Carbohydrate Research, 104 (1982) 21–32
Elsevier Scientific Publishing Company, Amsterdam – Printed in The Netherlands

ANOMERIC EFFECT IN SULFUR-CONTAINING SYSTEMS: AN *Ab-initio* STUDY

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(Received March 2nd, 1981; accepted for publication in revised form, November 10th, 1981)

ABSTRACT

The anomeric effect in S-C-S and O-C-S systems was studied by using closed-shell Hartree–Fock theory. A comparison of the STO-3G level with the 4-31G and 6-31G* levels was performed for the O-C-O system, and the STO-3G level found adequate for study of the anomeric effect. Optimization of bond lengths and angles was conducted at the STO-3G level and limited studies were made at the 4-31G level. The nature of the torsional potential curves is compared for the O-C-O, O-C-S, and S-C-S systems. The possible reasons for the decreased anomeric effect in sulfur systems are discussed.

INTRODUCTION

The anomeric effect[1,2] is known to influence the favored conformations in a number of systems. Extensive data[3,4] are available on the molecular geometries of the systems involved in anomeric effects associated with specific combinations of electronegative atoms X and Y. A series of crystallographic studies (see Tables VI–VIII in ref. 5) and various theoretical calculations[6–14] have helped in understanding the anomeric effect in general. By using dimethoxymethane as the model compound, it has been shown, in agreement with experiment, that methyl α-D-pyranosides favor a conformation where the C-5–O-5–C-1–O-1–C bond-sequence adopts the (*-sc*,*-sc*) orientation (the first value in parentheses refers to the dihedral angle θ and the second one to ϕ, as shown in Fig. 1), and in methyl β-D-pyranosides the foregoing sequence favors the (*ap*,*-sc*) orientation; the extended disposition (*ap*,*ap*) is not observed for the oxygenated systems. However, the (*ap*,*ap*) orientation has been reported for a crystalline 1,5-dithio-α-D-pyranoside, a system in which both hetero atoms are sulfur. N.m.r. studies[15] on various sulfur-containing D-ribopyranosides have also indicated significant differences in the conformational preference for the six-membered ring. These differences have been attributed to a lower anomeric effect in thioribopyranosides. Therefore, a systematic study of the anomeric effect in sulfur systems has been performed theoretically by *ab-initio* molecular orbital theory, and comparison is made with the oxygen analogues.

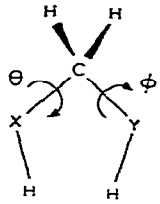

Fig. 1. Schematic representation of the dihedral angles θ and ϕ in X-C-Y systems, where $\theta = \phi = 0°$. In methanediol, X = Y = oxygen, in methanedithiol, X = Y = sulfur, and in thiolmethanol, X = sulfur and Y = oxygen.

METHODS

Closed-shell Hartree–Fock theory[16] at the STO-3G[17] level was used for most of the calculations, using the DEC-10 version of GAUSSIAN 74. The model compounds studied were methanedithiol and thiolmethanol. The energies were calculated for various θ and ϕ values, θ and ϕ being depicted in Fig. 1.

Standard geometries[18] were used for the first-row atoms. The C-S and S-H bond lengths were taken as 182 and 135 pm, respectively, and the C-S-H bond angle was taken[19] as 96.5°. The C-S-C bond angle was taken* as 100.3°. Energy optimizations were also performed as functions of the C-O or C-S bond lengths and as functions of the O-C-S or S-C-S bond angles. Single calculations were conducted on bis(methylthio) methane $[CH_2(SCH_3)_2]$ for the three staggered conformations: (*-sc,-sc*), (*ap,-sc*), and (*ap,ap*). For this system, standard values were used for all parameters except for the S-C-S angle, which was assumed to be the same as that obtained by optimization for the methanedithiol system. The 4-31G calculations[20] were also made for the three staggered conformations of methanedithiol, using geometries obtained by optimization at the STO-3G level.

