmatrix}0.2193\\0.0021\end{Bmatrix}{}^{1,3}\phi_{12\to18}-\begin{Bmatrix}0.0026\\0.0043\end{Bmatrix}{}^{1,3}\phi_{13\to18}\end{aligned}\tag{17}$$

$$\begin{aligned}|{}^{1,3}\mathrm{E}_{1u}\begin{Bmatrix}3\mathrm{B}\\2\mathrm{B}\end{Bmatrix}\rangle = &\begin{Bmatrix}0.0983\\0.5824\end{Bmatrix}({}^{1,3}\phi_{14\to16}-{}^{1,3}\phi_{15\to17})\\ &+\begin{Bmatrix}0.6829\\-0.4011\end{Bmatrix}({}^{1,3}\phi_{14\to17}+{}^{1,3}\phi_{15\to16})\\ &-\begin{Bmatrix}0.0026\\0.0043\end{Bmatrix}{}^{1,3}\phi_{12\to18}-\begin{Bmatrix}0.2193\\0.0021\end{Bmatrix}{}^{1,3}\phi_{13\to18}\end{aligned}\tag{18}$$

where the upper and lower figures in braces correspond to the singlet and triplet states, respectively, and each configurational wave function is constructed from the ground state configuration as in the following:

$$\begin{aligned}&(1a_{1g})^2(2,3e_{1u})^4(4,5e_{2g})^4(6a_{1g})^2(7b_{1u})^2(8b_{2u})^2(9,10e_{1u})^4\text{-}\\ &(11\pi a_{2u})^2(12,13e_{2g})^4(14\pi,15\pi e_{1g})^4(16\pi,17\pi e_{2u})^0(18b_{2u})^0\text{-}\\ &(19\pi b_{2g})^0(20,21e_{2g})^0(22a_{1g})^0(23,24e_{1u})^0(25b_{1u})^0(26,27e_{1u})^0\\ &(28,29e_{2g})^0(30a_{1g})^0\end{aligned}\tag{19}$$

In the above, each figure before the symmetry designation shows the orbital number in the order of increasing energy (double numbers are used for degenerate levels) and the simbol π after each figure denotes a π-electron MO, a specification for a σ-electron MO being omitted. With this orbital numbers we designate the configurational wave functions appearing in Eqs. 17 and 18 such as $\phi_{14\to16}$.

We obtained the following spin-contaminated wave functions for the ground state $|\mathrm{G^c}\rangle$ and the triplet E_{1u} state $|{}^3\mathrm{E}^c_{1u}\rangle$ needed to produce the ${}^3\mathrm{E}_{1u}$-${}^1\mathrm{A}_{1g}$ intercombination:

$$\begin{aligned}|\mathrm{G^c}\rangle &= |{}^1\mathrm{A}_{1g}\rangle+\sum_i\lambda_i^{so}|{}^3\mathrm{E}_{1g}(\sigma\pi^*,\pi\sigma^*;\ i)\rangle\\ &\quad+\sum_i\omega_i^{so}|{}^3\mathrm{A}_{2g}(\sigma\pi^*,\pi\sigma^*;\ i)\rangle\\ &= |{}^1\mathrm{A}_{1g}\rangle+0.7059\times10^{-4}|{}^3\mathrm{E}^x_{1g}(10\mathrm{A})\rangle\\ &\quad-0.7234\times10^{-5}|{}^3\mathrm{E}^y_{1g}(10\mathrm{A})\rangle\\ &\quad+0.7234\times10^{-5}|{}^3\mathrm{E}^x_{1g}(10\mathrm{B})\rangle\\ &\quad+0.7059\times10^{-4}|{}^3\mathrm{E}^y_{1g}(10\mathrm{B})\rangle\end{aligned}$$

$$\begin{aligned}&+0.5152\times10^{-4}|{}^3\mathrm{E}^x_{1g}(13\mathrm{A})\rangle\\ &+0.1836\times10^{-3}|{}^3\mathrm{E}^y_{1g}(13\mathrm{A})\rangle\\ &-0.1836\times10^{-3}|{}^3\mathrm{E}^x_{1g}(13\mathrm{B})\rangle\\ &+0.5152\times10^{-4}|{}^3\mathrm{E}^y_{1g}(13\mathrm{B})\rangle\\ &-0.7770\times10^{-4}|{}^3\mathrm{A}^z_{2g}(17)\rangle\end{aligned}\tag{20}$$

