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# The Nearly Octahedral Hexamethylsulfur and Hexamethylselenium Molecules: Lighter Counterparts to the Recently Synthesized Hexamethyltellurium

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**Abstract:** Self-consistent-field molecular orbital theory has been applied to the hypervalent molecules hexamethylsulfur and hexamethylselenium. Using a double-$\zeta$ basis set augmented by d-like polarization functions on the central atom, one minimum of $D_3$ symmetry is predicted for each compound. It is noted that these minima are only slightly distorted from octahedral ligand coordination. Molecular geometries, vibrational frequencies, and infrared intensities are predicted. Comparisons are made between these predictions and the predictions from the same level of theory applied to the dimethylchalcogens. The results of a preliminary investigation of hexamethyltellurium are also included.

## Introduction

Until recently, peralkylated derivatives of hexavalent main-group elements were completely unknown. Hexamethyltungsten had been made as early as 1973,[1] and by 1975 hexamethylrhenium had also been synthesized.[2] Of course, perfluorinated species, such as $SF_6$, have long been known to exist. A peralkylated derivative of a hexavalent main-group element had never been synthesized until Ahmed and Morrison reported the synthesis of one such breakthrough compound.[3] Their synthesis of hexamethyltellurium, following soon after the synthesis of tetramethyltellurium by Gedridge et al.,[4] proved that there is at least one main-group element for which a hexavalent peralkylated derivative is possible. These molecules are interesting not only as novel new species, but also as possible methylating agents. Due to the large size of the tellurium atom, it seems reasonable to assume that peralkylated derivatives of this element would be the easiest to synthesize, but what of the lighter group 16 elements? For the purpose of stimulating further experimentation in this area, we report the results of a theoretical study of both hexamethylsulfur and hexamethylselenium and the initial results of a hexamethyltellurium study.

## Theoretical Procedures

The basis set for the carbon and hydrogen atoms for each of the hexamethylchalcogens was constructed from the Huzinaga-Dunning[5] double-$\zeta$ contraction of Gaussian functions and is designated DZ. The basis set for sulfur was comparably constructed, but to this DZ set was added a set of pure-angular momentum d-like functions with an orbital $\alpha$ exponent of 0.70. The basis set for selenium was contracted from the (14s11p5d) primitive set of Dunning[6] and was augmented by one set of pure-angular momentum d-like polarization functions with an orbital exponent of 0.315 as derived by Binning and Curtiss.[7] The Se contraction was made as per unpublished research by Grev, Fowler, and Schaefer.[8] The basis set for tellurium came from the *Handbook of Gaussian Basis Sets*, Table 52.1.1,[9] and will be referred to throughout this paper as dz, because it is estimated by the authors to be of approximately double-$\zeta$ quality. The basis sets used here are designated H(4s/2s), C(9s5p/4s2p), S(11s7p1d/6s4p1d), Se(14s11p6d/7s5p3d), and Te(15s11p6d/10s8p4d). The hydrogen s functions were scaled by a factor of 1.2.

Due to the presence of the 18 hydrogen atoms, true octahedral symmetry ($O_h$) is not possible for the hexamethylchalcogens. The geometries of all molecules were fully optimized within the constraints of $C_2$ symmetry using SCF analytic first derivatives.[10] Once stationary points were found, SCF analytic second derivatives[11] were used to evaluate harmonic vibrational frequencies and to determine the nature of the stationary points. In order to compare these molecules to simpler species, these same methods were applied to dimethylsulfur, dimethylselenium, and dimethyltellurium. This study was completed using the PSI program system.[12]

## Results and Discussion

For each of the hexamethylchalcogens a single minimum of $D_3$ symmetry was located, the constraining $C_2$ axis being one of the three equivalent $C_2$ symmetry axes of the $D_3$ group. The hexamethylsulfur minimum geometry is displayed in Figure 1. All three minimum structures are quite similar and are interesting in two aspects. The ligand coordination is of interest as is the comparison of the chalcogen–carbon bonds to "normal" chalcogen–carbon single bonds.