RESULTS AND DISCUSSION

Table I shows the STO-3G results for methanediol. The data reported earlier[5] for this system using 4-31G and[21] 6-31G* methods are also included in this table for comparison. Table I shows that, although there are differences in the actual energy values, all of the methods lead to the same favored conformations, with (60,60) being the lowest. The energy maxima also occur at the same positions. Compared with the 6-31G* results, the STO-3G energy differences are underestimated and the 4-31G energy differences overestimated. The variation of the potential energy with respect to θ and ϕ (Fig. 1) obtained by STO-3G calculations is qualitatively the same as that reported by the 4-31G or the 6-31G* methods. The bond-length studies presented in Table II shows that STO-3G also predicts the shortening of C-O bonds, but to a lesser extent than predicted by the 4-31G method. This difference may be due

*The average crystal-structure value was taken for the C-S-C angle.

TABLE I

RELATIVE ENERGIES FOR VARIOUS CONFORMATIONS OF METHANEDIOL ($kJ.mol^{-1}$)

(θ, ϕ)	*STO-3G*	*4-31G*[b]	*6-31G**[c]
(60,60)	0.0[a]	0.0	0.0
(±60,180)	9.37	20	15.7
(180,180)	27.6	47	37.0
(180,0)	11.0	18	18.2
(180,±120)	25.1	40	30.5
(60,0)	16.0	20	16.7
(60,120)	9.67	16	12.9
(60,−120)	13.6	21	15.9
(60,−60)	11.97	23	17.2

[a]The total energy for this conformation is −187.38249 hartrees. [b]From ref. 7. [c]From ref. 5.

TABLE II

ENERGIES OF METHANEDIOL FOR OPTIMIZED C-O[a] BOND LENGTHS AND OPTIMIZED O-C-O ANGLES

Method	*Conformation*	*Optimized C–O-1 (pm)*	*Optimized C–O-2 (pm)*	*Optimized O-C-O (degrees)*	*Relative energy*[b] *kJ.mol*$^{-1}$
	(+*sc*,+*sc*)	142.7	142.7	111.76	0 (0)
STO-3G	(+*sc*,*ap*)	141.5	143.1	109.18	10.6 (9.37)
	(*ap*,*ap*)	142.2	142.2	106.31	26.9 (27.6)
	(+*sc*,+*sc*)	141.6	141.6	110.69	0 (0)
4-31G[c]	(+*sc*,*ap*)	139.6	142.8	108.76	18.8 (18)
	(*ap*,*ap*)	140.9	140.9	106.87	44.77 (46)

[a]Optimized C-O bond length in methanol is 143.7 (4-31G, ref. 7) and 143.3 pm (STO-3G, ref. 38). [b]Values in parentheses are relative energies calculated by using a standard value for the O-C-O angle. [c]From ref. 7.

to the limitation of the STO-3G method, which has less flexibility for the valence shell, which is well accommodated in 4-31G split-valence basis set. The optimum O-C-O bond angle predicted by both methods is very similar in methanediol. In this system, the optimization of bond lengths and bond angles does not significantly affect the energy differences between various conformations. There is thus qualitative agreement between the STO-3G, 4-31G, and 6-31G* results for methanediol, suggesting that the STO-3G method may be used to predict the favored conformations in these systems, as also found by other workers[9,12].

The concept of d-orbital participation as proposed by Pauling[22] has been investigated by several authors. A critical comparison[23] of the performance of various basis sets (including polarization functions) for second-row atoms has been made. Also, a number of sulfur-containing systems in particular have been studied with d

TABLE III

POTENTIAL SURFACE (STO-3G) FOR METHANEDITHIOL WITH RIGID ROTATION[a] (kJ.mol^{-1})

ϕ (degrees)	θ (degrees)						
	−180	*−120*	*−60*	*0*	*60*	*120*	*180*
180	4.06	6.49	0.75	8.40	0.75	6.49	4.06
120	6.49	13.7	6.36	13.39	6.86	11.6	6.49
60	0.75	6.36	4.14	11.3	0.0[b]	6.86	0.75
0	8.41	13.4	11.3	36.1	11.3	13.4	8.40

