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Ab Initio Study of the Conformations of Vinyl Mercaptan, Methyl Vinyl Sulfide, and Methyl Allenyl Sulfide
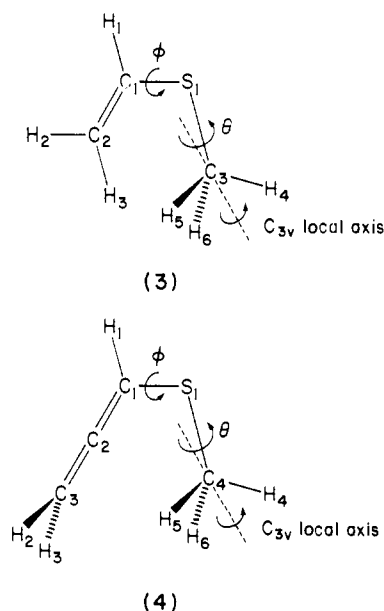
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Abstract: Ab initio (STO-3G and 44-31G) molecular orbital theory has been employed to investigate the rotational potential surfaces of methyl mercaptan, methyl vinyl sulfide, and methyl allenyl sulfide. Both STO-3G and 44-31G predict, for internal rotation along the C_{sp^2}–S bond, two stable conformations and the syn is the more stable one. However, for each molecule, a gauche form is found as the second stable conformation by 44-31G, as opposed to the anti by STO-3G. The corresponding rotational barriers predicted by STO-3G are apparently too high, while those by 44-31G are reasonable. The rotational barrier for a methyl group has also been studied for the syn and anti conformations of methyl vinyl sulfide and methyl allenyl sulfide. The methyl rotational barrier (STO-3G) for the syn is much larger in methyl vinyl sulfide (3.1 kcal mol^{-1}) than in methyl allenyl sulfide (1.9 kcal mol^{-1}) presumably due to steric interactions. Structural variations and conformational energies are rationalized in terms of orbital and steric interactions.

From the structural point of view, vinyl mercaptan (**1**), allenyl mercaptan (**2**), methyl vinyl sulfide (**3**), and methyl

(1)

(2)

(3)

(4)
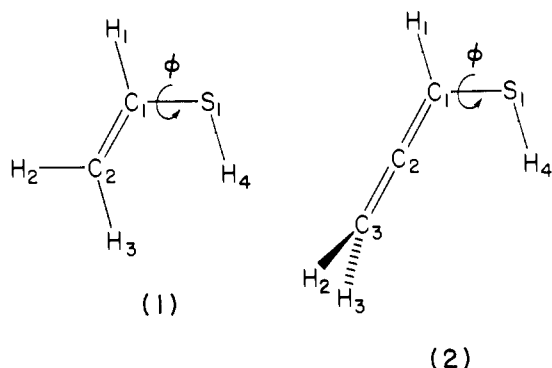
allenyl sulfide (**4**) can be considered as the second-row analogue of vinyl alcohol, allenyl alcohol, methyl vinyl ether, and methyl allenyl ether, respectively. Just as their oxygen counterparts,[1,2a] the potential function about the C_{sp^2}–S bond has been the subject of some controversy.[2-6] Only a syn form of methyl vinyl sulfide (syn is defined as the structure having $C_{sp^2}=C_{sp^2}$—S—R coplanar and having S—R and $C_{sp^2}=C_{sp^2}$ bonds on the same side of the C_{sp^2}—S bond) was reported to exist by microwave and photoelectron data.[3] A study of tem-

perature-dependent IR spectra showed, on the other hand, that methyl vinyl sulfide existed in two conformations.[5] Electron diffraction studies reported by two independent research

Table I. Calculated and Experimental Equilibrium Geometries (Å or deg)

structural parameter[a]	calcd[b]		exptl[c]
	STO-3G	44-31G	
methanethiol			
C_1-S_1	1.798[d]	1.885	1.819 (5)[e]
H_1-C_1	1.086	1.076	1.092 (10)
H_4-S_1	1.331	1.356	1.335 (10)
$H_1C_1S_1$	69.0	71.3	70.8 (0.5)
$H_4S_1C_1$	95.5	97.8	96.5 (0.5)
$H_{1,2,3}C_1S_1$	177.5	177.1	177.8 (0.5)
vinyl sulfide			
C_1-S_1	1.759[d]	1.823	
C_1-C_2	1.310	1.313	
H_1-C_1	1.084	1.070	
H_2-C_2	1.080	1.072	
H_3-C_2	1.081	1.072	
H_4-S_1	1.331	1.355	
$H_1C_1S_1$	112.9	110.8	
$H_2C_2C_1$	121.4	120.6	
$H_3C_2C_1$	122.8	122.9	
$H_4S_1C_1$	95.9	98.3	
$C_2C_1S_1$	127.3	127.0	
allenyl sulfide			
C_1-S_1	1.772[d]	1.837	
C_1-C_2	1.288	1.288	
C_2-C_3	1.288	1.295	
H_1-C_1	1.085	1.069	
H_2-C_3	1.084	1.073	
H_4-S_1	1.331	1.354	
$C_2C_1S_1$	126.3	125.6	
$H_4S_1C_1$	95.8	98.0	
$H_1C_1S_1$	113.5	111.8	
$H_2C_3C_2$	122.2	121.5	
methyl vinyl sulfide			
C_1-S_1	1.760	1.820	1.752 (12),[f] 1.747 (3)[g]
C_1-C_2	1.311	[1.313]	1.342 (7), 1.341 (3)
C_3-S_1	1.797	[1.885]	1.794 (12), 1.807 (3)
H_1-C_1	1.085	[1.070]	
H_2-C_2	1.079	[1.072]	} 1.082 (7), 1.086 (26)
H_3-C_2	1.080	[1.072]	
H_4-C_3	1.086	[1.076]	1.105 (9), 1.101 (26)
$C_1S_1C_3$	101.6	102.4	102.5 (2.0), 104.6 (0.8)
$C_2C_1S_1$	129.6	128.2	127.0 (1.5), 127.5 (0,4)
$H_2C_2C_1$	123.7	[120.6]	
$H_3C_2C_1$	120.9	[122.9]	
$H_1C_1S_1$	111.4	110.1	112.1 (1.9)
$H_4C_3S_1$	110.7	[71.3]	
$H_{4,5,6}C_3S_1$	176.9	[177.1]	
methyl allenyl sulfide			
C_1-S_1	1.771	1.831	1.745 (10)[f]
C_1-C_2	1.288	[1.288]	1.327 (10)
C_2-C_3	1.289	[1.295]	1.282 (10)
C_4-S_1	1.797	[1.885]	1.800 (10)
H_1-C_1	[1.085]	[1.069]	} 1.087 (8)
H_2-C_3	[1.084]	[1.073]	
H_4-C_4	[1.086]	[1.076]	1.107 (8)
$C_1S_1C_4$	100.3	101.4	98.1 (0.8)
$C_2C_1S_1$	127.5	126.7	125,4 (0,6)
$H_1C_1S_1$	112.8	111.5	
$H_2C_3C_2$	122.2	[121.5]	
$H_4C_4S_1$	110.7	[71.3]	
$H_{4,5,6}C_4S_1$	177.4	[177.1]	

