

Conformational Properties of Methyl Vinyl Sulfone: Ab Initio Geometry Optimization and Vibrational Analysis

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An ab initio conformational analysis of methyl vinyl sulfone ($\text{CH}_2\text{CHSO}_2\text{CH}_3$) has been carried out. Molecular geometry optimizations have been performed at the HF and MP2 levels of the theory. Relative energies of the stationary points have been determined by using different approaches, including electron correlation corrections up to the third order. The IR and Raman spectra of the liquid have been measured and a vibrational assignment is proposed. The height of the barrier to the methyl group internal rotation has been estimated. Theoretical calculations and vibrational spectra have shown that the predominant conformation of methyl vinyl sulfone has the $\text{C}=\text{C}$ bond eclipsed with one of the $\text{S}=\text{O}$ bonds. Similar eclipsed forms have been found in vinyl fluoro sulfone, vinyl chloro sulfone and divinyl sulfone by ab initio HF calculations.

KEY WORDS: Methyl vinyl sulfone; conformational properties; ab initio calculations; vibrational spectra.

INTRODUCTION

Recently we investigated the rotational spectrum of methyl vinyl sulfone (MVS) [1], and found that the eclipsed conformation (see Fig. 1) is more stable than any other form by at least 0.7 kcal/mole, such result contradicting the conclusions previously obtained from other methods. In fact, similar proportions of the eclipsed and *s-cis* conformers were posulated to account for E.D. [2] and vibrational spectroscopy results [3].

As a contribution to the clarification of the situation, a conformational analysis of MVS using ab initio molecular orbital theory at the Hartree-Fock (HF) and second order Møller-Plesset perturbation (MP2) [4] levels has been carried out.

In light of the results of such theoretical analysis we considered that a reinvestigation of the vibrational

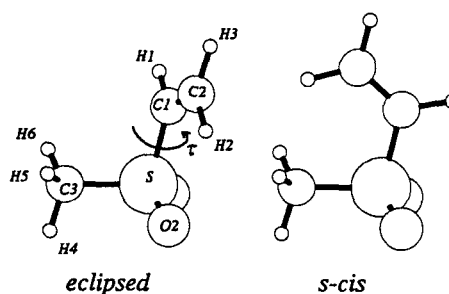


Fig. 1. Schematic representation of methyl vinyl sulfone.

spectra was indispensable. The IR and Raman spectra of the liquid MVS were then measured and a tentative assignment is proposed.

Since no definitive conclusions about the conformational properties could be drawn in the E.D. studies of the related molecules vinyl chloro sulfone ($\text{CH}_2\text{CHSO}_2\text{Cl}$) [5] and divinyl sulfone ($(\text{CH}_2\text{CH})_2\text{SO}_2$) [6], we felt that a theoretical conformational analysis of these molecules would be worthwhile. The results of this analysis, extended also to vinyl fluoro sulfone ($\text{CH}_2\text{CHSO}_2\text{F}$), have been included herein.

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CALCULATIONS

Throughout this study, molecular orbital calculations were performed with the GAUSSIAN 92 program [7], on a HP710 workstation. Geometry optimizations were done applying standard gradient techniques. Default convergence criteria were used for SCF and geometry optimizations. Residual forces were below 5×10^{-4} au. Vibrational frequencies were evaluated using analytical second differentiation.

EXPERIMENTAL

MVS was purchased from Aldrich and used without further purification. Infrared spectrum was obtained with a Bruker IFS 113 FT spectrometer, with a resolution of 2 cm^{-1} . Raman spectra were recorded with 4 cm^{-1} of resolution, with Raman accessory of the FT Bruker IFS 66 spectrometer equipped with a Nd-YAG laser. Polarization measurements were performed with a 90° geometry.

