Time-resolved EPR and ODMR studies on the lowest excited triplet states of α-silyl and α-germyl ketones

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Sublevel properties of the lowest excited triplet (T\(_1\)) n\(^\pi^+\) states of α-silyl and α-germyl ketones were examined by means of ODMR, time-resolved EPR and optical spectroscopy. The EPR parameters, \(D\), \(E\) and \(g\), population ratios, and triplet lifetimes were obtained. The \(D\) value and the triplet lifetime varied among the molecules. In contrast the \(E\) value and population ratio remains nearly the same. These properties together with their solvent dependence and emission properties are interpreted in terms of spin–orbit couplings between T\(_1\) (n\(^\pi^+\)) and higher S\(_1\) (n\(^\pi^+\)), T\(_2\) (\(\pi\pi^+\)) and S\(_2\) (\(\pi\pi^+\)) states. An origin of the remarkable red-shifts of 1,3(n\(^\pi^+\)) are discussed based on a model of delocalized n, \(\pi\) and \(\pi^+\) electrons over the Si and Ge atoms. This model is also consistent with all the triplet properties obtained.

1. Introduction

The lowest excited triplet (T\(_1\)) states of aromatic carbanions have been extensively studied by means of optical detection of magnetic resonance (ODMR) [1, 2] and time-resolved electron paramagnetic resonance (TREPR) [3, 4] techniques. In every case, an interaction between excited 3(\(\pi\pi^+\)) and 3(n\(^\pi^+\)) states is important and crucial for the properties of the T\(_1\) state. Among the properties, zero field splitting (zfs) parameters, \(D\) and \(E\), are highly sensitive to such interactions [5, 6]. The magnitude of interactions has been evaluated from the zfs parameters as represented in the paper of Hayashi and Nagakura [7]. They showed a nice correlation diagram between zfs parameters of T\(_1\) and mixing coefficients of 3(\(\pi\pi^+\)) and 3(n\(^\pi^+\)) from both view points of theory and experiment. However, there are no examples which show the almost pure 3(n\(^\pi^+\)) nature in aromatic carbanions; for example even benzophenone T\(_1\) (n\(^\pi^+\)) involves 15% of 3(\(\pi\pi^+\)) character [8]. This situation is based on the fact that aromatic carbanions usually provide 3(\(\pi\pi^+\)) with relatively low energy, while 3(n\(^\pi^+\)) is not red-shifted by interactions with other chromophores. On that point, α-silyl [9] and α-germyl ketones are rather rare molecules which show remarkably red-shifted 1,3(n\(^\pi^+\)) and almost unchanged 1,3(\(\pi\pi^+\)) states as compared with those of the corresponding C ketones, providing a nearly pure n\(^\pi^+\) character in the T\(_1\) state.

Triphenylsilyl phenyl ketone was synthesized as the first metalloid ketone (–M–CO–C) by Brook [10], and markedly red-shifted n\(^\pi^+\) absorptions of α-silyl (Si) and α-germyl (Ge) ketones were observed by Brook \textit{et al.} [11] and Corey \textit{et al.} [12]. Red-shifted n\(^\pi^+\) fluorescence and phosphorescence were later observed for these molecules [13]. Although the dual emission observed from the 1,3(\(n\pi^+\)) states is similar to that of aliphatic carbanions [14], the local structure around the carbonyl C=O group has turned out to be very different, showing our molecules to be almost planar and the aliphatic carbanions to be pyramidal, as shown in this study. There were several discussions concerning the origin of the large and small red-shifts of the 1,3(\(n\pi^+\)) and 1,3(\(\pi\pi^+\)) states, respectively, which seems to be unsettled as yet. Subjects of dispute have been: (1) the interactions between the metal d\(_e\) and carbonyl \(\pi\) orbitals [11, 15], (2) an inductive effect of the metal on the oxygen non-bonding orbital n\(_0\) [16], and (3) interactions between the metal–carbon \(\sigma\_M\) and n\(_0\) orbitals [17].