[a] The symbol $H_{i,j,k}$ denotes a point on the C_{3v} local axis of C–H_i, C–H_j, and C–H_k bonds. [b] Assumed values in brackets, see text. [c] The figures given in parentheses are reported standard deviations. [d] From ref 13. [e] From ref 23. [f] From ref 4. [g] From ref 2.

groups[2,4] suggested that a model with only one planar syn conformation was insufficient to explain the experimental intensity curves. It was at first concluded[4] that inclusion of a nonplanar conformation would improve the agreement between the observed and the calculated intensities, but no unique solution for one or more other conformations could be found without additional information. However, a further refinement favored the existence of a gauche form ($\phi = 116 \pm 7°$) as the second stable conformer. Most recently, photoelectron spectra of methyl vinyl sulfide have been recorded over the range of

Table II. Structural Variations Accompanying Internal Rotation (ϕ) in Vinyl Sulfide, Methyl Vinyl Sulfide, and Methyl Allenyl Sulfide (Å or deg)

Parameter[a]	STO-3G, ϕ =					44-31G, ϕ =				
	0°	60°	90°	120°	180°	0°	60°	90°	120°	180°
vinyl sulfide										
C_1-S_1	1.759	1.777	1.780	1.774	1.764	1.823	1.842	1.844	1.839	1.831
$C_2C_1S_1$	127.3	125.3	124.3	124.2	124.1	127.0	124.2	122.6	122.3	122.7
$H_1C_1S_1$	112.9	115.5	116.5	116.4	116.1	110.8	113.4	115.0	115.3	115.0
$H_4S_1C_1$	95.9	95.6	95.1	94.9	95.6	98.3	98.1	97.7	97.7	97.4
allenyl sulfide										
C_1-S_1	1.772				1.774					
$C_2C_1S_1$	126.3				124.2					
$H_1C_1S_1$	113.5				116.2					
$H_4S_1C_1$	95.8				95.0					
methyl vinyl sulfide										
C_1S_1	1.760	1.778		1.773	1.764	1.820	1.835		1.830	1.827
$C_1S_1C_3$	101.6	99.6		98.2	99.3	102.4	101.3		99.5	99.8
$C_2C_1S_1$	129.6	125.8		124.4	124.2	128.2	124.7		123.3	123.6
$H_1C_1S_1$	111.4	115.3		116.5	116.2	110.1	113.5		114.8	114.6
$H_{4,5,6}C_3S_1$	176.9	177.1		177.3	177.4					
methyl allenyl sulfide										
C_1-S_1	1.771	1.783		1.780	1.775	1.831	1.839		1.837	1.838
$C_1S_1C_4$	100.3	99.5		98.0	98.8	101.4	101.1		99.3	99.1
$C_2C_1S_1$	127.5	124.8		123.7	124.1	126.7	123.6		122.6	123.0
$H_1C_1S_1$	112.8	115.8		116.8	116.2	111.5	114.6		115.6	115.2

[a] See footnote *a* under Table I.

temperature 20–600 °C by Müller et al.[6] They have confirmed the existence of a gauche form as the second stable isomer. However, the cis-gauche energy difference estimated by them is quite different from those obtained from electron diffraction studies.[2] A second rotational isomer has also been proposed for methyl allenyl sulfide but its nature is still not clear.[4] Recently, microwave and IR spectra of vinyl mercaptan have been obtained and the predominant conformation of the molecule has been shown to be planar or near-planar syn.[7] No information regarding other possible conformations of vinyl mercaptan has been reported yet.

In this paper, single determinant ab initio molecular orbital theory is employed to investigate the structures as well as the rotational potential surfaces of vinyl mercaptan, methyl vinyl sulfide, and methyl allenyl sulfide. Ab initio calculations have previously been reported for vinyl mercaptan.[2a] However, only limited geometry optimization was performed. No detailed molecular orbital calculations, even at the semiempirical level, have previously been reported for allenyl mercaptan, methyl vinyl sulfide, and methyl allenyl sulfide. Therefore, a systematic and more complete treatment of these molecules seemed desirable.

We are interested in conformational analysis of these molecules because they are model compounds for future force field development[8] for this particular class of molecules. Furthermore, conformational analysis of methyl vinyl sulfide and methyl allenyl sulfide is interesting, because nonbonded attraction found in methyl vinyl ether[9] may exist in these two molecules.

Computational Aspects and Results

All results reported in this paper were carried out with a modified version of the Gaussian 70 system of programs.[10,11] Fully STO-3G[12] optimized geometries for the syn form of vinyl mercaptan and allenyl mercaptan have previously been reported.[13] In this work, all structural parameters for the syn conformation of methyl vinyl sulfide were fully optimized at the STO-3G level[12] assuming C_{3v} symmetry for the methyl group. This method was shown useful in several structural studies and conformational analyses of sulfides,[13–15] disul-

fides,[13,16,17] polysulfides,[13] and elemental sulfur.[19–21] Structural parameters of the syn form of methyl allenyl sulfide were similarly fully optimized with the exception that the C_4-H_4, C_3-H_2, and C_1-H_1 bond lengths were taken from the appropriate theoretical (STO-3G) structures[13] of allenyl mercaptan and dimethyl sulfide. This assumption, which was made for computing economy, is justified in light of the obtained theoretical C–H bond lengths for methyl vinyl sulfide, these being identical to those found in vinyl sulfide and dimethyl sulfide.[13] Structural parameters obtained in this manner are shown in Table I.

