

Mechanisms of Benzoylacetone $T \leftrightarrow S$ Processes in the Presence of Heavy-metal Ions and Their Effects on the Excited-state 3 (Borobenzoylacetonide) Complex Formation

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The mechanisms of $T \leftrightarrow S$ crossings of benzoylacetone (BZA) and its EDA [1] species with Ag^+ , Cd^{2+} , Hg^{2+} and Tl^+ , are investigated. It can be shown that perturbations are different in nature for EDA complexes (intramolecular) and BZA (extramolecular) but in the two cases and for all crossings ($S_1 \rightarrow T_1$, $T_1 \rightarrow S_0$ of EDA species and BZA) the initial-final state coupling elements are shown to be largely dominated by spin-orbit (SO) matrix elements. Experimental data [1] are found to be quantitatively correlated to the SOC factors ζ of the metal ions and this can be theoretically predicted if it is asserted that, for EDA species, SO couplings are dominated by one atomic (metal) center. In the indirect-mixing of states mechanism ($S_1 \rightarrow T_1$ and $T_1 \rightarrow S_0$ of BZA), Tl^+ shows striking departures from the quantitative correlations. A possible explanation can be given, if it is assumed that indirect-mixing takes place through EDA-BZA CT states. The above $T \leftrightarrow S$ mechanisms are shown to account for the observed [1] heavy-metal ion effects on the 3 BZA-boron species interaction.

Introduction

It has recently been shown [1] that Ag^+ , Cd^{2+} , Hg^{2+} and Tl^+ enhance the $T \leftrightarrow S$ crossings of benzoylacetone (BZA), thus affecting the rate of 3 BZA interaction with boron species. EDA species of BZA with the above metal ions, revealed by their characteristic $S_1 \rightarrow S_0$ and $T_1 \rightarrow S_0$ emissions and their $T_1 \rightarrow S_0$ radiative lifetimes, were also found to be responsible of the retardation of "Boron-BZA" ground-state chelate formation.

In the present work we investigate the $T \leftrightarrow S$ crossing mechanisms of BZA and its EDA complexes and discuss the experimental data obtained in ref. 1 on the basis of theoretical formulations for $T \leftrightarrow S$ transition probabilities.

Discussion

The $S_1 \rightarrow T_1$ Crossings of BZA and $(BZA-M)^{n+}$ Species

As was shown in part III [1] of this work, the 77K $S_1 \rightarrow S_0$ emission intensities of BZA and $(BZA-M)^{n+}$,

clearly depend on the metal ion. Frequencies of the F-C maxima of $(BZA-M)^{n+}$ were found to be correlated to I_P^{-1} (inverse of the 1st – for Ag and Tl – and 2nd – for Cd and Hg – ionisation potentials) as roughly expected for EDA complexes, but there is no relation between fluorescence intensity and I_P^{-1} . On the contrary, emission intensities of these complexes and of BZA are shown (Fig. 1) to be related to the SOC factors ζ of the metal ions, indica-

