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Articles

The S_6 Point Group Conformers of the Hexamethylchalcogens: Me_6S, Me_6Se, Me_6Te

Joseph E. Fowler and Henry F. Schaefer III*

Center for Computational Quantum Chemistry, University of Georgia, Athens, Georgia 30602

Kenneth N. Raymond*

Department of Chemistry, University of California, Berkeley, California 94720

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The synthesis of Me_6Te in 1990 stimulated the exploration of hexamethylchalcogen potential energy surfaces. This earlier *ab initio* work focused only on the D_3 conformers, but it has been noted that the pseudooctahedral $X(CH_3)_6$ compounds show either D_3 or S_6 symmetry. Here are reported the results of an *ab initio* molecular orbital study of the hexamethylchalcogens confined to S_6 symmetry. Stationary points were found for each of the three hexamethylchalcogens studied and were shown to be minima for the two larger hexamethylchalcogens. Each of the S_6 stationary points found was energetically higher lying than the earlier reported D_3 counterpart. These energy differences are discussed in terms of nuclear repulsion and molecular orbital bonding considerations.

Following soon after the isolation and characterization of Me_4Te[1] and Me_6Te[2] came the publication of an *ab initio* study of the series of hexamethylchalcogens, Me_6S, Me_6Se, and Me_6Te[3] (a study of the tetramethylchalcogens was recently completed[4]). This *ab initio* study found a stationary point on the potential energy surface of each hexamethylchalcogen that corresponded to a minimum of D_3 symmetry with slight deviations from octahedral ligand coordination decreasing with the larger chalcogens. Not long after this article appeared, it occurred to one of us that a conformation of S_6 symmetry might lie lower in energy than the D_3 structure. Indeed the S_6 point group had been completely overlooked by the original investigators as it so seldomly appears in the publications and conversations of chemistry. We report here for each of the three studied hexamethylchalcogens the location of a stationary point belonging to the S_6 point group. Except for the S_6 symmetry constraint in this case, the methods used in this study were exactly those used in the earlier work (simply, a double-ζ basis set for each atom augmented by a set of d functions on sulfur and selenium was used at the self-consistent field level of theory).[3]

For an “octahedral” $X(CH_3)_6$ molecule or ion, the full O_h symmetry is lowered by the local 3-fold symmetry of the CH_3 substituent. The highest symmetry possible for such a species is D_{3d}, but this subgroup requires a geometry that eclipses hydrogen atoms on adjacent groups. Relaxation of this very short H···H interaction by rotation of the CH_3 unit around the X−C bond involves a kind of gearing of all the CH_3 units. This can be done while either the 2-fold axis or the inversion symmetry of the parent D_{3d} point group is maintained. In the first case, D_3 is the resultant symmetry. The second case gives the less common molecular point group S_6. A search of the structural data base for species conforming to the $X(CH_3)_6$ structural unit (for either CH_3 or NH_3) shows that only homoleptic ammine cationic complexes and methyl anionic complexes appear to have been reported.

Among cations, $[Cr(NH_3)_6]^{3+}$ was found in 1968 to be present with crystallographic and molecular S_6 symmetry in the pentachlorocuprate salt.[5] In that early paper appears an explicit discussion of the lowering of the octahedral symmetry into the S_6 point symmetry, with concomitant maintenance of the inversion center. In general, this symmetry is found for all of the ammine cations. For the corresponding $[Co(NH_3)_6]^{3+}$ cation,[6] a careful analysis of the hydrogen bonding in the structure and complete location of all hydrogen atoms in one typical salt[6a] show that the cation has essentially S_6 symmetry, even though no crystallographic symmetry is required in that case. In other cases, crystallographic site symmetry does require S_6 symmetry, as is also found in one case of the corresponding $[Ni(NH_3)_6]^{2+}$ cation.[7]

