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The Tetramethylchalcogens (Me_4S, Me_4Se, Me_4Te): Bonding and Structure

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Abstract: The compound Me_4Te was recently isolated and characterized. Here is reported an *ab initio* study of this compound and the lighter tetramethylchalcogens. These systems were studied at the self-consistent field (SCF) level of theory (plus the singled and double excitation configuration interaction [CISD] level for tetramethylsulfur) and four stationary points were located on each potential energy surface: the equilibrium geometry, the pseudorotation transition state, and the axial and equatorial methyl rotation transition states. Comparisons to experiment are made, geometrical parameters, harmonic vibrational frequencies, infrared intensities, and total and relative energies are reported, and the bonding nature of the tetravalent chalcogens is explored.

Introduction

Until recently[1] no tetraalkylchalcogen compound had ever been isolated. Tetramethyltellurium and similar compounds had apparently been prepared in solution as early as 1968, but these species rapidly decomposed.[2] Gedridge, Harris, Higa, and Nissan[1] were the first to report the isolation and characterization of Me_4Te in 1989. This breakthrough synthesis and isolation procedure, involving the reaction of $TeCl_4$ with MeLi, instigated the synthesis and characterization of the first peralkylated hexavalent derivative of a main group element, Me_6Te, as reported by Ahmed and Morrison soon after.[3]

The structures of these compounds are of interest because of the hypervalence of the central atom. The hexavalent Me_6Te was thought by Ahmed and Morrison to have octahedrally coordinated ligands, but the uncertainty of the experimental data prompted a theoretical study[4] of Me_6Te and its lighter counterparts Me_6Se and Me_6S. An earlier theoretical work had already been completed on Me_6S, Me_4S, and Me_2S, but this work focused mainly on average bond strengths of the S–C bonds.[5] The Fowler, Hamilton, and Schaefer study found one minimum on the potential energy surface of each of the hexamethylchalcogens. These minima were of D_3 symmetry, and the ligand coordination was nearly octahedral with the slight deviances from octahedral coordination being the result of steric factors.[4] More recently, the S_6 structures of the hexamethylchalcogens have been investigated.[6]

The structural data obtained by Gedridge *et al.*[1] concerning the Me_4Te compound pointed toward a trigonal-bipyramidal geometry with a lone pair occupying one of the equatorial sites but was far from conclusive. The proton NMR spectrum of Me_4Te agreed with either a square-pyramidal structure or a trigonal-bipyramidal structure with rapid interchange of axial and equatorial groups, as the methyl groups were found to be equivalent. The IR and Raman spectra hinted at a trigonal-bipyramidal structure because of the number of observed peaks in the estimated Te–C stretching region, but since peak assignment was impossible, these data were inconclusive.[1]

Typically, tetravalent chalcogens have geometries characterized by trigonal-bipyramidal coordination with a lone pair occupying one equatorial site. The tetrahalide chalcogens exemplify this behavior quite well. The first molecular structure determination of one such compound was completed in 1940 by Stevenson and Schomaker.[7] Their electron diffraction data agreed with a $TeCl_4$ structure of distorted trigonal-bipyramidal configuration with C_{2v} symmetry. By the mid-1950's SF_4 had been shown by both NMR[8] and IR and Raman[9] methods to have a similar structure. The following years saw many publications investigating the structure of the tetrafluorochalcogens and it was established that all have distorted trigonal-bipyramidal geometries of C_{2v} symmetry,[10] although the crystal structure of TeF_4 appears to be of a more ionic ($TeF_3^+F^-$) character.[11]

Mono- and diorganochalcogen fluorides are also known to assume this trigonal-bipyramidal-like structure. CF_3SF_3 was first isolated in 1953[12] and $MeSF_3$ in 1976.[13] The first synthesis of Me_2SeF_2 was reported in 1968[14] and a study of its properties followed soon after, being supportive of a trigonal-bipyramidal geometry with the fluorines occupying the axial sites.[15] Electron diffraction experiments showed a similar conformation for the $(CF_3)_2SF_2$ molecule,[16] and NMR data later supported this same structure for Me_2SF_2.[17] A more recent report of electron diffraction and *ab initio* data is supportive of a distorted trigonal-bipyramidal geometry for both CF_3SF_3 and $MeSF_3$.[18]

From all these well-known data concerning the structure of tetravalent chalcogens it seems that it would be reasonable to assume that the tetramethytlchalcogens also would have trigonal-bipyramidal ligand coordination, but the hypothetical molecules

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SH_4, SeH_4, and TeH_4 cast at least a bit of doubt onto this postulate. The lack of a highly electronegative ligand in the case of the tetramethylchalcogens raises the question of whether or not an appropriate ligand for the axial bonding positions is present. SH_4 is without an electronegative ligand and is predicted to be rather radically different from SF_4 in geometry. The first theoretical study of SH_4 was reported in 1974 and the geometry in this semiempirical study was assumed to be trigonal-bipyramidal.[19] The first *ab initio* study found a similar geometry to be a minimum, but no d functions were present on the sulfur atom during the optimization.[20] No contradiction to this was offered by Chen and Hoffmann in their MO analysis of the electronic structure of sulfuranes.[21] The work of Gleiter and Veillard was the first to include d orbitals in the geometry optimization of SH_4, and they predicted a significantly different equilibrium geometry.[22] A minimum of C_{4v} symmetry was predicted by their SCF methods, which did predict a C_{2v} structure for SH_2F_2 having axial fluorines. This prediction of such a novel structure invited several additional publications from various sources,[23] and as recently as 1993 the system has been studied in more detail as to the elimination of H_2 from XH_4 where X = S, Se, Te.[24] A C_1 transition state to H_2 elimination was found in this last report with barriers of 16 kcal/mol for both SH_4 and SeH_4 and 23 kcal/mol for TeH_4.

