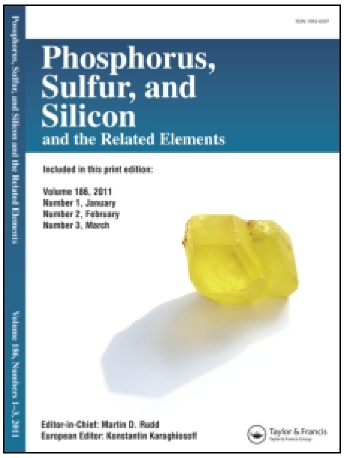

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CONFORMATIONAL ANALYSIS OF ETHANE-1,2-DITHIOL AND MERCAPTOETHANOL AN *AB INITIO* SCF HF/3-21G* AND 6-31G** STUDY

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CONFORMATIONAL ANALYSIS OF ETHANE-1,2-DITHIOL AND MERCAPTOETHANOL AN *AB INITIO* SCF HF/3-21G* AND 6-31G** STUDY

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A conformational analysis study has been carried out on ethane-1,2-dithiol and mercaptoethanol, using *ab initio* 3-21G* and 6-31G** bases set. The optimized geometries are very similar in both cases and suggest that very good results can be obtained by adopting the less time consuming 3-21G* basis. In contrast with literature findings based on electron diffraction and microwave spectra, the most stable conformer of ethane-1,2-dithiol, is the *gauche-trans-gauche* structure, but the *gauche-gauche-gauche* rotamers have less than 2 kJ mol^{-1} energy difference. On the contrary, mercaptoethanol is predicted to exist mainly as a mixture of *gauche-gauche-gauche* conformers, the *gtg* form being unfavoured. This is attributable to different hydrogen bond strengths due to different hydrogen bridges (S—H. . .S in the former and O—H. . .S in the latter molecules, respectively). Approximate hydrogen bond energies were also calculated. They are in line with experimental estimation and with expectation on the ground of literature semiempirical relations. Rotation barriers and interconversion pathways are also discussed.

Key words: Ethane-1,2-dithiol; mercaptoethanol; conformational analysis.

INTRODUCTION

The balance between intramolecular hydrogen bond energy and non bonded repulsive interactions is the main factor governing the relative stability of the *anti* and *gauche* conformers originating from rotation around the central single bond of 1,2-substituted ethanes. Hydrogen bond formation is particularly important when bridges like O—H. . .O or O—H. . .N are present; however there are evidences that also the weaker hydrogen bonding originating when oxygen is substituted by the less electronegative S atom is able to influence the conformational equilibrium, as occurs, e.g., in ethane-1,2-dithiol (dithioglycol). This compound has been studied extensively both from the experimental[1–4] and theoretical point of view.[5–8] On the ground of microwave[1] and electron diffraction spectra[2–4] it was deduced that the molecule exists, in gas phase, as a mixture of nearly equal amounts of *anti* (*trans-trans-trans*) and *gauche* (*trans-gauche-gauche*)† conformers. According to Reference 4, but in contrast to Reference 1, the *gauche* form (1.09 kJ mol^{-1} more stable than the *anti* one[7]) shows a S. . .H distance favourable to the formation of hydrogen bonding, whose strength was estimated[4] as *ca.* 4.18 kJ mol^{-1}.

That the *trans-gauche-gauche* (*tgg*) is slightly more stable than the *ggg* accommodation has been experimentally found[8] and theoretically confirmed[9] (4-21G, 6-

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†Here *anti* and *gauche* refer to the torsion angle around the C—C bond. In the following we'll use the symbols *c*, *t* and *g* to represent *cis*, *trans* and *gauche* conformations. Looking at Fig. 1, the order, from left to right, refers to the S—C, C—C and C—S or C—O bonds.