RESULTS AND DISCUSSION

Ab Initio Conformational Analysis

In Ref. 1 it was concluded that in the main conformation of MVS the dihedral angle τ between the C=C-S and C-S-C planes (see Fig. 1) must be greater than 109° . We used this value as the starting point for a geometry optimization at the HF level with the 3-21G* basis set, the only constraints being those of C_{3v} symmetry for the CH_3 group and planarity for the vinyl moiety. The calculation converged rather speedily to a minimum at $\tau = 110.9^\circ$. In a second step both restrictions were removed, and the fully optimized geometry reported in Table I was obtained.

In Table II the resulting rotational constants can be compared with the experimental values [1]. We have also included the deviations of the calculated second moments of inertia ($M_{aa} = -I_a + I_b + I_c$, etc.) with respect to the experimental values, since they indicate rather directly the "elongation" or "contraction" of the calculated geometry along the principal axes. The large negative deviation in the case of M_{aa} could be partly due to the apparently short values of the resulting S-C distances (see Table I), which could be considered a basis set deficiency, since this is also observed in methyl sul-

fone [8a], for which very reliable experimental data are available [9].

The 6-31G** basis set was then used, the fully optimized geometry being reported in Table I. As it was expected, the main difference with the 3-21G* geometry lies in the C-S distances, but the C-S-C angle is rather larger as well. The relative size of the two O-S-Cl angles is reversed, but the geometry of the SO_2 moiety is only slightly different.

As it can be seen in Table II, the agreement between calculated and experimental rotational constants is considerably improved with respect to the 3-21G* geometry, with deviations of second moments that can be considered more than satisfactory.

The addition of diffuse basis functions (6-31+G** set) has little influence on the optimized structural parameters and the agreement between experimental and calculated second moments of inertia is not further improved (see Tables I and II).

As regards the heavy atoms skeleton, the HF/6-31G** values of bond distances and angles are in reasonable agreement with those determined in the E.D. study of Ref. 2 (see Table I), with the exception of the C=C distance, whose calculated value is too short, a systematic deficiency at the HF level of the theory [8b]. The calculated S-O distance is somewhat larger than the experimental value, a rather unusual fact at the HF level. But in this case the experimental value could probably be in error, since it is 0.007 \AA shorter than those determined for $(\text{CH}_3)_2\text{SO}_2$ [9c] and $(\text{CH}_2\text{CH})_2\text{SO}_2$ [6].

Geometry optimizations were also performed for the two possible C_s structures. With the 3-21G* basis set, both ($\tau = 0^\circ$ and $\tau = 180^\circ$) are characterized by vibrational analysis to be transition states for the internal rotation around the S-Cl bond, while $\tau = 0^\circ$ corresponds to an energy minimum when the 6-31G** basis set is used. In the potential energy curve presented in Fig. 2, obtained by performing geometry optimizations at the HF/6-31G** level for fixed τ values, the shallowness of this second minimum is evident. The height of the *s-cis* to eclipsed rotational barrier can indeed be calculated to be only 0.1 kcal/mol from the relative energies reported in Table III. On the other hand, since the zero point energy of the *s-cis* form is just 0.1 kcal/mole higher than that of the transition state ($\tau = 29.8^\circ$), the existence of the second stable conformation cannot be established with certainty at the HF level.

In several molecular systems the potential energy curve has been observed to be drastically changed when electron correlation is included. In fact, not only the rel-

Table I. Optimized Geometries of the Eclipsed Conformer of Methyl Vinyl Sulfone.