Thus, the purposes of this study were several. As was the case in the earlier study of the hexamethylchalcogens,[4] a prompting of experimentation into the synthesis of the lighter peralkylated hypervalent chalcogens is intended. Second, a determination of the equilibrium geometries of these molecules is sought. Also, in order to elucidate the experimental NMR and vibrational data, stationary points in addition to the minima are investigated. Finally, it is the purpose of this paper to compare between these tetramethyl systems and the XH_4 and XF_4 systems.

Theoretical Methods

For all the tetramethylchalcogens in this study the basis for the carbons and hydrogens, designated double-ζ (DZ), was constructed from the Huzinaga–Dunning[25] set of contracted Gaussian functions. The basis for sulfur was comparably constructed, but a set of five pure-angular-momentum d-like functions [$\alpha_d(S) = 0.70$] was added to the DZ set as d orbitals have been shown to be very important in the geometry optimizations of hypervalent chalcogens.[22,26] For selenium the basis set was contracted as per unpublished research by Grev, Fowler, and Schaefer[27] from the (14s11p5d) primitive set of Dunning.[28] This selenium set was augmented by one set of five pure-angular-momentum d-like functions with an orbital exponent of $\alpha_d = 0.315$ as derived by Binning and Curtiss.[29] The basis for tellurium came directly from the *Handbook of Gaussian Basis Sets*, Table 52.1.1,[30] and will be referred to as dz because the authors estimate it as approximately double-ζ in quality. The basis set designations are as follows: 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.

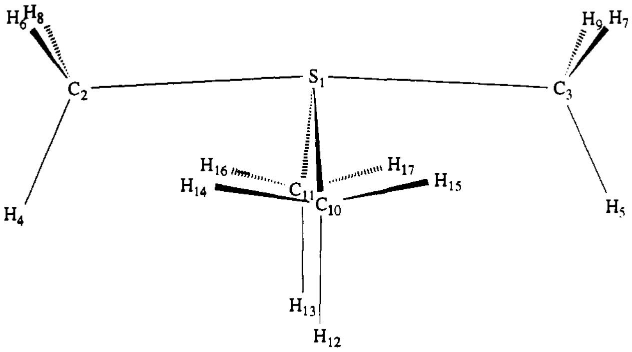

Figure 1. Tetramethylsulfur equilibrium geometry in C_{2v} symmetry.

All stationary points were fully optimized within the given symmetry restraints with closed shell self consistent field (SCF) analytic gradient techniques.[31] Residual Cartesian and internal coordinate gradients were less than 10^{-6} au. For each of the stationary points located, harmonic vibrational frequencies were obtained through the use of analytic second derivative techniques[32] in order to determine the nature of the stationary points. The tetramethylsulfur stationary points were further investigated through the use of single and double excitation configuration interaction (CISD) gradient techniques.[33] At this correlated level of theory, the five lowest-lying molecular orbitals were held doubly occupied (five frozen core), and the five highest virtuals were kept unoccupied (five frozen virtuals).

In an earlier study,[4] similar methods were applied to both the hexamethylchalcogens and the dimethylchalcogens for purposes of comparison to experiment.[34] The theory/experiment comparison for the dimethylchalcogens demonstrated the reliability of these methods. In this paper structures will also be compared to equilibrium structures of XF_4 and XH_4 predicted by equivalent methods. This study was completed with use of the PSI program package.[35]

Results

The equilibrium geometry for each tetramethylchalcogen is predicted at the SCF level of theory (and at the CISD level for tetramethylsulfur) to be of C_{2v} symmetry, as seen in Figure 1. As was the case for the tetrafluorochalcogens, the ligand coordination is found to be approximately trigonal-bipyramidal, one of the equatorial sites being occupied by a lone pair. The structural parameters for the three tetramethylchalogens are reported in Table 1. Table 2 lists the chalcogen–carbon harmonic vibrational frequencies and IR intensities, and Table 3 lists the harmonic vibrational frequencies and IR intensities associated with the methyl groups.