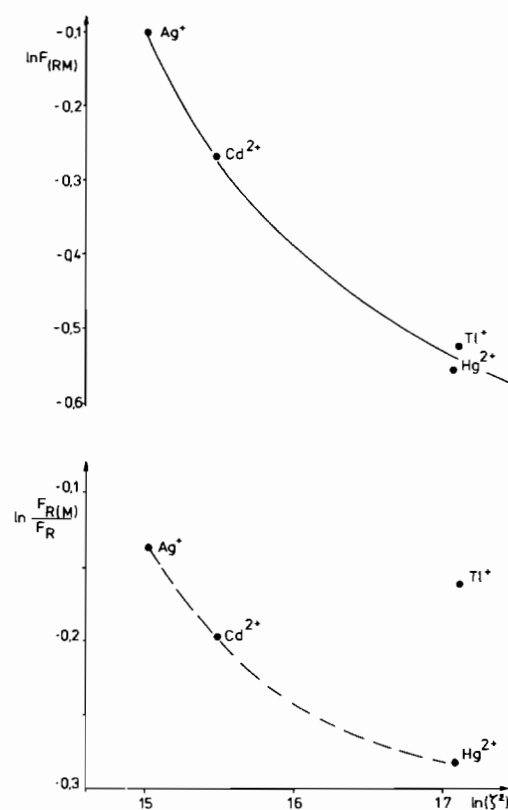


Figure 1. $\ln F_{(RM)}$ and $\ln = F_{R(M)}/F_R$ versus $\ln(\zeta^2)$. ζ were chosen according to the proposed [1] two-way type of bonding in $(BZA-M)^{n+}$. Thus ζ for Silver and Cadmium are those of Ag and Cd $4d^9 5s$ [21]. The value for the analogous configuration of Mercury is not known and Au $5d^9 6s$ [22] stands here for Hg. For Thallium ζ stands for Tl $6p$ [23] (values for other configurations are not known).

ting that heavy-metal ion effects are strongly operating and that spin-orbit (SO) elements are probably the leading terms of the matrix elements coupling the S_1, T_1 states.

In order to assign the inverse dependencies of BZA and $(BZA-M)^{n+}$ intensities upon ζ the following basic assumptions, as to nature of metal-ion perturbation, are made: since $(BZA-M)^{n+}$ are well defined species with definite binding energies in the ground as well as in the excited-state, the metal perturbation on these species is an intramolecular one, but for BZA, extramolecular perturbations make that an indirect coupling of states through perturber states, most probably $(BZA-M)^{n+} T$ and S states, is considered to operate.

Now, the choice of an appropriate expression for non-radiative ($n.r$) transition probabilities, is also necessary and for our purposes, the "golden-rule" [2, 3]

$$k_{n,r}(i \rightarrow f) = 2\pi h^{-1} \rho V_{i,f}^2 \quad (1)$$

will be utilised. This choice may be subject to some criticism, since the above expression is an approximate one* and since it appears that the final states density ρ and the coupling matrix element $V_{i,f}$ are difficult to evaluate.

However, the scope of this discussion is not to try the very ambiguous determination of exact $k_{n,r}$'s** but only to compare transition probabilities of BZA and $(BZA-M)^{n+}$, so that even if approximate, expression (1) is sufficient for significant deductions.

Starting, now, from the following expressions:

$$\begin{aligned} \Phi_{F(RM)} &= F_{(RM)}(K_{(1)} \epsilon_{RM} [(RM)^{n+}]^{-1}) \\ &= k_{F(RM)} / \sum_i k_{i(RM)} + k_{F(RM)} + k_{ST(RM)} \end{aligned} \quad (2)$$

$$\begin{aligned} \Phi_{F(R)} &= F_R(K_{(1)} \epsilon_R [R])^{-1} \\ &= k_{F(R)} / \sum_i k_{i(R)} + k_{F(R)} + k_{ST(R)}^{***} \end{aligned} \quad (3)$$

$$\begin{aligned} \Phi_{F(R)}^M &= F_{R(M)}(K_{(1)} \epsilon_R [R]_M)^{-1} \\ &= k_{F(R)} / \sum_i k_{i(R)} + k_{F(R)} + k_{STM(R)} \end{aligned} \quad (4)$$

where F : photomultiplier responses; $\Phi_{F(RM)}, \Phi_{F(R)}, \Phi_{F(R)}^M$: fluorescence yields of $(BZA-M)^{n+}$, of BZA and of BZA in the presence of metal-ion; ϵ : molar absorptivities; $K_{(1)}$: $2.3 u I_0^{-1}$; u : an apparatus constant; I_0 : incident intensity; $\sum_i k_i$: for other than fluores-

cence (k_F) and $S_1 \rightarrow T_1(k_{ST})$, degradative of S_1 processes (see ref. 1).

The fluorescence intensity to concentration ratio of $(BZA-M)^{n+}$ is:

$$q_{RM} = \frac{F_{(RM)}}{[(RM)^{n+}]} = \frac{K'' \epsilon_{(RM)}^2}{(\gamma + 1)} \left(\frac{2\pi}{h} \rho' V_{i,f}' \right)^{-1} \quad (5)$$

and the quotient of such ratios for BZA is given by:

$$q_R = \frac{F_{R(M)} [R]_M^{-1}}{F_R [R]^{-1}} = \frac{(\delta + 1)}{(\nu + 1)} \cdot \frac{\rho V_{i,f}^2}{\rho'' V_{i,f}''^2} \cong \frac{F_{R(M)}}{F_R}; \quad (6)$$

