Evidence of Tilt of the Methyl Top Axis in the \( r_s \)-structure of Dimethyl Selenide

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The complete \( r_s \)-structure of dimethyl selenide has been determined by using suitably chosen changes in principal moments of inertia of a number of isotopic species. The tilt of the methyl top axis with respect to the C—Se bond, as determined by the analysis of the internal rotation fine structure of the rotational transitions is also evidenced in the \( r_s \)-structure. The center of mass condition has been used.

In order to fit the internal rotation splittings in the rotational spectra of the molecules dimethyl ether\(^{1,2}\), dimethyl sulphide\(^{3,4}\), dimethyl selenide\(^5\) of the series \((\text{CH}_3)_2-X\), with \(X\) a group VI atom, it was found necessary to assume the symmetry axis of the methyl top to be tilted by few degrees with respect to the corresponding \(X-C\) bond. For the former two molecules, the tilt was also confirmed by determining the \(r_s\)-coordinates of the hydrogen atoms with suitable isotopic substitutions in the molecule. For the latter case, viz. dimethyl selenide, this could not be done\(^6\) because of the insufficient number of available isotopic substitutions for the hydrogen atoms. This was also done by Beecher\(^5\). The calculation of the hydrogen coordinates \((\pm a_1, b_1, 0)\) for the symmetric and \((\pm a_2, b_2, \pm c_2)\) for the asymmetric hydrogen atoms could not be done in the conventional ways\(^8,9\), because rotational constants for the singly deuterated species are not yet measured.

In what follows we describe a method, which can be used to determine the hydrogen coordinates in a molecule containing two equivalent methyl groups \([\text{such as } (\text{CH}_3)_2-X]\) by using only changes in the principal moment of inertia between normal and hexadeuterated and normal and trideuterated species of the molecule. We experienced, that the monodeuterated species of a molecule is, in general, costlier to prepare and its spectrum is also sometimes more difficult to interpret.

In going from the normal \((6H)\) to the hexadeuterated \((6D)\) species of the molecule, it can be stated that the \(C_{2v}\) symmetry axis and the symmetry plane of the molecule remain unchanged, only the origin is shifted along the \(b\)-axis. One has

\[
I_a(6D) - I_a(6H) = 2 \Delta m (b_1^2 + 2 b_2^2) + 4 \Delta m c_2^2 - 4 \mu_6 t^2, \\
I_b(6D) - I_b(6H) = 2 \Delta m (a_1^2 + 2 a_2^2) + 4 \Delta m c_2^2, \\
I_c(6D) - I_c(6H) = 2 \Delta m (a_1^2 + 2 a_2^2) + 4 \Delta m (b_1^2 + 2 b_2^2) - 4 \mu_6 t^2.
\]

where

\[
\Delta m = m_{1D} - m_{1H}, \\
\mu_6 = \frac{(\Delta m)^2}{M + 6 \Delta m}, \\
t = b_1 + 2 b_2.
\]
Table 1. The rotational constants and moments of inertia of the different isotopic species of dimethyl selenide used for working out the \( r_s \)-structure.

<table>
<thead>
<tr>
<th>((\text{CH}_3)_2^{\text{Se}}) (^{a})</th>
<th>((\text{CH}_3)_2^{\text{Se}}) (^{a})</th>
<th>(^{13}\text{CH}_3^{\text{Se}}\text{CH}_3) (^{a})</th>
<th>(^{13}\text{CH}_3^{\text{Se}}\text{CH}_3) (^{a})</th>
<th>((\text{CD}_3)_2^{\text{Se}}\text{CH}_3) (^{a})</th>
<th>((\text{CD}_3)_2^{\text{Se}}\text{CH}_3) (^{a})</th>
</tr>
</thead>
<tbody>
<tr>
<td>(A) (MHz)</td>
<td>11300.43</td>
<td>11369.93</td>
<td>11102.19</td>
<td>10013.31</td>
<td>8782.406</td>
</tr>
<tr>
<td>(B) (MHz)</td>
<td>6912.83</td>
<td>6912.76</td>
<td>6715.73</td>
<td>5960.13</td>
<td>5296.524</td>
</tr>
<tr>
<td>(C) (MHz)</td>
<td>4528.79</td>
<td>4539.91</td>
<td>4412.19</td>
<td>4017.77</td>
<td>3603.330</td>
</tr>
<tr>
<td>(I_a) (amu (\AA^2)) (^{c})</td>
<td>44.73555</td>
<td>44.46210</td>
<td>45.53435</td>
<td>50.48590</td>
<td>57.56179</td>
</tr>
<tr>
<td>(I_b) (amu (\AA^2)) (^{c})</td>
<td>73.12938</td>
<td>73.13012</td>
<td>75.27566</td>
<td>84.81879</td>
<td>95.44581</td>
</tr>
<tr>
<td>(I_c) (amu (\AA^2)) (^{c})</td>
<td>111.62606</td>
<td>111.35264</td>
<td>114.57598</td>
<td>125.82377</td>
<td>140.29550</td>
</tr>
</tbody>
</table>