31G*, MP2/6-31G* and 6-31G**) also for ethylene glycol, whilst microwave spectra indicate that the *gauche-gauche-gauche* (*ggg*) conformation is favoured in mercaptoethanol.[10]

Ab initio calculations limited to the *tgg* and *anti* structures of ethane-1,2-dithiol, carried out using 3-21G,[5] 4-31G,[6,11] and (while the present work was in progress) 6-31G** bases set,[12] confirm that the above conformers are nearly isoenergetic. However, 3-21G results obtained by Ohsaku[5] (who considered most of the possible conformations arising from rotation around the C—C bond and from rotation of the S—H groups) pointed out that one of the *gauche-trans-gauche* forms (*gtg'*) is the most stable conformer of ethane-1,2-dithiol, whilst the *trans-trans-trans*, (*ttt*) is the less stable structure.

Since the above conclusions are in contrast with some experimental suggestions, and bearing in mind that the position of the H atoms cannot be unambiguously determined from the electron diffraction and microwave data, we performed a complete conformational analysis study of ethane-1,2-dithiol and mercaptoethanol (see Figure 1) at *ab initio* SCF/HF level, using both the 3-21G* and 6-31G** bases set in order to determine the stability order of the various possible rotamers as well as the most significant interconversion barriers, and to evaluate the hydrogen bond strength, if any. Moreover the use of 3-21G* and 6-31G** bases allows to analyze which improvements occur when polarization functions are extended to the first and second row elements.

CALCULATIONS

All the geometrical parameters of the studied compounds were simultaneously optimized without symmetry restrictions, except for the *ttt* and *gtg* conformations of ethane-1,2-dithiol. The standard 3-21G* and 6-31G** bases set were adopted for calculations, which were carried out on a VAX 11/750 and a VAX-2000 computer using the GAUSSIAN82 program.[13] Owing to the limited hard disk capacity of the above machines it was not possible to enclose correlation energy evaluation.

RESULTS AND DISCUSSION

Ethane-1,2-dithiol

The 6-31G** optimized molecular geometries of the most significant minimum energy conformations of ethane-1,2-dithiol are collected in Table I. Other possible conformers (as, e.g., the *cis-cis-cis* and *cis-cis-trans*) are omitted on energetic grounds; however their bond lengths and bond angles are not very different from those of the most stable forms. In the same Table the energy differences, dipole moments and percentages of each conformer, evaluated according to the Boltzmann equation, are also reported.

Taking into account the rotation around the C—C bond as well as the possible accommodations of the S—H groups, two *gauche-gauche-gauche* (*ggg-A* and *ggg-B*) and two *gauche-trans-gauche* (*gtg-A* and *gtg-B*) structures were identified. These

TABLE I

Calculated (6-31G**) and experimental geometries of ethane-1,2-dithiol (distances in Å, angles in degrees, energies in kJ mol^{-1})