[a]This table and Table VI may be extended to negative ϕ values by using $V(-\theta,-\phi) = V(\theta,\phi)$.
[b]Total energy is −826.063507 hartrees.

functions[24-27]. In general, the molecular properties are described adequately without the addition of d-orbital contributions. Polarization functions are found to be important for describing such properties as dipole moment[28,29], the bond angle at the second-row atom with non-hydrogen substituents[23], and in the study of hypervalent

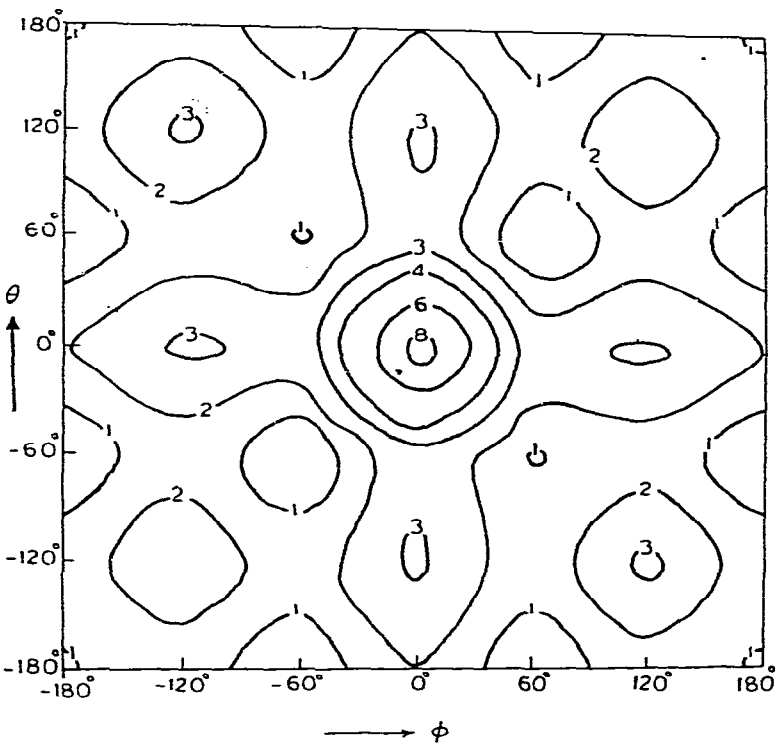

Fig. 2. Potential energy surface for methanedithiol as a function of the torsion angles θ and ϕ.

TABLE IV

OPTIMIZATION OF C-S[a] BOND LENGTH AND S-C-S BOND ANGLE IN METHANEDITHIOL
(The study is at STO-3G level unless otherwise specified)

Conformation	*Optimized C–S-1 (pm)*	*Optimized C–S-2 (pm)*	*Optimized S-C-S (degrees)*	*Relative energies kJ.mol*$^{-1}$			
				b	*c*	*d*	4-31G[e]
(+60,+60)	181.7	181.7	114.55	0	0	0	0
(+60,180)	181.5	180.5	112.54	4.27	0.46	0.75	9.04
(180,180)	180.9	180.9	110.37	9.24	3.56	4.06	18.6

[a]The STO-3G optimized C-S bond-length in methanethiol is[22] 180.4 pm. [b]Relative energies obtained by optimizing the C-S bond lengths and S-C-S bond angles. [c]Relative energies obtained by optimizing the C-S bond lengths; all other parameters are taken as standard values. [d]Relative energies obtained by assuming standard values for all parameters. [e]4-31G calculations were made for STO-3G optimized geometries.

molecules[30]. In view of these studies, we feel that the minimal basis-set is sufficient for our present study of sulfur systems.