Parameter ^a	HF/3-21G*	HF/6-31G**	MP2/6-31G**	HF/6-31+G**	E.D. ^b
S-C1	1.740	1.762	1.772	1.764	1.774(3)
S-C3	1.754	1.772	1.784	1.773	1.776
C1-C2	1.314	1.316	1.334	1.318	1.346(6)
S-O1	1.438	1.437	1.469	1.438	1.429(1)
S-O2	1.440	1.437	1.469	1.438	1.429(1)
H1-C1	1.072	1.075	1.082	1.075	
H2-C2	1.072	1.074	1.081	1.075	
H3-C2	1.072	1.075	1.081	1.075	
H4-C3	1.083	1.082	1.088	1.082	
H5-C3	1.080	1.081	1.086	1.081	
H6-C3	1.081	1.081	1.087	1.081	
C1-S-C3	102.6	104.1	103.1	104.2	103.2(0.6)
C2-C1-S	120.7	120.9	119.9	121.1	119.1(0.8)
O1-S-C1	108.8	107.7	107.3	107.6	109.5(0.6)
O2-S-C1	108.0	108.4	108.1	108.4	109.5(0.6)
H1-C1-S	115.9	114.8	115.5	114.7	
H2-C2-C1	120.8	121.1	120.3	121.2	
H3-C2-C1	121.5	120.7	121.0	120.6	
H4-C3-S	107.9	106.5	106.6	106.4	
H5-C3-S	110.2	109.4	109.1	109.3	
H6-C3-S	110.3	109.5	109.4	109.4	
C2-C1-S-C3	112.1	112.4	114.6	111.8	
O1-S-C1-C2	226.2	226.2	228.2	225.8	
O2-S-C1-C2	-2.1	-2.1	0.9	-2.7	
H1-C1-S-C3	-70.4	-70.5	-69.0	-70.8	
H2-C2-C1-H1	-178.5	-178.7	-178.7	-178.6	
H3-C2-C1-H1	0.7	0.6	0.5	0.6	
H4-C3-S-C1	178.6	178.0	178.2	178.0	
H5-C3-S-C1	-62.1	-62.9	-62.6	-62.8	
H6-C3-S-C1	59.9	59.3	59.4	59.3	
O...O ^c	2.492	2.493	2.563	2.494	2.475
O-S-O ^c	120.0	120.3	121.4	120.2	120.0(0.5)

^aDistances in Å and angles in degrees. For the atom numbering see Fig. 1.

^bFrom ref. [2]. Individual C₁ symmetry model with fixed S-C₃ distance.

^cDependent parameters.

Table II. Rotational Constants (MHz) and Deviations (Calc-Exp) of the Second Moments of Inertia (amu. Å²) of Methyl Vinyl Sulfone.

	HF/3-21G*	HF/6-31G**	MP2/6-31G**	HF/6-31+G**	Exp. ^a
A	4561.6	4548.9	4401.5	4543.7	4524.321(1)
B	2562.4	2514.0	2478.5	2507.3	2513.832(1)
C	2537.5	2504.0	2470.8	2497.7	2500.768(1)
ΔM_{aa}	-2.9	0.2	1.1	0.6	
ΔM_{bb}	0.0	-0.4	1.4	-0.4	
ΔM_{cc}	-0.9	-0.2	1.8	-0.1	

^aFrom Ref. 1.

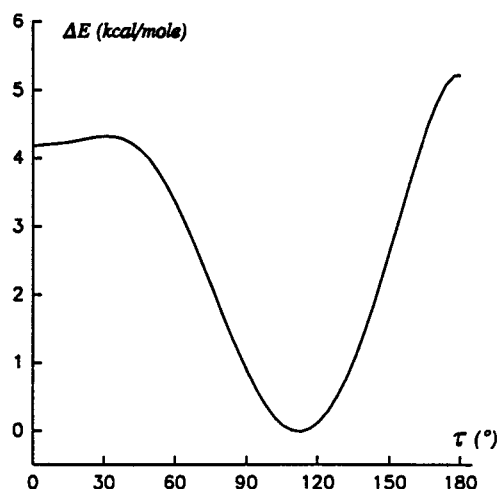


Fig. 2. Variation as a function of the C=C-S-C dihedral angle (τ) of the HF/6-31G** energy of methyl vinyl sulfone.

ative energies can be different, but also the location and even the number of stationary points.

Full geometry optimizations were also performed at the second order Møller-Plesset perturbation level (MP2) with the 6-31G** basis set, in order to analyze the influence of the electron correlation effects on the potential energy of MVS. The optimized geometry of the eclipsed conformation is reported in Table I.