where $\lambda_i{}^{so}$ and $\omega_i{}^{so}$ are the mixing coefficients for the ith perturbing triplets of symmetries ${}^3\mathrm{E}_{1g}$ and ${}^3\mathrm{A}_{2g}$, respectively, and each figure in a parenthesis is the state number in order of increasing energy, a symbol A or B after figure showing either of the degenerate states (see Table 1): and

$$\begin{aligned}|{}^3\mathrm{E}^c_{1u}(2\mathrm{A})\rangle &= |{}^3\mathrm{E}_{1u}(\pi\pi^*,\sigma\sigma^*;\ 2\mathrm{A})\rangle\\ &\quad+\sum_i\nu_i^{so}|{}^1\mathrm{E}_{1u}(\pi\pi^*,\sigma\sigma^*;\ i)\rangle\\ &\quad+\sum_i\mu_i^{so}|{}^1\mathrm{A}_{2u}(\sigma\pi^*,\pi\sigma^*;\ i)\rangle\\ &= |{}^3\mathrm{E}_{1u}(2\mathrm{A})\rangle+0.3689\times10^{-6}|{}^1\mathrm{E}^z_{1u}(3\mathrm{A})\rangle\\ &\quad+0.1828\times10^{-6}|{}^1\mathrm{E}^z_{1u}(3\mathrm{B})\rangle\\ &\quad+0.9425\times10^{-5}|{}^1\mathrm{A}^x_{2u}(4)\rangle\\ &\quad-0.1834\times10^{-4}|{}^1\mathrm{A}^y_{2u}(4)\rangle\\ &\quad-0.2521\times10^{-6}|{}^1\mathrm{E}^z_{1u}(14\mathrm{A})\rangle\\ &\quad-0.6792\times10^{-6}|{}^1\mathrm{E}^z_{1u}(14\mathrm{B})\rangle\end{aligned}\tag{21}$$

$$\begin{aligned}|{}^3\mathrm{E}^c_{1u}(2\mathrm{B})\rangle &= |{}^3\mathrm{E}_{1u}(2\mathrm{B})\rangle+0.1828\times10^{-6}|{}^1\mathrm{E}^z_{1u}(3\mathrm{A})\rangle\\ &\quad+0.3689\times10^{-6}|{}^1\mathrm{E}^z_{1u}(3\mathrm{B})\rangle\\ &\quad-0.1834\times10^{-4}|{}^1\mathrm{A}^x_{2u}(4)\rangle\\ &\quad-0.9424\times10^{-5}|{}^1\mathrm{A}^y_{2u}(4)\rangle\\ &\quad+0.6792\times10^{-6}|{}^1\mathrm{E}^z_{1u}(14\mathrm{A})\rangle\\ &\quad-0.2510\times10^{-6}|{}^1\mathrm{E}^z_{1u}(14\mathrm{B})\rangle.\end{aligned}\tag{22}$$

This computational output is in accord with a group-theoretical consideration given by Clementi,4) apart from the numerical factors. We have thus a hypothetical transition moment between the ${}^3\mathrm{E}_{1u}$ and the ground ${}^1\mathrm{A}_{1g}$ states (in a.u.):

$$\begin{aligned}\sum_{i=2\mathrm{A},2\mathrm{B}}\langle\mathrm{G^c}|\vec{M}|{}^3\mathrm{E}^c_{1u}(i)\rangle &= 2.2890\times10^{-7}\vec{e}_x\\ &\quad-7.1426\times10^{-7}\vec{e}_y\\ &\quad-9.4013\times10^{-5}\vec{e}_z.\end{aligned}\tag{23}$$

If we assume that the main contribution to the phosphorescence polarization comes from the transition ${}^3\mathrm{E}_{1u}\rightarrow{}^1\mathrm{A}_{1g}$, the phosphorescence spectrum of benzene is predicted to be almost 100% out-of-plane polarized.

