# Theoretical study of structure of the 1,2-disubstituted derivatives of ethane. I. Conformations of 1,2-ethanediol, 2-aminoethanol, and 1,2-ethanediamine

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All staggered and eclipsed conformations of 1,2-ethanediol, 2-aminoethanol, and 1,2-ethanediamine have been studied by the semiempirical CNDO/2 method with optimization of structural parameters. The conformations of the -OH and  $-NH_2$  functional groups have been also investigated. The results obtained are compared with available experimental and theoretical data. The energy of particular conformations is mainly influenced by interatomic repulsion and possible formation of intramolecular hydrogen bond.

Полуэмпирическим методом CNDO/2 с полной оптимализацией структурных параметров были изучены все скошенные и заслоненные конформации 1,2-этандиола, 2-аминоэтанола и 1,2-этандиамина. Был сделан также конформационный анализ – OH и – NH<sub>2</sub> групп. Полученные результаты сравниваются с доступными экспериментальными и теоретическими данными. Наибольшее влияние на энергию отдельных конформаций оказывает межатомное отталкивание и возможность образования внутримолекулярной водородной связи.

The 1,2-disubstituted derivatives of ethane were for a long time topic of the conformational studies carried out by experimental as well as theoretical methods. The rotation about the C-C bond can give rise to 3 staggered (2 synclinal and 1 antiperiplanar) and 3 eclipsed forms (2 anticlinal and 1 synperiplanar). The present results show that the antiperiplanar form prevails in most cases. That appears with those compounds the potential energy curve of which is determined by interatomic repulsion, *e.g.* with 1,2-dihalogen ethane. The situation is different if a hydrogen bond may arise in the derivative. Such intramolecular hydrogen bond is able to stabilize the synclinal conformer, *e.g.* with 1,2-ethanediol. The hydrogen bond may also produce a change in bond lengths and bond angles. If the substituent is represented by a functional group, the conformations formed by its rotation must be also taken into consideration.

In this study we were concerned with theoretical investigation of the optimum geometry and its influence on energetic stability of the conformations of 1,2-ethanediol, 2-aminoethanol, and 1,2-ethanediamine. All these compounds may form an intramolecular hydrogen bond. The experimental measurements performed with these compounds were mainly aimed at the conformations on the C-C bond and, to a lesser extent, at the conformation of the functional groups. The theoretical papers hitherto published are aimed at the conformational analysis of the C-C bond in the functional groups, too. However, the bond lengths and bond angles have not been optimized. In most papers, the subject of study involves only the staggered conformations which are, in general, energetically preferable. Nevertheless, it may be assumed that the hydrogen bond can, to a certain degree, stabilize the eclipsed conformation in some cases. Therefore, the purpose of this study is to find out the optimum structural parameters of all conformations corresponding to the staggered as well as eclipsed arrangement and simultaneously to verify the suitability of the semiempirical CNDO/2 method for the study of this problem.

## Method of calculation

For calculations, we used the semiempirical CNDO/2 method [1-3] which proved to be good for the study of the hydrogen bonds [4]. We optimized the structural parameters of the investigated compounds using the gradient method [5, 6] and the optimization programme DERIVAL [7]. The bond lengths and bond angles were automatically optimized. The method used being symmetry-conserving, the dihedral angles cannot be directly optimized because it would be connected with a passage from one symmetry into another. Therefore we investigated all staggered and eclipsed conformations of the above compounds, originating from rotation about the C-C bond. We took, to a certain extent, into consideration the conformations of the -OH and -NH, groups, as well. We took into account the torsional angle of 0 and 180° for the -OH group and 0 and 90° for the -NH, group. Provided a formation of hydrogen bond was possible, we also investigated the gauche conformations of the functional groups, i.e. the angle of 60 or 300°. A survey of the investigated conformations of 1,2-ethanediol, 2-aminoethanol, and 1,2-ethanediamine is presented in Figs. 1-3. The numbering of individual atoms is in Scheme 1. The experimental data obtained by the X-ray analysis were used as input data [8]. The results obtained were compared with available experimental or theoretical data.



Scheme 1



Fig. 1. Investigated conformations of 1,2-ethanediol.



Fig. 2. Investigated conformations of 2-aminoethanol.



Fig. 3. Investigated conformations of 1,2-ethanediamine.

#### **Results and discussion**

#### 1,2-Ethanediol

According to the experimental studies hitherto published [9-11]. 1,2-ethanediol occurs in the synclinal form which is stabilized by the hydrogen bond. The measurements based on the <sup>1</sup>H-n.m.r. spectra [12] also admit occurrence of the antiperiplanar form. The theoretical studies with nonempirical methods [13-15] also prefer the synclinal arrangement. In most theoretical publications, the authors take into account only the staggered arrangement of conformations.