	tgg^{a}	ggg-A	ggg-B	tgt	ggt	Exp.^{a}		gtg-A^{b}	gtg-B^{b}	ttt
r_{C-C}	1.527	1.526	1.526	1.525	1.525	1.537	r_{C-C}	1.524	1.524	1.525
r_{C2-S3}	1.821	1.822	1.819	1.829	1.829	1.824	r_{C-S}	1.824	1.826	1.827
r_{C1-S4}	1.829	1.822	1.823	1.829	1.822		r_{S-H}	1.328	1.327	1.327
r_{S3-H5}	1.326	1.327	1.326	1.327	1.327	1.373	r_{C-H}	1.082	1.082	1.082
r_{S4-H6}	1.326	1.327	1.328	1.327	1.328		$r_{S...S}$	4.472	4.475	4.391^{c}
r_{C-H}	1.083^{d}	1.082^{d}	1.083^{d}	1.082^{d}	1.083^{d}	1.081^{d}	$r_{C2...H6}$	3.017	3.024	3.719^{c}
$r_{S3...S4}$	3.603	3.609	3.604	3.448	3.462	3.522	δ_{S-C-C}	113.2	113.2	108.9
$r_{S4...H5}$	3.054	3.224	3.042	4.554	4.668	2.70	δ_{C-S-H}	98.0	97.3	97.6
$r_{S3...H6}$	4.469	3.225	4.155	4.554	3.882	4.104	δ_{H-C-C}	110.7	110.7	110.2
$\delta_{S3-C2-C1}$	115.6	115.6	115.5	111.7	112.2	113.1	$\omega_{S-C-C-S}$	176.3	179.9	180.0
$\delta_{S4-C1-C2}$	111.0	115.6	115.2	111.7	115.7		$\omega_{H5-S-C-C}$	67.7	69.6	180.0
$\delta_{C2-S3-H5}$	98.3	98.2	98.1	96.8	96.7	94.0^{e}	$\omega_{H6-S-C-C}$	67.7	-69.6	180.0
$\delta_{C1-S4-H6}$	97.9	98.2	97.7	96.8	97.8		$\omega_{H7-C-C-S}$	58.3	59.4	60.1
$\delta_{H7-C2-C1}$	111.0	110.8	110.9	110.2	110.4		$\omega_{H8-C-C-S}$	-60.7	-59.6	-60.1
$\delta_{H8-C2-C1}$	108.5	108.6	108.7	108.1	108.1					
$\delta_{H9-C1-C2}$	108.9	108.6	109.5	108.1	109.0					
$\delta_{H10-C1-C2}$	110.1	110.8	110.3	110.2	110.2					
$\omega_{S-C-C-S}$	- 75.1	- 68.4	- 68.6	- 67.9	62.0	69.0				
$\omega_{H5-S-C-C}$	64.9	77.5	63.6	173.5	155.5	- 40.0				
$\omega_{H6-S-C-C}$	161.4	77.5	- 70.1	173.5	62.0	-141.0				
$\omega_{H7-C-C-S}$	50.8	56.4	56.5	54.2	- 60.5					
$\omega_{H8-C-C-S}$	168.1	174.3	174.1	172.7	181.4					
$\omega_{H9-C-C-S}$	165.2	174.3	168.5	172.7	185.2					
$\omega_{H10-C-C-S}$	45.9	56.4	50.1	54.2	- 56.9					
ΔE	7.36	2.39	2.74	13.91	11.22			0.00	1.32	6.96
E_{HB}	6.55^{f}	11.52^{g}	8.48^{h}			4.18				
μ(Debye)	1.99	1.02	2.32	2.93	3.24	2.03		1.64	0.00	0.00
W%^{i}	2	14	13	-	-			37^{b}	22^{b}	2

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a) Ref.4. This geometry refers to the tgg conformation.

b) The ttg conformer shows geometrical parameters practically equal to those of the gtg-A and gtg-B ones (the main difference is $\delta_{S3-C2-C1}$ 109.0°). It is characterized by $\Delta E = 3.50$ kJ mol^{-1}, $\mu = 1.33$ D and 9% of Boltzman population).

c) Experimental values: $r_{S...S}$=4.471 Å; r_{C2-H6}=3.735 Å (ref.4).

d) Average value. e) Assumed value.

f) ΔE between the tgt and tgg conformations.

g) ΔE between the tgt and ggg-A conformations (two hydrogen bridges).

h) ΔE between the ggt and ggg-B conformations.

i) Calculated according to the Boltzman equation.

latter differ from each other for having equal or opposite sign on the torsion angles ω_{5321} and ω_{6123}. The calculated bond lengths agree satisfactorily with those coming from microwave and electron diffraction spectra, except $r_{S—H}$, for which theory predicts a value shorter than experimentally suggested. The *gtg-A* and *gtg-B* forms were found to be the most stable conformations, but the former is favoured by only 1.32 kJ mol^{-1} with respect to the latter. According to the Boltzmann equation, their percentages are 37% and 22%, respectively, whilst the population of the intermediate structure, *ttg*, ($\Delta E = 3.5$ kJ mol^{-1}) is about 9%. The *tgg* (corresponding to that reported in Reference 4) and the *all-trans* (*ttt*) conformers are *ca.* 7 kJ mol^{-1} less stable than the *gtg-A* one, so that their percentages are negligible and the conformational equilibrium suggested on the ground of microwave and electron diffraction spectra, is not confirmed by theory, at least at room temperature.