The results for methanedithiol, using standard bond lengths and angles, are presented in Table III and Fig. 2. The various optimization studies and the 4-31G studies for this system are presented in Table IV. Interestingly, although the (*sc,sc*) conformation is of the lowest energy, the energy differences between the (*sc,sc*) and (*ap,sc*) [or (*sc,ap*), which has the same energy as the (*ap,sc*)] conformations (ΔE_1 = 4.27 kJ.mol^{-1}) and the difference between the (*sc,ap*) and (*ap,ap*) conformations (ΔE_2 = 4.98 kJ.mol^{-1}) are much less than the corresponding differences (ΔE_1 and ΔE_2 are 10.7 and 16.2 kJ.mol^{-1}, respectively) for the methanediol system. These energy differences are quite insensitive to the bond-length optimization studies. As with methanediol, the optimized C-S bond-length varies as a function of conformation. However, it is noteworthy that all C-S bonds are longer than the STO-3G-optimized C-S bond for methanethiol (CH_3SH), in contrast to the methanediol system, where all C-O bonds are shorter than in methanol. The S-C-S bond-angle optimization studies show that these angles depend significantly on conformation. The largest is 114.6° for the (*sc,sc*) conformation, and the smallest is 110.4°, for the (*ap,ap*) conformation; this is the same trend as observed in -O-C-O- systems. As there are only limited experimental studies on thiopyranosides[14,15,31–34], a comparative study of the present, theoretically predicted bond lengths and angles with experimental values is not attempted in this paper.

Unlike the case of halomethanols[13], the 4-31G studies on methanediol and methanedithiol (see Tables I and III) agree qualitatively with the STO-3G studies that is the ΔE_1 [(*sc,sc*):(*sc,ap*)], and the ΔE_2 [(*sc,ap*):(*ap,ap*)] values are smaller for the S-C-S system than for the O-C-O system. However, the ΔE_1 and ΔE_2 values predicted by 4-31G studies are higher in both systems than those predicted by STO-3G studies. In view of the comparative studies conducted earlier on methanediol, we

TABLE V

COMPARATIVE STUDY OF DIMETHOXYMETHANE AND BIS(METHYLTHIO)METHANE AT THE STO-3G LEVEL

Conformation	$CH_2(SCH_3)_2$[a] *Relative energy* $kJ.mol^{-1}$	$CH_2(OCH_3)_2$ *Relative energy* $kJ.mol^{-1}$
(+*sc*,+*sc*)	0.0[b]	0[c] (0)[d]
(+*sc*,*ap*)	4.23	6.57 (2.76)
(*ap*,*ap*)	7.36	13.8 (13.7)

[a]Standard geometry is used except for the S-C-S angle, which is assumed to be the same as the optimized value in methanedithiol, given in Table IV. [b]Total energy for this conformation is −903.23627 hartrees. [c]The values are for optimized O-C-O angles and are taken from ref. 5. [d]The values in parentheses are computed for standard geometry. The total energy for the (+*sc*,+*sc*) conformation is −264.550262 hartrees. The values reported for standard geometry in ref. 5 are different from these values, as those authors used 108° for the O-C-O angle instead of 109.5°.

expect the 6-31G* estimate for ΔE_1 and ΔE_2 to be intermediate between the STO-3G and the 4-31G values.

As $CH_2(XCH_3)_2$ are better model compounds for the methyl aldopento-pyranosides, some studies at the STO-3G level on these compounds were performed, and the results are presented in Table V. The ΔE_1 values seem to be sensitive to the level of optimization. However, ΔE_2 values and the energy differences between the (*sc*,*sc*) and (*ap*,*ap*) conformations are clearly decreased when oxygen is replaced by sulfur, thus supporting the conclusions drawn from study of the $CH_2(XH)_2$ system. Furthermore, as these values apply to an isolated system in a vacuum, they may be further decreased, either in the solid state or in solution[35,36]. This factor may account for the existence of the (*ap*,*ap*) conformation in crystalline methyl 1,5-dithio-α-D-ribopyranoside[13]. These studies also suggest that the decrease in anomeric effect may increase the stability of the $^1C_4$ and $^4C_1$ conformations, respectively, in the 1,5-dithio-α-D- and β-D-pyranosides as compared with their oxygen analogues, which is in agreement with solution studies of these compounds[15]. However, as these results strictly apply to isolated systems in a vacuum, it must be kept in mind that the environment and the nature of intramolecular hydrogen-bonds[32] may also influence the favored ring-conformation.

