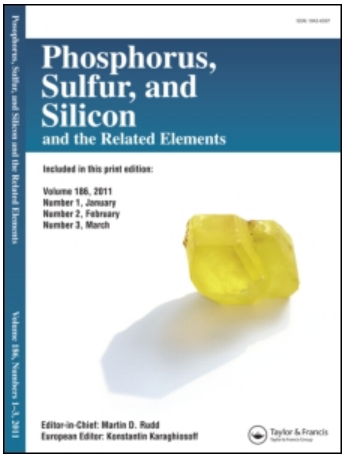

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Origin of ^{77}Se NMR Chemical Shifts Revealed for Pre-α, α, β, and γ Effects

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The origin of δ(Se) is revealed based on the MO theory. The pre-α effect in H_2Se, defined in the text, is the generation of double σ(Se—H) and σ(Se—H) through the protonation to spherical Se^{2-}. The extension of HOMO-n (n = 0, 1, and 2) over the whole molecule of Me_2Se is mainly responsible for the α effect. The β effect originates not from the occupied-to-unoccupied transitions but from the occupied-to-occupied transitions. The γ effect of the upfield shifts is the results of the subtle balance between two types of transitions. Contributions from each MO (ψ_i) and each $\psi_i \rightarrow \psi_a$ transition are evaluated separately, using a utility program (NMRANAL-NH03G).*

Keywords Ab initio calculations; $\alpha\beta\gamma$ effects; GIAO; origin of ^{77}Se NMR chemical shifts; paramagnetic shielding constants; pre-α effect

INTRODUCTION

^{77}Se NMR chemical shifts (δ(Se)) are typically used to determine the structures.[1,2] Indeed, empirical rules are useful to assign the spectra, but they are of no use when the origin of δ(Se) is considered.[3] How do δ(Se) of selenium compounds originate depending on the respective structures? The origin is elucidated for various selenides based on the MO theory, as a first step to establish plain rules founded in theory and familiar to experimental chemists. An idea called the "pre-α effect" is proposed for the better understanding of δ(Se).[4] The pre-α effect is defined as the downfield shift by a proton added to a lone pair orbital of Se, as shown in Scheme 1.

The δ(Se) value of H_2Se (δ(Se: H_2Se)) from Se^{2-} would be most practical for the pre-α effect. The α and β effects[1,5] are downfield shifts in the processes from H_2Se to Me_2Se then to Et_2Se, respectively, and the

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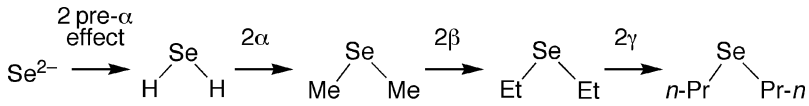

SCHEME 1 Pre-α, α, β, and γ effects.

γ effect of upfield shifts is that from Et_2Se to *n*-Pr_2Se, for example.[1,5] The magnitudes of the effects in the processes are two times larger than defined values. The origin of the pre-α, α, β, and γ effects are elucidated, employing calculated absolute paramagnetic shielding constants (σ^{p}(Se)).

RESULTS AND DISCUSSION

Calculation Method

QC calculations are performed employing the 6–311+G(3df) basis sets for Se and the 6–311+G(3d,2p) basis sets for other nuclei in the *Gaussian 03* program.[6] The structural optimization is performed at the DFT level (B3LYP). The gauge-independent atomic orbital (GIAO) method is applied to evaluate the absolute magnetic shielding tensors of Se (σ^{p}(Se)) at the DFT (B3LYP) level, applying on the structures optimized with the same basis sets (the GIAO–DFT method). σ(Se: Se^{2-}) is chosen as the standard since σ^{p}(Se: Se^{2-}) = 0 ppm is favorable for the standard. Table I lists the calculated σ(Se) and observed δ(Se) values of various selenides.

Pre-α Effect

The pre-α effect is analyzed employing σ^{p}(Se) and the components of H_2Se. Figure 1a depicts the occupied-to-unoccupied ($\psi_i \rightarrow \psi_a$) transitions in H_2Se. It well explains how the pre-α effect originates from the transitions under the control of the angular momentum operator. Since Se^{2-} is chosen as the standard, σ^{p}(Se-pα: H_2Se) is explained by the generation of double σ(Se–H) and σ^*(Se–H) through the protonation by two protons at the spherical Se^{2-}. The four orbitals act as σ(H_2Se: a_1), σ(H_2Se: b_2), σ^*(H_2Se: a_1), and σ^*(H_2Se: b_2). Figure 1b explains the results. The newly formed orbitals lead effective $\psi_i \rightarrow \psi_a$ transitions, together with n_p(Se) of $4p_z$(Se), which mainly arise the pre-α effect in H_2Se.