Ahmed and Morrison[3] conjectured that the ligand coordination would be essentially octahedral for hexamethyltellurium. This is nearly the case for both hexamethylsulfur and hexamethylselenium. For both of these molecules the bond lengths of the central chalcogen atom to the carbons are all equal to within 0.0001 Å. The only significant differences with respect to octahedral ligand coordination come in the C–S–C bond angles. In these angles, the largest deviations from the octahedral 90° prediction are the $C_5$–S–$C_6$ angle (87.4°) and the $C_3$–S–$C_4$ angle (93.7°). These discrepancies are slightly less in the selenium case: 87.6° for $C_5$–Se–$C_6$ and 93.2° for $C_3$–S–$C_4$. The methyl groups themselves are also nearly symmetrical. The C–H bond lengths have a range of 1.080 to 1.082 Å in the hexamethylsulfur

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[12] Distributed by PSITECH Inc., Watkinsville, Ga.

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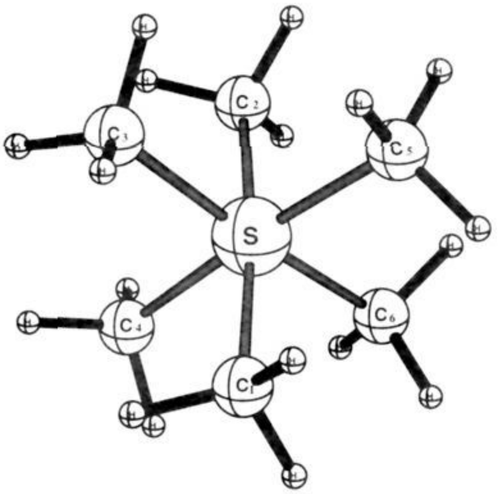

**Figure 1.** Hexamethylsulfur

case, and in hexamethylselenium they are all within 0.0005 Å of 1.083 Å. The S–C–H angles, too, show little variance, the smallest being 108.3° and the largest 111.3°. The Se–C–H angles vary from 108.1° to 110.7°.

All these results point clearly toward octahedral ligand coordination hindered by steric effects. The best evidence for the steric argument is that in the hexamethylselenium case, all departures from the "octahedral" model are less than in the hexamethylsulfur case. As is expected from the atomic radii, the bond lengths between the central chalcogen atom and the carbons are significantly larger in the hexamethylselenium molecule. The S–C bond lengths are 1.916 Å and the Se–C bond lengths are 2.029 Å—a difference of 0.113 Å. This distancing of the methyl groups allows more space for the congested hydrogens and thus the steric effects are less pronounced.

As to the comparison with "normal" S–C and Se–C single bonds, again we find that moving down the periodic table lessens the differences. The bonds that we shall refer to as "normal" are those predicted by the same level of theory as used on hexamethylsulfur and hexamethylselenium, but applied to the dimethyl compounds. At this level of theory, the agreement with experiment for $S(CH_3)_2$ and $Se(CH_3)_2$ is quite good, the largest differences being in the carbon–chalcogen–carbon bond angles (see Table I). The dimethylsulfur S–C bond length is 1.806 Å, 0.110 Å shorter than the 1.916 Å predicted for the S–C bonds of hexamethylsulfur. Hexamethylselenium has a Se–C bond length of 2.029 Å, which is only 0.075 Å longer than the predicted dimethylselenium Se–C bond length of 1.954 Å.