\(^{a}\) J. F. Beecher, Reference 5.  
\(^{b}\) G. K. Pandey and H. Dreizler, Reference 6.  
\(^{c}\) Conversion factor \(5.05531 \times 10^5\) MHz·amu \(\AA^2\); mass scale \(^{16}\)O.

From these equations one can readily get

\[
c_2^2 = \frac{P_a(6D) - P_a(6H)}{4 \Delta m} \quad (3)
\]

\[
a_1^2 + 2a_2^2 = \frac{P_a(6D) - P_a(6H)}{2 \Delta m} \quad (4)
\]

\[
b_1^2 + 2b_2^2 = \frac{P_b(6D) - P_b(6H)}{2 \Delta m} + \frac{2 \mu_3}{\Delta m} t^2 \quad (5)
\]

where

\[
P_a = \frac{1}{2} (a + b + c)
\]

with cyclic permutation for \(P_b\) and \(P_c\).

Also in going from the normal to the 3 deuterated species (CD\(_3\) – X – CH\(_3\)) of the molecule the plane of the symmetry remains but the C\(_{2v}\) symmetry of the molecule is destroyed. Thus again one can show that

\[
I_c(3D3H) - I_c(6H) = \Delta m(b_1^2 + 2b_2^2) + \Delta m(a_1^2 + 2a_2^2) - \mu_3 t^2 - \mu_3(a_1 + 2a_2)^2 \quad (6)
\]

with

\[
\mu_3 = (\Delta m)^2 / (M + 3 \Delta m).
\]

Inserting Eqs. (3), (4) and (5) in Eq. (6) one gets

\[
|a_1 + 2a_2| = \left| \frac{P_b(6D) - P_b(6H)}{2 \mu_3} + \frac{2 \mu_6 t^2}{\mu_3} - t^2 \right| \quad (7)
\]

\[
+ \frac{P_a(6D) - P_a(6H)}{2 \mu_3} - \frac{I_c(3D3H) - I_c(6H)}{\mu_3} \right|^{1/2}.
\]

\(t\) in Eq. (2) can be calculated from the known \(b\)-coordinates of the X and C atoms and using the center of mass condition for the parent (CH\(_3\))\(_2\) – X molecule. The values of \(b_1\) and \(b_2\) can then be determined by solving Eq. (2) and (5) and of \(a_1\) and \(a_2\) by solving Eqs. (4) and (7)\(^*\).

\(^*\) As the solution involves a quadratic equation one gets two sets of values for \(b_1\) and \(b_2\), corresponding to which four sets of values for \(a_1\) and \(a_2\) are obtained. The correct set is chosen on the basis of plausibility and a comparison with the \(r_s\)-structure.

In order to check the validity of this method, we first tried it on dimethyl ether, where sufficient experimental data are available to evaluate the hydrogen coordinates from singly deuterated species data employing normal substitution method and also by the proposed method. We found general agreement (within experimental uncertainty) between the two sets of calculated coordinates.

The results of the calculation for dimethyl selenide are given in Table 2. Some checks can be made on these calculated \(r_s\)-coordinates. In the above calculations \(I_a(3D3H) - I_a(6H)\) and \(I_b(3D3H) - I_b(6H)\) have not been used, so they can be used as independent checks on the calculated structure. Also the experimental data for \((\text{CD}_3)_2^{13}\text{Se}\) and \((\text{CD}_3)_2^{75}\text{Se}\) are available and can be used as checks. For these the calculated \(\Delta I\)'s were found to differ at the worst by 0.008 amu \(\AA^2\) from the corresponding experimental data (Table 3). This shows the correctness of the determined structure. The reason for such a consistency could be that none of the atoms lied very near to any of the principle coordinate axis, making thereby the structure determination to be less contaminated by the zero point vibrational effects.