TABLE I Calculated σ(Se) and Observed δ(Se) Values of Various Selenides

Compound	σ^d(Se)	σ^p(Se)	σ^t(Se)	Effect[a,b]	δ(Se)[c]	Effect[c,d]
Se^{2-} (O_h)	3005.7	0.0	3005.7	—	—	—
HSe^- ($C_{\infty v}$)	3001.3	−501.2	2500.2	−505.5: p-α	−447[e]	—
H_2Se (C_{2v})	2998.0	−931.3	2066.7	−469.5: p-α	−331.7[f,g]	222: p-α
MeSeH (C_s)	2998.2	−1155.0	1843.2	−223.5: α	−141.6[g,h]	111: α
EtSeH (C_s)	3000.1	−1235.0	1765.1	−78.1: β	36[i]	151: β
i-PrSeH (C_s)	3004.5	−1469.7	1534.8	−154.2: β	161[i]	151: β
t-BuSeH (C_s)	3009.3	−1553.5	1455.8	−129.1: β	28[i]	144: β
Me_2Se (C_{2v})	2999.1	−1349.0	1650.1	−208.3: α	0.0[i,j]	115: α
Et_2Se (C_{2v})	3006.2	−1516.6	1489.6	−80.3: β	230[i]	115: β
n-Pr_2Se (C_{2v})	3009.1	−1489.3	1519.7	15.1: γ	155[i]	−38: γ
i-Pr_2Se (C_{2v})	3015.3	−1777.1	1238.2	−103.0: β	429[i]	107: β
t-Bu_2Se (C_{2v})	3027.1	−1970.7	1056.4	−99.0: β	614[i]	102: β

[a]In the σ(Se) scale; [b]values and the corresponding effects are shown; [c]observed values (see, ref. 1); [d]in the δ(Se) scale; [e]in DMF; [f] δ(Se) = −225.5 in neat; [g]gas phase; [h] δ(Se) = −115 in $CDCl_3$; [i]in $CDCl_3$; [j] δ(Se) = 13.1 in gas phase.

α Effect

The α effect is analyzed exemplified by Me_2Se, employing σ^p(Se) and the components. The α effect is the downfield shift caused by the replacement of Se—H with Se—Me. Figure 2 shows HOMO, HOMO-1, and HOMO-2 of Me_2Se, which clearly shows the extension of the MOs over

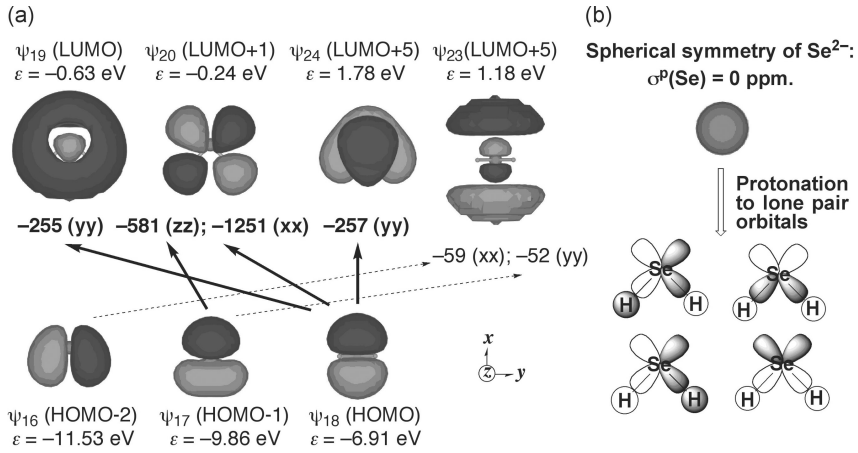

FIGURE 1 (a) Contributions from each $\psi_i \rightarrow \psi_a$ transition to the components of σ^p(Se) in H_2Se; and (b) schematic drawing of origin for the pre-α effect.

FIGURE 2 HOMO, HOMO-1, and HOMO-2 of Me_2Se.

the whole molecule of Me_2Se. The extension is responsible for the α effect.

β Effect

The β effect seems more complex to understand intuitively based on the MO theory than the cases of the pre-α and α effects. The $\psi_i \rightarrow \psi_a$ transitions do not contribute to the β effect but the occupied-to-occupied ($\psi_i \rightarrow \psi_j$) transitions do to the effect. Although the $\psi_i \rightarrow \psi_j$ transitions are usually positive, the positive value in Me_2Se becomes smaller then to negative when a proton in Me_2Se is substituted by a methyl group, one after the other.

γ Effect

The γ effect seems more complex. To examine the effect, $\Delta\sigma^{\mathrm{p}}(\text{Se-}\gamma)$ contributed from the $\psi_i \rightarrow \psi_j$ transitions ($\Delta\sigma^{\mathrm{p}}(\text{Se-}\gamma\colon \psi_i \rightarrow \psi_j)$) are plotted versus $\Delta\sigma^{\mathrm{p}}(\text{Se-}\gamma\colon \psi_i \rightarrow \psi_a)$ for n-PrSeR (R = H, Me, and n-Pr). Equation (1) shows the correlation, which is fairly good (r = 0.986, n = 7).

$$\Delta\sigma^{\mathrm{p}}(\text{Se-}\gamma : \psi_i \rightarrow \psi_j) = -1.17 \times \Delta\sigma^{\mathrm{p}}(\text{Se-}\gamma : \psi_i \rightarrow \psi_a) + 24.1 \qquad (1)$$

The γ effect of the upfield shift is the results of the well-balanced contributions from the $\psi_i \rightarrow \psi_j$ and $\psi_i \rightarrow \psi_a$ transitions.

Investigations to evaluate the electron population factor $\langle r^{-3} \rangle$ are in progress. The results with the applications will be reported elsewhere.

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[5] Downfield shifts of about 110–170 and 100 ppm are observed for the α and β effects, respectively, although the values depend on the conditions of measurements such as solvents (see Table I).[1] The γ effect is the upfield shift of about 30 ppm.[1]
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