Harmonic vibrational frequencies and infrared intensities for hexamethylsulfur and hexamethylselenium are seen in Tables III–VI. The comparison of vibrational frequencies is a bit more complicated because of the fact that the dimethylsulfur and dimethylselenium have only two S–C stretches and one C–S–C bend—much simpler than the six stretches and nine bends of the hexamethyl systems. The S–C stretching frequencies of dimethylsulfur are ($a_1$) 745 cm$^{-1}$ and ($b_2$) 806 cm$^{-1}$. The hexamethylsulfur S–C stretching frequencies are (e) 595 cm$^{-1}$, ($a_2$) 590 cm$^{-1}$, ($a_1$) 572 cm$^{-1}$, and (e) 457 cm$^{-1}$. For dimethylselenium the ($a_1$) stretching mode has a frequency of 639 cm$^{-1}$ and the ($b_2$) mode 660 cm$^{-1}$. The Se–C stretching frequencies of hexamethylselenium are ($a_1$) 564 cm$^{-1}$, (e) 555 cm$^{-1}$, ($a_2$) 553 cm$^{-1}$, and (e) 483 cm$^{-1}$. Again, we note that the frequency reductions are smaller for selenium, the difference of averages being −231 cm$^{-1}$ for the sulfur compounds and −118 cm$^{-1}$ in the case of selenium. The lower vibrational frequencies for the hexacoordinate molecules imply that their chalcogen–carbon bonds are significantly weaker.

**Table I.** Comparison of Theory and Experiment for Dimethylchalcogens

Structural Parameters for Dimethylsulfur

| | DZ+d(S)/SCF | expt[a] |
|---|---|---|
| $r$(CS), Å | 1.806 | 1.802 |
| $r(\mathrm{CH_a})$, Å | 1.082 | 1.090 |
| $r(\mathrm{CH_s})$, Å | 1.082 | 1.090 |
| Θ(CSC), deg | 100.2 | 98.8 |
| $\Theta(\mathrm{SCH_a})$, deg | 111.4 | 110.8 |
| $\Theta(\mathrm{SCH_s})$, deg | 107.8 | 106.7 |

Structural Parameters for Dimethylselenium

| | DZ+d(Se)/SCF | expt[b] |
|---|---|---|
| $r$(CSe), Å | 1.954 | 1.943 |
| $r(\mathrm{CH_a})$, Å | 1.081 | 1.093 |
| $r(\mathrm{CH_s})$, Å | 1.082 | 1.093 |
| Θ(CSeC), deg | 97.5 | 96.2 |
| $\Theta(\mathrm{SeCH_a})$, deg | 110.4 | 109.6 |
| $\Theta(\mathrm{SeCH_s})$, deg | 107.5 | 106.7 |

Structural Parameters for Dimethyltellurium

| | dz/SCF | expt[c] |
|---|---|---|
| $r$(CTe), Å | 2.168 | 2.142 |
| $r(\mathrm{CH_a})$, Å | 1.080 | 1.07 |
| $r(\mathrm{CH_s})$, Å | 1.081 | *d* |
| Θ(CTeC), deg | 95.4 | 94 |
| $\Theta(\mathrm{TeCH_a})$, deg | 110.4 | 112 |
| $\Theta(\mathrm{TeCH_s})$, deg | 108.1 | *d* |

[a] Hayashi, M.; Nakata, N.; Miyazaki, S. *J. Mol. Spectrosc.* **1989**, *135*, 270. [b] Beecher, J. F. *J. Mol. Spectrosc.* **1966**, *21*, 414. [c] Blom, R.; Haaland, A.; Seip, R. *Acta Chem. Scand., Ser. A* **1983**, *A37* (7), 595. [d] Assumed $C_{3v}$ symmetry of methyls.

**Table II.** Structural Parameters for Hexamethylchalcogens

Structural Parameters for Hexamethylsulfur

| | DZ+d(S)/SCF | | DZ+d(S)/SCF |
|---|---|---|---|
| $r$(SC), Å | 1.916 | $r(\mathrm{C_1H_3})$, Å | 1.082 |
| $r(\mathrm{C_1H_1})$, Å | 1.081 | $r(\mathrm{C_1H_5})$, Å | 1.080 |
| $\Theta(\mathrm{SC_1H_1})$, deg | 110.7 | $\Theta(\mathrm{C_1SC_3})$, deg | 89.6 |
| $\Theta(\mathrm{SC_1H_3})$, deg | 108.3 | $\Theta(\mathrm{C_1SC_4})$, deg | 87.4 |
| $\Theta(\mathrm{SC_1H_5})$, deg | 111.3 | $\Theta(\mathrm{C_1SC_6})$, deg | 93.7 |