Three additional stationary points were located on the potential energy surface of each molecule. These stationary points correlated with transition states for pseudorotation (Figure 2), rotation of an axial methyl group (Figure 3), and rotation of an equatorial methyl group (Figure 4). Both of the methyl rotation transition states were of C_s symmetry in each of the tetramethylchalcogens. The pseudorotation transition state was seen to have C_4 symmetry in the case of Me_4S, but for the heavier chalcogens this transition state had C_{4v} symmetry. The geometries for the pseudorotation transition states are given in Table 4, those

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Table 1. Structural Parameters for the Tetramethylchalcogen Equilibrium Geometries in C_{2v} Symmetry

parameter	Me_4S (SCF)	Me_4S (CISD)	Me_4Se	Me_4Te
$r(XC_2)$, Å	2.035	2.057	2.136	2.266
$r(XC_{10})$, Å	1.805	1.816	1.949	2.171
$\theta(C_2XC_3)$, deg	175.2	174.5	169.6	156.5
$\theta(C_{10}XC_{11})$, deg	112.4	111.6	110.3	118.6
$r(C_2H_4)$, Å	1.090	1.102	1.090	1.086
$r(C_2H_6)$, Å	1.088	1.100	1.089	1.085
$r(C_{10}H_{12})$, Å	1.082	1.095	1.082	1.082
$r(C_{10}H_{14})$, Å	1.077	1.091	1.078	1.079
$\theta(XC_2H_4)$, deg	115.9	115.7	114.5	111.6
$\theta(XC_2H_6)$, deg	107.3	107.0	108.0	109.3
$\theta(XC_{10}H_{12})$, deg	109.4	109.2	108.6	109.1
$\theta(XC_{10}H_{14})$, deg	109.4	109.3	108.8	109.3

Table 2. Harmonic Vibrational Frequencies (cm^{-1}) and Infrared Intensities in Parentheses (km/mol) for the Tetramethylchalcogens Involving Chalcogen–Carbon Motions

assignment	Me_4S	Me_4Se	Me_4Te
a_1 equatorial X–C stretch	714 (2)	629 (<1)	537 (1)
a_1 axial X–C stretch	415 (1)	428 (<1)	432 (<1)
a_1 $\Delta(C_2XC_3) + \Delta(C_{10}XC_{11})$	328 (<1)	257 (<1)	208 (6)
a_1 $\Delta(C_2XC_3) - \Delta(C_{10}XC_{11})$	188 (3)	159 (3)	73 (1)
a_2 deformation	438 (0)	368 (0)	316 (0)
b_1 deformation	435 (<1)	330 (143)	277 (20)
b_1 axial X–C stretch	334 (657)	399 (238)	455 (142)
b_2 equatorial X–C stretch	782 (3)	662 (<1)	555 (11)
b_2 deformation	369 (4)	288 (4)	243 (11)

for the axial methyl rotation in Table 5, and those for equatorial methyl rotation in Table 6.

Total energies for each of the located stationary points (minima and transition states) can be found in Table 7. Energies for each of the transition states relative to the C_{2v} minima are reported in Table 8, as are the zero point vibrational energy corrections to these simple energy differences.

Discussion

The Minimum. On each of the potential energy surfaces of the tetramethylchalcogens the minimum (equilibrium geometry) was found to be a structure of distorted trigonal-bipyramidal ligand coordination and of C_{2v} symmetry. The equilibrium structure of Me_4S is depicted in Figure 1, and the structures of Me_4Se and Me_4Te are similar.

Examination of Table 1 reveals that the differences in axial and equatorial methyls are reduced in the heavier chalcogens. The differences in the bond lengths are 0.230 Å in Me_4S, 0.187 Å in Me_4Se, and 0.095 Å in Me_4Te, a 19% decrease from Me_4S to Me_4Se and a 49% decrease from Me_4Se to Me_4Te. This pattern can be seen in the bond angles also, where the differences between axial and equatorial methyl bond angles are 62.8° in Me_4S, 59.3° in Me_4Se, and 37.9° in Me_4Te. Again the percentage change is larger from Me_4Se to Me_4Te: −6% for Me_4S to Me_4Se vs −36% for Me_4Se to Me_4Te.

The effect of electron correlation upon the tetramethylsulfur equilibrium geometry is similar to electron correlation effects in other systems that SCF theory describes well: the bond lengths increase. We note that the angles change only slightly despite the significant changes in bond length. The axial S–C bonds are lengthened by 0.022 Å, while the equatorial S–C bonds are only lengthened by 0.011 Å.

These trends are also borne out in the predictions of these methods concerning the tetrafluorochalcogens which agree reasonably well with a recent *ab initio* study.[36] The predicted differences in axial and equatorial X–F bond lengths are 0.101 Å for SF_4, 0.080 Å for SeF_4, and 0.049 Å for TeF_4 and those of the F–X–F bond angles are 69.0° for SF_4, 61.4° for SeF_4, and 51.6° for TeF_4. Although the percentage changes are not as great in the tetrafluoro case, it is still seen that the step from selenium to tellurium is the more significant.

Table 3. Harmonic Vibrational Frequencies (cm^{-1}) and Infrared Intensities in Parentheses (km/mol) for the Tetramethylchalcogen Normal Modes Involving Methyl Motions