How large is the effect of many-center spin-orbit coupling integrals? Clementi,4) after the manner of Hameka and Oosterhoff, estimated the contribution of three-center spin-same-orbit coupling integrals and three- and four-center spin-other-orbit coupling integrals to the $|{}^3\mathrm{E}^c_{1u}(2\mathrm{A})\rangle$ and $|{}^3\mathrm{E}^c_{1u}(2\mathrm{B})\rangle$ states of pure π character. If we use his estimated value of such contribution

$$|{}^3\mathrm{E}^{cm}_{1u}(i)\rangle = |{}^3\mathrm{E}^c_{1u}(i)\rangle+2.15\times10^{-5}\sum_{i=3\mathrm{A},3\mathrm{B}}|{}^1\mathrm{E}_{1u}(i)\rangle\tag{24}$$

we have the following transition moment (in a.u.):

$$\begin{aligned}\sum_{i=2\mathrm{A},2\mathrm{B}}\langle\mathrm{G^c}|\vec{M}|{}^3\mathrm{E}^{cm}_{1u}(i)\rangle &= -5.1001\times10^{-5}\vec{e}_x\\ &\quad+5.0516\times10^{-5}\vec{e}_y\end{aligned}$$

$$- 9.4013\times 10^{-5}\vec{e}_z. \qquad (25)$$

Thus, the ratio of the out-of-plane to the in-plane polarizations of the phosphorescence ${}^3E_{1u}\rightarrow{}^1A_{1g}$ turns out to be 81 : 51 which is in accord with the observation (*ca.* 3 : 2) of Russel and Albrecht.1) However, Eq. 25 does not lead to the almost out-of-plane polarized ${}^3B_{1u}\rightarrow{}^1A_{1g}$ phosphorescence which is the more recent experimental result obtained by van Egmond and van der Waals2) (*vide infra*). The value 2.15×10^{-5} in Eq. 24 seems to be overestimated, even from the fact that the contribution of the one-center integrals in $CH_2$26,27) and H_2CO16,20) is calculated to be from ten to fifty times larger than that of many-center integrals.

Vibronically Induced ${}^3B_{1u}\rightarrow{}^1A_{1g}$ *Emission* via ${}^3E_{1u}$-${}^1A_{1g}$ *Intercombination.* If we take account of the vibronic coupling H_{vib} as well as the spin-orbit coupling neglecting spin-vibronic terms, spin- and vibronically-contaminated wave functions for excited triplet states might be given by the second-order perturbation theory, because of relatively large values of vibronic coupling integrals compared with spin-orbit coupling integrals.

$$\begin{aligned}|T_i^c\rangle = |T_i\rangle &+ \sum_{j\neq i}\frac{\langle T_j|H_{\text{vib}}|T_i\rangle}{E(T_i)-E(T_j)}|T_j\rangle \\ &+ \sum_j\frac{\langle S_j|H_{\text{so}}|T_i\rangle}{E(T_i)-E(S_j)}|S_j\rangle \\ &+ \sum_j\sum_{k\neq i}\frac{\langle S_j|H_{\text{vib}}|S_k\rangle\langle S_k|H_{\text{so}}|T_i\rangle}{[E(T_i)-E(S_j)][E(T_i)-E(S_k)]}|S_j\rangle \\ &+ \sum_j\sum_{k\neq i}\frac{\langle S_j|H_{\text{so}}|T_k\rangle\langle T_k|H_{\text{vib}}|T_i\rangle}{[E(T_i)-E(S_j)][E(T_i)-E(T_k)]}|S_j\rangle \qquad (26)\end{aligned}$$

or in an abbreviated form

$$\begin{aligned}|T_i^c\rangle = |T_i\rangle &+ \sum_{j\neq i}\delta_j^{\text{vib}}|T_j\rangle + \sum_j\gamma_j^{\text{so}}|S_j\rangle \\ &+ \sum_j\sum_{k\neq i}\alpha(S_j|S_k|T_i)|S_j\rangle \\ &+ \sum_j\sum_{k\neq i}\beta(S_j|T_k|T_i)|S_j\rangle \qquad (27)\end{aligned}$$

