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AB INITIO STUDY ON THE CONFORMATIONAL BEHAVIOUR OF ETHANE-1,1-DIOL and ETHANE-1,1,2-TRIOL IN SOLUTION

SAFİYE SAĞ ERDEM, TEREZA VARNALI* AND VİKTORYA AVİYENTE
Chemistry Department, Boğaziçi Univerisity, 80815 Bebek-Istanbul, Turkey

Ab initio optimizations at the HF/6–31G level and single-point calculations at the MP2/6–31G//6–31G level were performed on ethane-1,1-diol and ethane-1,1,2-triol. Their conformational properties are discussed in terms of the anomeric effect, *gauche* effect and internal O–H interactions. The results showed a parallel behaviour with ethane-1,2-diol. The solvent effect was taken into account using the SCRF theory with a general cavity shape which is defined by the molecular surface. © 1997 by John Wiley & Sons, Ltd.**

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INTRODUCTION

The study of the conformational preference of substituted ethanes has been the focus of considerable attention for a long time because many interactions that occur in them serve as a key to understanding the structures of large cyclic and acyclic compounds. In addition to many experimental and theoretical studies, a considerable amount of *ab initio* work has been reported in the literature on ethane derivatives.[1] The small size of these molecules allows high-level treatments, in terms of both basis sets and electron correlation.

Among the substituted ethanes and propanes, polyhydroxylated molecules have been widely studied by both experimental[2] and theoretical methods.[3] These structures are related with biological chemistry, such as carbohydrates.[4] On the other hand, carbohydrates are complex molecules whose structural features are strongly influenced by special conformational effects such as the ‘anomeric effect’ and ‘*gauch* effect’ or intramolecular hydrogen bonding. Whereas sugars are too large for full conformational analysis using *ab initio* calculations, polyhydroxyethanes are attractive models for studying these types of interactions. In this study, we focused out attention on the structural and conformational properties of ethane-1,1,2-triol, ethane-1,1-diol, and ethane-1,2-diol. These are the simplest representatives of the functional groups of carbohydrates and cyclic compounds such as dioxanes and acetals, and will be of help in understanding the conformational effects related to their analogues. The most dominant conformational effect controlling the structural features in carbohydrates is known as the ‘anomeric effect.’ This refers to the tendency for an electronegative substitutent at C1 of a pyranoid ring to prefer the axial rather than equatorial orientation,[5] despite the predictions based on only steric interactions. It soon became clear that this phenomenon is not restricted to carbohydrates or six-membered heterocycles. Molecules containing an R—O—C—O atomic arrangement prefer the *gauche* (axial) orientation, which is associated with variations of C—O bond lengths and O—C—O bond angles.[6] The variations have been explained as arising from interactions between the non-bonded electrons on oxygen (n_p) and antibonding C—O bond orbital (σ^*c—O) which form the basis of the anomeric effect. There is a stereoelectronic preference for the conformation in which non-bonded electrons on one oxygen adopt an antiperiplanar orientation with respect to the C—O bond involving the other oxygen, as seen in the *gauche* orientation in Figure 1. This arrangement produces lengthening of the C—O (acceptor σ^*) bond and shortening

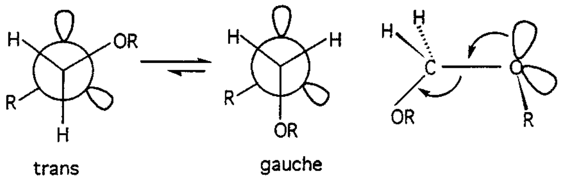

Figure 1. Anomeric effect

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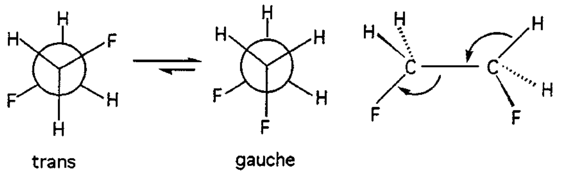


Figure 2. *Gauche* effect

of the C—O (donor oxygen) bond.[5a,6a,d]

Apart from anomeric effect, a related effect exists in systems X—C—C—Y, where X and Y are electronegative groups. For example, in the series X—C—C—X (X = halogen) there is a gradual increase in the proportion of the *gauche* conformation as the electronegativity of *X* increases, so that *gauche*-1,2-difluoroethane clearly predominates in the gas phase.[1c,d,h,i] The origin of this attractive *gauche* preference, which overcomes unfavourable steric and dipolar interactions, was rationalized in terms of stabilizing overlap between bonding and antibonding orbitals, in particular α—σ^* interactions. Therefore, in the *gauche* conformation of 1,2-difluoroethane, C—H bonds serve as donors to the antiperiplanar C—F acceptor bonds as depicted in Figure 2.[5a] On the other hand, Wiberg *et al.*,[1k] explained the *gauche* effect using the bond path method of Runtz *et al.*[7] as being due to a destabilizing interaction in the *trans* rotamer in which the C—C bond orbitals are bent in opposite directions, giving a decreased overlap and thus a poorer bond.