assignment	Me_4S	Me_4Se	Me_4Te
a_1 C–H stretch	3347 (15)	3345 (16)	3336 (20)
	3244 (166)	3241 (151)	3278 (75)
	3241 (14)	3235 (4)	3224 (21)
	3145 (<1)	3142 (<1)	3172 (<1)
a_1 methyl deformation	1642 (25)	1631 (23)	1617 (21)
	1614 (4)	1610 (2)	1588 (<1)
a_1 methyl umbrella	1549 (9)	1494 (5)	1458 (6)
	1385 (<1)	1367 (<1)	1379 (2)
a_1 methyl rock	1164 (8)	1060 (14)	999 (53)
	932 (9)	860 (14)	855 (18)
a_2 C–H stretch	3378 (0)	3368 (0)	3359 (0)
	3253 (0)	3245 (0)	3282 (0)
a_2 methyl deformation	1628 (0)	1623 (0)	1612 (0)
	1600 (0)	1601 (0)	1585 (0)
a_2 methyl rock	1166 (0)	1090 (0)	1040 (0)
	868 (0)	799 (0)	786 (0)
a_2 methyl rotation	283 (0)	246 (0)	184 (0)
	88 (0)	104 (0)	121 (0)
b_1 C–H stretch	3378 (20)	3369 (22)	3358 (25)
	3243 (<1)	3241 (<1)	3278 (3)
	3142 (187)	3139 (181)	3170 (185)
b_1 methyl deformation	1634 (9)	1626 (12)	1610 (15)
	1610 (<1)	1608 (<1)	1597 (<1)
b_1 methyl umbrella	1398 (44)	1378 (44)	1389 (37)
b_1 methyl rock	1167 (114)	1082 (79)	1023 (106)
	786 (18)	739 (12)	782 (8)
b_1 methyl rotation	90 (4)	110 (<1)	123 (<1)
b_2 C–H stretch	3346 (29)	3344 (23)	3337 (20)
	3254 (141)	3246 (134)	3283 (69)
	3241 (5)	3235 (7)	3224 (53)
b_2 methyl deformation	1629 (4)	1619 (1)	1599 (<1)
	1605 (17)	1605 (18)	1591 (19)
b_2 methyl umbrella	1528 (1)	1476 (<1)	1446 (3)
b_2 methyl rock	1065 (<1)	981 (<1)	922 (16)
	955 (20)	859 (29)	859 (49)
b_2 methyl rotation	272 (2)	236 (2)	181 (2)

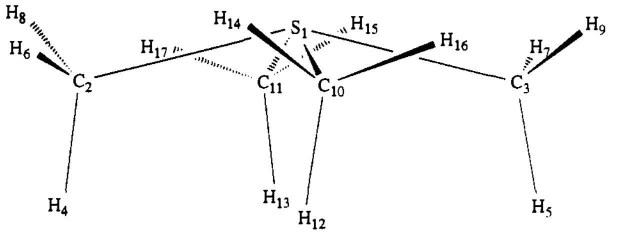

Figure 2. Tetramethylsulfur pseudorotation transition state in C_4 symmetry.

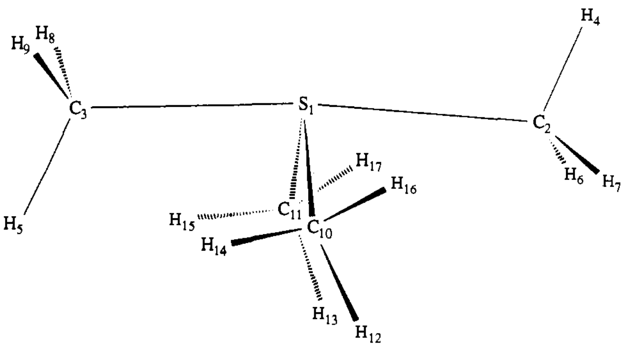

Figure 3. Tetramethylsulfur axial methyl rotation transition state in C_s symmetry.

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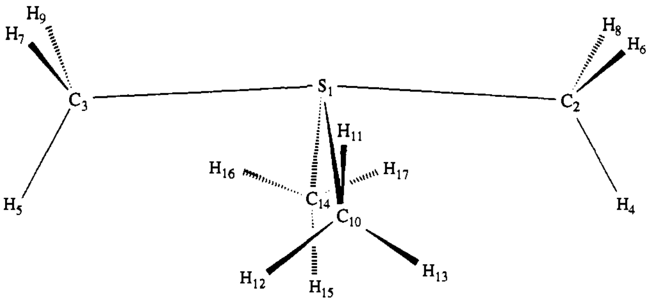

Figure 4. Tetramethylsulfur equatorial methyl rotation transition state in C_s symmetry.

Table 4. Structural Parameters for the Tetramethylchalcogen Pseudorotation Transition States (Me_4S in C_4 Symmetry, Me_4Se and Me_4Te in C_{4v} Symmetry)

parameter	Me_4S (SCF)	Me_4S (CISD)	Me_4Se	Me_4Te
$r(XC_2)$, Å	1.908	1.922	2.037	2.218
$\theta(C_2XC_3)$, deg	152.4	153.1	145.9	140.3
$r(C_2H_4)$, Å	1.085	1.097	1.085	1.083
$r(C_2H_6)$, Å	1.079	1.093	1.082	1.082
$r(C_2H_8)$, Å	1.081	1.095	a	a
$\theta(XC_2H_4)$, deg	110.5	110.4	110.2	110.1
$\theta(XC_2H_6)$, deg	110.2	110.4	108.9	109.3
$\theta(XC_2H_8)$, deg	108.7	107.8	a	a
$\tau(H_4C_2XC_3)$, deg	-8.8	-15.6	0.0	0.0
$\tau(H_6C_2XC_3)$, deg	112.0	105.5	120.2	120.0
$\tau(H_8C_2XC_3)$, deg	-128.7	-135.2	-120.2	-120.0

[a] Determined by C_{4v} symmetry [$r(C_2H_8) = r(C_2H_6)$; $\theta(HC_2H_8) = \theta(XC_2H_6)$].