where in Albrecht's notation5) we write

$$H_{\text{vib}} = \sum_a(\partial H/\partial Q_a)_0 Q_a. \qquad (28)$$

If we adopt the possible phosphorescence routes suggested by Albrecht,5) we have

$$\begin{aligned}|{}^3B_{1u}^c(1)\rangle = |{}^3B_{1u}(1)\rangle &+ \sum_{i=2A,2B}\delta_i^{\text{vib}}|{}^3E_{1u}^c(i)\rangle + \gamma_1^{\text{so}}|{}^1B_{2u}(1)\rangle \\ &+ \sum_{i=3A,3B}[\alpha({}^1E_{1u}(i)|{}^1B_{2u}(1)|{}^3B_{1u}(1)) \\ &+ \sum_{j=2A,2B}\beta({}^1E_{1u}(i)|{}^3E_{1u}(j)|{}^3B_{1u}(1))]|{}^1E_{1u}(i)\rangle \\ &+ [\sum_{i=5A,5B}\alpha({}^1A_{2u}(4)|{}^1E_{2u}(i)|{}^3B_{1u}(1)) \\ &+ \sum_{i=2A,2B}\beta({}^1A_{2u}(4)|{}^3E_{1u}(i)|{}^3B_{1u}(1))]|{}^1A_{2u}(4)\rangle \\ &+ \sum_{i=3A,3B}[\sum_{j=5A,5B}\{\alpha({}^1E_{1u}(i)|{}^1E_{2u}(j)|{}^3B_{1u}(1)) \\ &+ \beta({}^1E_u(i)|{}^3E_{2u}(j)|{}^3B_{1u}(1))\} \\ &+ \beta'({}^1E_{1u}(i)|{}^3A_{2u}(7)|{}^3B_{1u}(1))]|{}^1E_{1u}(i)\rangle \qquad (29)\end{aligned}$$

where

$$\delta_i^{\text{vib}} = \frac{\langle{}^3E_{1u}^c(i)|H_{\text{vib}}|{}^3B_{1u}(1)\rangle}{E({}^3B_{1u}(1))-E({}^3E_{1u}^c(i))} \cong \frac{\langle{}^3E_{1u}(i)|H_{\text{vib}}|{}^3B_{1u}(1))\rangle}{E({}^3B_{1u}(1))-E({}^3E_{1u}(i))} \qquad (30)$$

and $|{}^3E_{1u}^c(i)\rangle$ corresponds to Eqs. 21 and 22. These individual contribution are schematically shown in Fig. 1, where (a), (b), (c), (d) and (e) correspond to the second, third, fourth, fifth and the last terms of Eq. 29, respectively. In order to obtain the mixing coefficients of Eq. 29, we adopt experimental values of excitation energies, if available, and otherwise use the corresponding calculated values. For vibronic integrals we use the values determined by Albrecht.5) The last term of Eq. 29 is cut off, since the values of