The *ggg-A* and *ggg-B* conformations appear to be only slightly less stable than the *gtg-A* and *gtg-B* are. Although no symmetry was imposed, the *ggg-A* structure shows a binary symmetry axis and a dipole moment *ca.* 50% lower than the experimental value. On the contrary, a dipole moment of 2.32 D is calculated for the *ggg-B* rotamer, in good agreement with the experimental datum (2.03 D), deduced from the second order Stark effect theory.[1] Moreover, the geometry of this rotamer shows the best agreement with that deduced from electron diffraction spectra: in particular, r_{S4-H5} and r_{S3-H6} are closer to the experimental findings than those of the *tgg* and *ggg-A* forms. On this ground, an equilibrium between the *ggg* and *gtg* structures, justified also by the low energy differences, is conceivable. It would be very interesting to test if the present *ab-initio* geometrical parameters are able to account for the microwave and electron diffraction spectra. Apart from the slight difference concerning the ΔE between the two *tgt* rotamers, the stability order found in the present work is in line with that reported by Ohsaku,[5] except for the *ttt* conformer. Comparative analysis of the present and the Ohsaku results suggests that the disagreement can be attributable to the different basis set used for calculations.

Mercaptoethanol

Analysis of the molecular geometries of the various rotamers of mercaptoethanol, reported in Table II, evidences that the geometrical parameters of the left side framework (—CH_2SH) does not change appreciably with respect to those of ethane-1,2-dithiol and that (differently from ethane-1,2-dithiol), the three *ggg* and the *gtt* rotamers are favoured with respect to the *gtg* ones. The geometrical parameters and dipole moment value of the most stable conformation, *ggg-C*, agree with the experimental findings better than those of the *ggg-A* and *ggg-B* structures. The *ggg-C* and *ggg-A* are expected to be the predominating conformers (according to the Boltzmann equation, their percentages are 49% and 22%, respectively). Populations ranging from 5% to 7% are calculated for the *ggg-B*, *gtg* and *gtt* conformations. The *ctt*, *ctc* and *ttc* are the less stable conformations (their geometries are not reported for space saving). The stability order of *gtg-A* and *gtg-B* forms is reversed with respect to that found for the corresponding structures of ethane-1,2-dithiol.

The greater stability of the *ggg* conformations of mercaptoethanol can be justified on the ground of possible formation of hydrogen bonds stronger than those of ethane-1,2-dithiol, as it will be discussed in the following.

Comparison with 3-21G Results*

The geometrical parameters obtained at 321-G* level are omitted, being, on the whole, very similar to those obtained by 6-31G** calculations. The most relevant

TABLE II

Optimized 6-31G** geometries of 2-mercaptoethanol[a] (distances in Å, angles in degrees, energies in kJ mol^{-1})