(BZA) \gg [(RM) $^{n+}$]

where:

$$\gamma = \left(\sum_i k_{i(RM)} + k_{F(RM)} \right) k_{ST(RM)}^{-1} \quad (7)$$

$$\delta = \left(\sum_i k_{i(R)} + k_{F(R)} \right) k_{ST(R)}^{-1} \quad (8)$$

$$\vartheta = \left(\sum_i k_{i(R)} + k_{F(R)} \right) k_{STM(R)}^{-1} \quad (9)$$

and $K'' \sim 10^4 K_{(1)}$ (from the rough $k_{F(RM)} \sim 10^4 \epsilon_{(RM)}$ approximation).

Expressions (5) and (6) show an inverse dependance of $F_{RM} [(RM)^{n+}]^{-1}, F_{R(M)} [R]_M^{-1}$ upon the interactions $V_{i,f}$ and one might roughly conclude that, if SO matrix elements in $V_{i,f}$ are overwhelming, the above relations are qualitatively in agreement with the experimental results.

More quantitative deductions are however necessary and this requires the formulation of the coupling elements $V_{i,f}$. Unfortunately, formulation of matrix elements for $T \leftrightarrow S$ crossings, continues to be subject of controversies* and for our problem an appropriate choice is not an unambiguous task.

However, we shall align ourselves to the thought and theoretical developments of H. Siebrand *et al.* [3, 7-9], and use his recent three-type intersystem-crossing overall expression [9]

$$V_{i,f} = V_{i,f}(1) + V_{i,f}(2) + V_{i,f}(3) \quad (10)$$

$V_{i,f}(1), V_{i,f}(2), V_{i,f}(3)$ standing for direct SO, adiabatically induced SO and non-adiabatic couplings.

For the formulation of $V_{i,f}'$ and $V_{i,f}$ in expressions (5) and (6) we shall, moreover, tacitly admit that for $S_1 \rightarrow T_1$ crossings of $(BZA-M)^{n+}$ and BZA, the first order term is largely overwhelming:

$$V_{i,f}(1) \gg V_{i,f}(2), V_{i,f}(3),$$

so that

$$V_{i,f}' \approx V_{i,f}(1) = \langle \psi_i | H_{so} | \psi_f \rangle \langle \Lambda_i | \Lambda_f \rangle \quad (11)$$

with ψ and Λ standing for electron and vibrational wavefunctions.

*See, however, in ref. 3 arguments in favor of its applicability.

**One must note that not only "golden-rule" rates given by a rigorous expression depart from the exact ones, but when one chooses different Born-Oppenheimer approximations, results are unexpectedly discordant [5, 6].

***Any metal ion effect on k_F can safely be disregarded [4].

*See for exemple refs. 8, 10, 11 and 9.

Expressions (5) and (6) can now be written as:

$$q_{RM} = M\rho^{-1} |\langle \Lambda_i' | \Lambda_f' \rangle|^{-2} |\langle \psi_i' | H_{SO} | \psi_f' \rangle|^{-2} \quad (12)$$

$$q_R = N\rho' |\langle \Lambda_i | \Lambda_f \rangle|^{-2} |\langle \psi_i | H_{SO} | \psi_f \rangle|^{-2} |\rho''^{-1} V_{i,f}''^{-1}| \quad (13)$$

but before proceeding to the q_{RM} and q_R connection to ζ , the $V_{i,f}''$ matrix element must be formulated.

In principle this is not a straightforward problem, because it happens that in the quasi-majority of cases, mechanisms accounting for external perturbations concern $S_0 \rightarrow T_1$ [12-14] and $T_1 \rightarrow S_0$ non radiative [15] or $T_1 \rightarrow S_0$ radiative processes [15, 16]

However, our relevant datum (the preparation of S_1 and T_1 states of EDA (BZA-M) $^{n+}$ complexes) leads us to consider an indirect mixing through these EDA states*. This may not be implausible and can be supported by the fact that metal acetylacetonates assist $S_0 \rightarrow T_1$ transitions [17, 18] of some aromatics.