Conformations with the dihedral angle ϕ equal to 60°, 120°, and 180° for vinyl mercaptan, methyl vinyl sulfide, and methyl allenyl sulfide were studied and a flexible rotor model was employed (Table II). However, only the anti form of allenyl mercaptan was studied in addition to the syn, because of the anticipated close relationship between the conformational characteristics of vinyl mercaptan and allenyl mercaptan. Unoptimized structural parameters were taken from their corresponding syn conformations. Optimized structural parameters and calculated total and relative energies are shown respectively in Tables II and IV. The calculated energy values for ϕ = 0°, 60°, 120°, and 180° allow the determination of the potential function $V(\phi)$ in the truncated Fourier expansion

$$V(\phi) = \tfrac{1}{2}V_1(1 - \cos\phi) + \tfrac{1}{2}V_2(1 - \cos 2\phi) + \tfrac{1}{2}V_3(1 - \cos 3\phi) \quad (1)$$

The potential functions obtained in this manner are depicted in Figures 1–3. The potential barrier hindering rotation of the methyl group was studied for the syn and the anti conformations of each molecule. Again, a flexible rotor model was employed and the results are displayed in Tables III and IV.

To describe the rotational potential surface along the C–S bond more accurately, calculations using the extended 44-31G basis set[22] were carried out. The 44-31G set is the larger and more reliable basis for conformational analysis, but because of the computational expenses, only partial geometry optimization for molecules as large as methyl vinyl sulfide and methyl allenyl sulfide is practically feasible. Therefore, only four parameters of the syn form of methyl vinyl sulfide and methyl
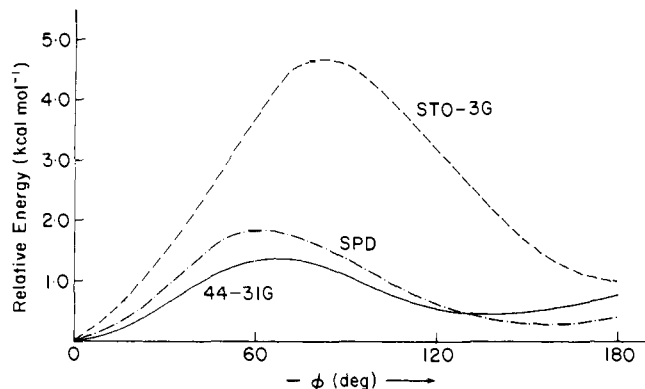
Figure 1. Calculated potential functions describing internal rotation (ϕ) about the C_{sp^2}–S bond in vinyl sulfide.
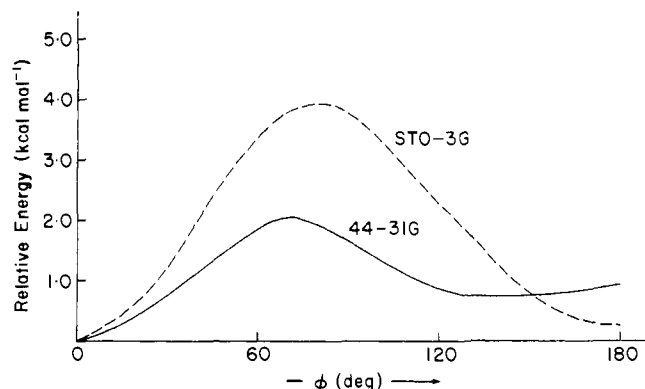

Figure 2. Calculated potential functions describing internal rotation (ϕ) about the C_{sp^2}–S bond in methyl vinyl sulfide.

allenyl sulfide were optimized while the rest of the parameters were taken from the 44-31G optimized geometries of methanethiol, vinyl mercaptan, and allenyl mercaptan. This is justified in light of the STO-3G results for these compounds. The theoretical 44-31G structures of methanethiol (**5**), vinyl

(5)
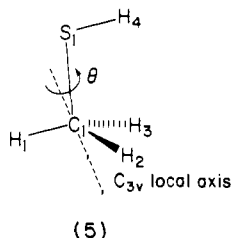
mercaptan, and allenyl mercaptan were determined in this work and are shown in Table I. A flexible rotor model similar to the one used in STO-3G calculations was also employed for 44-31G studies of conformations of vinyl mercaptan, methyl vinyl sulfide, and methyl allenyl sulfide. The 44-31G structural parameters and energetic data obtained in this manner are also shown in Tables II and III and Figures 1-3.

Discussion

Comparison of Calculated and Experimental Geometries. Available experimental structures for methanethiol,[23] methyl vinyl sulfide,[2,4,5] and methyl allenyl sulfide[4] are shown in Table I along with calculated results. The theoretical STO-3G and 44-31G structures for methanethiol have previously been reported,[14] but the data shown in Table I are more complete and reliable. A superficial inspection of Table I shows that STO-3G and 44-31G structures are rather similar to each other, with the exception that C-S and S-H bonds obtained by 44-31G are consistently longer than those by STO-3G. STO-3G results appear to be more in line with experimental values. However,
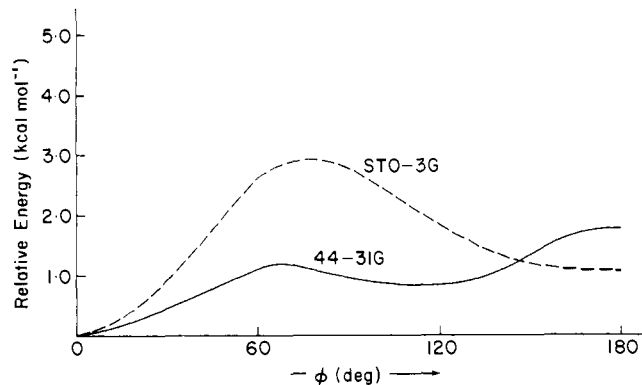

Figure 3. Calculated potential functions describing internal rotation (ϕ) about the C_{sp^2}–S bond in methyl allenyl sulfide.