Thiolmethanol (CH_2OHSH) is a model compound for monothiopyranosides. The STO-3G energies of this molecule, for standard geometrical parameters, as functions of θ and ϕ, are presented in Table VI and Fig. 4. The optimization studies are presented in Table VII. The bond-length optimization shows that, in general, there is a small shortening of the C-O bond and lengthening of the C-S bond in various conformations [except in the (+*sc*,*ap*) conformation, where the length of the C-O bond is unchanged and the C-S bond is shorter than that in methanethiol by 0.36 pm]. The S-C-O bond-angle optimization again gives rise to a larger S-C-O angle for the (+*sc*, +*sc*) conformation and a smaller angle for the (*ap*,*ap*) conformation. In this

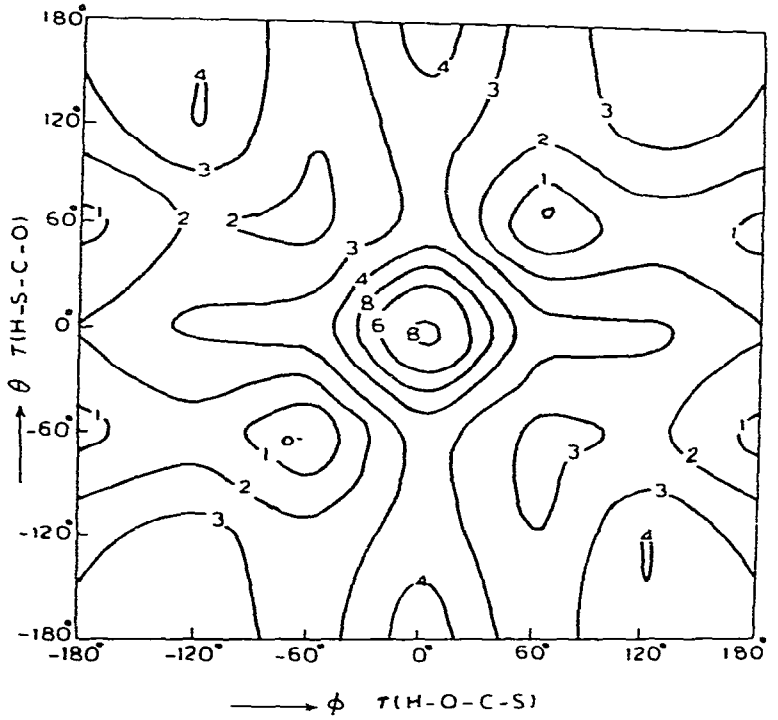

Fig. 3. Potential-energy surface for thiolmethanol as a function of the torsion angles θ and ϕ.

case also, the relative energies between various conformations are more dependent on S-C-O bond angles and not on the bond lengths.

The energy difference between the $(+sc,+sc)$ and (ap,ap) conformations in this molecule is intermediate between that of methanediol and methanedithiol, and the $(+sc, ap)$ conformation is more stable than the $(ap,+sc)$ conformation by $\sim$5.0 kJ.mol^{-1}. This result indicates different stability for the ring conformations of 5-thioribopyranosides and 1-thioribopyranosides. The stability of various monothio sugars given in ref. 14 may be understood in general from the energy calculations (except for a 5-thio-β-D-ribopyranoside, where the energy differences suggest that the conformational preferences should be closer to the situation for methyl β-D-ribopyranoside. However, as mentioned before, the role of hydrogen bonding and the environment is not considered here).