Triplet sublevel properties, such as the zfs parameters, the g value, the \(S_1\)–T\(_1\) intersystem crossing (isc) rate and the T\(_1\)–S\(_0\) decay rate, are useful parameters...
for elucidation of $T_1$ character in terms of interactions between the $T_1$ and higher excited states. ODMR and TREPR were utilized to obtain these parameters in rigid glass solutions. UV–vis absorption spectra, emission spectra of fluorescence and phosphorescence and their excitation spectra were also measured, making the discussion more quantitative. The following M ketones ($M = Si$ or Ge) (figure 1) were examined in this report; phenyldimethylsilyl phenyl ketone Ph(Me)$_2$SiCOPh (I), trimethylsilyl phenyl ketone (Me)$_3$SiCOPh (II), triphenylgermyl phenyl ketone (Ph)$_3$GeCOPh (III), phenyldimethylgermyl phenyl ketone Ph(Me)$_2$GeCOPh (IV), trimethylgermyl phenyl ketone (Me)$_3$GeCOPh (V). As a reference for these ketones, $t$-butyl phenyl ketone (Me)$_3$CCOPh (VI), a C ketone, was also examined. The axes are taken as shown in figure 1, where the $z$ and $x$ axes are parallel to the $C=O$ direction and perpendicular to the $>C=O$ plane, respectively.

2. Experimental

Compounds I–V were synthesized as described in the literature [11, 13]. The solid compounds were purified by chromatography on silica gel (Wakogel C100) eluted with n-hexane, followed by recrystallization and sublimation. Liquid compounds were purified by chromatography and distillation. Spectral grade methylcyclohexane (MCH), toluene (Tol), 2,2,2-trifluoroethanol (TFE) and ethanol (EtOH) were purchased from Wako Chemicals, and n-pentane and n-heptane from Tokyo Chemical Industry Co., and these were used as solvents without further purification. The solutions were degassed by repeated freeze–pump–thaw cycles using a vacuum line.

TREPR and steady state EPR measurements were carried out at various temperatures using a modified X-band JEOL JES FE2XG EPR spectrometer. Temperature was controlled by using a JEOL ES –DVT3 nitrogen gas flow system. A small amount of oxygen gas was intermixed into the nitrogen gas to quench paramagnetic species produced on the quartz wall under 266 nm excitation. EPR signals from a modified EPR unit were integrated over a certain gate time period by a NF BX-531 boxcar integrator, giving rise to TREPR spectra. A method of two gates (before and after the laser pulse) was employed to remove low frequency noises. Other details of the TREPR apparatus have been described elsewhere [18]. An OPO laser (Spectra Physics MOPO-710) pumped by a Nd:YAG laser (Spectra Physics GCR-170) and the fourth harmonics of the Nd:YAG laser were employed to excite the molecule selectively to the $S_1$ and $S_2$ states at 445 and 266 nm, respectively. For a magnetophotoselection experiment, polarized light with a horizontal or vertical electric field vector is generated by changing a number of inserting prisms. Depolarized light was obtained by use of a depolarizer.

UV–visible absorption measurements were made with a Shimadzu UV-160 spectrometer. Phosphorescence and fluorescence spectra were observed with a Hitachi 850 fluorometer. Phosphorescence lifetimes were measured by using a Nikon G250 monochromator and a Hamamatsu Photonics R928 photomultiplier tube under excimer laser excitation (308 nm; Lambda Physik LPX 100).

A nitrogen gas laser (337.1 nm) was used for ODMR and the method of fast-passage [19] was used to determine sublevel decay rate constants. The details of the ODMR experiments have been described elsewhere [20].

3. Results and interpretation

3.1. Optical measurements

Absorption spectra of silyl and germyl ketones (I–V) were observed in non-polar (MCH) and polar (TFE + EtOH (3:2)) solvents at room temperature. The typical spectrum of compound II in MCH is shown in figure 2 together with that of the corresponding C ketone (VI). As already reported for these compounds, it was found from the figures that $S_2$ ($\pi\pi^*$) is red-shifted a little (294 versus 288 nm), but $S_1$ ($\pi\pi^*$) shifted remarkably (442 versus 375 nm) by metal (Si or Ge) substitution. Fluorescence (F) and phosphorescence (P) spectra were both observed in all compounds at 77 K as typically shown for compound I in figure 3. The ratio of the emissions ($I_F/I_P$) varied sensitively with solvent as shown in figure 3 and table 1, where the phosphorescence is more intense in polar solvents. A phosphorescence spectrum of VI in MCH is also shown in figure 3. The $T_1$ ($\pi\pi^*$) state is red-shifted also remarkably in the Si and Ge ketones. A well-resolved phosphorescence spectrum was observed for II (figure 4) in pentane at 4.2 K. The $C=O$ stretching band in these M ketones was very weak in contrast to typical $C=O$ progressions observed in the $3(\pi\pi^*)$ emissions of carbonyls (figure 3(c)).