Table III. Structural Variations Accompanying Internal Rotation (θ) in Methanethiol, Methyl Vinyl Sulfide, and Methyl Allenyl Sulfide (Å or deg)

Parameter[a]	STO-3G		44-31G	
	staggered	eclipsed	staggered	eclipsed
		methanethiol		
C_1–S_1	1.798	1.804	1.885	1.894
H_1–C_1	1.086	1.086	1.076	1.076
H_4–S_1	1.331	1.329	1.356	1.354
$H_1C_1S_1$	69.0	68.9	71.3	71.2
$H_4S_1C_1$	95.5	95.9	97.8	98.2
$H_{1,2,3}C_1S_1$	177.5	179.8	177.1	179.1
		methyl vinyl sulfide		
		(syn)		
C_3–S_1	1.797	1.802		
$C_1S_1C_3$	101.6	104.9		
$H_4C_3S_1$	110.7	111.1		
$H_{4,5,6}C_3S_1$	176.9	177.9		
		(anti)		
C_3–S_1	1.797	1.804		
$C_1S_1C_3$	99.3	100.8		
$H_4C_3S_1$	110.7	111.0		
$H_{4,5,6}C_3S_1$	177.4	179.3		
		methyl allenyl sulfide		
		(syn)		
C_4–S_1	1.797	1.802		
$C_4S_1C_1$	100.3	102.2		
$H_4C_4S_1$	110.7	110.8		
$H_{4,5,6}C_4S_1$	177.4	179.2		
		(anti)		
C_4–S_1	1.797	1.804		
$C_4S_1C_1$	98.8	100.3		
$H_4C_4S_1$	110.7	111.0		
$H_{4,5,6}C_4S_1$	177.4	179.2		

[a] See footnote *a* under Table I.

when bond variation in going from C_{sp^3}–S to C_{sp^2}–S is considered, the 44-31G basis set gives better results than the STO-3G (experimentally, 0.07Å; STO-3G, 0.03 Å; 44-31G, 0.07 Å). The results presented here are consistent with recent observations[14] that the addition of a full set of valence orbitals to a minimal basis set tends to increase bond lengths and that although the absolute errors for 44-31G bond lengths are generally large, the calculated bond lengths are expected to be consistently too long.

The carbon–carbon double bond of methyl vinyl sulfide is consistently and characteristically[24] underestimated by about 0.03 Å. However, the situation in methyl allenyl sulfide is more complex. Both STO-3G and 44-31G calculations predict that the C_2=C_3 bond should be slightly longer than the C_1=C_2 bond (by 0.001 Å for STO-3G and 0.007 Å for 44-31G). The electron diffraction data[4] on the other hand showed that the

Table IV. Calculated Total and Relative Energies

conformation		total, hartrees		relative, kcal mol^{-1}	
		STO-3G	44-31G	STO-3G	44-31G
		methanethiol			
staggered		−432.89607	−437.18374	0	0
eclipsed		−432.89375	−437.18200	1.46	1.09
		vinyl sulfide			
$\phi = 0°$		−470.25715	−474.97033	0	0
60°		−470.25087	−474.96818	3.94	1.35
90°		−470.24997	−474.96874	4.51	1.00
120°		−470.25203	−474.96946	3.21	0.55
180°		−470.25559	−474.96911	0.98	0.77
		allenyl sulfide			
$\phi = 0°$		−507.60390	−512.74447	0	
180°		−507.60214		1.10	
		methyl vinyl sulfide			
$\phi = 0°$	staggered	−508.84193	−513.95150	0	0
	eclipsed	−508.83696		3.12	
60°	staggered	−508.83645	−513.94851	3.44	1.88
120°	staggered	−508.83832	−513.95014	2.27	0.85
180°	staggered	−508.84152	−513.95000	0.26	0.94
	eclipsed	−508.83910		1.78	
		methyl allenyl sulfide			
$\phi = 0°$	staggered	−546.19005	−551.72652	0	0
	eclipsed	−546.18699		1.92	
60°	staggered	−546.18586	−551.72476	2.63	1.10
120°	staggered	−546.18715	−551.72525	1.82	0.80
180°	staggered	−546.18831	−551.72368	1.09	1.78
	eclipsed	−546.18567		2.75	

$C_1\!=\!C_2$ bond is much longer (0.045 Å) than the $C_2\!=\!C_3$ bond. Furthermore, if the underestimation of C=C bonds by theory is taken for granted, the experimental $C_2\!=\!C_3$ bond is then apparently too long while the $C_1\!=\!C_2$ bond is about correct. No immediate answers for this discrepancy can be afforded here. But, since not all independent structural parameters were taken into account before, a refinement of electron diffraction data by considering the present work may result in an improved structure.

For bond angles agreement between theoretical and experimental values is generally acceptable. It is also found that the 44-31G method seems to reproduce the experimental bond angles a little bit better than the STO-3G. The deviations between 44-31G and experimental values for the angles are within three times the quoted esd values, with the single exception of the $C_1S_1C_4$ angle of methyl allenyl sulfide. The experimental $C_1S_1C_4$ bond angle is surprisingly low (98.1°) compared with the observed values in methyl vinyl sulfide (102.5 or 104.6°). The theoretical value, on the other hand, appears to be more in line with the corresponding value in methyl vinyl sulfide. Again, we suggest that by taking the theoretical results into account a further refinement of the experimental results may lead to an improved structure.