A visual inspection of the lowest vacant molecular orbitals showed that they have antibonding character. Electron promotion into these unfilled orbitals, implicit in the MP2 perturbation treatment, would be expected to lead to bond lengthening with respect to the HF values, which is consistent with the large positive deviations in the second moments (Table II) calculated with the MP2 geometry.

The effect of the correlation correction on the calculated C=C bond length is of particular interest. While the highest occupied molecular orbital (HOMO) is almost entirely a π -type bonding orbital on this bond, the

lowest unoccupied molecular orbital (LUMO) consists mainly of the corresponding π^* (antibonding) orbital. The significant lengthening of the C=C bond distance can be attributed to a large contribution to the MP2 wave function of the double substitution involving these two orbitals, with the concomitant reduction of the double-bond character.

It is worth noting that this is the only skeletal bond distance for which the agreement with the experimental value is improved by the correlation correction.

However, the most significant difference between the HF and MP2 geometries is to be found in the SO₂ group, being this effect also observed in (CH₃)₂SO₂ [10]. In fact, at the MP2 level the S-O bond distances lengthen by 0.03 Å with respect to the HF values, while the OSO angle increases by about 1°. The resulting O···O nonbonded distance is definitively out of the range within which that distance has been observed to vary in a relatively large series of sulfone molecules.

This behavior is related to the significant depletion of charge density that correlation correction produces around the S=O bond critical point, being this effect clearly observed when the MP2 electronic density is compared with the SCF density.

The relative energies of the eclipsed and *s-cis* conformations, and that of the transition structure connecting them ($\tau = 36^\circ$), obtained by full geometry optimizations at the MP2 level, are shown in Table III. The relative energy of the two minima is sensibly lowered by the inclusion of the second order correction. The *s-cis* to *trans* barrier, on the other hand, is twice that obtained at the HF level, but this difference can hardly be considered relevant because the barrier height is still of the same order of the zero point energy difference.

The results of single point MP2 and MP3 calculations based on HF geometries are also gathered in Table III. Although, as expected, the second-order corrections are considerably different from those obtained within the MP2//MP2 scheme, there are only slight differences as regards the relative energies of the three stationary points considered.

The third order corrections, on the other hand, have no effect on the relative energies of the two minima.

Table III. Relative Energies (kcal/mol) of the Stationary Points in the Potential Energy of Methyl Vinyl Sulfone.

	<i>s-cis</i>	TS	Eclipsed	<i>s-trans</i>
E(HF/3-21G*)	5.7		0.0	6.3 ^a
E(HF/6-31G**)	4.2	4.3	0.0	5.2
E(HF/6-31+G**)	4.1		0.0	
E(MP2/6-31G**)	3.3	3.5	0.0	
E(MP2/6-31G**//HF/6-31G**)	3.4	3.5	0.0	
E(MP3/6-31G**//HF/6-31G**)	3.4		0.0	

^aTransition state.

Vibrational Spectra

Figure 3 shows the Raman spectrum of liquid MVS. The number of fundamental modes observed, and the fact that all the Raman bands were clearly polarized, are consistent with the presence in a detectable amount of an only conformer with C₁ symmetry, in agreement with theoretical predictions and microwave results [1].