For the relatively small manganese(IV) ion in the methyl complex $[Mn(CH_3)_6]^{2-}$, the crystallographic site symmetry has inversion symmetry, with the anion having essentially S_6 point symmetry.[8] In contrast, the somewhat larger chromium(III) complex $[Cr(CH_3)_6]^{3-}$ lies on a crystallographic D_3 point symmetry position[9] in its $Li(TMED)_2$ salt, as do the isostructural iridium(III) and rhodium(III) anions.[10] The unusual zirconium

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Table 1. Vibrational Frequencies (cm^{-1}) and Infrared Intensities (km/mol) for the S_6 Symmetry Conformation of $S(CH_3)_6$ Which Involve Sulfur−Carbon Stretching and Carbon−Sulfur Bending

S−C vib	ω	I	S−C vib	ω	I
a_u S−C str	590	126	a_u C−S−C bend	488	3
e_u S−C str	586	248	e_g C−S−C bend	476	0
a_g S−C str	570	0	e_g S−C str	442	0
a_g C−S−C bend	510	0	e_u C−S−C bend	366	0
e_u C−S−C bend	491	2	a_u C−S−C bend	360	1

Table 2. Vibrational Frequencies (cm^{-1}) and Infrared Intensities (km/mol) for the S_6 Symmetry Conformer of $Se(CH_3)_6$ Which Involve Selenium−Carbon Stretching and Carbon−Selenium−Carbon Bending

S−C vib	ω	I	S−C vib	ω	I
a_g Se−C str	563	0	e_g C−Se−C bend	380	0
a_u Se−C str	554	78	e_u C−Se−C bend	365	39
e_u Se−C str	551	151	a_u C−Se−C bend	362	20
e_g Se−C str	481	0	e_u C−Se−C bend	297	1
a_g C−Se−C bend	415	0	a_u C−Se−C bend	294	0

Table 3. Vibrational Frequencies (cm^{-1}) and Infrared Intensities (km/mol) for the S_6 Symmetry Conformer of $Te(CH_3)_6$ Which Involve Telurium−Carbon Stretching and Carbon−Telurium−Carbon Bending

Te−C vib	ω	I	Te−C vib	ω	I
a_g Te−C str	524	0	e_g C−Te−C bend	280	0
a_u Te−C str	515	58	e_u C−Te−C bend	263	49
e_u Te−C str	515	113	a_u C−Te−C bend	259	24
e_g Te−C str	472	0	e_u C−Te−C bend	216	2
a_g C−Te−C bend	301	0	a_u C−Te−C bend	213	0

Table 4. Vibrational Frequencies (cm^{-1}) Associated with the Methyl Group Rotations of the Hexamethylchalcogens

	mode	ω
$S(CH_3)_6$	a_g	204
	a_u	190
	e_g	78
	e_u	31i
$Se(CH_3)_6$	a_g	162
	a_u	160
	e_g	69
	e_u	15
$Te(CH_3)_6$	a_g	123
	a_u	109
	e_g	49
	e_u	19

complex $[Zr(CH_3)_6]^{2-}$ cannot be compared with the others because it has a trigonal prismatic geometry around the metal center.[11]

In short, both D_3 and S_6 symmetries are found for these pseudooctahedral molecular species. In general, the smaller central ions seem to favor S_6 symmetry for these species as found in solid state structures of their salts.

With this experimental background in mind, we turn to the present *ab initio* quantum mechanical results. Vibrational frequency analyses of the stationary points reveal that while both the Me_6Se and Me_6Te potential energy surfaces have a minimum of S_6 symmetry, no genuine minimum in the S_6 point group exists for the Me_6S molecule at this level of theory. Tables 1−4 list the most interesting harmonic vibrational frequencies and their intensities. In the case of Me_6S, a doubly degenerate E_u vibrational frequency corresponding to methyl rotation was found to be imaginary. This same mode was of very low frequency in the heavier hexamethylchalcogens (Me_6Se, 15 cm^{-1}; Me_6Te, 19 cm^{-1}) but does show these stationary points to be minima. The frequency of the doubly degenerate E_g mode of methyl rotation is also quite low in each of the S_6 conformers, but is in all cases positive (Me_6S, 78 cm^{-1}; Me_6Se, 69 cm^{-1}; Me_6Te, 49 cm^{-1}).

