

Theoretical study of structure of the 1,2-disubstituted derivatives of ethane

II. Conformations of 2-mercaptoethanol and 1,2-ethanedithiol

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The conformations of 2-mercaptoethanol and 1,2-ethanedithiol were studied by the semiempirical CNDO/2 and PCILO methods. As for 2-mercaptoethanol, there are small energetic differences between energetically preferable conformations and the order of particular conformations is not quite in agreement with experimental data. As for 1,2-ethanedithiol the interatomic repulsion is the decisive factor which is in agreement with experiment.

Семиэмпирическими методами CNDO/2 и PCILO были изучены конформации 2-меркаптоэтанола и 1,2-этандитиола. В случае 2-меркаптоэтанола имеются малые энергетические различия между энергетически выгодными конформациями, последовательность отдельных конформаций не совсем соответствует экспериментальным данным. В случае 1,2-этандитиола решающим фактором является в соответствии с экспериментом межатомное отталкивание.

The problems of conformations of the 1,2-disubstituted derivatives of ethane belong among fundamental problems of stereochemistry. The energetically preferable conformation of a certain derivative is given by equilibrium of the interactions of attraction and repulsion not only of heteroatoms but also of other atoms in molecule. The interactions of substituents, however, play a substantial role in stabilization of the *gauche* or *anti* conformation. An important type of interaction which usually stabilizes the *gauche* conformation is intramolecular hydrogen bond.

In preceding paper [1] we studied the conformations of 1,2-ethanediol, 2-aminoethanol, and 1,2-ethanediamine by the CNDO/2 method with full optimization of geometrical parameters. It has been found that the CNDO/2 method overestimates interatomic repulsion in case of electronegative atoms (1,2-ethanediol) while the results obtained with other two compounds were conformable to experimental data. Moreover, it has been ascertained that the major factor determining total energy of the system is the angle of rotation whereas the change in bond lengths and bond angles is less significant.

In this study we tested semiempirical methods with respect to conformational effects and theoretically investigated 2-mercaptoethanol and 1,2-ethanedithiol by using the quantum chemical CNDO/2 and PCILO methods.

Method of calculation

The calculations were performed by the semiempirical CNDO/2 [2–4] and PCILO [5–8] methods. The following experimental values [9] were used for bond lengths and bond angles: C—C: 0.1538 nm, C—O: 0.1423 nm, C—S: 0.1806 nm, O—H: 0.1015 nm, S—H: 0.1340 nm, C—H: 0.1015 nm, \sphericalangle CCO: 111.4°, \sphericalangle CCS: 113.5°, \sphericalangle 104.4°, \sphericalangle CSH: 96.5°, \sphericalangle CCH: 110.2° (for —CH₂—OH segment), \sphericalangle CCH: 110.7° (for —CH₂—SH segment).

Individual conformations are denoted by the symbols *C*, *T*, *G*, *G'* which have this meaning: *C* — *cis* form, rotational angle 0°; *T* — *trans* form, rotational angle 180°; *G* — *gauche* form, angle of rotation 60°; *G'* — *gauche* form, angle of rotation —60°. The conformations which arise by rotation about the C—C bond are denoted by capital letters while the conformations on functional groups are denoted by small letters. The first small letter denotes the rotation about the C—O bond, the second one denotes the rotation about the C—S bond. The total energy of individual compounds was calculated as a function of rotation about the C—C bond (by 10°). The fundamental conformations on functional groups (*t*, *g*, *g'*, *c*) were also calculated.

Results and discussion

2-Mercaptoethanol

The experimental measurements based on infrared and Raman spectra [10] have shown that both the *trans* and *gauche* conformers are present in the liquid state. The study based on microwave spectra has confirmed that a molecule in the gaseous phase occurs in the *gGg* conformation. This conformation is stabilized by an intramolecular hydrogen bond of the type O—H ... S, the distance H ... S being 0.2565 nm.