The relative values of energy for the conformations studied by us are given in Table 1. We can see that the CNDO/2 method gives the smallest value of energy for the antiperiplanar conformer exhibiting the lowest inferatomic repulsion. Conformation 2, in which the synperiplanar arrangement is stabilized by the hydrogen bond, has the energy higher by 4.4 kJ mol<sup>-1</sup>. For conformations where the hydrogen bond may arise, we also investigated the influence of the arrangement in functional groups. For conformation 2, we also considered the arrangement with the torsional C-1-C-2-O-2-H-2 angle of 60°. This conformation has the relative energy of 14.4 kJ mol<sup>-1</sup> and is less favourable than original conformation 2. Another conformation where a hydrogen bond may arise is conformation 5. This

Conformation	1,2-Ethanediol	2-Aminoethanol	1,2-Ethanediamine
1	0.0	0.0	0.0
2	4.427	1.765	6.923
3	10.406	4.639	9.017
4	10.425	11.023	11.483
5	12.383	12.074	18.343
6	13.036	16.858	19.355
7	18.854	17.003	26.232
8	19.327	19.684	62.648
9	23.001	21.641	67.875
10	23.869	24.535	72.090
11	34.044	25.595	74.491
12	36.233	28.277	113.318
13		32.896	
14		52.107	
15		52.483	
16		59.244	

Table 1 Relative potential energy  $(kI mol^{-1})$  of the 1.2-disubstituted derivatives of ethane<sup>a</sup>

a) Conformations are numbered in conformity with Figs. 1-3.

arrangement with the torsional O-1-C-1-C-2-O-2 angle  $\sim 60^{\circ}$  is regarded on the basis of experimental data and theoretical calculation as the most favourable. We investigated the influence of the torsional C-1-C-2-O-2-H-2 angle on total energy. Provided the value of this angle was  $60^{\circ}$ , we obtained a reduction in relative energy to 8.3 kJ mol<sup>-1</sup>, owing to which this conformation got to the third place from the view-point of energetic preference. The optimization of molecular geometry of particular conformations resulted in a tightening of the C-C bond approximately to 0.147 nm and the C-O bond to 0.138 nm whereas the O-H bond was extended to 0.103 nm. The values of the resulting bond angles are given in Table 2. We can see that the C-C-O angle changes only slightly in conforma-

Resulting bond angles in 1,2-ethanediol						
Conformation	Bond angles [°]					
	C-2-C-1-O-1	C-1-C-2-O-2	C-1-O-1-H-1	С-2-О-2-Н-2		
1	109.83	109.83	106.69	106.69		
2	107.22	111.88	106.98	105.02		
3	108.15	108.72	106.89	106.81		
4	109.96	114.89	106.79	108.11		
5	113.97	109.16	107.49	106.96		
6	110.74	108.96	107.15	106.97		
7	110.92	110.38	107.43	106.91		
8	114.43	110.23	106.20	107.06		
9	113.96	113.96	107.89	107.89		
10	115.00	115.00	108.00	108.00		
11	111.11	116.05	107.48	108.58		
12	119.21	119.21	110.77	110.77		

Table 2

tions 1-4, and increases in conformations 5-12, the most in unfavourable arrangement 12. The C-O-H angle decreases in all cases and approaches the tetrahedral arrangement of bonds and lone electron pairs in oxygen. Its smallest value is in conformation 2 where a hydrogen bond may be assumed while its highest value is in conformation 12. The presence of hydrogen bond in conformation 2 is also indicated by a high value of positive charge on the hydrogen atom of the hydroxyl group (0.164). The Wiberg index of the O-H bond (0.928) also implies a weakening of this bond.

## 2-Aminoethanol

The measurements with microwave [16] and infrared [17] spectra have shown that the molecule is likely to occur in a synclinal arrangement which is stabilized by hydrogen bond. The nonempirical calculations [14] have disclosed that the three forms containing the hydrogen bond are energetically the most favourable while the arrangement with the N...H-O bond processes the lowest energy.

As obvious from Table 1, the CNDO/2 method also gives the lowest energy for the synclinal arrangement. In contrast to nonempirical calculations, this conformer is, however, stabilized by the N-H...O hydrogen bond where the H...O distance is 0.275 nm. Antiperiplanar conformer 2 has the energy higher by 1.7 kJ mol<sup>-1</sup>. Other three conformations 3—5 are also stabilized by a hydrogen bond and conformation 4 is eclipsed. We have also calculated the conformation which is according to experimental measurements as well as nonempirical calculations energetically the most favourable. This conformation exhibits a synclinal arrangement of the central O-C-1-C-2-N atoms and the torsional angles of the functional groups are: C-2-C-1-O-H=60°, C-1-C-2-N-H-1=300°, C-1-C-2-N-H-2=180°. According to the CNDO/2 method we have, however, obtained the energy which is higher than that of conformation 5 from which the most favourable conformer has been derived. The optimization of bond lengths