Table 5. Structural Parameters for the Tetramethylchalcogen Axial Methyl Rotation Transition States in C_s Symmetry[a]

parameter	Me_4S (SCF)	Me_4S (CISD)	Me_4Se	Me_4Te
$r(XC_2)$, Å	2.140	2.144	2.185	2.284
$r(XC_3)$, Å	1.993	2.027	2.127	2.264
$r(XC_{10})$, Å	1.805	1.806	1.950	2.175
$\theta(C_2XC_3)$, deg	177.1	176.0	171.3	156.4
$\theta(C_{10}XC_{11})$, deg	111.5	111.1	109.8	121.0
$r(C_2H_4)$, Å	1.089	1.101	1.089	1.085
$r(C_2H_6)$, Å	1.088	1.100	1.088	1.084
$\theta(XC_2H_4)$, deg	103.1	103.1	105.1	108.0
$\theta(XC_2H_6)$, deg	114.3	113.9	113.3	111.3
$\theta(XC_3H_5)$, deg	116.1	116.0	114.8	111.5
$\theta(XC_3H_8)$, deg	107.0	106.8	107.7	109.3
$\theta(XC_{10}H_{12})$, deg	109.6	109.4	108.8	109.3
$\theta(XC_{10}H_{14})$, deg	110.4	110.4	109.5	109.5
$\theta(XC_{10}H_{16})$, deg	107.9	107.7	107.8	108.7
$\tau(H_{12}C_{10}XC_{11})$, deg	20.9	21.5	18.0	10.8
$\tau(H_{14}C_{10}XC_{11})$, deg	-110.2	-99.7	-102.7	-109.3
$\tau(H_{16}C_{10}XC_{11})$, deg	139.0	139.5	136.4	129.8

[a] The bond distances $r(C_3H_5)$ and $r(C_3H_8)$ are in all cases within 0.005 Å of 1.09 Å. Equatorial C-H bond lengths are all within 0.005 Å of 1.08 Å.

Comparison to the equilibrium geometries of the dimethylchalcogens predicted at these levels of theory is also interesting. The equatorial methyl groups and the methyl groups of the dimethylchalcogens are remarkably similar in X–C bond length, the largest difference being in the case of selenium for which the difference is 0.005 Å. A radical difference, however, can be noted in the C–X–C bond angles, both in absolute values and in trends down the periodic table. The C–X–C bond angles of the dimethylchalcogens are 100.2° for Me_2S, 97.5° for Me_2Se, and 95.4° for Me_2Te. The equatorial C–X–C bond angles are all greater than their dimethyl counterparts, as would be expected for trigonal-bipyramidal coordination. Also, while this angle lessens in going from Me_4S to Me_4Se, it increases on the step to Me_4Te. This is in marked contrast to the dimethylchalcogens for which the bond angle decreases with each step down the periodic table, as does the H–X–H angle in the XH_4 series.

Table 6. Structural Parameters for the Tetramethylchalcogen Equatorial Methyl Rotation Transition States in C_s Symmetry[a]

parameter	Me_4S (SCF)	Me_4S (CISD)	Me_4Se	Me_4Te
$r(XC_2)$, Å	2.039	2.062	2.140	2.267
$r(XC_{10})$, Å	1.810	1.821	1.954	2.180
$r(XC_{14})$, Å	1.800	1.810	1.945	2.169
$\theta(C_2XC_3)$, deg	176.9	176.0	171.5	157.7
$\theta(C_{10}XC_{14})$, deg	111.0	110.5	109.1	118.7
$\theta(XC_2H_4)$, deg	116.6	116.4	115.1	111.8
$\theta(XC_2H_6)$, deg	107.0	106.9	107.7	109.0
$\theta(XC_2H_8)$, deg	106.8	106.5	107.5	109.3
$\theta(XC_{10}H_{11})$, deg	107.4	107.2	107.1	108.3
$\theta(XC_{10}H_{12})$, deg	110.3	110.2	109.6	109.7
$\theta(XC_{14}H_{15})$, deg	109.8	109.6	108.8	109.3
$\theta(XC_{14}H_{16})$, deg	109.1	109.0	108.6	109.1
$\tau(H_4C_2XC_3)$, deg	24.1	20.6	10.2	6.2
$\tau(H_6C_2XC_3)$, deg	-98.0	-101.4	-111.6	-114.3
$\tau(H_8C_2XC_3)$, deg	146.3	142.7	131.9	127.0

[a] Carbon-hydrogen bond lengths of the axial methyls are in all cases within 0.005 Å of 1.09 Å, and those of the equatorial methyls are within 0.005 Å of 1.08 Å.

The harmonic vibrational frequencies involving chalcogen–carbon motions shown in Table 2 provide insight into the differences between the tetramethylchalcogens. Note that the frequency differences between axial and equatorial stretches steadily decreases and that the axial stretching frequencies actually increase in the heavier tetramethylchalcogens. Not shown is the coupling between these two modes, which was insignificant in the case of Me_4S but was of importance in Me_4Te—another sign that the axial and equatorial methyls are more similar in Me_4Te than in Me_4S. It is also noticeable from the harmonic frequencies that the potential energy surface becomes more flat with regards to angular C–X–C motions as the size of the central atom is increased. Both of the a_1 bends attest to this as do all of the deformation modes.