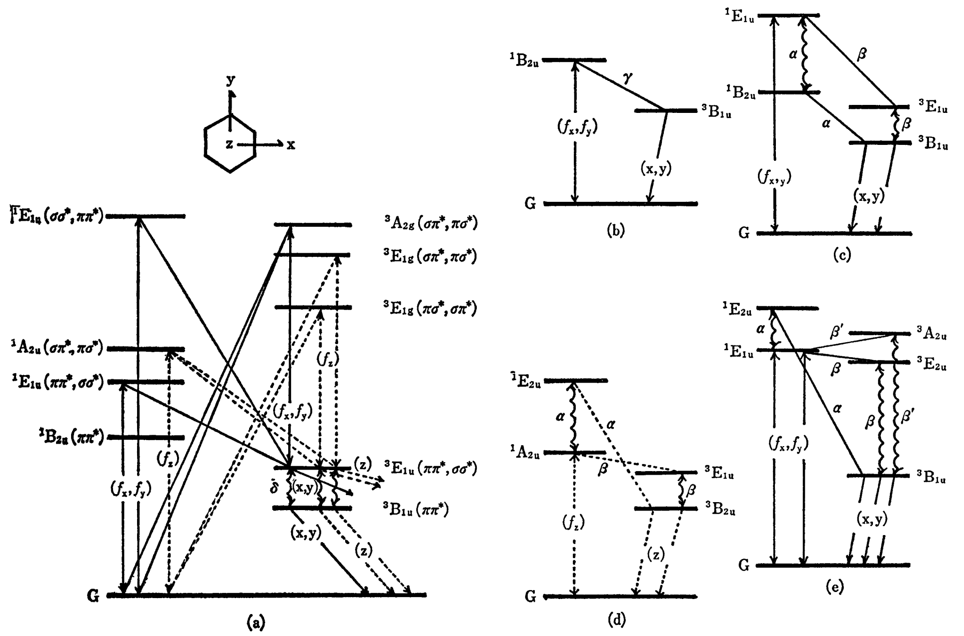

Fig. 1. Possible phosphorescence mechanisms in benzene. (a), (b), (c), (d), and (e) correspond to the 2nd, 3rd, 4th, 5th and 6th terms of Eq. 29 in the text, respectively. Solid arrow: in-plane polarized transition; dashed arrow: out-of-plane polarized transition.

these vibronic integrals are unknown. Matrix elements over many-center integrals are neglected by the reason mentioned before. Only exception is the element $\langle {}^1B_{2u}|H^z_{so}|{}^3B_{1u}\rangle$ which is included in the following in order to estimate the effect of Route (b). The forbidden transition moment $\langle {}^1A_{1g}|M_{x,y}|{}^1B_{2u}\rangle$ is estimated to be $\pm 1.013\times 10^{-2}$ atomic unit from an experimental point of view.

Equation 29 is now calculated to be[28]

$$\begin{aligned}|{}^3B^c_{1u}(1)\rangle = {} & 0.9025|{}^3B_{1u}(1)\rangle \\ & - 0.3047[|{}^3E^c_{1u}(2A)\rangle + |{}^3E^c_{1u}(2B)\rangle] \\ & + 0.1190\times 10^{-4}|{}^1B_{2u}(1)\rangle \\ & + 0.1473\times 10^{-5}|{}^1E_{1u}(3A)\rangle \\ & + 0.1411\times 10^{-5}|{}^1E_{1u}(3B)\rangle \\ & - 0.3239\times 10^{-5}|{}^1A_{2u}(4)\rangle. \end{aligned} \tag{31}$$

Finally, we have

$$\begin{aligned}\langle G^c|\vec{M}|{}^3B^c_{1u}(1)\rangle = {} & -0.3047[\langle G^c|\vec{M}|{}^3E^c_{1u}(2A)\rangle \\ & + \langle G^c|\vec{M}|{}^3E^c_{1u}(2B)\rangle] \\ & + 0.1190\times 10^{-4}\langle {}^1A_{1g}|\vec{M}|{}^1B_{2u}(1)\rangle \\ & + 0.1473\times 10^{-5}\langle {}^1A_{1g}|\vec{M}|{}^1E_{1u}(3A)\rangle \\ & + 0.1411\times 10^{-5}\langle {}^1A_{1g}|\vec{M}|{}^1E_{1u}(3B)\rangle \\ & - 0.3239\times 10^{-5}\langle {}^1A_{1g}|\vec{M}|{}^1A_{2u}(4)\rangle \\ = {} & (-3.411\pm 0.060)\times 10^{-6}\vec{e}_x \\ & + (3.838\pm 0.060)\times 10^{-6}\vec{e}_y \\ & + 2.825\times 10^{-5}\vec{e}_z. \end{aligned} \tag{32}$$

Fractional contributions of the four phosphorescence routes shown in Fig. 1 to the transition moment $\langle G^c|\vec{M}|{}^3B^c_{1u}(1)\rangle$ are listed in Table 3. The final result given in Eq. 32 clearly shows that the phosphorescence from the ${}^3B_{1u}(1)$ state is almost 100% out-of-plane polarized. This is in accord with the results of the Zeeman and MIDP experiments obtained by van Egmond and van der Waals.[2] If we use the observed energy separation 3.95 eV between the ${}^3B_{1u}(1)$ state and the ground state, Eqs. 5 and 6 yield the oscillator strength $f({}^3B_{1u}\rightarrow{}^1A_{1g})=0.7940\times 10^{-10}$ and the lifetime $\tau=55.8$ second.