If both S_1 and T_1 states of BZA interact with BZA-M) $^{n+}$ states, $V_{i,f}''$ is given in the third order by:

$$V_{i,f}'' = \frac{\vartheta^{(I)} \vartheta^{(II)} \langle \psi_i' | H_{SO} | \psi_f' \rangle \langle \Lambda_i' | \Lambda_f' \rangle}{({}^3E - {}^3E')({}^1E - {}^1E')} \quad (14)$$

where primed wave functions and energies refer to EDA states**

$$\vartheta^{(I)} = \langle \psi_f' | H_{SO} | \psi_i' \rangle \quad (15)$$

$$\vartheta^{(II)} = \langle \psi_i' | H_{SO} | \psi_f' \rangle \quad (16)$$

and the q_R expression now takes the form:

$$q_R = \frac{N\rho \rho''^{-1} m^2 \lambda^2}{\vartheta^{(I)2} \vartheta^{(II)2}} |\langle \psi_i' | H_{SO} | \psi_f' \rangle|^{-2} (\Delta^3E)^2 (\Delta^1E)^2 \quad (17)$$

where:

$$\lambda = \langle \Lambda_i | \Lambda_f \rangle \langle \Lambda_i' | \Lambda_f' \rangle^{-1} \quad (18)$$

$$m = \langle \psi_i | H_{SO} | \psi_f \rangle \vartheta^{(I)} \vartheta^{(II)} \quad (19)$$

$$\Delta^3E = ({}^3E - {}^3E'); \Delta^1E = ({}^1E - {}^1E')$$

Reductions of SO matrix elements and assertions that SO couplings are dominated by one atomic center, leading to a direct relation between V_{SO} and ζ :

$$V_{SO} = C_{AO} \zeta \quad (20)$$

(where C_{AO} stands for a two AO coefficient product), were shown by McGlynn *et al.* [20] to be applicable to 1-halonaphthalenes and to group IV tetraphenyls.

Since our basic assumption is that in the case of (BZA-M) $^{n+}$ the perturbation caused by M^{n+} is an intramolecular one, we may use analogous simplifications and check the applicability of (see (12)):

$$q_{RM} = M' \rho^{-1} |\langle \Lambda_i' | \Lambda_f' \rangle|^{-2} \zeta^{-2} \quad (21)$$

to the (BZA-M) $^{n+}$ species and of (see (14)):

$$q_R = N' \rho \rho''^{-1} \lambda^2 m^2 (\Delta^3E)^2 (\Delta^1E)^2 \zeta^{-2} \quad (22)$$

to BZA.

Fig. 2 shows that $\ln q_{RM}$ and $\ln q_R$ are well correlated to $\ln(\zeta^{-2})$ and $\ln[(\Delta^3E)^2 (\Delta^1E)^2 \zeta^{-2}]$ but the linearity of these correlations and the striking departure of Tl^+ in the indirect-mixing mechanism, should be discussed.

In the case of (21) linearity implies constancy or little variation of $(1 + \gamma)$ (see (5)), vibrational factors, density of final states and products of A.O. coefficients in the assumption of SO coupling domination by one atomic center (the metal), with the nature of (BZA-M) $^{n+}$

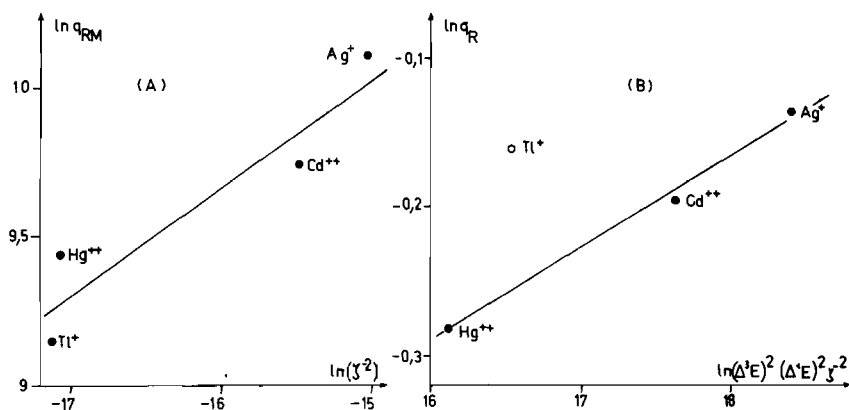


Figure 2. $\ln q_{RM}$ vs. $\ln(\zeta^{-2})$ and $\ln q_R$ vs. $\ln[(\Delta^3E)^2 (\Delta^1E)^2 \zeta^{-2}]$ variations.