The calculated $H_{1,2,3}C_1S_1$ angle in methanethiol ($H_{1,2,3}$ here represents a point on the C_3 local axis of C_1–H_1, C_1–H_2, and C_1–H_3 bonds) is 177.5° for STO-3G and 177.1° for 44-31G, respectively, compared with 177.8° obtained from microwave data. The corresponding angle, which shows the symmetry axis of the methyl group tilted with respect to the S–C(methyl) bond, in methyl vinyl sulfide as well as methyl allenyl sulfide is respectively 176.9 and 177.4° for STO-3G. No experimental value is currently available for comparison. However, the corresponding angle in dimethyl sulfide is known; 177.5° experimentally[25] and 177.0° theoretically.[13]

Conformational Analysis

(A) **Vinyl Mercaptan.** Vinyl mercaptan is of considerable experimental and theoretical interest.[2,7,26,27] Recently, microwave and infrared spectroscopic measurements[7] have shown that the predominant conformation of vinyl mercaptan is the planar or near-planar syn arrangement. Ab initio calculations have previously been carried out by Samdal and Seip[2a] to study the structure and conformations of vinyl mercaptan but only very limited geometry optimization was employed. However, their calculations involve d orbitals and hence offer an opportunity to judge qualitatively whether d orbitals are important for the present study. They used a {(C/7,3), (H/4), (S/10,6,1)} basis contracted to {[C/4,2], [H/2], [S/6,4,1]}.[28] For convenience in our later discussion, we will refer to the basis set adopted by them as an spd basis set.

Shown in Figure 1 are the rotational potential curves for three different basis sets. The STO-3G and 44-31G curves depicted in Figure 1 were obtained by fitting four points ($\phi = 0°, 60°, 120°$, and 180°) into eq 1. An extra point ($\phi = 90°$) was calculated both at STO-3G and 44-31G levels of theory in order to check how well the potential curve obtained in this manner is. In fact, the relative energies obtained from direct calculations are very similar to those obtained from the three-term curves (within 0.1 kcal mol^{-1}).

As can be seen from Figure 1, results obtained from the STO-3G method are quite different from those by spd and 44-31G calculations. Although the STO-3G method does correctly predict that the planar syn is most stable among all conformations, the barrier (4.7 kcal mol^{-1}) is probably overestimated (vide infra) and hence the second stable conformation is probably incorrectly predicted to be anti instead of gauche.

The 44-31G potential function is very similar to the one involving d orbitals. They both predict that the planar syn is the most stable conformation and a gauche constitutes the second stable conformation. The stable gauche form occurs at $\phi \simeq 135°$ with 44-31G calculations while $\phi \simeq 156°$ with spd calculations. Both spd and 44-31G calculations predict that the syn-gauche barrier occurs at about $60 \sim 70°$. However, the 44-31G barrier is smaller than the spd barrier (1.4 vs. 1.8 kcal

mol^{-1}). The low barrier to internal rotation in thiophenol (<0.8 kcal mol^{-1})[29] compared to phenol (3.3–3.5 kcal mol^{-1})[30] seems to favor the 44-31G value. Nevertheless, the smaller flexibility of rotor model employed in spd calculations may contribute to less acceptable agreement with experiment. Results presented here clearly indicate that neglecting d orbitals would not cause any serious drawbacks for the present study as long as an extended basis set is employed.

The conformational characteristics of vinyl mercaptan are similar to (but not identical with) those of vinyl alcohol.[2] By way of introduction, we might recall that propene exists preferentially in the eclipsed form, and the staggered form corresponds to the rotational transition state.[31,32] The methyl group's preference to be eclipsed rather than staggered with respect to the carbon–carbon double bond has been rationalized in terms of the overlap between the carbon component of $\pi^*_{CH_3}$ and $\pi_{C=C}$ (or π_{CH_3} and $\pi^*_{C=C}$).[32] We now turn our attention to the vinyl mercaptan system. At first, one might try to visualize vinyl mercaptan as an analogue of propene by assuming that sulfur lone pairs would approximately replace two methyl group orbitals in propene. This would seem to explain well the order of stabilities of syn and anti conformations. However, this rationale seems questionable from the following two points of view. First, population analysis[33] shows that a pair of lone-pair electrons occupies essentially a p_z orbital for H_2O or H_2S and the use of an sp^3 hybridization picture for the divalent dicoordinate oxygen or sulfur atom to predict molecular properties remains to be explored.[34] Second, the ratio of the barriers in the series ethane, methylamine, and methanol is close to the ratio of the number of vicinal hydrogen–hydrogen interactions. This suggests that interactions between vicinal hydrogens are probably playing an important role for conformational analysis of these molecules.

The situation in vinyl mercaptan (or vinyl alcohol) is probably best rationalized in terms of orbital interactions as well as steric effects. Interaction (6) between HOMO of a double


(6)
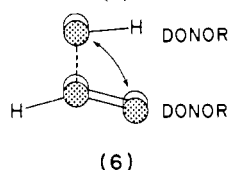
bond and the appropriate p_z orbital occupied by two lone-pair electrons involves four electrons and hence is destabilizing.[35] This unfavorable interaction should lead to a bond-angle widening of $C_2C_1S_1$. Obviously, the unfavorable orbital interaction is more easily relieved in the syn form (6) than in the anti (7) because of the existence of steric repulsion between

(7)
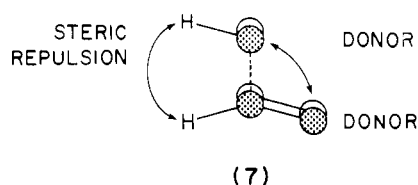
a vinyl hydrogen (H_1) and the hydrogen (H_4) attached to sulfur in the anti. Therefore, one expects that the anti would be less stable than the syn as predicted by calculations.[36] The Mulliken overlap population analysis provides some insight into the unfavorable steric repulsion. The overlap populations between H_1 and H_4 in syn and anti conformations are respectively 0.0011 and −0.0004 for STO-3G and 0.0017 and −0.0058 for 44-31G. These results clearly indicate some antibonding character between H_1 and H_4 hydrogens in the anti form. The obtained structures also support the proposed orbital and steric interactions. The obtained $C_2C_1S_1$ angle for the anti form (124.1° with STO-3G, 122.7° with 44.31G) is substantially smaller than the one in the syn form (127.3° for STO-3G,

127.0° for 44-31G) but is close to the corresponding value in ethylene (HCC; 122.2° for STO-3G and 122.0° for 44-31G).[24b] Furthermore, the C_1-S_1 bond length in the anti conformation is substantially longer than in the syn (0.005 Å with STO-3G and 0.008 Å with 44-31G) presumably also due to the unfavorable interaction being more severe in the anti (7 vs. 6).