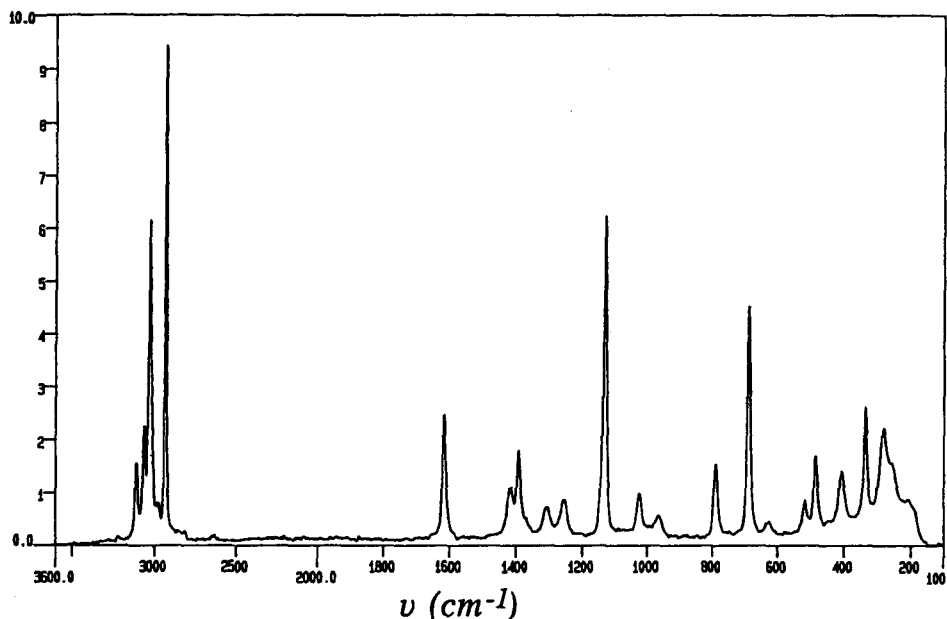


Fig. 3. Raman spectrum of methyl vinyl sulfone.

The wavenumbers observed in the IR and Raman spectra of liquid MVS are collected in Table IV.

The fundamental vibrations were assigned mainly on the basis of the HF/6-31G** calculated vibrational frequencies and normal modes characterization, but the assignments were tested with spectra of related molecules [6, 11].

Assignment of bands over 600 cm^{-1} did not present major difficulties; therefore we thought that only the portion of the spectrum below that frequency deserved some discussion.

The assignment of the SO_2 deformations is difficult because, on the one hand, there are no regularities in their order for various sulfonyl compounds, and, on the other hand, the sequence predicted for the ab initio calculations is not always coincident with the experimental results. In fact, HF/6-31G** frequency calculations [10] are successful in reproducing the order proposed for the sulfonyl deformations in a vibrational analysis of divinyl sulfone [6], but fail in the case of dimethyl sulfone [11], where experimental evidences would seem to be conclusive. Since in the case of MVS, due to its low symmetry, the analysis should have been done on the basis of relative intensities and depolarization ratios of Raman bands, we thought any conclusion drawn would have been controvertible. The order predicted theoretically was then maintained.

Characterization of the ν_3 and ν_4 fundamentals as the SCC and CSC deformation modes is rather arbitrary

because a considerable mixing is predicted, and they could also be described as an antisymmetric (ν_3) and a symmetric (ν_4) deformation of the C-S-C=C chain.

Finally, the assignment of the feature at 205 cm^{-1} in the Raman spectra to the methyl group torsion is supported not only by the calculated frequency but also by the value obtained in Ref. 1.

Barrier to the Methyl Group Internal Rotation

In Ref. 1 a lower limit of 2.8 kcal/mole was established for the barrier to the methyl group internal rotation in MVS. To calculate the barrier height, we performed a HF/6-31G** full geometry optimization, starting with the CH_3 moiety rotated 60° from its equilibrium position (see Table I). Including the zero-point energies, a barrier height of 2.7 kcal/mole was obtained, a value only slightly below the above mentioned experimentally determined limit.

The reliability of the method used here for MVS was tested by determining the barrier to the methyl group internal rotation in methane sulfonyl fluoride, the only tetracoordinate S(VI) compound for which a reliable experimental value is available [8a]. The agreement between the calculated and experimental values was better than 0.5%, and then the method can be considered successful within the experimental error, equivalent to a 7.5%.

Table IV. Observed and Calculated^a Frequencies (cm⁻¹) and Vibrational Assignment for Methyl Vinyl Sulfone.