Triplet lifetimes were obtained from the decay of phosphorescence as summarized in table 2. The energy levels of compounds I–VI were obtained from the emis-
sion spectra and excitation spectra of emission as summarized in table 3. A striking feature of large red-shifts of $1\alpha_1$(n$p^*\alpha$) is clearly seen from the table. Among these ketones, the $1\alpha_1$(n$p^*\alpha$) energies are a little more red-shifted and the $T_1$ lifetime becomes shorter by methyl substitution. A heavy atom effect is also found for the $T_1$ lifetime with Si and Ge substitution.

3.2. ODMR studies

The zero-field splitting (zfs) parameters $D$ and $E$ were obtained for I–V from three ODMR transitions in $n$-pentane as typically shown for Ph(Me)$_2$SiCOPh (I) in figure 5. The sublevel decay rate constants $k_i$ ($i = x,y,z$) were measured at 1.2 K with the fast passage method and from the non-exponential decay curves of the 0–0 transitions of the phosphorescence. The zero-field schemes obtained were shown for I and

![Absorption spectra](image)

**Figure 2.** Absorption spectra of (a) (Me)$_3$SiCOPh and (b) (Me)$_3$CCOPh in methylecyclohexane at room temperature.

![Emission spectra](image)

**Figure 3.** Emission spectra of Ph(Me)$_2$SiCOPh in (a) ethanol + toluene and (b) $n$-heptane and of (c) (Me)$_3$CCOPh in methylecyclohexane at 77 K. The vibrational frequencies are shown in cm$^{-1}$. F and P denote fluorescence and phosphorescence, respectively.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>$I_F/I_P^a$</th>
<th>$T_1$(n$p^*$)</th>
<th>$S_1$(n$p^*$)</th>
<th>$S_2$(n$p^*$)</th>
<th>$E_{exc}$/cm$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>EtOH + Tol</td>
<td>0.046</td>
<td>19 740</td>
<td>22 090</td>
<td>31 750</td>
<td></td>
</tr>
<tr>
<td>MCH</td>
<td>0.053</td>
<td>19 660</td>
<td>22 070</td>
<td>32 500</td>
<td></td>
</tr>
<tr>
<td>$n$-pentane</td>
<td>0.25</td>
<td>19 440</td>
<td>22 000</td>
<td>32 400</td>
<td></td>
</tr>
<tr>
<td>$n$-pentaneur</td>
<td>0.34</td>
<td>19 310</td>
<td>21 920</td>
<td>32 260</td>
<td></td>
</tr>
</tbody>
</table>

$^a$ Intensity ratio of fluorescence (F) and phosphorescence (P).
Assignment of the sub-levels is made on the basis of the results of TREPR, which will be discussed in section 3.3. It is found that only one sublevel decays very fast among the three sublevels. The validity of the decay rate constants is ascertained by the following equation.

\[ k_{av} = \frac{1}{3}(k_x + k_y + k_z) = k_{77K}. \]  

The value of \( k_{av} \) is compared with the decay rate \( k_{77K} \) of phosphorescence measured at 77 K where the decay curve was analysed with a single exponential function. The \( k_{av} \) and \( k_{77K} \) obtained are 1450 and 1370 s\(^{-1}\) for \( I \) and 2840 and 2700 s\(^{-1}\) for \( II \) with experimental relative uncertainties of 5%. The coincidence of these two values is satisfactory enough to justify the sublevel decay rate constants obtained.