*One could possibly think of metal ion states as perturbing states. Nevertheless, for the metal ions used in part III, low-lying excited states, except for Tl^+ : 3P , are 3D , so that ν^{II} in (14) is virtually zero because its electronic part vanishes by dipole and spin restrictions.

**A formulation analogous to (14) was first derived [19] for heavy-atom solvent perturbation and then extended to perturbations by CT or atom-like states [15].

- (i) If $k_{ST(RM)}$ is larger than $\sum k_{i(RM)} + k_{F(RM)}$, γ may not be important before 1, so that its variations in the series of $(BZA-M)^{n+}$ may have little repercussions to $(1 + \gamma)$.
- (ii) The vibrational factor must be some, but definite direct function of the energy difference ΔE_{i-t} and as for the $(BZA-M)^{n+}$ series, $\Delta E_{S_1-T_1}$ does not vary much, values of these factors may not be very different.
- (iii) Finally, little variations in ρ and in the A.O. coefficient products are expected for very close electronic structures and same geometries as is the case of these complexes [1].

Uncertainties, however, arise from the q_{RM} values in which $BZA-M^{n+}$ concentrations were calculated from room temperature formation constants [1]. So, unless stability constants at 77K are nearly the same fractions or multiples of room temperature constants for all the $(BZA-M)^{n+}$, the data may in fact not be so well correlated as in figure 2(A).

As far as the $\ln q_R$ correlation is concerned (fig. 2 B), assumptions analogous to (i)–(iii) can show that in (22), N' (see the first quotient in (6) and our anticipations as to the same A.O. coefficient product for all $(BZA-M)^{n+}$ in the assertion of SO coupling domination by one atomic center), λ (see (18) and (ii)) and the final states density quotient, may not vary much.

The size of the electrostatic matrix elements $\vartheta^{(1)}$ and $\vartheta^{(1D)}$ is unknown. If, however, we anticipate close values for these elements mixing BZA with $(BZA-M)^{n+}$ states, expression (17) accounts well for the Ag^+ , Cd^{2+} , Hg^{2+} data (fig. 2B).

The striking departure of Tl^+ is, nevertheless, not at all straightforward. Of course, we took the ζ value for Tl $6p$ (see fig. 1) while, in the two-way bonding with the benzene ring of BZA [1], we must have $Tl5d^9 6s^2 6p$. However, q_{RM} for Tl^+ is quite well correlated in fig. 2A and anyhow the q_R value for Tl^+ had to fall near the value of Hg^{2+} .

The main difference between $(BZA-Tl)^+$ and the other three EDA complexes is that in the two-way bonding ($d\pi_y$ to π_2^* M.O. of benzene ring and π_2 or π_3 to M^{n+} A.O.) [1] the accepting orbital of Tl^+ is the $6p$, while for Ag^+ , Cd^{2+} and Hg^{2+} it is the s A.O.

Since $(BZA-M)^{n+}$ are definite species in the ground as well in the excited state [1], it may not be excluded that indirect-mixing takes place through $BZA-(BZA-M)^{n+}$ CT states* in which case ${}^3\psi'$, ${}^1\psi'$ in (14) would stand for these states.

In this case, the CT action in the excited-state could be orbitally thought as electron donation from π_2 or π_3 (benzene ring) to s A.O. of Ag^+ , Cd^{2+} , Hg^{2+}

and $6p$ A.O. of Tl^+ and $d\pi_y$ electron donation of the metal in $(BZA-M)^{n+}$ to the π_2^* benzene ring M.O. of another BZA molecule.

Some screening of this latter donation by the $6s^2$ pair would be expected in the case of Thallium and this may possibly explain its deviation which, interestingly enough, is a negative one (fig. 2B) meaning that its perturbing action is lesser than the expected one.