Interaction 8 involves two electrons and is hence stabilizing.

(8)
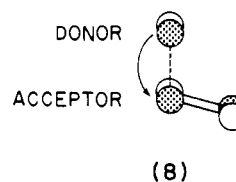
Deviation from planarity would certainly reduce this favorable interaction. Accordingly, the C_1-S_1 bond increases its length due to the decreasing π delocalization as the dihedral angle ϕ deviates from planarity.

While it is apparent that deviation from planarity decreases the favorable 2π electron interaction 8, it should also be borne in mind that rotating away from planarity would at the same time decrease the unfavorable 4π electron interaction 6 or 7. Therefore, there are two opposite interactions which counteract each other and the net gain as a result of such a distortion depends on their relative magnitudes. Since interaction 8 is not extremely strong as evidenced from experimental as well as theoretical barriers (vide infra) and interaction 7 is greater than 6, a gauche form occurring at $\phi = 135°$ is in fact not surprising.

Other structural variations ($H_1C_1S_1$ and $H_4S_1C_1$) presented in Table II may similarly be rationalized in terms of interactions 6–8. Another point of interest is that structural variations predicted by the STO-3G method are rather similar to those by the 44-31G method.

By way of contrast, let us consider the relationship between conformational characteristics of vinyl alcohol and vinyl mercaptan. The major conformational difference between vinyl alcohol and vinyl mercaptan occurs in the second stable conformation, which is related to the size of barrier height. The barrier is as high as 4.2 kcal mol^{-1} (spd) in vinyl alcohol while only about 1.4 kcal mol^{-1} (44-31G) or 1.8 kcal mol^{-1} (spd) in vinyl mercaptan. The high barrier in vinyl alcohol thus masks the stable gauche form found in vinyl mercaptan. Since the barrier height is approximately proportional to the magnitude of interaction 8, the result here indicates the difference in π character between C–S and C–O bonds. In fact, spd calculations[2] show that there is a large reduction in π overlap population in going from C–O to C–S (0.040 vs. 0.005 for the syn form). On the other hand, STO-3G calculations give a π overlap population in the C–S bond comparable to that in the C–O bond[37] (0.046 vs. 0.029 for the syn form). Apparently, the overestimation of π character by STO-3G is the principal factor for the less accurate results of STO-3G compared with the extended basis sets.

(B) Allenyl Sulfide. In light of the close relationship between structures and orbital interactions of vinyl sulfide and allenyl sulfide, one expects that their potential functions for internal rotation (ϕ) along the C_{sp^2}–S bond would be rather similar. The energy difference between syn and anti conformations of allenyl sulfide, for which STO-3G calculations were actually carried out, is indeed very close to that found in vinyl mercaptan (1.1 vs. 1.0 kcal mol^{-1}).

(C) Methyl Vinyl Sulfide. The most stable structure for methyl vinyl sulfide has experimentally been suggested to be the syn form.[2-6] Electron diffraction studies[2,4] seemed to favor a nonplanar gauche structure as the next most stable conformer, the angle ϕ lying in the range 116–123°. A study of temperature dependent photoelectron spectra also suggested

the existence of a gauche form but its nature is not clear.[6] In fact, the 44-31G calculations do predict that the syn and a gauche (Figure 2) are two stable conformations with the syn being lower in energy by 0.7 kcal mol^{-1}. The anti form represents a little energy bump (0.2 kcal mol^{-1}) which separates the two gauche forms from each other. The energy barrier which separates the syn from the gauche is about 2.1 kcal mol^{-1}. The maximum of the potential function for the C–C–S–C torsion occurs at $\phi = 70°$. This potential barrier which is lower than that found for methyl vinyl ether (4–5 kcal mol^{-1})[1,9] also supports the contention that the π delocalization in sulfides is much smaller than that in ethers. As can be seen from Figure 2, the obtained (44-31G) potential function is very flat indeed. However, the real potential function may even be flatter because of the possible coupling between the torsion about the C_{sp^2}–S bond and the torsion about the C_{sp^3}–S bond. One would therefore expect that the gauche form can oscillate almost freely through the anti and rotate to the syn without any big problem at room temperature.

According to our calculations, the cis-gauche energy difference is about 0.7 kcal mol^{-1} and this implies that there are approximately 38% of the molecules in the gauche conformation at room temperature. A slightly larger value (1.4 kcal mol^{-1}) for the energy difference was obtained from IR spectroscopy.[5] An even larger value (2.3 kcal mol^{-1}) was obtained from the temperature dependent photoelectron spectra.[6] On the other hand, electron diffraction studies[2] suggest zero (or near zero) energy difference. The results are contradicting each other. Previously, it has been shown that the barrier in internal rotation in thiophenol (<0.8 kcal mol^{-1})[29] is much lower than in phenol (3.3–3.5 kcal mol^{-1}).[30] One might expect a similar trend here. Thus, it seems to us that any value greater than 1 kcal mol^{-1} for the cis-gauche energy difference for methyl vinyl sulfide is probably questionable since the corresponding value in methyl vinyl ether is only 1.2 kcal mol^{-1} experimentally[38] and 1–2 kcal mol^{-1} theoretically.[1]

For methyl vinyl sulfide, the second conformer seems definitely to have a nonplanar arrangement on the basis of theoretical and experimental data. For methyl vinyl ether, the results are not consistent. Theoretical studies[1,2,9,39] predicted that the second conformer of methyl vinyl ether should be anti but most experimental data[40,41] favored a gauche form. However, the recent refinement[2] of electron diffraction data seemed to favor the anti although a gauche form with a torsional angle close to 180° could not be ruled out. The discrepancy in methyl vinyl ether is possibly due to the fact that experimental data represent the averaged dihedral angle (ϕ) while theoretical calculations deal with single conformations.

The STO-3G method predicts correctly that the syn conformation is most stable but predicts incorrectly that the anti is the next stable conformation. The energy barrier is also largely overestimated.