Fig. 1 represents the results obtained by the CNDO/2 method. We started from the conformers *tCt*, *cCc*, *tCc*, and *cCt* and investigated the influence of the rotation about the C—C bond on energy of the molecule. Furthermore, we took interest in conformation of the functional groups O—H and S—H. The results are given in Table 1. We can see that the lowest energy corresponds to the *tGt* conformer which may be stabilized solely by *gauche* effect because no hydrogen bond occurs there. The conformers *tGg'* and *tGg* which are stabilized by a hydrogen bond of the O ... H—S type have only a little higher energy (0.61 and 1.68 kJ mol⁻¹, respectively). This kind of hydrogen bond also stabilizes the conformers *tGc* and *tCc*. The conformers *g'Gt* and *gGt* have the S ... H—O hydrogen bond and their

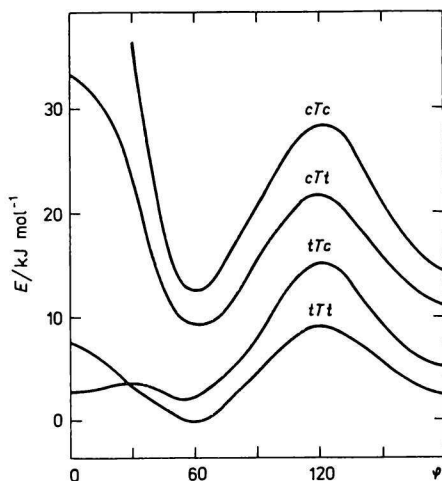


Fig. 1. Variation of total energy of conformers of 2-mercaptoethanol with the angle of rotation about the C—C bond (CNDO/2 method).

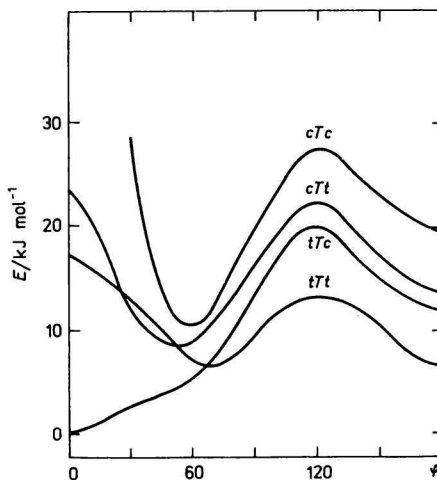


Fig. 2. Variation of total energy of conformers of 2-mercaptoethanol with the angle of rotation about the C—C bond (PCILO method).

Table 1

Relative total energies (kJ mol^{-1}) of conformations on functional groups of 2-mercaptoethanol

Conformation	Energy	
	CNDO/2	PCILO
tGt	0.0	7.05
tGg'	0.61	1.95
tGg	1.68	8.54
$g'Gt$	4.54	3.08
gGt	5.57	10.00
gGg'	6.37	6.29
gGg	7.15	9.82
gGc	7.88	6.03
tCg	9.63	13.78
cGg	10.71	8.65
gCt	15.30	16.19
gCg	18.56	15.80
gCg'	19.91	21.23
gCc	23.97	18.91
cCg	41.83	33.19

energy is also only a little higher. It is also obvious from Fig. 1 that individual curves show the minimum energy for the *G* arrangement on the C—C bond. The *C* conformation on the C—C bond appears to be disadvantageous because of repulsion of the heteroatoms except the *tCc* conformation where a stabilization by the O ... H—S hydrogen bond takes place.

Analogous calculations were performed by the PCILO method. The results are represented in Fig. 2 and Table 1. The most stable *tCc* conformation has the O ... H—S hydrogen bond. The *tGg'* conformer has only little higher energy (by 1.95 kJ mol⁻¹). The *g'Gt* conformation which is stabilized by the S ... H—O hydrogen bond appears to be energetically advantageous. The course of the curves obtained by the PCILO method is similar to that obtained by CNDO/2. But according to PCILO, the hydrogen bond more stabilizes the molecule (*tCc* conformer) and the repulsion of heteroatoms is also more significant (*tCt* conformer).

1,2-Ethanedithiol

The experimental data resulting from infrared spectra [11] show that this compound occurs in the *tTt* and *tGt* forms while the first one is more stable. This fact was confirmed by electron diffraction [12].