<table>
<thead>
<tr>
<th>Ketones</th>
<th>( n)-pentane</th>
<th>MCH in TFE + EtOH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ph(Me(_2))SiCOPh (I)</td>
<td>0.73</td>
<td>0.84</td>
</tr>
<tr>
<td>(Me(_3))SiCOPh (II)</td>
<td>0.37</td>
<td>0.53</td>
</tr>
<tr>
<td>(Ph)(_2)GeCOPh (III)</td>
<td>—</td>
<td>0.27</td>
</tr>
<tr>
<td>Ph(Me(_2))GeCOPh (IV)</td>
<td>0.079</td>
<td>0.10</td>
</tr>
<tr>
<td>(Me(_3))GeCOPh (V)</td>
<td>0.035</td>
<td>0.023</td>
</tr>
<tr>
<td>(Me(_3))CCOPh (VI)</td>
<td>—</td>
<td>3.5</td>
</tr>
</tbody>
</table>

The energies of the \( T_1(\pi\pi^*) \), \( S_1(\pi\pi^*) \), and \( S_2(\pi\pi^*) \) states are obtained from emission and their excitation spectra in methylcyclohexane and the values in parentheses are those in TFE + EtOH (3:2).
3.3. Time-resolved EPR studies

Time-resolved RPR (TREPR) signals were observed for all compounds I–VI in non-polar MCH at 77 K under depolarized light excitation of 266 nm. The TREPR spectra of Ph(Me)$_2$SiCOPh (I) and (Me)$_3$SiCOPh (V) obtained at 0.8 µs after the laser pulse are shown in figure 7. All the spectra provide similar electron spin polarization. The polarity of the signals is an absorption (A) and an emission (E) of microwave at every stationary field of low and high field sides, respectively and A at the minimum field ($B_{\text{min}}$; $\Delta m_s = 2$), providing an A,AAA/EEE pattern. These spectra were simulated with the zfs parameters $D$, $E$ and $g$ values, and a $S_1$–$T_1$ intersystem crossing (isc) ratio $P_i$ ($i = x, y, z$), under an assumption of random orientation. Linewidths of 5–8 mT were used for the simulation. The isc ratio was $P_z - P_y$: $P_x - P_y = 1 : 0$, which is consistent with the fact that only one sublevel is active in this population process. The simulated spectra are shown in figure 7 and the parameters used are summarized in table 4. The TREPR spectra were also observed for compounds I and V in polar solvent (TFE+EtOH) and simulated using the parameters summarized in table 4. It is found that the $D$ value decreases from I to V, whereas $E$ remains nearly unchanged. $D$ decreases also in polar solvents. For the $g$ value, we obtained $g_{ii} = 2.002$ ($i = x, y, z$) and could not observe any anisotropy within the experimental error ($\pm 0.001$).

In order to assign the triplet sublevel, we utilized a method of magnetophotoselection using polarized light excitation. It has been already reported that the electronic transition moment ($E$) of the $S_0$–$S_2$ ($\pi\pi^*$) and $S_0$–$S_1$ ($\pi\pi^*$) transitions for carbonyls is polarized towards the $y$ [21] and $x$ axes, respectively. The TREPR spectra were observed in MCH under the $S_2$ (266 nm) and $S_1$ (450 nm) excitation as shown in figure 8, with $E \parallel B$ and $E \perp B$, where $B$ denotes a magnetic field vector. From the figures with $E \parallel B$, it is easily found that the middle pair of stationary fields (figure 8(a)) and the inner-most pair fields (figure 8(b)) correspond to the fields at $B \parallel y$ (266 nm) and $B \parallel x$ (450 nm), respectively, because of the directions of their transition moment, $y$ ($S_2$) and $x$ ($S_1$), respectively. Then the outer most fields are those at $B \parallel z$. When we take into account the result that only one sublevel is dominant both in the decay (figure 6) and isc (table 4) processes, we can safely assign the active sublevel to be

![Figure 6](image)

Figure 6. Zero field scheme of (a) Ph(Me)$_2$SiCOPh and (b) (Me)$_3$SiCOPh. Zero-field splittings and lifetimes of the sublevels are shown.

![Figure 7](image)

Figure 7. Time-resolved EPR spectra of (a) Ph(Me)$_2$SiCOPh and (b) (Me)$_3$GeCOPh in methylecylexane at 0.8 µs and 77 K together with their simulations ($a'$ and $b'$).