As evident from Eq. 32, the main contribution to the phosphorescence lifetime comes from the term δ^{vib} for which we have used Albrecht's value $\langle {}^3E^c_{1u}(i)|H_{vib}|{}^3B_{1u}(1)\rangle=0.27$ eV, $i=2A$ and $2B$. Comparison of the calculated lifetime with the observed value 4.75 second[29,30] suggests that the value of δ^{vib}, namely the value of $\langle {}^3E^c_{1u}|H_{vib}|{}^3B_{1u}\rangle$, is underestimated. In fact, van der Waals *et al.*[31] estimated the value of the δ^{vib} to be -0.4031 which yields $f({}^3B_{1u}\rightarrow{}^1A_{1g})=1.390\times 10^{-10}$ and $\tau=31.9$ second. If one wants to reproduce the observed lifetime 4.75 second by making use of the same computational scheme as above, δ^{vib} must be taken the value 0.55 and one has

$$\begin{aligned}|{}^3B^c_{1u}(1)\rangle = {} & 0.63|{}^3B_{1u}(1)\rangle \\ & - 0.78\frac{1}{\sqrt{2}}\{|{}^3E^c_{1u}(2A)\rangle + |{}^3E^c_{1u}(2B)\rangle\} + \cdots. \end{aligned}$$

Thus the mixing coefficients of the triplet B_{1u} and E_{1u} states come out to be absolutely improbable. On the other hand, if the value of δ^{vib} is fixed to be around -0.4, a value of the z-component of the transition moment between the ${}^3E_{1u}$ and the ground states $-1.3\times 10^{-4}\vec{e}_z$ instead of our calculated value $-9.40\times 10^{-5}\vec{e}_z$ yields the lifetime which is in accord with the observed value. Though further studies are needed to clarify this matter, our conclusion at present is that molecular wave functions to calculate the transition moment due to the ${}^3E_{1u}$-${}^1A_{1g}$ intercombination are very sensitive to the prediction cf the triplet lifetime in benzene.

TABLE 3. CONTRIBUTION OF POSSIBLE PHOSPHORESCENCE ROUTES TO TRANSITION MOMENT $\langle G^c|\vec{M}|{}^3B^c_{1u}(1)\rangle$

Route in Fig. 1	M_x	M_y	M_z
a	-0.6978×10^{-7}	2.1756×10^{-7}	2.8646×10^{-5}
b	$\pm 0.6027\times 10^{-7}$	$\pm 0.6027\times 10^{-7}$	0
c	-0.3341×10^{-5}	0.3612×10^{-5}	0
d	0	0	-0.0401×10^{-5}
e	—	—	—

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28) In the case that the mixing coefficient δ^{vib} between the ${}^3\mathrm{B}_{1\mathrm{u}}^{\mathrm{c}}$ and ${}^3\mathrm{E}_{1\mathrm{u}}^{\mathrm{c}}$ states is calculated not from the second-order perturbation method but from the Ritz variation method, the value of δ^{vib} comes out to be -0.3408 instead of -0.3047 in Eq. 31. This value yields $\langle \mathrm{G}^{\mathrm{c}} | \vec{M} | {}^3\mathrm{B}_{1\mathrm{u}}^{\mathrm{c}}(1) \rangle = -0.0078 \times 10^{-5}\vec{e}_{\mathrm{x}} + 0.0243 \times 10^{-5}\vec{e}_{\mathrm{y}} + 3.2040 \times 10^{-5}\vec{e}_{\mathrm{z}}$, $f({}^3\mathrm{B}_{1\mathrm{u}} \rightarrow {}^1\mathrm{A}_{1\mathrm{g}}) = 0.9933 \times 10^{-10}$ and $\tau = 44.6$ second.

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