	ggg-A	ggg-B	ggg-C	Exp.[a]	tgt	tgg	ggt	ttt	gtg-A	gtg-B	ttg	gtt
r_{C-C}	1.523	1.523	1.524	1.538	1.516	1.524	1.518	1.519	1.524	1.524	1.525	1.518
r_{C-O}	1.397	1.401	1.393	1.423	1.399	1.396	1.397	1.401	1.400	1.400	1.400	1.401
r_{C-S}	1.826	1.820	1.826	1.806	1.829	1.827	1.823	1.826	1.820	1.821	1.826	1.820
r_{O-H}	0.943	0.943	0.945	1.015	0.942	0.944	0.942	0.943	0.943	0.943	0.943	0.943
r_{S-H}	1.327	1.326	1.328	1.340	1.327	1.327	1.328	1.326	1.328	1.328	1.326	1.328
r_{C-H}	1.087[b]	1.082[b]	1.090[b]	1.094[b]	1.087[b]	1.082[b]	1.088[b]	1.088[b]	1.082[b]	1.083[b]	1.084[b]	1.085[b]
$r_{S...O}$	3.199	3.215	3.209	3.148	3.060	3.084	3.225	3.976	4.056	4.057	4.017	4.011
$r_{S...H5}$	2.935	3.676	2.788	2.565	3.807	3.378	3.966	4.667	4.377	4.364	4.340	4.719
$r_{O...H6}$	3.000	2.638	3.717	3.573[c]	4.241	4.268	3.860	4.737	4.306	4.269	4.805	4.275
δ_{C-C-O}	112.7	112.5	112.8	111.4	108.4	113.6	108.7	106.8	111.3	111.4	111.1	107.0
δ_{C-C-S}	113.9	113.9	113.7	113.5	110.8	110.7	115.0	109.6	113.6	113.4	109.7	113.4
δ_{C-O-H}	109.3	109.9	109.4	104.4	110.3	110.3	110.3	109.9	110.1	109.9	110.0	110.0
δ_{C-S-H}	98.0	97.3	97.9	96.5	97.2	97.0	97.6	97.5	98.1	97.9	97.6	98.1
δ_{H7-C-C}	109.8	110.0	109.9	110.7	109.7	109.9	110.0	109.9	109.7	110.0	109.9	109.9
δ_{H8-C-C}	108.6	108.9	108.6		108.5	108.3	108.3	109.9	110.2	109.9	110.2	109.7
δ_{H9-C-C}	109.9	109.7	110.8		109.1	108.9	110.3	109.3	111.0	110.3	110.0	109.6
$\delta_{H10-C-C}$	110.5	110.4	109.5		109.5	110.3	109.0	109.3	109.4	110.2	109.2	110.2
$\omega_{S-C-C-O}$	- 61.3	-63.3	- 62.6	58.3	-69.2	-55.8	62.1	180.0	176.1	178.3	177.7	180.7
$\omega_{C-C-O-H}$	77.5	-72.7	60.4	307.3	167.1	299.5	193.6	180.0	72.0	72.1	72.3	180.0
$\omega_{C-C-S-H}$	81.5	51.4	- 70.7	67.1	206.6	196.0	76.6	- 4.0	60.1	- 68.5	180.0	- 71.9
$\omega_{H7-C-C-S}$	63.2	55.3	62.3		59.4	62.8	- 53.2	- 59.3	58.1	60.6	60.0	60.1
$\omega_{H8-C-C-S}$	-179.2	173.4	-180.4		177.3	180.3	189.4	59.3	- 60.1	- 57.5	- 58.5	- 58.2
$\omega_{H9-C-C-O}$	-179.7	178.6	173.8		177.8	184.0	192.8	59.5	- 60.2	- 64.2	- 62.2	- 61.3
$\omega_{H10-C-C-O}$	61.3	60.4	54.6		58.7	65.5	-49.2	-59.5	58.2	54.4	57.1	56.9
ΔE[d]	2.08	4.94	0.00		11.50	11.23	11.76	9.31	5.88	5.18	10.11	4.68
E_{HB}	9.43[e]	6.29[f]	11.76[g]									
μ(Debye)	0.65	2.83	2.03	1.87[a]	2.83	3.30	3.25	1.00	2.33	0.83	2.08	2.21
W%[h]	22	7	49		-	-	-	1	5	6	1	7

a) Ref.10. b) Average value. c) Calculated by us from the coordinates reported in ref.10.

d) For space saving the geometries of the unfavoured ctt (ΔE=15.21 kJ mol^{-1}, μ = 2.71 D), ctc (ΔE=24.80 kJ mol^{-1}, μ =0.74 D) and ttc (ΔE=20.65 kJ mol^{-1}, μ = 2.56 D) conformations are not reported.

e) ΔE between the tgt and tgg-A conformations.

f) ΔE between the tgg and ggg-B conformations.

g) ΔE between the ggt and ggg-C conformations.

h) Calculated according to the Boltzman equation.

differences observed in ethane-1,2-dithiol concern the C—C bond and the S. . .S distance, which are *ca.* 0.01 Å longer and *ca.* 0.03 Å shorter, respectively, than those found at 6-31G** level. However, it is noteworthy that $r_{C—C}$ coming from 3-21G* basis matches the experimental value better than that obtained by 6-31G** calculations. The contrary is true for $r_{S...S}$. Both bases predict an average value of *ca.* 1.825 Å for the C—S bond length, which is much more close to the experimental datum than found by the simple 3-21G calculations carried out on mercaptans and sulphides.[14]

Bond and torsion angle variations are generally limited to less than one degree, except for ω_{6412}, which decreases by *ca.* 5°. Variations limited to about 1 kJ mol^{-1} are observed in the energy difference (ΔE) among the various conformers. In both molecules the 6-31G** and 3-21G* bases predict opposite stability order for the *ggg-A* and *ggg-B* rotamers, which, in any case, are nearly isoenergetic structures.