The dipole moments obtained from STO-3G calculations are respectively 0.59 and 1.09 D for syn and anti forms while those obtained from 44-31G calculations are 1.58 and 1.84 D, respectively. These values are very similar to those found in vinyl mercaptan (syn: 0.50 D for STO-3G and 1.55 D for 44-31G; anti: 1.02 D for STO-3G and 1.68 D for 44-31G). The STO-3G method probably underestimates these dipole moments.[13]

Since there is a close contact distance between the methyl group and the ethylene fragment if molecular model is considered, one might expect that the most stable conformation of methyl vinyl sulfide is the anti. However, this is certainly not the case both experimentally and theoretically. Interactions similar to 6 and 7 are possibly key factors dictating the unexpected conformational preference on the grounds of a simple steric interaction model. However, according to 44-31G cal-

culations, the syn-anti energy difference in methyl vinyl sulfide is even slightly larger than in vinyl mercaptan. This is contradictory to what is expected from steric considerations since the syn of methyl vinyl sulfide is indeed more crowded than the syn of vinyl mercaptan. Apparently, the methyl vinyl sulfide molecule should have gained extra stability by some procedures other than interactions 6 and 7, which still need to be accounted for. The extra stability may be rationalized in terms of interaction 9 between the HOMO of the methyl group and the LUMO of the C=C—S fragment or interaction 10 between

(9) (10)
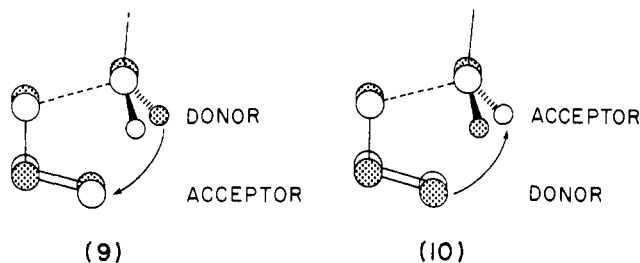
the LUMO of the methyl group and the HOMO of the C=C—S fragment. There is another qualitative MO approach to look at this problem as proposed by Bernardi et al.[9] for methyl vinyl ether. This would involve interaction 11 between

(11)
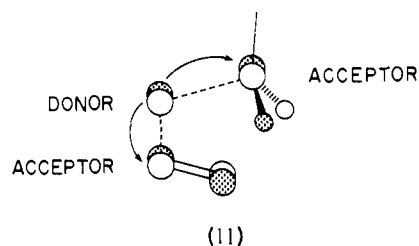
the filled $3p_z$ orbital of S and the LUMO of the group orbitals constructed by methyl and ethylene fragments. The extra stability gain by orbital interactions in methyl vinyl sulfide as opposed to vinyl mercaptan may equivalently be interpreted as saying that the former involves 6π electrons and is hence aromatic while the latter has 4π electrons and is hence nonaromatic.[9,32,42]

Although STO-3G calculations have some shortcomings as mentioned above, the obtained structural changes accompanying internal rotation from syn to anti are similar to those by 44-31G calculations. The structural variations for methyl vinyl sulfide are similar to those for vinyl mercaptan (Table II) and may be summarized as follows. As the dihedral angle ϕ deviates from planarity, the C_1–S_1 bond length increases due to the decreasing π delocalization. The $H_1C_1S_1$ bond angle usually opens because of the increasing steric repulsion between H_1 and the methyl group in going from 0 to 180°. On the other hand, the $C_1S_1C_3$ and $C_2C_1S_1$ angles usually decrease due to the relief of the corresponding steric repulsion as ϕ increases from 0 to 180°. The $H_{4,5,6}C_3S_1$ angle opens but quite insignificantly as ϕ rotates away from 0°.

The methyl rotational barriers for the syn and anti forms were also studied. The conformation involving a staggered arrangement of the methyl with respect to the C_1–S_1 bond was found to be more stable than the corresponding eclipsed form by 3.1 kcal mol^{-1} for the syn and 1.5 kcal mol^{-1} for the anti. The barrier to internal rotation calculated for the syn form is in good agreement with the experimental estimate (3.2 kcal mol^{-1}).[3] The methyl rotational barrier in dimethyl sulfide (single rotor) is 2.1 kcal mol^{-1} experimentally[25] and 2.5 kcal mol^{-1} theoretically.[13] An even lower value is found in methanethiol (1.3 kcal mol^{-1} experimentally,[43] 1.5 kcal mol^{-1} with STO-3G and 1.1 kcal mol^{-1} with 44-31G) and in dimethyl disulfide (1.6 kcal mol^{-1} experimentally[44] and 1.4 kcal mol^{-1} theoretically[13,17]). The higher value for the syn methyl

rotational barrier in methyl vinyl sulfide reflects the importance of interaction **9–11** and the existing unfavorable close contact between the eclipsed methyl hydrogen (H_4) and the vinyl hydrogen (H_3) in the syn conformation.

(D) Methyl Allenyl Sulfide. The calculated potential functions describing the $C_{sp^2}-C_{sp^2}-S-C_{sp^3}$ torsion for methyl allenyl sulfide are displayed in Figure 3. Both STO-3G and 44-31G calculations predict that the syn form is the most stable and the first rotational transition state for the syn–anti interconversion occurs at about $\phi = 65-70°$. However, this is the end of agreement between STO-3G and 44-31G calculations. The 44-31G method predicts that the second stable conformation occurs at $\phi = 120°$ and the anti form is another transition state while the STO-3G method shows that the anti is the second stable conformation. It seems thus that similar STO-3G drawbacks as found in vinyl mercaptan as well as methyl vinyl sulfide occur here too.

According to 44-31G calculations, the syn form would go to a gauche form through a barrier height of about 1.2 kcal mol^{-1}. There is a barrier height of about 1.0 kcal mol^{-1} separating two gauche forms from each other. Since these two barrier heights are small and about equal as seen from the gauche, the gauche–gauche transformation may proceed either through the anti form or by going back through the syn form. Therefore, the conformational characteristics between methyl vinyl sulfide and methyl allenyl sulfide are different.