<table>
<thead>
<tr>
<th></th>
<th>$D$/GHz</th>
<th>$E$/GHz</th>
<th>$P_z$ : $P_y : P_x$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ph(Me)$_2$SiCOPh (I)</td>
<td>4.25 (4.08)</td>
<td>0.26 (0.26)</td>
<td>1 : 0</td>
</tr>
<tr>
<td>(Me)$_3$SiCOPh (II)</td>
<td>4.19</td>
<td>0.26</td>
<td>1 : 0</td>
</tr>
<tr>
<td>(Ph)$_3$GeCOPh (III)</td>
<td>3.66</td>
<td>0.20</td>
<td>1 : 0</td>
</tr>
<tr>
<td>Ph(Me)$_2$GeCOPh (IV)</td>
<td>3.24</td>
<td>0.22</td>
<td>1 : 0</td>
</tr>
<tr>
<td>(Me)$_3$GeCOPh (V)</td>
<td>2.97 (2.75)</td>
<td>0.23 (0.21)</td>
<td>1 : 0</td>
</tr>
</tbody>
</table>

*Values in parentheses are those in TFE + EtOH (3 : 2).
on the basis of numerous previous data for carbonyl compounds. We will come back to this point and discuss it in more detail in the following section. It is concluded that the energy levels of $T_z$, $T_x$ and $T_y$ are located from the top to the bottom in this order as shown in Figure 6 and Table 4. Now the ZFS parameters are defined as $D = 3/2E_z$, $E = (1/2)(E_y + E_x)$, where $E_i$ ($i = x, y, z$) denotes the sublevel energy.

4. Discussion

4.1. States and orbitals

When properties of the excited state are discussed, the wavefunctions of the states and orbitals should be known. In carbonyls, the non-bonding (n) orbital, which is usually localized on the carbonyl oxygen atom ($n_O$), is always important to evaluate a $T_1$ property whether a $3(n\pi^*)$ state lies lowest or not. If we notice the results for M ketones that only one triplet sublevel is active both in the population and decay processes and that $1,3(n\pi^*)$ transitions are remarkably red-shifted whereas $1(\pi\pi^*)$ transitions remain nearly the same as compared with those of the corresponding C ketones, we conclude that spin–orbit couplings are selective and the $n_O$ orbital interacts with the other orbitals. When we consider measurable heavy atom and substitution effects on the $T_1$ properties of these Si and Ge ketones, the n, $\pi$ and $\pi^*$ molecular orbitals involved in the lower excited states must be delocalized over (and interact with) the atomic orbitals of M (=Si and Ge). Then

$$n = C_{Ox}^n p_{Ox} + \sigma_{Mx}$$

where $C_{Ox}$ and $p_{Ox}$ denote a coefficient and a p orbital, respectively. These delocalized orbitals and transitions among the orbitals are schematically shown in Figure 9. The $n_O$ orbital interacts strongly with the $\sigma_{Mx}$ orbital of M and C(O), providing the destabilized n orbital. The $\pi$ and $\pi^*$ orbitals are destabilized and stabilized by an inductive effect of M and delocalization of $\pi$ ($\pi^*$) electrons over M, respectively. Although we do not know exactly which is more effective, we consider that delocalization dominates the inductive effect based on the observed normal small red shift of $S_2$ ($\pi\pi^*$). This scheme explains qualitatively the shifts of the transitions.

The results that the population ($P_i$) and decay ($k_i$) of the $T_z$ sublevel (Table 4 and Figure 6) dominate those of the other two sublevels are also shown to be consistent

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**Figure 8.** Time-resolved magnetophotoselection EPR spectra of Ph(Me)$_2$SiCOPh in methycyclohexane at 77 K with $E || B$ and $E \perp B$ under selective excitation of (a) $S_0-S_1$ (450 nm) and (b) $S_0-S_2$ (266 nm) transitions.