It was of interest to study the change in the shape of the potential curve in comparing methanediol and methanedithiol. As already mentioned, the major differences between the two systems are: (*1*) the occurrence of an energy minimum at the (180,180) conformation for methanedithiol, which is an energy maximum in the methanediol molecule; (*2*) the energy differences (ΔE_1 and ΔE_2) are smaller for methanedithiol. Unlike the case of the S-C-S or O-C-O systems, in the O-C-S system (thiolmethanol), the shape of the potential curve depends on whether it is a θ rotation

TABLE VI

POTENTIAL SURFACE (STO-3G) FOR THIOLMETHANOL WITH RIGID ROTATION ($kJ.mol^{-1}$)

ϕ (degrees)	θ (degrees)						
	−180	*−120*	*−60*	*0*	*60*	*120*	*180*
180	14.1	16.6	9.79	19.4	9.79	16.6	14.1
120	11.2	16.9	8.33	15.1	9.25	14.6	11.2
60	2.76	8.83	6.99	13.6	0.0[a]	6.74	2.76
0	8.83	13.8	14.1	34.7	14.1	13.8	8.83

[a]The total energy is −506.72100 hartrees.

or a ϕ rotation (compare Figs. 2 and 3). A comparison of θ rotation (rotation around the C-S bond) in thiomethanol and methanediol is given in Fig. 4 for ϕ values of 60 and 180°. A similar comparison of ϕ rotation (rotation around the C-O bond) for thiolmethanol and methanedithiol is given in Fig. 5 for θ values of 60 and 180°. Qualitatively, it may be seen from these graphs that the rotation around C-S bond in thiolmethanol resembles that of methanediol (Fig. 4) and the rotation around the C-O bond resembles that of methanedithiol (Fig. 5). The (180,180) conformation in

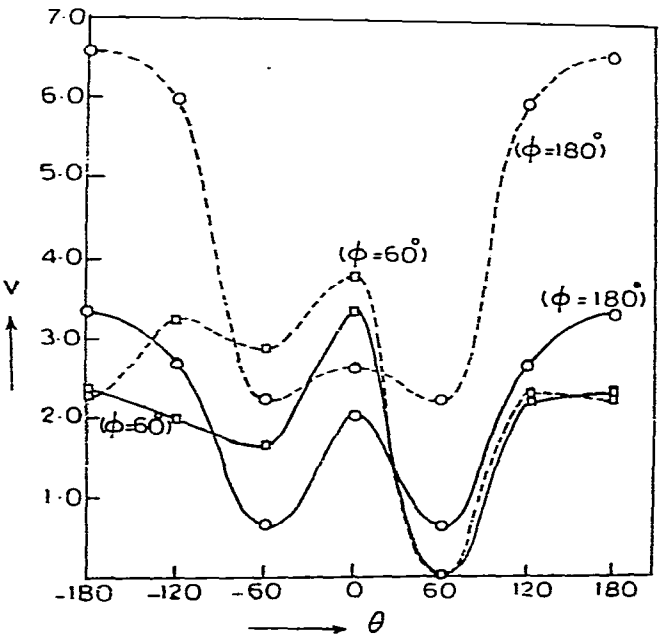

Fig. 4. Sections, V(θ), of the potential surface for internal rotation in the X-C-Y system for fixed values of ϕ. The solid lines refer to thiolmethanol and the dotted lines are for methanediol.

TABLE VII

OPTIMIZATION STUDIES (STO-3G) FOR THIOLMETHANOL

Conformation	*Optimized C-S (pm)*	*Optimized C-O (pm)*	*Optimized S-C-O (degrees)*	*Relative energies in kJ.mol^{-1}*		
(+*sc*,+*sc*)	181.7	143.0	113.08	0[a]	(0)[b]	(0)[c]
(+*sc*,*ap*)	180.0	143.3	110.06	4.86	(1.97)	(2.76)
HSCO = 60° (*ap*,+*sc*)	182.5	142.5	111.61	11.8	(9.83)	(9.79)
HOCS = 60° (*ap*,*ap*)	181.1	142.8	108.12	16.6	(13.9)	(14.1)