Mode	Approximate description	HF/6-31G**	IR	Raman
ν_{30}	asym. CH ₂ stretch	3051	3107	3107
ν_{20}	CH stretch	3005	3059	3060
ν_{28}	asym. CH ₃ stretch	2963	3022	3026
ν_{27}	sym. CH ₂ stretch	2963	3022	3026
ν_{26}	asym. CH ₃ stretch	2954	3022	3026
ν_{25}	sym. CH ₃ stretch	2864	2934	2930
ν_{24}	CC stretch	1638	1614	1615
ν_{23}	asym. CH ₃ def.	1408	1414	1414
ν_{22}	asym. CH ₃ def.	1406	1414	1414
ν_{21}	CH ₂ def.	1375	1389	1390
ν_{20}	sym CH ₃ def.	1341		
ν_{19}	asym. SO ₂ stretch	1289	1302	1306
ν_{18}	CH def.	1246	1259	1254
ν_{17}	sym. SO ₂ stretch	1104	1132	1126
ν_{16}	CH ₂ wag	1031	1018	
ν_{15}	CH ₂ rock	1008		1021
ν_{14}	CH rock	975	984	963
ν_{13}	CH ₃ rock	967	984	963
ν_{12}	CH ₃ rock	956	966	963
ν_{11}	asym. CS stretch	785	789	790
ν_{10}	sym. CS stretch	684	687	687
ν_9	CH rock	621	627	625
ν_8	SO ₂ wag	503	515	516
ν_7	SO ₂ def.	467	484	483
ν_6	SO ₂ rock	393		405
ν_5	SO ₂ tors.	310		333
ν_4	CSC def.	252		280
ν_3	SCC def.	238		257
ν_2	CH ₃ tors.	199		206
ν_1	vinyl tors.	104		

^aScaled by 0.89.

Conformational Analysis of Vinyl Fluoro Sulfone, Vinyl Chlorosulfone, and Divinyl Sulfone

In order to comprehend to which extent the conformational properties of CH₂CHSO₂X molecules depend on the X substituent, our theoretical analysis was extended to vinyl fluoro sulfone (VFS), vinyl chlorosulfone (VCS), and divinyl sulfone (DVS). The HF/6-31G** optimized geometries of the stable forms are reported in Table V, and the relative energies of the stationary points are shown in Table VI.

The results obtained for VFS are very similar to those previously obtained for MVS. The absolute minimum of the potential energy was located at $\tau = 113^\circ$ (eclipsed) and a very shallow minimum at $\tau = 0^\circ$ (*s-cis*), with the transition structure between them at $\tau = 41.2^\circ$.

For VCS, on the other hand, only one energy min-

imum was located, since the *s-cis* form was characterized to be a transition structure. In light of these theoretical results, the hypothesis on the conformational composition used in the E.D. investigation of Ref. 5 should be revised. The bond lengths and angles determined there, however, were found to be independent on the refinement scheme used, and therefore no significant changes should be expected even if the E.D. data were refined under the assumption of an only conformation. The agreement between experimental and calculated values is very good (see Table V), specially for the S=O bond length. As previously noted for MVS, the exception is the C=C distance, whose calculated value is too short.

In the case of DVS, the two eclipsed structures with C₂ ($\tau' = \tau$) and C_s ($\tau' = -\tau$) symmetry correspond to minima on the potential energy surface, with transition structures for the internal rotation around both C—S bonds located at $(\tau, \tau') = (109.2^\circ, 36.7^\circ)$, while no other stationary points could be found. The results on the conformational equilibrium obtained in the E.D. study of Ref. 6 would then be at least controvertible, since, even within the refinement scheme (set B) more consistent with our theoretical results, a significant relative abundance of the C₁ form was determined, and the same conformational ratio for both the C₂ and C_s conformers was obtained.

But also in this case, the results on the bond lengths and angles were found to be independent on the conformational properties, with the exception of the C—S—O and C—S—C angles. For the remaining parameters there is good agreement between experimental and calculated values, except for the C=C bond, whose calculated value is again too short.