**Figure 9.** (a) Orbital interaction between $n_O$ and $\sigma_M$ and delocalization of $\pi$ ($\pi^*$) electrons and (b) red-shifts of the excited states in M ketones.
with the proposed wavefunctions (equations (2) and (3)) and equations (4) and (5).
\[ P_j \propto |\langle S_1 | R | T_1 \rangle |^2 \]  \hspace{1cm} (4)
\[ k_{pp}^\text{nr} \propto |\langle T_1 | R | S_0 \rangle |^2 \]  \hspace{1cm} (5)
\[ R = H_{SO} + T_N \]  \hspace{1cm} (6)
\[ H_{SO} = \alpha \cdot s = \sum \xi_i s_i \quad (i = x, y, z). \]  \hspace{1cm} (7)

Here \( k_{pp}^\text{nr} \) and \( T_N \) represent a nonradiative decay rate constant and the Hamiltonian of nuclear kinetic energy, respectively. If we consider that both \( T_1 \) and \( S_1 \) are \( n\pi^* \) in nature, we can write down the matrix elements as the following \[ \langle S_1 | R | T_1 \rangle = \langle 1^n \pi^* | H_{SO} | 3^n \pi^* \rangle + \langle 1^n \pi^* | T_N | 1^n \pi^* \rangle \]
\[ \times \langle 1^n \pi^* | H^\prime_{SO} | 3^n \pi^* \rangle / \Delta E_{SS} \]
\[ + \langle 1^n \pi^* | H_{SO} | 3^n \pi^* \rangle \times \langle 3^n \pi^* | T_N | 1^n \pi^* \rangle / \Delta E_{ST}, \]  \hspace{1cm} (8)
\[ \langle T_1 | R | S_0 \rangle = \langle 3^n \pi^* | H_{SO} | 1^n \rangle \text{nn}. \]  \hspace{1cm} (9)

The first term of equation (8) is less important due to the three centre terms involved [23]. Then all terms in both equations include the matrix element of \[ \langle 1^n \pi^* | H_{SO} | 3^n \pi^* \rangle \], which is important in the \( T_1 \) properties of carbonyls. This element is expanded to those composed of atomic orbitals by use of equations (2) and (3).
\[ \langle 1^n \pi^* | H_{SO} | 1^n \rangle \text{nn} \]  \hspace{1cm} (10)

Here only one centre term is included [23]. If we consider the properties of the angular momentum operator \( l_n \), we obtain the important formulas
\[ \langle 1^n \pi^* | H^\prime_{SO} | 1^n \rangle \text{nn} \neq 0 \quad (i = z) \]  \hspace{1cm} (11 a)
and
\[ \langle 1^n \pi^* | H^\prime_{SO} | 1^n \rangle \text{nn} = 0 \quad (i = x \text{ or } y). \]  \hspace{1cm} (11 b)

These provide selective preference for the \( T_2 \) sublevel both in the isc and the decay processes. In other words, the \( n \) and \( \pi \) (\( \pi^* \)) MOs (molecular orbitals) mostly consist of the \( p_y \) and \( p_x \) AOs (atomic orbitals), respectively, indicating a planarity of the centre part (\( \text{M(C} \text{C} \text{C} \text{O}) \)) of the molecules. This result also indicates that the fine structure axes (\( x, y \) and \( z \)) are almost parallel to the molecular axes, as shown in figure 1.

4.2. Location of \( T_2 \) (\( \pi\pi^* \))

In order to discuss the \( T_1 \) properties of \( M \) ketones quantitatively, we need to know the location of \( T_2 \) (\( \pi\pi^* \)). We refer to the energies of the excited states of \( t \)-butyl phenyl ketone (Me\(_2\)CCOPh: VI). \( S_2 \) (\( \pi\pi^* \)) of VI lies at 32,900 cm\(^{-1}\) in TFE + EtOH, and \( T_1 \) (\( \pi\pi^* \)) lies around 25,600 cm\(^{-1}\) in ethylene glycol + H\(_2\)O (1:1) solution [24]. \( T_2 \) (\( \pi\pi^* \)) is also estimated at ca. 25,500 cm\(^{-1}\) in MCH from the analysis of the zfs parameters [24]. In the corresponding Ge ketone \( V \), \( S_2 \) (\( \pi\pi^* \)) lies at 31,900 cm\(^{-1}\), which is a little lower (1000 cm\(^{-1}\)) than that of VI (32,900 cm\(^{-1}\)). When we consider that a little smaller shift is expected for \( 3^n \pi^* \) as compared with \( 1^n \pi^* \), we have determined the location of \( T_2 \) (\( \pi\pi^* \)) as 24,700 cm\(^{-1}\) for the \( M \) ketone. This value is also consistent with the value (7300 cm\(^{-1}\)) of \( \Delta E_{ST}(\pi\pi^*) \) for benzaldehyde (7500 cm\(^{-1}\)) and acetonaphone (8000 cm\(^{-1}\)) [25]. As a result, \( T_2 \) (\( \pi\pi^* \)) lies at ca. 5000 cm\(^{-1}\) above \( T_1 \) (\( \pi\pi^* \)) in \( M \) ketones, which is very different from the usual value for aromatic carboxyls and ketones.