Structural Parameters for Hexamethylselenium

| | DZ+d(Se)/SCF | | DZ+d(Se)/SCF |
|---|---|---|---|
| $r$(SeC), Å | 2.029 | $r(\mathrm{C_1H_3})$, Å | 1.083 |
| $r(\mathrm{C_1H_1})$, Å | 1.083 | $r(\mathrm{C_1H_5})$, Å | 1.083 |
| $\Theta(\mathrm{SeC_1H_1})$, deg | 110.2 | $\Theta(\mathrm{C_1SeC_3})$, deg | 89.7 |
| $\Theta(\mathrm{SeC_1H_3})$, deg | 108.1 | $\Theta(\mathrm{C_1SeC_4})$, deg | 87.6 |
| $\Theta(\mathrm{SeC_1H_5})$, deg | 110.7 | $\Theta(\mathrm{C_1SeC_6})$, deg | 93.2 |

Structural Parameters for Hexamethyltellurium

| | dz/SCF | | dz/SCF |
|---|---|---|---|
| $r$(TeC), Å | 2.203 | $r(\mathrm{C_1H_3})$, Å | 1.083 |
| $r(\mathrm{C_1H_1})$, Å | 1.083 | $r(\mathrm{C_1H_5})$, Å | 1.082 |
| $\Theta(\mathrm{TeC_1H_1})$, deg | 110.1 | $\Theta(\mathrm{C_1TeC_3})$, deg | 89.7 |
| $\Theta(\mathrm{TeC_1H_3})$, deg | 108.6 | $\Theta(\mathrm{C_1TeC_4})$, deg | 88.0 |
| $\Theta(\mathrm{TeC_1H_5})$, deg | 110.6 | $\Theta(\mathrm{C_1TeC_6})$, deg | 92.7 |

For hexamethylsulfur and hexamethylselenium the bending degrees of freedom are significantly hindered compared to those of dimethylsulfur and dimethylselenium. The single dimethylsulfur bending mode has a frequency of 293 cm$^{-1}$. The nine hexamethylsulfur modes range from 338 to 490 cm$^{-1}$, with an average difference from the dimethylsulfur frequency of +142 cm$^{-1}$. The dimethylselenium bending frequency is located at 223 cm$^{-1}$ while the nine hexamethylselenium modes range from 279 to 399 cm$^{-1}$, the average difference in this case being +110 cm$^{-1}$. These data follow the same trend—the differences between the dimethyl and hexamethyl molecules become smaller as one goes from sulfur to selenium.

Other data supporting the near octahedral coordination are the near degeneracies of the frequencies of the vibrations

**Table III.** Vibrational Frequencies (in $cm^{-1}$) and Infrared Intensities (in km/mol) for $S(CH_3)_6$ Which Involve Sulfur–Carbon Stretching and Carbon–Sulfur–Carbon Bending[a]

| sulfur–carbon vibrations | $\omega$ | $I$ |
|---|---|---|
| e ($t_{1u}$-like stretching) | 595.1 | 126.9 |
| $a_2$ ($t_{1u}$-like stretching) | 589.6 | 123.6 |
| $a_1$ ($a_{1g}$-like stretching) | 572.0 | 0.0 |
| $a_1$ ($t_{2g}$-like deformation) | 490.4 | 0.0 |
| e ($t_{1u}$-like deformation) | 489.4 | 1.11 |
| $a_2$ ($t_{1u}$-like deformation) | 481.6 | 2.42 |
| e ($e_g$-like stretching) | 456.8 | 0.630 |
| e ($t_{2g}$-like deformation) | 447.8 | 0.477 |
| e ($t_{2u}$-like deformation) | 366.4 | 0.004 |
| $a_1$ ($t_{2u}$-like deformation) | 338.2 | 0.0 |

[a] Symmetry labelings as per the hypothetical $O_h$ coordination are given in parentheses.