The CNDO/2 calculations of energy of 1,2-ethanedithiol are given in Fig. 3 and Table 2. The procedure was equal to that with preceding compound. We can see that the *tTt* conformer is the most stable, which is a logical expression of the superiority of the interatomic repulsion to a weak S—H ... S hydrogen bond. The second most stable conformer is the *tGt* conformer where the only possibility of

Table 2

Relative total energies (kJ mol⁻¹) of conformations on functional groups of 1,2-ethanedithiol

Conformation	Energy	
	CNDO/2	PCILO
<i>tTt</i>	0.0	0.0
<i>tGg</i>	7.15	6.19
<i>tGg'</i>	7.69	2.71
<i>gGg</i>	9.77	8.78
<i>g'Gg</i>	11.03	8.38
<i>cGg</i>	12.90	9.30
<i>tCg</i>	20.06	18.55
<i>gCg</i>	34.68	34.17
<i>g'Cg</i>	36.35	37.56
<i>cCg</i>	73.95	71.31

stabilization is the *gauche* effect without hydrogen bond. The conformations with hydrogen bond *tGg* (7.15 kJ mol^{-1}) and *tGg'* (7.69 kJ mol^{-1}) are less stable. These results are very well consistent with experimental data.

The course of energetic relationships shows that the *T* arrangement corresponds to the lowest energy in all cases, which evidences the predominant role of interatomic repulsion of the SH groups. The PCILO method gives similar results. It follows from Fig. 4 that the course of energetic relationships is equal to that obtained by the CNDO/2 method and the *tTt* conformer is again the most stable. The second most advantageous *tGg'* conformer has a hydrogen bond (Table 2).

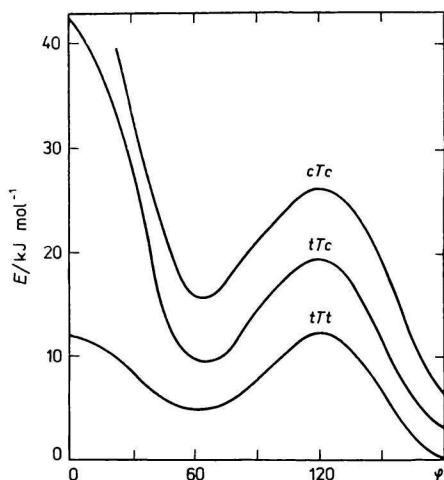


Fig. 3. Variation of total energy of conformers of 1,2-ethanedithiol with the angle of rotation about the C—C bond (CNDO/2 method).

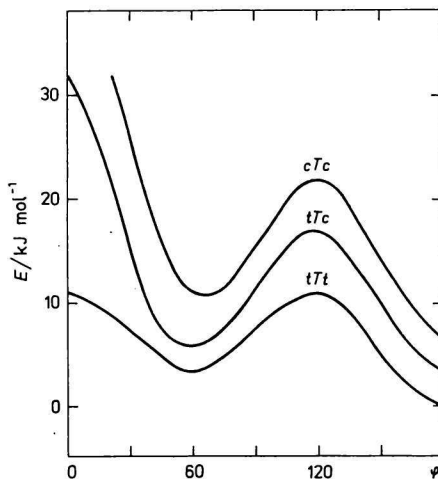


Fig. 4. Variation of total energy of conformers of 1,2-ethanedithiol with the angle of rotation about the C—C bond (PCILO method).

Conclusion

The results of the study of conformation of the 1,2-disubstituted derivatives of ethane obtained by theoretical methods have shown that the conformations stabilized by hydrogen bond are significantly effective in 2-mercaptoethanol. The replacement of oxygen by sulfur brings about that the interatomic repulsion becomes the decisive factor. It may be pointed out that the semiempirical CNDO/2 and PCILO methods are useable for such studies. Though the theoretical results

are not in full agreement with experimental results for 2-mercaptoethanol, it is worth noticing that the order of conformations need not be precise because of very small energetic differences between advantageous conformations (among which the conformer found experimentally occurs). The results obtained by CNDO/2 for 1,2-ethanedithiol are in good agreement with experiments.

Both methods used give similar results. However, the PCILO method prefers conformations with hydrogen bond while the CNDO/2 method prefers conformations with the *G* arrangement without hydrogen bond.

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