Conformation -	5 000 5	Bond angles [°]					
	C-C-0	C-C-N	С-О-Н	C-N-H-1	C-N-H-2		
1	109.99	110.54	106.64	110.35	110.05		
2	109.75	119.68	106.66	110.54	110.54		
3	109.70	115.35	106.75	108.23	107.79		
4	109.12	115.13	106.84	108.18	108.17		
5	114.12	110.25	107.76	111.54	111.01		
6	114.28	119.36	107.66	109.79	109.79		
7	114.76	116.22	108.02	108.72	109.16		
8	110.95	111.92	107.34	112.02	110.87		
9	114.84	117.22	107.85	110.11	110.11		
10	111.37	117.09	107.42	108.73	108.70		
11	110.28	111.75	106.99	123.55	121.41		
12	114.50	120.32	106.20	110.10	110.13		
13	115.30	111.92	106.45	118.24	117.09		
14	117.52	114.73	106.84	126.80	119.85		
15	108.93	109.69	106.60	110.55	122.15		
16	115.39	111.30	107.46	123.36	121.67		

 Table 3

 Resulting bond angles in 2-aminoethanol

resulted again in tightening of the C-C bond to 0.147 nm, the C-O bond to 0.138 nm, and the C-N bond to 0.142 nm while the O-H bond and N-H bond were extended to 0.103 and 0.107 nm, respectively. The calculated optimum values of bond angles are given in Table 3. The change in the C-2-C-1-O bond angle is small and its value approximately corresponds to tetrahedral arrangement. The C-1-C-2-N angle of all conformers increased, in some cases in a rather great degree (conformation 2). The C-1-O-H angle decreased approximately to 107°. In all cases, except energetically unfavourable conformations 15 and 16, the resulting arrangement of the  $-NH_2$  group is pyramidal and the value of the C-2-N-H angle indicates an approximate tetrahedral arrangement on the nitrogen atom. A great difference between the C-2-N-H-1 and C-2-N-H-2 angle in case of great repulsion of the functional groups (conformations 14 and 15) is interesting.

## 1,2-Ethanediamine

On the basis of measurements by electron diffraction [18, 19], it may be assumed that the molecule predominantly occurs in the synclinal form. A nonempirical calculation also predicts [14] the existence of two synclinal forms stabilized by hydrogen bond which have the lowest energy. The antiperiplanar arrangement has the energy higher by  $4.77 \text{ kJ mol}^{-1}$ .

Our results are in agreement with the experimental as well as nonempirical data. Two of the most favourable conformations, *i.e.* conformations 1 and 2, are synclinal whereas conformation 3 is antiperiplanar. The energetic differences are, however, somewhat greater than they are in nonempirical calculations. The optimization of structural parameters exhibited equal trend as with foregoing compounds. The C-C and C-N bond tightened and the N-H bond became longer. The values of the bond angles are given in Table 4. The C-C-N angle changed considerably and the most favourable conformation 1 shows a sizeable difference between the C-1-C-2-N-2 angle and C-2-C-1-N-1 angle. The resulting arrangement of the  $-NH_2$  group in energetically favourable conformations is pyramidal.

### Conclusion

The results of conformational study obtained by the CNDO/2 method with optimization of structural parameters for 2-aminoethanol and 1,2-ethanediamine are in agreement with experimental data and for the second substance with nonempirical calculations as well. For 1,2-ethanediol, the order of energetically favourable conformations is not in harmony with available data. Since the energetic

Resulting bond angles in 1,2-ethanediamine						
Conformation	Bond angles [°]					
	C-2-C-1-N-1	C-1-C-2-N-2	C-1-N-1-H-1	C-1-N-1-H-2	C-2-N-2-H-3	C-2-N-2-H-4
1	117.02	112.51	108.07	108.48	108.69	108.83
2	111.83	111.74	110.48	109.58	109.45	110.31
3	114.57	113.27	111.03	111.87	108.18	108.01
4	118.06	118.14	108.68	108.74	108.69	108.76
5	119.03	119.02	109.63	109.63	109.66	109.66
6	120.60	120.59	109.35	109.35	109.36	109.36
7	118.56	118.56	109.59	108.79	108.81	109.95
8	116.88	112.05	108.40	108.26	121.89	120.44
9	118.48	111.41	108.51	108.56	122.84	122.35
10	114.98	119.00	121.25	123.67	108.70	108.68
11	113.97	113.88	121.72	123.54	117.11	116.05
12	116.36	116.34	120.98	124.50	124.50	120.99

Table 4

differences between particular conformations are small, the overestimation of interatomic repulsion rooted in the method used may lead to an incorrect order of conformers. The optimization of structural parameters has shown that the resulting bond angles have real values and irrespective of initial geometry, the changes in bond lengths are too large.

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