The use of 3-21G* and 6-31G** gives rise to relevant differences in the geometrical parameters of the right end moiety (—CH_2—OH) of mercaptoethanol. In particular, the 3-21G* basis predicts lower values for $r_{C—O}$ (about 0.04 Å), r_{OH} (*ca.* 0.02 Å), and $\delta_{C—C—O}$ (*ca.* 4°), whose cumulative effect is a decrease of the S. . .O distance. These changes are to be ascribed to the extension of polarization functions to the first and second row elements.

Hydrogen Bonding

The S—H. . .S, S—H. . .O and/or O—H. . .S distances in the rotamer showing *gauche* accommodation, are lower or nearly equal to the sum of the van der Waals radii of oxygen and sulphur, so suggesting the possible formation of intramolecular hydrogen bonds, favoured also by the small negative charge calculated for the S atom.

To evaluate the strength of such hydrogen bridges we need to select a reference structure free from hydrogen bonds. In the present case we assume that the hydrogen bond energy (E_{HB}) is the difference between the energy of the examined conformation and the energy of the corresponding optimized structure having the H atom involved in the bridge rotated in *trans* position. Obviously, optimization of the reference structure give rise to a minimum energy rotamer having a geometry rather different from that of the hydrogen bridged one and, consequently, the related E_{HB} value can be affected by contributions extraneous to the hydrogen bond interactions; for this reason it cannot be considered as absolute hydrogen bond energy. Notwithstanding this, the E_{HB} values so obtained are very useful for comparison purposes and can help in understanding the conformational equilibria.

Following the above procedure, on the ground of 6-31G** results, we calculated E_{HB} = 6.55 kJ mol^{-1} for the *tgg* conformer of ethane-1,2-dithiol $r_{S...S}$ = 3.6 Å), which is a figure in acceptable agreement with the literature datum[4] of *ca.* 4.18 kJ mol^{-1} deduced from electron diffraction measurements. Although the comparison is not strictly appropriate, these theoretical and experimental findings are not far from the value of 4.6 kJ mol^{-1} calculated at 6-31G** level (adopting the 4-31G optimized geometries) for the chelate tautomer of dithiomalondialdehyde,[11] where $r_{S...S}$ is 3.528 Å).

In the *ggg-A* conformation, where two equivalent hydrogen bridges seem to be present ($r_{S4...H5}$ and $r_{S3...H6}$ are *ca.* 3.22 Å), E_{HB} is 11.52 kJ mol^{-1}, corresponding to *ca.* 5.75 kJ mol^{-1} per hydrogen bridge. In the *ggg-B* conformation E_{HB} is 8.48 J mol^{-1}. These values are nearly coincident with those coming from the 3-21G* basis.

As far as mercaptoethanol is concerned, a O—H. . .S bridge is certainly present in the *ggg-A* ($r_{S4...H5}$ is 2.935 Å, to be compared with the value of the sum of the S (1.85 Å) and H (1.2 Å) van der Waals radii (3.05 Å) and *ggg-C* conformers ($r_{S4...H5}$ = 2.788 Å). For these rotamers, E_{HB} values of 9.43 and 11.76 kJ mol^{-1}, respectively, were calculated. The rather low strengths for such bridges reflect correctly the fact that the O. . .S distance (*ca.* 3.2 Å) is remarkably longer than found by X-ray diffractometric measurements for the O—H. . .S bridge present in the 1-(1-methylcyclopropyl)-3-thioxabutan-1-one cyrstalline structure.[15]