For the purposes of comparison to experiment, it has been recommended that SCF frequencies be scaled by a factor of 0.91.[37] It was not the intention of this study to match the observed experimental frequencies and, truthfully, it is fortuitous that such was not our goal. The basis set for tellurium is the least complete of our chalcogen sets, and this may explain why even with the 0.91 scaling our SCF frequencies do not well match the frequencies observed by Gedridge *et al.*[1] (699, 623, 520, 507, 383, 263, and 219 cm^{-1}). We do suspect, though, that two of their "probable" and "possible" Te–C stretching bands at 699, 520, and 623 cm^{-1} may be too high, and perhaps some of their lower frequency peaks may be due to Te–C stretching. The experimentally observed Te–C stretch in Me_2Te is at 528 cm^{-1},[38] so the 520 cm^{-1} peak could reasonably be associated with equatorial methyl stretching and would not be too far from our predicted 555 cm^{-1} (505 cm^{-1} after scaling) frequency for the b_2 equatorial stretch. The longer bond distances for the axial methyls would imply that their stretching frequencies should be lower than the equatorial stretching frequencies and indeed we predict them to be quite a bit lower (455 and 432 cm^{-1} for the axial methyl stretches vs 555 and 537 cm^{-1} for the equatorial stretches). Thus, it is with reasonable confidence that we suggest their 699 and 623 cm^{-1} frequencies might not be due to Te–C stretching.

Pseudorotation Transition State. In order to find the pseudorotation transition state, the a_1 [$\Delta(C_2XC_3) - \Delta(C_{10}XC_{11})$] normal coordinate of the minimum was maximized while all other

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Table 7. Total Energies (Hartrees) for Each of the Stationary Points

stationary point	Me_4S (SCF)	Me_4S (CISD)	Me_4Se	Me_4Te
C_{2v} minimum	−555.746 02	−556.270 27	−2 557.928 11	−6 731.210 01
C_4 pseudorotation TS[a]	−555.733 66	−556.260 65	−2 557.918 72	−6 731.209 23
C_s axial methyl rotation TS	−555.740 20	−556.265 47	−2 557.923 26	−6 731.206 94
C_s equatorial methyl rotation TS	−555.744 55	−556.268 84	−2 557.926 48	−6 731.208 28

[a] C_4 symmetry for Me_4S, C_{4v} symmetry for Me_4Se and Me_4Te.

Table 8. Relative Energies (kcal/mol) for Each of the Stationary Points (C_{2v} minimum = 0.0) and Zero Point Vibrational Energy Corrections in Parentheses

stationary point	Me_4S (SCF)	Me_4S (CISD)	Me_4Se	Me_4Te
C_4 pseudorotation TS[a]	7.8 (+0.4)	6.0	5.9 (+0.2)	0.5 (+0.1)
C_s axial methyl rotation TS	3.7 (−0.2)	3.0	3.0 (−0.1)	1.9 (+0.2)
C_s equatorial methyl rotation TS	0.9 (−0.3)	0.9	1.0 (−0.3)	1.1 (0.0)

[a] C_4 symmetry for Me_4S, C_{4v} symmetry for Me_4Te and Me_4Te.

coordinates were minimized (only C_2 symmetry was enforced). On the Me_4S SCF and CISD surfaces stationary points of C_4 symmetry were found. Here again the CISD method has the effect of lengthening bonds. The CISD torsional angles also deviate from C_{4v} orientation more than do the SCF values. For each of the heavier tetramethylchalcogens a stationary point of C_{4v} symmetry was located. In a separate search, a stationary point of C_{4v} symmetry was also found on the Me_4S SCF surface by restriction of symmetry, but vibrational frequency analysis showed this stationary point to be of Hessian order two with one of the imaginary frequencies corresponding to methyl rotation. When the molecule was relaxed along this coordinate, the C_4 stationary point was located. The C_4 stationary point of the Me_4S surface and the two C_{4v} stationary points of the heavier tetramethylchalcogens were shown to be true transition states with one imaginary vibrational frequency corresponding to the coordinate $\Delta(C_2XC_3) - \Delta(C_{10}XC_{11})$, pseudorotation.

Since the C_4 transition state of Me_4S does not deviate much from C_{4v} symmetry and the larger tetramethylchalcogens do have a C_{4v} pseudorotation transition state, it seems safe to blame the Me_4S deviance from C_{4v} symmetry on simple steric factors. The larger tetramethylchalcogens already have sufficient distance between the hydrogens of adjacent methyls such that no rotation is necessary to add distance between these hydrogens. The smaller Me_4S, however, experiences crowding which is best alleviated by minor methyl rotation.

Note that this stationary point has the ligand coordination of a square pyramid with an apical lone pair. This structure is related to those of the XH_4 series and is one of the possible structures with which the proton NMR of Me_4Te agrees, the other being a trigonal-bipyramid with rapid axial–equatorial ligand interchange.[1] However, this stationary point is a transition state. Specifically, this is the transition state for pseudorotation or, in other words, axial–equatorial ligand interchange. Thus, the identification of this stationary point as the pseudorotation transition state along with the location of the trigonal-bipyramidally-coordinated minimum makes a definite statement that this level of theory predicts each of the tetramethylchalcogens to be of distorted trigonal-bipyramidal equilibrium geometry.