**Table IV.** Vibrational Frequencies (in $cm^{-1}$) and Infrared Intensities (in km/mol) Associated with the Methyl Groups of $S(CH_3)_6$

| | | $\omega$ | $I$ |
|---|---|---|---|
| C–H stretching | $a_1$ | 3342.6 | 0.0 |
| | e | 3339.2 | 48.0 |
| | $a_2$ | 3328.9 | 125.2 |
| | e | 3324.8 | 35.3 |
| | e | 3319.2 | 47.4 |
| | $a_1$ | 3314.6 | 0.0 |
| | e | 3310.3 | 0.006 |
| | $a_2$ | 3310.1 | 6.97 |
| | $a_1$ | 3232.5 | 0.0 |
| | e | 3219.7 | 49.9 |
| | $a_2$ | 3216.4 | 57.4 |
| | e | 3212.1 | 4.43 |
| methyl deformation | e | 1653.6 | 4.90 |
| | $a_2$ | 1647.1 | 0.332 |
| | $a_1$ | 1646.9 | 0.0 |
| | e | 1640.3 | 2.87 |
| | e | 1628.0 | 9.00 |
| | $a_1$ | 1624.5 | 0.0 |
| | e | 1617.5 | 0.385 |
| | $a_2$ | 1612.5 | 15.7 |
| methyl umbrella | $a_1$ | 1520.2 | 0.0 |
| | e | 1493.2 | 33.7 |
| | $a_2$ | 1486.1 | 32.8 |
| | e | 1460.2 | 1.33 |
| methyl rocking | e | 1146.0 | 139.1 |
| | $a_2$ | 1131.8 | 149.7 |
| | $a_1$ | 1111.6 | 0.0 |
| | e | 1106.9 | 2.24 |
| | e | 1026.9 | 0.030 |
| | $a_1$ | 1024.8 | 0.0 |
| | $a_2$ | 921.6 | 0.033 |
| | e | 914.2 | 0.004 |
| methyl rotation | $a_2$ | 302.6 | 0.079 |
| | $a_1$ | 241.0 | 0.0 |
| | e | 200.5 | 0.001 |
| | e | 139.7 | 0.048 |

**Table V.** Vibrational Frequencies (in $cm^{-1}$) and Infrared Intensities (in km/mol) for $Se(CH_3)_6$ Which Involve Selenium–Carbon Stretching and Carbon–Selenium–Carbon Bending[a]

| selenium–carbon vibrations | $\omega$ | $I$ |
|---|---|---|
| $a_1$ ($a_{1g}$-like stretching) | 563.5 | 0.0 |
| e ($t_{1u}$-like stretching) | 554.9 | 77.4 |
| $a_2$ ($t_{1u}$-like stretching) | 553.1 | 77.0 |
| e ($e_g$-like stretching) | 482.8 | 0.012 |
| $a_1$ ($t_{2g}$-like deformation) | 398.9 | 0.0 |
| e ($t_{2g}$-like deformation) | 379.7 | 4.57 |
| $a_2$ ($t_{1u}$-like deformation) | 357.3 | 19.28 |
| e ($t_{1u}$-like deformation) | 349.9 | 14.8 |
| e ($t_{2u}$-like deformation) | 296.7 | 0.199 |
| $a_1$ ($t_{2u}$-like deformation) | 278.5 | 0.0 |

[a] Symmetry labelings as per the hypothetical $O_h$ coordination are given in parentheses.

**Table VI.** Vibrational Frequencies (in $cm^{-1}$) and Infrared Intensities (in km/mol) Associated with the Methyl Groups of $Se(CH_3)_6$