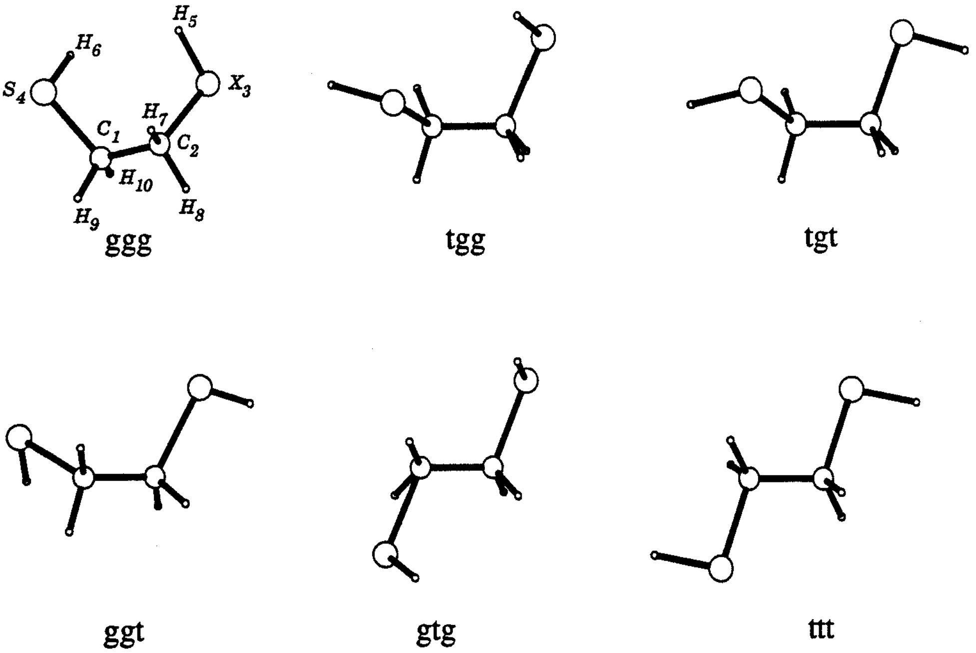
Only a S—H. . .O hydrogen bridge is present in the *ggg-B* conformation, where $r_{O...H}$ = 2.638 Å (the sum of the van der Waal radii of O and H atoms is 2.7 Å). For this conformer E_{HB} was estimated as 6.29 kJ mol^{-1}.

The above results, although approximate, appear to be reliable since the energy of the O—H. . .S bridge is higher than that of the S—H. . .O and S—H. . .S ones, as expected also on the ground of the Lippincott semiempirical relation.[16]

Analysis of the predicted hydrogen bond energies points out that the highest figure was found in the *ggg-C* conformation of mercaptoethanol, which is also the most stable conformer, notwithstanding the non bonded repulsive interactions are certainly stronger than in the *gtg* form. In ethane-1,2-dithiol the weaker hydrogen bond is not able to overcome such non bonded repulsions and the *gtg* conformers become more stable than the *ggg* ones.

Rotation Barriers

Since double bonds are absent, the title compounds are highly flexible and interconversions among the various rotamers are possible. The main factor governing such interconversions is the related rotation barrier. Some of these barriers, concerning the most stable conformations, were estimated in the present study and are here discussed (see also Figure 1).



ggg tgg tgt

ggt gtg ttt

FIGURE 1 Main conformations and numbering system of the studied molecules. *g* = gauche; *t* = trans. Ethane-1,2,-dithiol: X = S.—Mercaptoethanol: X = O.

From the most stable conformer of ethane-1,2-dithiol, *gtg-A*, it is possible to reach the *gtg-B* conformations by rotating one of the S—H framework around the C—S bond. If S—H rotation occurs counterclockwise the transition state is reached when ω_{6412} is zero and the barrier to be overcome is 9.5 kJ mol^{-1} for the *gtg-A* → *gtg-B* pathway and 8.3 kJ mol^{-1} for the opposite one. If a clockwise rotation occurs the system crosses through the *gtt* conformation after a barrier of *ca.* 5.7 kJ mol^{-1} (4.5 kJ mol^{-1} for the opposite pathway). This latter is of the same order of the barriers calculated by Ohsaku at 3-21G level.[5] Analogous rotation barrier values were found when the *ggg-A* → *ggg-B* interconversion was taken into account.