Table 5. Structural Parameters for the Hexamethylchalcogen Stationary Points in S_6 Symmetry[a]

param	Me_6S	Me_6Se	Me_6Te
r(XC), Å	1.921	2.032	2.204
$\theta(C_1XC_3)$, deg	89.1	89.3	89.4
$\theta(C_1XC_4)$, deg	90.9	90.7	90.6
$\theta(XC_1H_8)$, deg	109.5	109.0	109.2
$\theta(XC_1H_{14})$, deg	110.0	109.5	109.6
$\theta(XC_1H_{20})$, deg	111.1	110.6	110.4
$\tau(C_3XC_1H_8)$, deg	−137.0	−136.8	−136.6
$\tau(C_3XC_1H_{14})$, deg	−17.9	−17.6	−17.2
$\tau(C_3XC_1H_{20})$, deg	102.7	103.0	103.2

[a] All C−H bond lengths are within 0.001 Å of 1.081 Å, and all H−C−H angles are within 0.5° of 108.5°.

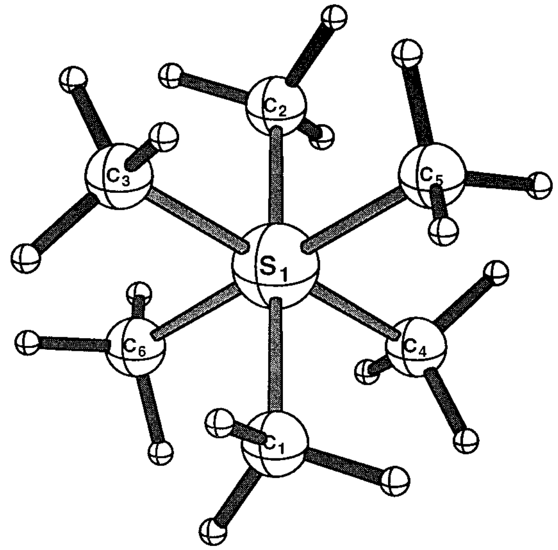

Figure 1. Hexamethylsulfur in S_6 symmetry.

Table 6. Total Energies (hartrees) for Each of the Stationary Points, Relative Energies (kcal/mol), and ZPVE Corrections in Parentheses (kcal/mol)

	Me_6S	Me_6Se	Me_6Te
D_3 stationary point	−634.823 01	−2637.029 87	−6810.336 98
S_6 stationary point	−634.818 97	−2637.027 65	−6810.336 16
rel energy (D_3 = 0.0)	2.53 (−0.73)	1.39 (−0.46)	0.51 (−0.27)

The structural parameters for the S_6 stationary points are given in Table 5. The X−C bond lengths are all a bit longer in the S_6 conformer than the X−C bond lengths of the earlier studied D_3 structures. The S_6 S−C bond is 0.005 Å longer than the S−C bond in the D_3 conformer. This difference is reduced to 0.003 Å in the case of Me_6Se and 0.001 Å in the Me_6Te case. Note that octahedral ligand coordination is not ensured by the S_6 symmetry constraint but the deviation from this coordination is very small. The difference between the bond angles $\theta(C_1XC_3)$ and $\theta(C_1XC_4)$ is only 1.8° in the Me_6S case and shrinks to 1.2° in the case of Me_6Te. Thus, the deviation from octahedral coordination is even less in the S_6 case than it was for the D_3 conformer, where the greatest angle discrepancy was 6.3° for Me_6S and 4.7° for Me_6Te.