[a]The values are for optimized C-S, C-O bond lengths and the O-C-S bond angle. [b]The values are for optimized C-S, C-O bond lengths and a standard (109.5°) O-C-S angle. [c]The values are obtained by assuming all parameters to have standard geometry.

thiolmethanol is at an energy minimum for ϕ rotation as in methanedithiol, and is at the potential maximum for θ rotation, as in methanediol. Thus it seems that in the X-C-Y sequence, the energy for rotation around the C-X bond is very much influenced by the nature of Y and the ϕ value, and vice-versa. This factor may be due to the difference in polarizability of oxygen and sulfur, which may influence the dipolar contribution to the total energy, as described in ref. 7. The discussion in the following two paragraphs may also support this idea.

Mulliken population-analysis was conducted for the various systems studied here to understand more about the decrease in anomeric effect in the S-C-S system.

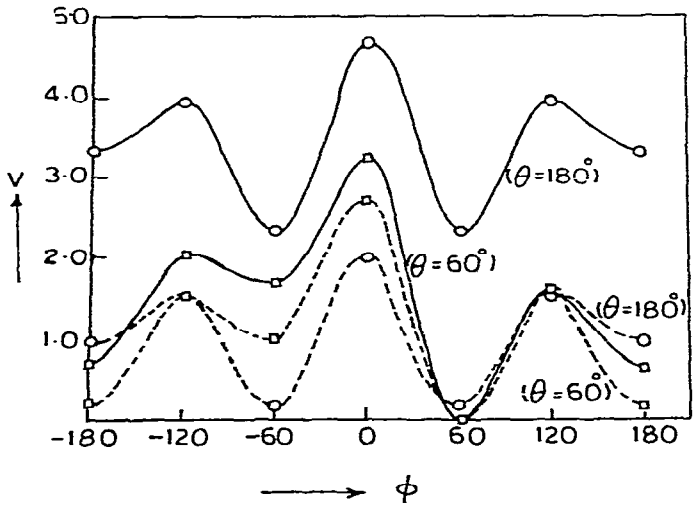

Fig. 5. Sections, V(θ), of the potential surface for internal rotation in X-C-Y systems for fixed values of θ. The solid lines refer to thiolmethanol and the dotted lines are for methanedithiol.

TABLE VIII

STO-3G CALCULATED CHARGE DISTRIBUTIONS AND DIPOLE MOMENTS IN X-C-Y SYSTEMS (X = Y = O AND OR S)

Conformation	*Molecule*	*Net charges on*			*Total electron density*[b] *in*		*Dipole moment (debyes)*
		C	X	Y	$P_y(X)$	$P_y(Y)$	
1	2	3	4	5	6	7	8
	$CH_2(OH)(OH)$	+0.124	−0.325	−0.325	1.51	1.51	0.14
	$CH_2(OCH_3)(OCH_3)$	+0.117	−0.258	−0.258	1.47	1.47	0.14
(+*sc*,+*sc*)	$CH_2(OH)(SH)$	−0.081	−0.310	+0.090	1.51	1.31	0.50
	$CH_2(SH)(SH)$	−0.278	+0.108	+0.108	1.31	1.31	0.19
	$CH_2(SCH_3)(SCH_3)$	−0.283	+0.140	+0.140	1.31	1.31	0.03
	$CH_2(OH)(OH)$	+0.133	−0.307	−0.320	1.51	1.98	2.05
	$CH_2(OCH_3)(OCH_3)$	+0.120	−0.240	−0.260	1.48	1.95	1.84
(+*sc*,*ap*)	$CH_2(OH)(SH)$	−0.084	−0.313	+0.120	1.32	1.98	1.80
	$CH_2(SH)(SH)$	−0.280	+0.106	+0.123	1.31	1.99	1.31
	$CH_2(SCH_3)(SCH_3)$	−0.281	+0.140	+0.160	1.30	1.98	1.25
(*ap*,+*sc*)[a]	$CH_2(OH)(SH)$	−0.076	−0.300	+0.090	1.99	1.51	1.61
(*ap*,*ap*)	$CH_2(OH)(OH)$	+0.134	−0.305	−0.305	1.97	1.97	2.91
	$CH_2(OCH_3)(OCH_3)$	+0.133	−0.242	−0.242	1.95	1.95	2.61
	$CH_2(OH)(SH)$	−0.080	−0.310	+0.130	1.98	1.99	2.41
	$CH_2(SH)(SH)$	−0.279	+0.118	+0.118	1.99	1.99	1.93
	$CH_2(SCH_3)(SCH_3)$	−0.281	+0.150	+0.150	1.98	1.98	1.88