$T_1 \rightarrow S_0$ Crossings of BZA and its EDA Species with Metal Ions

Radiative lifetimes τ_R of BZA in the presence of M^{n+} and of its EDA species τ_{RM} were obtained from the analysis of phosphorescence-decay semilogarithmic plots [1].

τ_R can be related to the following [15] matrix elements:

$$\tau_R^{-1} = k_{P(R)} + k_{TS(R)} = \frac{A|\langle {}^3\psi | H | {}^3\psi' \rangle \langle {}^3\psi' | H_{SO} | {}^1\psi' \rangle|^2}{({}^3E' - {}^1E')^2} + \frac{B|\langle {}^3\psi | H | {}^3\psi' \rangle \langle {}^1\psi | H | {}^1\psi' \rangle \langle {}^3\psi' | H_{SO} | {}^1\psi' \rangle|^2}{({}^3E' - {}^1E')^2 ({}^1E' - E_0)^2} \quad (23)$$

where ${}^1\psi_0$ stands for S_0 of BZA, A is a constant factor and B stands for the product of $2\pi h^{-1}$ with final state density and squared vibrational factor.

We can take (23) in the following form:

$$({}^3E' - {}^1E')^2 \tau_R^{-1} = \langle {}^3\psi | H | {}^3\psi' \rangle^2 \times \left[A + \frac{B|\langle {}^1\psi' | H | {}^1\psi_0 \rangle|^2}{({}^1E' - E_0)^2} \right] K_{AO}^2 \zeta^2, \quad (24)$$

(where, as above, K_{AO} is an A.O. coefficient product), and check the applicability of (24).

As shown in Fig. 3A the $({}^3E' - {}^1E') \tau_R^{-1}$ vs. ζ^2 function is a curve with diminishing slope. This is to be expected since, in going from Ag^+ to Hg^{2+} , $({}^1E' - E_0)$ increases, making in the meantime the ${}^1\psi'$, ${}^1\psi_0$ mixing less effective. However, ${}^3E'$ does not vary to much and the sizes of $\langle {}^3\psi | H | {}^3\psi' \rangle$ may not be very different.

Tl^+ again presents a marked deviation, but our above assumptions as to the indirect-mixing of states mechanism for $S_{1(R)} \rightarrow T_{1(R)}$ may also possibly explain the Tl^+ deviation for the $T_{1(R)} \rightarrow S_{0(R)}$ crossing.

As shown in Fig. 3B, the radiative lifetimes τ_{RM} are also related to ζ^2 . The $\ln(\tau_{RM}^{-1})$ vs. $\ln(\zeta^2)$ curve shows that the following relation:

* $aS_0 \rightarrow T_1$ assistance of some aromatics by metal acetylacetonates [17, 18] has been attributed to the "aromatic-metal acetylacetonate" CT complexes.

*Data taken from ref. 1.

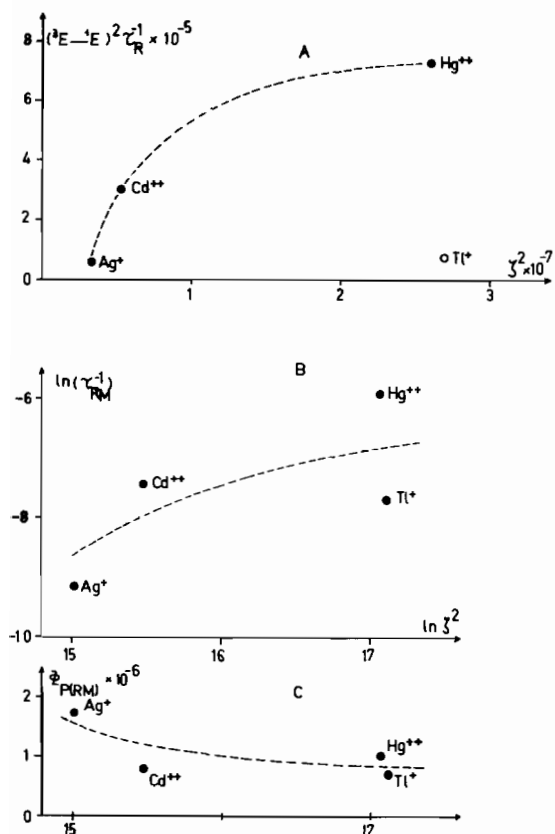


Figure 3. $(^3E - ^1E)^2 \tau_R^{-1}$ vs. ζ^2 , $\ln(\tau_{RM}^{-1})$ and $\Phi_{P(RM)}$ vs. $\ln \zeta^2$ variations.