CONCLUSIONS

The theoretical conformational analysis presented here predicts that methyl vinyl sulfone exists predominantly in a conformation in which one of the S=O bonds almost exactly eclipses the C=C bond (C=C—S=O dihedral angle < 3°). The *s-cis* form cannot be definitively characterized as a second stable conformation, but, in any event, it would be less stable than the eclipsed conformer by at least 3.3 kcal/mole. This result is consistent with the conclusion obtained in Ref. 1, where a lower limit of 0.7 kcal/mol was determined for the energy difference between conformers.

Our vibrational analysis showed that the eclipsed conformation is the only one detectable in the liquid.

Table V. HF/6-31G** Optimized Geometries of Vinyl Fluoro Sulfone, Vinyl Chloro Sulfone, and Divinyl Sulfone.

Parameter ^a	Vinyl fluoro sulfone	Vinyl chloro sulfone		Divinyl sulfone		
	X=F	X=Cl		X=C3		
	HF	HF	E.D. ^b	HF		E.D. ^c
				C ₂	C _s	
S-Cl	1.745	1.753	1.744(5)	1.761	1.761	1.769(4)
S-X	1.562	2.031	2.035(5)	1.761	1.761	1.769(4)
C1-C2	1.315	1.315	1.357(18)	1.316	1.315	1.332(4)
S-O1	1.413	1.419	1.420(6)	1.437	1.436	1.438(3)
S-O2	1.414	1.420	1.420(6)	1.437	1.437	1.438(3)
H1-C1	1.074	1.074		1.075	1.075	
H2-C2	1.074	1.074		1.074	1.074	
H3-C2	1.075	1.075		1.075	1.075	
C1-S-X	99.2	101.2	100.2(6)	103.5	103.9	
C2-C1-S	120.5	120.2	121.3(17)	121.0	121.1	121.5(3)
O1-S-C1	110.0	109.0	109.8(4)	107.6	107.2	
O2-S-C1	110.9	110.0	109.8(4)	108.1	108.3	
H1-C1-S	114.3	114.0		114.5	114.6	
H2-C2-C1	121.6	121.6		121.1	121.2	
H3-C2-C1	120.3	120.1		120.7	120.7	
C2-C1-S-X	113.0	112.0		112.1	114.1	
O1-S-C1-C2	223.7	223.5		226.4	227.4	
O2-S-C1-C2	-0.6	1.6		-1.9	-0.9	
H1-C1-S-X	-69.1	-70.3		-70.2	-69.0	
H2-C2-C1-H1	-179.9	-179.5		-178.9	-178.7	
H3-C2-C1-H4	-0.2	0.3		0.4	0.8	
O...O ^d	2.474	2.480	2.484	2.496	2.496	2.485
O1-S-O2 ^d	122.1	121.6	122.0(10)	120.6	120.6	119.5(12)

^aDistances in Å and angles in degrees. For the atom numbering refer to Fig. 1 with X replacing C3.

^bFrom Ref. 5.

^cFrom Ref. 6.

^dDependent parameters.

The results obtained for vinyl chloro sulfone, vinyl fluoro sulfone, and divinyl sulfone make evident that the high relative stability of the eclipsed conformation in

CH₂CHSO₂X molecules is a characteristic of the electronic distribution on the C=C-S=O chain, while the subtle differences in their conformational properties can be attributed to the different steric effect of each substituent.

Table VI. HF/6-31G** Relative Energies (kcal/mole) of the Stationary Points in the Potential Energy of Vinyl Chloro Sulfone, Vinyl Fluoro Sulfone, and Divinyl Sulfone.

	Eclipsed	TS ^a	<i>s-cis</i>	C ₂	C _s
VFS	0.0	3.4	3.0		
VCS	0.0		4.6 ^b		
DVS		4.8		0.0	0.6

^aThe transition state corresponds to $\tau = 41.2^\circ$ for VFS and to $(\tau, \tau') = (36.7^\circ, 109.2^\circ)$ for DVS (see text).

^bTransition state.

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