A simultaneous rotation of the two S—H groups allows to go from the *gtg-A* to the *ttt* form and vice versa. The associated barriers are 11.7 and 4.8 kJ mol^{-1}, respectively. It is noteworthy that the 11.7 figure is nearly twice that found for a single SH group rotation, i.e. each SH group rotation can occur nearly independently from the other.

On the ground of these values, following the Boltzmann equation and the most favoured pathway, about 10% of the *gtg-A* rotamer is able to reach the *gtg-B* structure and less than 1% (assuming the simultaneous rotation) is able to transform itself in the *ttt* conformation, at room temperature.

Rotation around the C—C bond allows the following interconversions:

$$gtg\text{-}A \underset{16.6}{\overset{19.1}{\rightleftarrows}} ggg\text{-}A$$

$$gtg\text{-}B \underset{15.2}{\overset{16.5}{\rightleftarrows}} ggg\text{-}B$$

Here no percentages of *gtg-A* and *gtg-B* conformers are able to overcome the rotation barriers at room temperature.

From the most stable conformation of mercaptoethanol (*ggg-C*) it is possible to reach the *ggg-A* conformer by rotating the SH group. The barriers for this pathway and for the opposite one are 9.50 and 7.42 kJ mol^{-1}, respectively. Rotation of the OH group allows to reach the *ggg-B* conformation starting from *ggg-A*. The barriers to overcome are 6.30 kJ mol^{-1} on going from *ggg-A* to *ggg-B* and 3.50 kJ mol^{-1} on going from *ggg-B* to *ggg-A*.

The pathway from *ggg-C* to *gtg-B* implies rotation around the C—C bond with an associated barrier amounting to 22.59 kJ mol^{-1} (17.4 kJ mol^{-1} for the opposite pathway).

On the ground of these values, only 8% of the *ggg-C* population can interconvert to *ggg-A*, at room temperature; in turn, about 18% of *ggg-A* is able to overcome the barrier for interconversion to *ggg-B*. The *ggg-C* → *gtg-B* interconversion is unfavoured.

The *gtg-B* → *ttg* → *gtg-A* interconversion can occur by rotating the SH group, whose rotation barrier is 7.1 kJ mol^{-1} for the *gtg-B* → *ttg* pathway and 6.39 kJ mol^{-1} for the *gtg-A* → *ttg* pathway. These values are comparable with those calculated for ethane-1,2-dithiol.

The OH group rotation barrier was calculated to be about 3.2 kJ mol^{-1}, so that the *gtt* → *gtg* interconversion can occur easily at room temperature.

CONCLUSIONS

The present results evidence that the *gtg-A*, *gtg-B*, *ggg-A* and *ggg-B* are the preferred conformers of ethane-1,2-dithiol. The rotation barrier around the C—S bond is not relevant and it has been estimated that about 10% if the *gtg-A* population can interconvert in the *gtg-B* conformation at room temperature. The equilibrium between the *tgg* and *ttt* structures, suggested on the basis of electron diffraction and microwave studies are not confirmed. Owing to a greater hydrogen bond strength, due to a O—H. . .S bridge, a *ggg* rotamer is predicted to be the most stable conformation of mercaptoethanol. Calculations indicate that the rotation barrier around the C—S bond is higher than that around the C—O bond. In both molecules the *ab initio* optimized geometries are in good agreement with the experimental ones.

Although the hydrogen bond strengths (E_{HB}) here reported are to be considered with somewhat a caution owing to the difficulties in defining the reference free hydrogen bond structure, they are in line with the predictions of the Lippincott semiempirical relation.[14] In particular, the E_{HB} value of *ca.* 6.5 kJ mol^{-1} found for the *tgg* conformation of ethane-1,2-dithiol is in good agreement with the experimental datum[4] (4.18 kJ mol^{-1}). The most stable conformation of mercaptoethanol shows also the highest hydrogen bond energy.

The geometries calculated at 3-21G* level are good as those predicted by the very onerous 6-31G** basis set. The E_{HB} values in the two cases are also very close to each other.

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