Axial Methyl Rotation Transition State. In order for the proton NMR of a trigonal-bipyramidally-coordinated Me_4Te to display a singlet as was observed,[1] not only must the axial and equatorial methyl groups be able to rapidly interchange, but also the methyl groups must be able to rotate. Thus, transition states for both axial and equatorial methyl rotation were sought. The first of these, the axial methyl rotation transition state, was found to be a stationary point of C_s symmetry with the axial methyl groups staggered. This stationary point was shown to have only one imaginary frequency which corresponded to rotation of the $C_2H_4H_6H_7$ methyl group (see Figure 3).

It is obvious from Table 5 that axial methyl rotation has a larger effect on the geometry of the lighter tetramethylchalcogens than it does on the heavier. The bond length difference between the two axial methyls in the Me_4S transition state is a whopping 0.147 Å while that for Me_4Te is only 0.020 Å. Electron correlation significantly reduces the differences between the two axial S–C bonds. The S–C_3 bond shows an increase of 0.034 Å in going from the SCF to the CISD method while the S–C_2 bond length increases a mere 0.004 Å. The rotation of equatorial groups to accommodate the rotating axial methyl is also greater in the smaller tetramethylchalcogen: 20.9° [$\tau(H_{12}C_{10}XC_{11})$] in Me_4S vs 10.8° in Me_4Te. Certainly, simple steric arguments would explain these angular differences, as Me_4Te has significantly longer X-C bonds.

Equatorial Methyl Rotation Transition State. The final stationary points located in this study were of C_s symmetry on each tetramethylchalcogen surface, and the Me_4S version is depicted in Figure 4. These stationary points were identified as transition states by analytic second derivative methods at the SCF level. By these methods one imaginary vibrational frequency was found which corresponded to rotation of the $C_{10}H_{11}H_{12}H_{13}$ methyl group, making this stationary point the transition state for equatorial methyl rotation. The CISD method again lengthens the bonds of the tetramethylsulfur stationary point, the axial bonds more than the equatorial bonds.

The differences between the rotating and non-rotating methyl X–C bond lengths were not as great in the equatorial methyl rotation transition state as they were in the axial methyl rotation transition state, being only about 0.01 Å in each tetramethylchalcogen case. The axial groups do, however, show significant rotation in this transition state as did the equatorial groups in the axial rotation transition state, and again the difference between Me_4S and Me_4Te is quite pronounced.

The Potential Energy Hypersurface. The potential energy surfaces of the various tetramethylchalcogens are rather flat along all coordinates investigated. Although the pseudorotation transition state is 8.2 kcal/mol above the minimum in the case of Me_4S at the SCF level (the CISD method lessens the classical barrier by 1.8 kcal/mol), this difference is reduced to 0.6 kcal/mol in the Me_4Te case. Note that the zero-point vibrational energy correction is positive in each of the pseudorotation transition state cases. This is a bit unusual as transition state zero-point vibrational energies are usually smaller than the zero-point vibrational energies of minima. This is true because transition states have one less vibrational frequency contributing to the total zero-point vibrational energy. In the case of the tetramethylchalcogens, two factors work toward the positive zero-point vibrational energy correction. The first is that the $\Delta(C_2XC_3) - \Delta(C_{10}XC_{11})$ coordinate has a very low frequency in the minimum. Thus, the loss of this coordinate's contribution to the zero-point vibrational energy does not much affect the zero-point vibrational energy. The second factor is that the crowding of the methyl groups in the C_4 or C_{4v} transition states causes the methyl rotation frequencies to increase and thereby the loss of the positive $\Delta(C_2XC_3) - \Delta(C_{10}XC_{11})$ coordinate is offset. The fact that the Me_4Te barrier to axial–equatorial ligand exchange is 0.6 kcal/mol at this level of theory agrees well with the rapid interchange hypothesis of Gedridge *et al.*[1] However, it should be noted the pseudorotational barriers are significantly higher for both Me_4S and Me_4Se, implying that the proton NMR results for these compounds should indicate separate peaks for the axial and equatorial methyl hydrogens.

For the axial and equatorial methyl rotation transition states we again see the trend in reduction of differences as we progress down the periodic table. The axial methyl rotation transition state lies 2.9 kcal/mol above the equatorial methyl rotation transition state on the Me_4S surface, but this difference is reduced to 2.2 kcal/mol on the Me_4Se surface and a meager 1.0 kcal/mol on the Me_4Te surface. The CISD method lessens the difference between the Me_4S axial and equatorial methyl rotation transition states because the classical barrier to axial methyl rotation is reduced from the SCF value by 0.7 kcal/mol while the equatorial methyl rotation classical barrier is unaffected. It is rather interesting that the axial methyl rotation transition state lies above the transition state for equatorial methyl rotation. The axial bond lengths are in all cases longer than the equatorial bond lengths (0.230 Å longer in Me_4S), and first impressions would place the axial methyl rotation barrier below that for equatorial rotation as the axial methyls are more weakly bound. This implies that the bonding characters of the two different types of methyl groups must be quite different (see Bonding Considerations below). Now, finally, the absolute values of 2.1 and 1.1 kcal/mol as barriers to methyl rotation in Me_4Te qualitatively are low enough so that the methyl hydrogens might appear equivalent in the proton NMR spectrum and again our predictions agree with the observations and hypotheses of Gedridge *et al.*[1]

Bonding Considerations. We have seen throughout this work that the most stable structure for the tetramethylchalcogens is one of distorted trigonal-bipyramidal ligand coordination maintaining C_{2v} symmetry, an equilibrium geometry similar to that of the tetrafluorochalcogens and in contrast to that of the tetrahydrochalcogens. In addition, we have seen that the axial and equatorial bonds are different not only in strength but also in character, and that these differences become less as the central atom becomes larger. What comment, then, can we make about the bonding character of the tetramethylchalcogens?