4.3. Zero field splitting parameters

The zfs parameters \( D \) and \( E \) were obtained as summarized in table 4, where \( D \) varies from 4.25 to 2.75 GHz for different substituents and solvents but \( E \) remains nearly unchanged at 0.20–0.26 GHz. These results are discussed in terms of spin–spin (ss) and spin–orbit (so) interactions together with delocalization of the \( n \) and \( \pi \) (\( \pi^* \)) electrons over the metal (Si and Ge) and also a heavy atom effect.

The spin Hamiltonian (\( H_s \)) of the zero field splitting is expressed by
\[ H_s = H_{SS} + H_{SO}. \]  \hspace{1cm} (12)
\[ H_{SS} = D_{SS}(S_z^2 - (1/3)S^2) - E_{SS}(S_1^2 - S_y^2). \]  \hspace{1cm} (13)

The spin–orbit Hamiltonian is described in equation (7). As the \( E \) value does not vary so much among the molecules examined, we consider \( E_{SS} \) remains nearly constant (ca. 0.23 GHz) in this system. Two important states of \( T_2(\pi\pi^*) \) and \( S_2(\pi\pi^*) \) should be considered for contributions of the spin–orbit coupling to sublevel energies, \( D_{SO} \), which is calculated by the second order perturbation theory as [26]
Here we consider only the \( z \) component \( H_{SO}^z \) of the spin–orbit contribution, because \( H_{SO}^x \) and \( H_{SO}^y \) contribute differently to \( T_x \) and \( T_y \), providing changes in \( E \) which are inconsistent with the observed result. The predominance of the matrix element \( \langle H_{SO}^z \rangle \) agrees well with the discussion on the population and decay of the \( T_1 \) state described in section 4.1. The spin–orbit contribution to the sublevel energies is represented schematically in figure 10. \( T_z \) is stabilized by the spin–orbit contribution from \( S_{pp}^\pi \) and \( T_x \) and \( T_y \) stabilized by the contribution from \( T_2(\pi^\pi) \), both via \( H_{SO}^z \). Then equation (14) is rewritten by

\[
D_{SO} = \frac{(\xi^2/4)|n|\langle n | \pi \rangle|^2[1/(E_{T_z} - E_{T_1})] - 1/(E_{S_i} - E_{T_1})].
\]

From this equation it is concluded that the spin–orbit contribution to \( D_{SO} \) is negative, because \( E_{S_i} > E_{T_z} > E_{T_1} \).

As the observed \( D = -(3/2)E_2 \) is positive (figure 8), the larger decrease in \( D \) indicates the larger spin–orbit contribution in the molecule. It is easily understood now that the Ge ketones have a smaller \( D \) than the Si ketones. When we compare \( D \) among the Ge ketones, methyl substitution is found to increase the spin–orbit contribution. Quantitative analyses are made by using equations (15) and (16).

\[
D = D_{SS} + D_{SO}.
\]