| | | $\omega$ | $I$ |
|---|---|---|---|
| C–H stretching | $a_1$ | 3325.6 | 0.0 |
| | e | 3322.8 | 40.7 |
| | $a_2$ | 3314.8 | 117.6 |
| | e | 3312.6 | 35.6 |
| | e | 3308.2 | 47.9 |
| | $a_1$ | 3304.4 | 0.0 |
| | e | 3301.5 | 0.031 |
| | $a_2$ | 3301.3 | 6.60 |
| | $a_1$ | 3213.2 | 0.0 |
| | e | 3203.4 | 57.6 |
| | $a_2$ | 3201.2 | 64.5 |
| | e | 3198.1 | 3.17 |
| methyl deformation | e | 1638.0 | 5.31 |
| | $a_2$ | 1635.9 | 0.239 |
| | $a_1$ | 1632.5 | 0.0 |
| | e | 1627.7 | 2.91 |
| | e | 1619.9 | 9.03 |
| | $a_1$ | 1617.6 | 0.0 |
| | e | 1611.2 | 0.277 |
| | $a_2$ | 1606.0 | 15.2 |
| methyl umbrella | $a_1$ | 1469.3 | 0.0 |
| | e | 1447.2 | 33.4 |
| | $a_2$ | 1441.8 | 33.8 |
| | e | 1422.1 | 1.17 |
| methyl rock | $a_1$ | 1034.8 | 0.0 |
| | e | 1033.8 | 8.94 |
| | e | 1020.5 | 96.0 |
| | $a_2$ | 1008.1 | 108.8 |
| | e | 949.3 | 0.003 |
| | $a_1$ | 946.1 | 0.0 |
| | $a_2$ | 848.6 | 0.132 |
| | e | 842.4 | 0.027 |
| methyl rotation | $a_2$ | 233.0 | 0.146 |
| | $a_1$ | 186.9 | 0.0 |
| | e | 150.4 | 0.0 |
| | e | 108.1 | 0.002 |

associated with the motions of the carbons with respect to each other and to the central atom. Again, as has been the case with all other data, the selenium derivative is shown to be closer to the hypothetical octahedral ligand coordination. Octahedrally coordinated compounds, such as $SF_6$, have $a_{1g}$, doubly degenerate $e_g$, and triply degenerate $t_{1u}$ stretching modes, and triply degenerate $t_{1u}$, $t_{2g}$, and $t_{2u}$ deformation modes. Tables III and V show the frequencies of the sulfur–carbon vibrations and the selenium–carbon vibrations, respectively. Also given parenthetically in these tables are the symmetries of the vibrations as if the molecules were truly octahedrally coordinated. In the case of hexamethylsulfur, there are discrepancies of 5.5 $cm^{-1}$ in the $t_{1u}$-like stretchings, 42.6 $cm^{-1}$ in the $t_{2g}$-like deformations, 7.8 $cm^{-1}$ in the $t_{1u}$-like deformations, and 28.2 $cm^{-1}$ in the $t_{2u}$-like deformations. These differences are reduced in the hexamethylselenium case to 1.8, 19.2, 7.4, and 18.2 $cm^{-1}$ (same order as above). The average size of this variance from degeneracy is 21.0 $cm^{-1}$ for $S(CH_3)_6$ and 11.7 $cm^{-1}$ for $Se(CH_3)_6$. These results, too, reveal the approximate octahedral coordination of both species and the tendency for the selenium derivative to be closer to octahedral coordination than its sulfur counterpart.

The preliminary results of the hexamethyltellurium study follow the same trends as the hexamethylsulfur and hexamethylselenium results. The tellurium–carbon bond length is predicted at this level to be 0.174 Å larger than that of the selenium–carbon bond, and this greatly reduces steric hindrance. C–Te–C angle discrepancies are reduced to 4.7° and those of the Te–C–H angles to 2.0°. The dimethyltellurium Te–C bond is predicted to be only 0.035 Å shorter than the hexamethyltellurium Te–C bond. The average of the stretching frequencies of hexamethyltellurium is 57.6 $cm^{-1}$ lower than the average of the two stretching frequencies of dimethyltellurium, and the average of the C–Te–C bending frequencies of hexamethyltellurium is 64.1 $cm^{-1}$ greater than the predicted C–Te–C bending frequency of dimethyltel-