It seems that the best clues for unraveling the mystery of bonding in the tetravalent chalcogens come from two sources: comparison of the XF_4, XH_4, and XMe_4 equilibrium geometries and examination of the XMe_4 methyl rotation transition states. As recently as 1989 Ewig and Van Wazer[23] wrote that the reasons for the C_{4v} equilibrium geometry of SH_4 were "presently not well understood". This also implies that the bonding character of SF_4 is not completely understood. If it were, then the difference between SF_4 and SH_4 would be obvious, and predictions could be confidently made concerning the structure of Me_4S without *ab initio* methods. In the introduction, it was mentioned that in the heterosubstituted tetravalent chalcogens the more electronegative ligands assume the axial positions and that both XH_4 and XMe_4 lacked highly electronegative ligands. If this had been the reason for the C_{4v} coordination of the XH_4 molecules, then surely the XMe_4 molecules would have been more similar to the XH_4 series than the XF_4 series. The molecular orbitals reveal where the difference actually lies. The molecular orbitals of the XMe_4 series reveal large participation of the axial carbon p orbitals in bonding to the central chalcogen. This is also the case in the XF_4 series, but the XH_4 molecules lack appropriate p orbitals on the ligands. Thus the hydrogens of the XH_4 molecules are unable to participate in the type of bonding that results in trigonal-bipyramidal coordination in tetravalent chalcogens because they have no occupied or low-lying p orbitals. This C_{4v} XH_4 equilibrium structure shows the importance of the p orbitals in the bonding of the trigonal-bipyramidally-coordinated tetravalent chalcogens.

The methyl rotation transition states also provide information concerning the angular nature of the axial bonds. The fact that the bond length differences for the equatorial methyls in the equatorial methyl rotation transition states are very small compared to the axial bond length differences in the axial methyl rotation transition states and the fact that the equatorial methyl rotation transition states lie below the axial methyl rotation transition states show that the axial bonds are much more angularly dependent. This holds well with the theory of hyperconjugation[39] with the chalcogen lone pair donating to the axial methyl groups. Of course, without appropriate p orbitals, the XH_4 molecules cannot bond in this manner and again the differences between XH_4 and XMe_4 are emphasized and the similarities of XF_4 and XMe_4 accentuated.

Electron correlation reduces the effects of hyperconjugation and reinforces the argument that the axial and equatorial bonds are fundamentally different. The reduction of hyperconjugation effects by the CISD method is seen for every stationary point; the axial bond lengths are regularly increased more than the equatorial bond lengths, and the barriers to pseudorotation and axial methyl rotation are lowered while the equatorial methyl rotation barrier is almost unaffected. Special note should be taken of the axial methyl rotation transition state for which the CISD method substantially increases the bond length of the axial methyl capable of hyperconjugation with the sulfur lone pair yet hardly affects the bond length of the rotated axial methyl which has its hyperconjugative ability "turned off".

Even the ever-present reduction of axial–equatorial differences in the heavier tetramethylchalcogens is consistent with this bonding explanation. As the bond length is increased, the π-type bonding is weakened and the whole system tends toward the more symmetric C_{4v} coordination. Hence, we see that one explanation holds well with all the obtained data. The equilibrium geometries of XH_4, XF_4, and XMe_4, the character of the axial and equatorial rotation transition states, the effects of electron correlation, and the periodic trends all exemplify the angular nature of the axial bonds and hold well with the predictions of hyperconjugation.

Conclusions

The potential energy surfaces of the three tetramethylchalcogens, Me_4S, Me_4Se, and Me_4Te, have been investigated. Four stationary points were found on each surface corresponding to the minimum, the pseudorotation transition state, and transition states for axial and equatorial methyl rotation. In all cases the minimum was found to be a C_{2v} structure of distorted trigonal-bipyramidal ligand coordination.

Each surface was found to be rather flat with respect to pseudorotation, or axial–equatorial ligand interchange, and methyl rotation, especially in the case of Me_4Te. This prediction is in good agreement with the observed singlet in the proton NMR of Me_4Te and the hypothesis of trigonal-bipyramidal ligand coordination with rapid ligand interchange as proposed by Gedridge *et al.*[1] The pseudorotation barriers of the other tetramethylchalcogens are, however, large enough that a proton NMR singlet would not be expected.

Examination of these potential energy surfaces and those of XF_4 and XH_4 has revealed much about the nature of bonding in the tetravalent chalcogens. Comparison with the equilibrium geometries of XF_4 and XH_4 has shown the importance of ligand p orbitals in forming a trigonal-bipyramidally-coordinated molecule and the methyl rotation transition states have illustrated the angular nature of the axial bonds. All data agree well with the theory of hyperconjugation.

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