Total and relative energies can be found in Table 6. The D_3 minimum is in each case found to be slightly lower (0.5−2.5 kcal/mol) in energy than the S_6 stationary point. The energy difference does decrease with an increase in the size of the central atom, a testament to the increasing flatness of the potential energy surface with respect to methyl rotation and CXC

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bends. This flattening is also evident in the vibrational frequencies corresponding to modes involving methyl rotation and ligand deformation, which frequencies become smaller with the larger chalcogens in both the D_3 and S_6 cases.

For an analysis of why the S_6 conformer should be higher in energy than the D_3 stationary point, we shall focus on the Me_6S case in looking at steric arguments, as the greatest differences can be found in the Me_6S molecule. The shortest H−H distance between hydrogens of adjacent methyls in the D_3 structure is 2.101 Å. This is shorter than the similar measure in the S_6 conformer, where this distance is 2.123 Å. There is an additional factor of interest, though. There are six H−H distances of 2.123 Å in the S_6 case but only three of these shortest 2.101 Å H−H distances in the D_3 case. Taking an average of the six shortest H−H distances for each conformer yields 2.224 Å for the D_3 case and, of course, 2.123 Å for the S_6 structure. Extending this averaging to include more H−H distances we find that the D_3 conformer continues to have a longer average H−H distance. Twelve shortest: D_3, 2.307 Å; S_6, 2.215 Å. Eighteen shortest: D_3, 2.354 Å; S_6, 2.284 Å. Thus, we see that while the D_3 conformer has a shorter minimum H−H distance, it is on the average less sterically hindered than the S_6 conformer if equal weight is given to each interaction.

However a nonlinear force field that approximates the repulsion leading to van der Waals contact distances heavily weights the shorter distances and gives a different result in the calculated structure. The Pauling force field approximation for the H−H interaction gives a pairwise repulsion proportional to d_{ij}^{-5} where d_{ij} is the distance between hydrogen atoms i and j on different CH_3 (or NH_3) groups. The maximum in this case, as expected, is for the eclipsed D_{3d} configuration. If $\tau(C_3XC_1H_{14})$ represents the rotation angle around the X−C bond of one CH_3 (or NH_3) group (see Table 5; this angle is 0° for the D_{3d} geometry and is periodic at $\tau + 120$ and $\tau + 240°$), then the energy minimum for the D_3 symmetry conformer is calculated to occur at $-13.6°$ while the S_6 minimum occurs at $-14.5°$. However the S_6 minimum is calculated to be lower in energy than the D_3 minimum. Relative to the energy difference between the D_{3d} maximum and the S_6 minimum (100%), the minimum for the D_3 conformer is 6.6% higher in energy than the S_6 minimum. These angles and the observed S_6 minimum agree with several of the ion structures described in the introduction. We conclude that the weak hydrogen−hydrogen repulsion forces are not perfectly accounted for in the *ab initio* calculation.

The methyls on opposite sides of the central atom have an eclipsed conformation in the D_3 stationary point and a staggered configuration in the S_6 case. It has been shown that the eclipsed conformation is that preferred by the axial methyls of the tetramethylchalcogens, and this has been explained in terms of three-center−four-electron bonding and hyperconjugation.[4] The bonding in the hexamethylchalcogens should be similar to that of the axial methyls in the tetramethylchalcogens, and therefore the nature of bonding in the hexamethylchalcogens would seem to prefer the D_3 conformer over the S_6 conformer.

Doubtless the forces which determine the global minimum on the hexamethylchalcogen potential energy surfaces are many and the subtle interplay of the forces must indeed be complex. We have reported here the location of an S_6 stationary point which is a minimum on both the Me_6Se and Me_6Te potential energy surfaces but has a doubly degenerate E_u mode of imaginary frequency in the Me_6S case. For each of the hexamethylchalcogens, this stationary point is higher in energy than the previously reported D_3 stationary point, but the energy difference is rather small. Because of the number of interacting forces, it is possible that the global minimum might not yet have been discovered and more stationary points surely exist. We have shown that the D_3 conformer is calculated to be slightly preferred over the S_6 conformer by bonding forces but the reverse is the case using a van der Waals model.

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