Table VII. Vibrational Frequencies (in cm$^{-1}$) and Infrared Intensities (in km/mol) for $Te(CH_3)_6$ Which Involve Tellurium–Carbon Stretching and Carbon–Tellurium–Carbon Bending[a]

| tellurium–carbon vibrations | $\omega$ | $I$ |
|---|---|---|
| $a_1$ ($a_{1g}$-like stretching) | 524.1 | 0.0 |
| e ($t_{1u}$-like stretching) | 517.1 | 57.43 |
| $a_2$ ($t_{1u}$-like stretching) | 516.8 | 58.85 |
| e ($e_g$-like stretching) | 472.8 | 0.01 |
| $a_1$ ($t_{2g}$-like deformation) | 289.4 | 0.0 |
| e ($t_{2g}$-like deformation) | 280.2 | 4.04 |
| $a_2$ ($t_{1u}$-like deformation) | 256.2 | 24.03 |
| e ($t_{1u}$-like deformation) | 253.3 | 21.42 |
| e ($t_{2u}$-like deformation) | 214.0 | 0.22 |
| $a_1$ ($t_{2u}$-like deformation) | 204.9 | 0.0 |

[a] Symmetry labelings as per the hypothetical $O_h$ coordination are given in parentheses.

Table VIII. Vibrational Frequencies (in cm$^{-1}$) and Infrared Intensities (in km/mol) Associated with the Methyl Groups of $Te(CH_3)_6$

| | | $\omega$ | $I$ |
|---|---|---|---|
| C–H stretching | $a_1$ | 3325.7 | 0.0 |
| | e | 3324.6 | 30.4 |
| | $a_1$ | 3319.8 | 75.5 |
| | e | 3316.6 | 14.1 |
| | e | 3315.2 | 46.8 |
| | e | 3312.5 | 0.223 |
| | $a_1$ | 3312.3 | 0.0 |
| | $a_2$ | 3311.3 | 10.2 |
| | $a_1$ | 3209.4 | 0.0 |
| | e | 3202.7 | 76.7 |
| | $a_2$ | 3201.6 | 82.2 |
| | e | 3200.0 | 1.55 |
| methyl deformation | $a_2$ | 1610.1 | 0.282 |
| | e | 1610.1 | 6.86 |
| | $a_1$ | 1605.6 | 0.0 |
| | e | 1601.8 | 5.47 |
| | e | 1599.1 | 2.95 |
| | $a_1$ | 1596.4 | 0.0 |
| | e | 1590.6 | 0.256 |
| | $a_2$ | 1583.9 | 11.7 |
| methyl umbrella | $a_1$ | 1454.4 | 0.0 |
| | e | 1428.4 | 42.8 |
| | $a_2$ | 1426.5 | 44.6 |
| | e | 1408.8 | 0.680 |
| methyl rock | e | 993.3 | 5.63 |
| | $a_1$ | 987.9 | 0.0 |
| | e | 973.8 | 145.2 |
| | $a_2$ | 959.7 | 152.2 |
| | $a_1$ | 903.8 | 0.0 |
| | e | 901.6 | 0.293 |
| | $a_2$ | 824.4 | 0.147 |
| | e | 820.8 | 0.030 |
| methyl rotation | $a_2$ | 155.2 | 0.412 |
| | $a_1$ | 130.1 | 0.0 |
| | e | 97.4 | 0.015 |
| | e | 66.9 | 0.010 |

Table IX. Atomic Coordinates (in bohr)[a]

Atomic Coordinates for Hexamethylsulfur

| | $X$ | $Y$ | $Z$ |
|---|---|---|---|
| S | 0.00000 | 0.00000 | 0.00019 |
| $C_1$ | 3.61521 | 0.12504 | 0.14112 |
| $C_3$ | –0.16024 | 2.63524 | 2.47690 |
| $C_5$ | 0.04302 | 2.50028 | –2.61745 |
| $H_1$ | 4.31188 | 1.85525 | –0.69292 |
| $H_3$ | 4.18424 | 0.07103 | 2.10340 |
| $H_5$ | 4.45199 | –1.46914 | –0.82194 |
| $H_7$ | 1.60989 | 3.65185 | 2.56667 |
| $H_9$ | 1.39793 | 1.92370 | –4.03484 |
| $H_{11}$ | –1.63555 | 3.94073 | 1.93202 |
| $H_{13}$ | 0.61021 | 4.31657 | –1.87317 |
| $H_{15}$ | –0.60186 | 1.89128 | 4.32631 |
| $H_{17}$ | –1.78763 | 2.67972 | –3.50379 |