[a]Because of symmetry, the (*ap*,*sc*) conformation is same as (*sc*,*ap*) in all the molecules except thiol-methanol. [b]P_y refers to $2P_y$ in oxygen and $3P_y$ in sulfur.

The charge distributions and dipole moments for $CH_2(OH)_2$, $CH_2(OCH_3)_2$, CH_2OHSH, $CH_2(SH)_2$, and $CH_2(SCH_3)_2$ are given in Table VIII. The charge distribution on the anomeric carbon atom and on the electronegative atom changes significantly from the oxygen to the sulfur system. Irrespective of the model system, the anomeric carbon atom is positive (+0.12) when attached to two oxygen atoms, and is slightly negative (−0.08) when bonded to an oxygen and a sulfur atom, and is clearly negative (−0.28) when bonded to two sulfur atoms. Furthermore, the oxygen atom is always negative (−0.24 to −0.3) and sulfur atom is always positive (+0.09 to +0.15). This difference is consistent with the electronegative properties of oxygen and sulfur as observed by gas-phase experimental studies[37] and also as predicted by theoretical calculations[25]. The net charge on oxygen 2Py or sulfur 3Py (1.91–2.0) is almost the same when this atom takes *trans*-disposition with respect to the group attached to the other electronegative atom (O or S). On the other hand, when the O or S atom is gauche to the substituent on the other electronegative atom, the oxygen 2Py has a different charge (1.51) than the sulfur 3Py (1.31).

Comparison of all of the molecules in various conformations shows that the (*sc*,*sc*) conformation has the lowest dipole moment and the (*ap*,*ap*) the highest

dipole moment, with the (*sc*,*ap*) conformation having an intermediate value. However, the dipole moments of the sulfur system in the (*sc*,*ap*), (*ap*,*sc*), and the (*ap*,*ap*) conformations are decreased as compared with their oxygen counterparts. As there are some differences in the dipole moments of Mulliken charge-distributions between the oxygen and sulfur systems, these may influence the dipolar contribution[7] to the total energy and thus may cause a decrease in the energy differences between various favored conformations. This conclusion is consistent with the recognised fact[39] that the electronic distribution and dipole moment are the major factors that determine the differences in physical properties and chemical behavior of alcohols and thiols.

SUMMARY AND CONCLUSIONS

Ab initio SCF-MO theory at the STO-3G level reproduces the trend in rotational behavior in methanediol. When compared with calculations at the 6-31G* level, the STO-3G energies are underestimated and the 4-31G energies overestimated. The shortening of C-O bonds in methanediol is reproduced at the STO-3G level, but the shortening predicted at this level is small.

Study of dithiomethanol at the STO-3G level shows a decreased anomeric effect that is, the energy difference between the (*sc*,*sc*) and (*sc*,*ap*) conformations is small as compared with the oxygen analogue. Furthermore, the (*ap*,*ap*) conformation is at a potential minimum, thus accounting for the occurrence of this conformation in the crystal of methyl 1,5-dithio-α-D-ribopyranoside.

The potential energy curves for θ and ϕ rotations in thiolmethanol resemble those of methanediol and methanedithiol, respectively.

In sulfur systems, the lower anomeric effect is attributed to the change in dipolar contribution to the total energy, as compared with the oxygen systems.

ACKNOWLEDGMENT

We thank Professor G. A. Jeffrey and Dr. J. H. Yates for their help in adopting GAUSSIAN-74 to the DEC-10 computer.

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