Here we assume that \( D_{SS} \) equals to 4.3 GHz, a slightly larger value than \( D \) (4.25 GHz) of Ph(Me)\(_2\)SiCOPh (I), for two reasons. One is that the \( D \) value for \( 3(\pi^\pi) \) formaldehyde \( H_2CO \) is calculated to be 4.5 GHz [27] and used as \( D \) of pure \( 3(\pi^\pi) \) in the Hayashi–Nagakura diagram [7], by which the spin–orbit contribution is explained nicely for various carbonyl compounds. M ketones provide an extended \( \pi \) (\( \pi^\pi \)) system where a slightly smaller \( D \) is expected. The other is that \( D_{SO} \) in the Si ketones should be very small (\( \approx 0.03 \) GHz) as compared with those of Ge ketones (1.04 and 1.25 GHz for \( D(I) < D(IV) \) and \( D(II) < D(V) \), respectively; table 4), based on equation (15) and \( \xi_{Ge}^2/\xi_{Si}^2 = 40 \) (\( \xi_{Ge} = 940 \) and \( \xi_{Si} = 149 \) cm\(^{-1} \)) [28]. \( D_{SO} \) is expressed by a sum of \( D_{SO}^{(1)} \) (I= M,O,C) on each atom using equations (2), (3) and (15).

\[
D_{SO} = \frac{(\xi^2/4)|n|\langle n | \pi \rangle|^2[1/(E_{S_i} - E_{T_{1n}})] - 1/(E_{S_i} - E_{T_{1n}})}{E(\xi^2/4)|n|\langle n | \pi \rangle|^2[1/(E_{S_i} - E_{T_{1n}})] - 1/(E_{S_i} - E_{T_{1n}})}.
\]
Phosphorescence properties

The triplet lifetime becomes shorter with methyl and Ge substitution as shown in table 2. On the basis of discussion in the previous two sections, it is easily expected that the shortening is due to the increased spin–orbit contribution on the Ge atom. When we look at the spin–orbit matrix element carefully, however, we find that the spin–orbit elements involved are different depending on the properties. The decay rate involves the element of $\langle n | \xi | \pi^e \rangle$ and the EPR parameters $D$, $E$ and $g$ involve $\langle n | \xi | \pi^e \rangle$, where the $n$ orbital is common but the $\pi^e$ orbital is different. The larger effect was observed for the decay rate with methyl substitution. This must be interpreted by the larger increase in the spin–orbit matrix element on Ge, that is, $C_{Gex}^{E}$ increases more than $C_{Gex}^{e}$ in equation (10), though the MNDO calculation does not support this idea. With Ge substitution the increased spin–orbit contributions to the isc and decay processes are similar, which is consistent with the MNDO calculation (section 4.3).

The phosphorescence was remarkably red-shifted and the spectra were very different from those of $3\pi^e$ carbonyl compounds (figure 3) [1, 2]. The intensity of the C–O band is very weak and the frequency is red-shifted; for example from 1630 (IV) to 1585 or 1598 cm$^{-1}$ (II), in M ketones. These features are consistent with our interpretation that the $n_M$ orbital interacts measurably with the $\sigma_M$ orbital as demonstrated in figure 9. These features were similarly observed for fluorescence.

The relative intensity of phosphorescence increased whereas the triplet lifetime decreased in polar solvent, as shown in figure 3 and table 2. As the radiative rate of $3\pi^e$ is not considered to vary with solvent, the $S_{T_1}$–$T_1$ isc rate must increase in polar solvent. This is interpreted in terms of the red-shift of $T_2(\pi^e)$ and the blue-shift of $S_1(\pi^e)$, inducing a decrease of the energy denominator $\Delta E_{ST}(=E_{T_2}-E_{S1})$ in equation (8) and making the isc rate $P$ faster and the fluorescence weaker in a polar solvent.

5. Conclusion

We have concluded that the lowest excited triplet ($T_1$) states of a series of $\alpha$-silyl and $\alpha$-germyl ketones I–V show nearly pure $3\pi^e$ character with very little $3\pi^e$ character. The different $D$ values and decay rate constants of the molecules were explained by a proposed model of spin–orbit coupling induced $3\pi^e$–$1\pi^e$ mixings. The spin–orbit character on the metal (M=Si and Ge) is important to determine the triplet properties, together with that on the O atom. The nearly constant $E$ and $g$ values and the population ratio were also interpreted by the same model. The delocalized $n$, $\pi$ and $\pi^*$ molecular orbitals are proposed and established based on these results. The delocalization coefficient on the Ge atom was obtained from the $D$ value. The solvent dependence of the triplet properties also supports the proposed spin–orbit coupling scheme.
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