$$\begin{aligned} \ln(\tau_{RM}^{-1}) &= \ln[(q+1)2\pi h^{-1} \rho''' \langle ^3\Lambda' | ^1\Lambda_o \rangle^2] + \\ &\quad + \ln|\langle ^3\psi | H_{SO} | ^1\psi_o \rangle|^2 \\ &= \ln[(q+1)2\pi h^{-1} \rho''' \langle ^3\Lambda' | ^1\Lambda_o \rangle^2 K_{AO}^2] + \\ &\quad + \ln(\zeta^2) \end{aligned}$$

(where $q = k_{P(RM)}/k_{TS(RM)}$)

very roughly correlates the experimental data [1] and this is to be expected since q undoubtedly varies. As shown, however, in Fig. 3C the apparent phosphorescence quantum yields ($\Phi_{P(RM)} = KP/[RM^{n+}]$)* of the EDA species approximatively diminishes from $(BZA-Ag^+)$ to $(BZA-Tl^+)$ so that the $\tau_{(RM)}$ correlation may not, in fact, be so rough as shown in Fig. 3B.

The influence of Ag^+ , Cd^{2+} , Hg^{2+} and Tl^+ on the 3BZA interaction with boron species was investigated [1]. It was shown that the metal ions M^{n+} enhance the $S_1 \rightarrow T_1$ crossing of BZA, thus affecting the rate of the excited-state 3 (Borobenzoylacetone) complex formation [1].

Relative increases in the triplet quantum yield of BZA (Φ_{STM}/Φ_{ST}) in the presence of M^{n+} were

calculated from kinetic data of "boron-BZA" complexation under continuous ligand excitation.

The calculated [1] Φ_{STM}/Φ_{ST} ratios can now be checked by the following relations (see also previous relations in this paper):

$$\begin{aligned} \frac{\Phi_{STM}}{\Phi_{ST}} &= \frac{k_{STM} [^1R]_M}{k_{ST} [^1R]} \frac{\varphi_M'''}{\varphi''} \cdot \frac{k_{STM}}{k_{ST}} = \\ &= \frac{\varphi_M'''}{\varphi''} \cdot \frac{\rho'' \varrho^{(I)2} \varrho^{(II)2}}{\rho \lambda^2 m^2} \frac{|\langle ^3\psi | H_{SO} | ^1\psi \rangle|^2}{(\Delta^3E)^{-2} (\Delta^1E)^{-2}} \quad (25) \\ &\approx K \frac{\varphi_M'''}{\varphi''} \zeta^2 (\Delta^3E)^{-2} (\Delta^1E)^{-2} \end{aligned}$$

and as

$$\varphi_M''''' = {}^1k_A - {}^1k_B Q_M,$$

expression (25) can be transformed in:

$$\frac{\Phi_{STM} (\Delta^3E)^2 (\Delta^1E)^2}{\Phi_{ST} \zeta^2} = R_\Phi = K I^{-1} {}^1k_A - K {}^1k_B Q_M; \quad (\varphi_M''/\varphi'' = 1) \quad (26)$$

Considering the approximations introduced in the above development and the fact that Q_M were calculated from experimental kinetic data, Table I shows that the R_Φ , Q_M values are rather satisfactorily correlated.

TABLE I. R_Φ and Q_M Values.

M^{n+}	Ag^+	Cd^{2+}	Hg^{2+}	Tl^+
$R_\Phi \times 10^{-7}$	17.9	8.29	2.33	2.80
Q_M	0.11	0.548	0.303	0.207

Finally, it has been assumed [1] that, owing to the enhancement of the $T_1 \rightarrow S_0$ crossing of the conjugate chelate form (R) of BZA, by the HMI, the excited path leading to the RH form which interacts with boron species is more actively quenched and our present deductions are, of course, in agreement with these assumptions.

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*See relation (27) in ref. 1.

**From relation (32) in ref. 1.

*Calculated from data in ref. 1.

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