The potential curve for methyl allenyl sulfide is more flat than the one for methyl vinyl sulfide. The flat potential curve obtained here reveals the possible difficulty for accurately determining the dihedral angle ϕ for stable conformations by experimental methods. Indeed, the available experimental results[4] are inconclusive. It was proposed, based on the gas phase electron diffraction study at 40 °C, that a slightly distorted planar syn with $\phi = 10-25°$ and a gauche form with $\phi = 94-108°$ were possible forms. Since the potential function is so flat, slight deviations from the planar syn conformation might be expected for experimental determination of the dihedral angle ϕ. However, a dihedral angle of 90° for the stable gauche form seems too small according to the present study.

The barrier height corresponding to the syn–anti interconversion for methyl allenyl sulfide is about 1 kcal mol^{-1} less than the one found in methyl vinyl sulfide (3.0 vs. 3.9 kcal mol^{-1} for STO-3G and 1.3 vs. 2.1 kcal mol^{-1} for 44-31G). This is presumably due to π character of the C–S bond being weaker in allenyl mercaptan than in vinyl mercaptan (for example, Mulliken population analysis (STO-3G) shows that π_{C-S} is 0.033 for the syn conformation of vinyl mercaptan while 0.023 for the syn conformation of allenyl mercaptan). The population analysis also shows that the π charge transferred from the S atom to the ethylene fragment in allenyl mercaptan is about 0.01 e less than that in vinyl mercaptan. Furthermore, the C–S bond in methyl allenyl sulfide is about 0.01 Å longer than in methyl vinyl sulfide and this displays a trend as shown by π overlap population analysis.

The methyl allenyl sulfide molecule is apparently less congested than the methyl vinyl sulfide molecule because of the absence of the close contact between a vinyl hydrogen (H_3) and the methyl group. This structural difference is possibly the main cause that the syn–anti energy difference is larger for methyl allenyl sulfide than for methyl vinyl sulfide (1.1 vs. 0.3 kcal mol^{-1} for STO-3G and 1.8 vs. 0.9 kcal mol^{-1} for 44-31G). The syn–anti energy difference in methyl allenyl sulfide compared with that in vinyl mercaptan is approximately a measure of intrinsic stability due to interactions **9–11**. The value obtained in this manner is 1.0 kcal mol^{-1} for 44-31G calculations.

Presumably, the lack of the unfavorable vinyl hydrogen–methyl group interaction in methyl allenyl sulfide also leads to a bond angle closing (1–2°) for $C_2C_1S_1$, $C_1C_1S_4$, and

$H_{4,5,6}C_4S_1$, as compared with corresponding values in the syn conformation in methyl vinyl sulfide. For methyl vinyl sulfide, rotating away from the planar syn would greatly reduce the unfavorable steric interaction. However, no such interaction is available for methyl allenyl sulfide. Therefore, structural variations for CCS and CSC accompanying internal rotation ϕ are smaller in methyl allenyl sulfide than in methyl vinyl sulfide. Other structural features accompanying internal rotation along the C_1-S_1 bond for methyl allenyl sulfide are quite similar to those for methyl vinyl sulfide and vinyl mercaptan and they will not be discussed further here.

The calculated rotational barriers hindering rotation of the methyl group in methyl allenyl sulfide are 1.92 and 1.66 kcal mol^{-1} respectively for the syn and the anti conformations, with the methyl staggered to the C_1-S_1 bond being always more stable. The methyl rotation barrier for the anti is as expected quite similar to that in methyl vinyl sulfide (1.66 vs. 1.52 kcal mol^{-1}). However, the syn barrier is much smaller than that found in methyl vinyl sulfide (1.92 vs. 3.12 kcal mol^{-1}) owing to the missing unfavorable methyl–vinyl hydrogen interaction.

Another point of interest is the derived reaction heats for the following isodesmic[45] reactions:

$$\begin{array}{c} \text{(2)} \end{array}$$

$$\begin{array}{c} \text{(3)} \end{array}$$
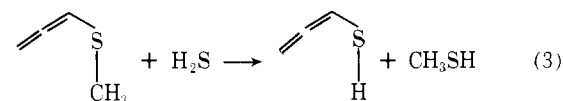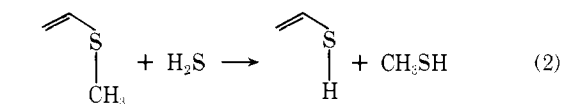
These reactions are a measure of germinal interactions at the sulfur atom. The obtained STO-3G values are respectively 0.2 and 1.1 kcal mol^{-1} for reactions 2 and 3. The corresponding 44-31G values are 0.9 and 1.4 kcal mol^{-1}, respectively, and they are almost systematically higher than STO-3G values. These results suggest that there are favorable geminal interactions in both molecules, and it seems that this interaction is more favorable in methyl allenyl sulfide while one can think of the unfavorable methyl group–vinyl hydrogen interaction in methyl vinyl sulfide.

Conclusions

Theoretical (STO-3G and 44-31G) structures as well as rotational potential surfaces for vinyl mercaptan, methyl vinyl sulfide, and methyl allenyl sulfide are reported here. Predictions are made for allenyl mercaptan. The theoretical (44-31G) structure and the rotational barrier for methanethiol are also presented here. Agreement between calculated and experimental structural data is generally good. However, 44-31G calculations are superior to STO-3G calculations for conformational analysis. On the basis of 44-31G results, it is concluded that the syn and a gauche form with $\phi \simeq 130°$ are the only two stable conformations for each molecule considered in this paper, with the syn being lower in energy. We have also attempted to rationalize structural variations and conformational energies in terms of orbital and steric interactions. Nonbonded attraction found in methyl vinyl ether is also found in methyl vinyl sulfide and methyl allenyl sulfide. Comparison of syn–anti energy differences between vinyl mercaptan and methyl allenyl sulfide reveals that the nonbonded attraction in this class of compounds is probably on the order of 1 kcal mol^{-1}. The lower syn–anti energy difference in methyl vinyl sulfide is ascribed to the fact that nonbonded attraction is partially masked by the unfavorable methyl group–vinyl hydrogen interaction. The methyl rotational barrier for the syn is much larger in methyl vinyl sulfide than in methyl allenyl

sulfide presumably due to the steric repulsions between a vinyl hydrogen and the eclipsed methyl group.

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