Table 2. The \(r_s\)-coordinates of dimethyl selenide in the principle axis system of \((\text{CH}_3)_2^{\text{Se}}\). Center of mass condition used for \(b\)-coordinates, see text.

<table>
<thead>
<tr>
<th>(a)</th>
<th>(b)</th>
<th>(c)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Se</td>
<td>0.0 (^*)</td>
<td>-0.3667</td>
</tr>
<tr>
<td>C</td>
<td>±1.4490</td>
<td>+0.9309</td>
</tr>
<tr>
<td>H(_s)</td>
<td>±2.3595</td>
<td>+0.3360</td>
</tr>
<tr>
<td>H(_a)</td>
<td>±1.3982</td>
<td>+1.5584</td>
</tr>
</tbody>
</table>

\(^*\) Assumed by symmetry.
Table 3. Comparison between calculated and observed changes in moments of inertia, which are not used in the structure determination of Table 2 and Table 4.

<table>
<thead>
<tr>
<th></th>
<th>Observed (amu Å²)</th>
<th>Calculated (amu Å²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$I_a[\text{CH}_3\text{SeCD}_3]$ - $I_a[\text{CH}_3\text{Se}]$</td>
<td>5.75035</td>
<td>5.75305</td>
</tr>
<tr>
<td>$I_b[\text{CH}_3\text{SeCD}_3]$ - $I_b[\text{CH}_3\text{Se}]$</td>
<td>11.6894</td>
<td>11.6840</td>
</tr>
<tr>
<td>$I_c[\text{CH}_3\text{SeCD}_3]$ - $I_c[\text{CH}_3\text{Se}]$</td>
<td>13.8719</td>
<td>13.8719</td>
</tr>
</tbody>
</table>

Table 4. Structural parameters derived from the $r_s$-coordinates of Table 2. Errors in brackets. Derived from the uncertainties of the rotational constants.

<table>
<thead>
<tr>
<th></th>
<th>$r(\text{Se} - \text{C})$</th>
<th>1.945 (0.4) Å</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$r(\text{C} - \text{H}_a)$</td>
<td>1.088 (13) Å</td>
</tr>
<tr>
<td></td>
<td>$r(\text{C} - \text{H}_b)$</td>
<td>1.096 (4) Å</td>
</tr>
<tr>
<td></td>
<td>$\angle \text{C} - \text{Se} - \text{C}$</td>
<td>96° 19' (5')</td>
</tr>
<tr>
<td></td>
<td>$\angle \text{Se} - \text{C} - \text{H}_a$</td>
<td>105° 0' (40')</td>
</tr>
<tr>
<td></td>
<td>$\angle \text{Se} - \text{C} - \text{H}_b$</td>
<td>110° 20' (15')</td>
</tr>
<tr>
<td></td>
<td>$\angle \text{H}_a - \text{C} - \text{H}_b$</td>
<td>109° 37' (30')</td>
</tr>
<tr>
<td></td>
<td>$2\angle 2 - \Theta$</td>
<td>101° 34' (1° 40')</td>
</tr>
<tr>
<td></td>
<td>angle of tilt</td>
<td>2° 38' (50')</td>
</tr>
</tbody>
</table>

Table 4 presents the structural parameters of the molecule as derived from the coordinates of Table 2. The interesting feature of the structure concerns the methyl group. First, the methyl groups are found to be somewhat asymmetric, the angles $\angle \text{H}_a - \text{C} - \text{H}_a$ and $\angle \text{H}_a - \text{C} - \text{H}_b$ differ by 44', which is more than twice the estimated uncertainty of 20' for the angles. (This estimated uncertainty allows the zero point contribution of 0.01 amu Å² to the $\Delta I$'s for replacement of H by D.) Secondly, the methyl groups do not have their symmetry axes coincident with the C–Se bond direction but are tilted by 2° 38', which makes the angle between the symmetry axes 5° 16' larger than the C–Se–C angle. This angle of tilt agrees both in magnitude and sign with the tilt angle of 1° 58' obtained by the analysis of the internal rotation splittings of the lines.

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