Atomic Coordinates for Hexamethylselenium

| | $X$ | $Y$ | $Z$ |
|---|---|---|---|
| Se | 0.00000 | 0.00000 | 0.01649 |
| $C_1$ | 3.83076 | 0.11899 | 0.15044 |
| $C_3$ | –0.15639 | 2.78249 | 2.65090 |
| $C_5$ | 0.03654 | 2.65361 | –2.75188 |
| $H_1$ | 4.51319 | 1.84516 | –0.71186 |
| $H_3$ | 4.39851 | 0.07767 | 2.11691 |
| $H_5$ | 4.63717 | –1.49521 | –0.81331 |
| $H_7$ | 1.63520 | 3.76772 | 2.74309 |
| $H_9$ | 1.40292 | 2.07879 | –4.16384 |
| $H_{11}$ | –1.62222 | 4.09964 | 2.09640 |
| $H_{13}$ | 0.58619 | 4.46848 | –1.98177 |
| $H_{15}$ | –0.61073 | 2.01050 | 4.49002 |
| $H_{17}$ | –1.80584 | 2.80886 | –3.62725 |

Atomic Coordinates for Hexamethyltellurium

| | $X$ | $Y$ | $Z$ |
|---|---|---|---|
| Te | 0.00000 | 0.00000 | 0.01649 |
| $C_1$ | 4.15874 | 0.12857 | 0.13864 |
| $C_3$ | –0.15344 | 3.00920 | 2.88838 |
| $C_5$ | 0.02249 | 2.89168 | –2.97756 |
| $H_1$ | 4.83358 | 1.84962 | –0.73821 |
| $H_3$ | 4.75600 | 0.09669 | 2.09539 |
| $H_5$ | 4.95620 | –1.48648 | –0.82966 |
| $H_7$ | 1.64535 | 3.97943 | 2.98484 |
| $H_9$ | 1.38731 | 2.34704 | –4.40137 |
| $H_{11}$ | –1.60683 | 4.34719 | 2.35545 |
| $H_{13}$ | 0.55840 | 4.70553 | –2.19717 |
| $H_{15}$ | –0.60476 | 2.22836 | 4.72374 |
| $H_{17}$ | –1.82342 | 3.04246 | –3.84461 |

[a] Given are the symmetry unique atoms if only $C_2$ symmetry is assumed. The $z$ axis is one of the three $C_2$ axes of the $D_3$ group.

lurium. The splittings of the frequencies which would be triply degenerate in the octahedral case are as follows: $t_{1u}$-like stretching, 0.3 cm$^{-1}$; $t_{2g}$-like deformation, 9.2 cm$^{-1}$; $t_{1u}$-like deformation, 2.9 cm$^{-1}$; and $t_{2u}$-like deformation, 9.1 cm$^{-1}$.

## Conclusions

It should come as no surprise that peralkylated derivatives of hexavalent elements are sterically strained. All the data are consistent with a sterically strained system: the increase in chalcogen–carbon bond length, due not only to weaker bonds, but also to overcrowding; the lowering of the stretching vibrational frequencies, again due to weaker bonds and also to the fact that an increase in bond length will help reduce the crowding problem; and the increased bending frequencies, as changing any C–S–C angle will move some methyl groups closer to others. Even the deviations from octahedral ligand coordination can be explained in terms of steric factors. The methyl groups must rotate and distort slightly from octahedral coordination in order to achieve the best possible packing. Neither should it be shocking that moving down the periodic table lessens the dissimilarity between the dimethyl and hexamethyl compounds, as the best way to relieve steric stress is to increase the size of the central atom. All these factors imply that indeed hexamethyltellurium should be the most stable of the three molecules hexamethyltellurium, hexamethylselenium, and hexamethylsulfur and that hexamethylselenium should be more stable than hexamethylsulfur. The present theoretical predictions do not, however, imply that the synthesis of either hexamethylselenium or hexamethylsulfur is impossible.

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