Ethane-1,2-diol is another well known example of the *gauche* preference. It is the simplest compound representing polyhydroxyethanes and therefore important for the purpose of comparison. Although the structures studied in this work are not known experimentally, ethane-1,2-diol has been studied extensively by both experimental and theoretical methods. Experimental techniques, including microwave spectroscopy, electron diffraction and IR spectroscopy, showed that the central O—C—C—O dihedral prefers to adopt a *gauche* conformation.[2a—d,3h] While tGg′ is the predominant conformer, a number of weak signals was assigned to the gGg′ conformer in recent IR and microwave studies.[3h] An appreciable amount of theoretical work, mainly *ab initio* and DFT calculations, has been reported in the literature.[3a—h] All of these investigations agree that the most stable conformer is tGg′ and the next stable conformer is gGg′. The *gauche* preference of ethane-1,2-diol has been attributed to the intramolecular H-bonding and therefore the situation is not exactly the same as in difluorethane.

It is obvious that structural and conformational properties are very much influenced by the solvation effects. Likewise, investigations in liquid state showed that tTt isomer of ethane–1,2-diol is better solvated than tGg′.[3a,3h] Including the effect of the solvent in theoretical studies is a crucial task for computational chemists since most of the experimental work is performed in liquid phase.

We present here the conformational effects operating on ethane-1,1,2-triol and ethane-1,1-diol including the effect of the solvent using a dielectric continuum model and discuss our results refering to a well-studied molecule, ethane-1,2-diol.

METHOD OF CALCULATION

Full geometry optimizations have been carried out at HF/6—31G level using Gausian 92[8] both in the gas phase and in acetonitrile which is selected as a polar solvent. Each minimum has been checked by force calculations, for all positive vibrational frequencies. The optimized geometries have also been subjected to single point MP2/6—31G** calculations to observe the effect of electron correlation. The role of the solvent has been included in the calculations using a SCRF model[9] implemented in Gaussian 92[10]. In this model, the solvent is represented by an infinite dielectric and polarizable continuum in which a cavity is created. The charge distribution of the solute placed in this cavity polarizes the continuum and an electric field is created inside the cavity. The main variations of the total solvation energy have been assumed to come from electrostatic and induction energies while the cavitation and the dispersion energies remain almost constant. In this approach, the shape of the cavity is crucial.[11] A general cavity shape which is a more sophisticated version of the continuum solvation model has been used.[12] In this model, the cavity is modelled on the shape of the solute, which is defined by the so-called molecular surface. The electrostatic and the induction perturbations on the molecular structure do not depend dramatically on the shape of the cavity.

For ethane-1,1-diol, conformational isomerism differs in the specification of the two possible rotameric dihedral angles about each of the two C—O bonds. Assuming a minimum for each staggered conformation for angles near 60°, 180° and 300° gives rise to six distinct conformations (symmetry is also considered), but only five of them could be located in 6—31G calculations as given in Figure 3.

Ethane-1,1,2-triol shows more conformational freedom with the possibility of changing four rotameric dihedral angles (Figure 4). In order to simplify the procedure, we performed a series of PM3 calculations and obtained five contour diagrams as described elsewhere.[11c] Each minimum obtained from the contour diagrams was subjected to 6—31G calculations and six minima were located as shown in Figure 4.

The notations *g*, *t* and *g*′ stand for the *gauche* clockwise, *trans* and *gauche* counterclockwise C—O torsions, which correspond to the dihedral angles 60°, 180° and 300°, respectively. Similarly *G*, *T* and *G*′ stand for the C—C torsions.

RESULTS AND DISCUSSION

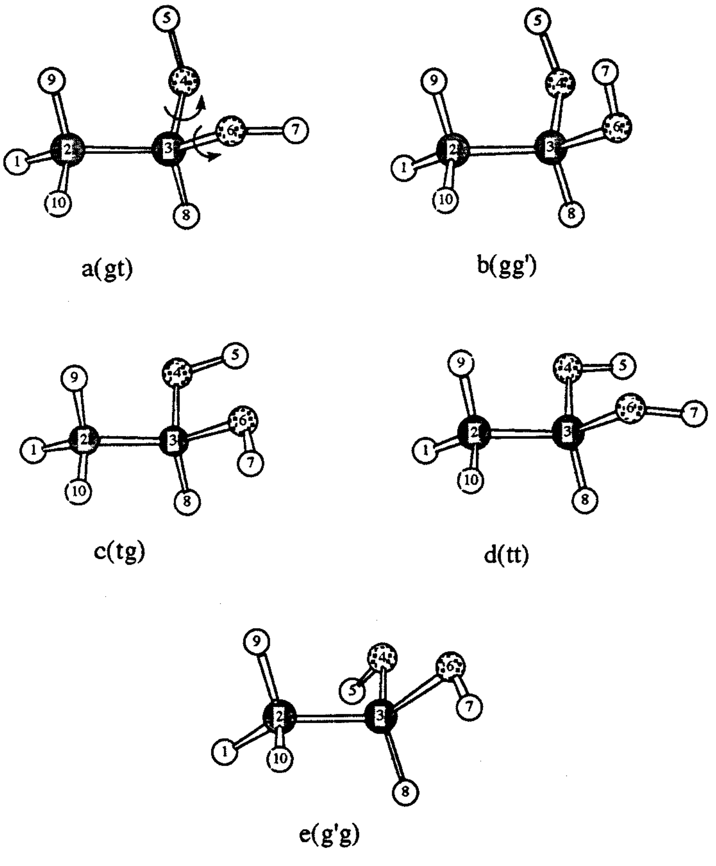
Ethane-1,1-diol

Five conformations located by 6—31G optimizations are given in Figure 3. The *e*(*g*′*g*) conformation has been identified as a transition state producing only one imaginary vibrational frequency in force calculations while the other structures have been proved to be minima.

The results of calculations are given in Table 1. In the gas phase, *a*(*gt*) is the most stable conformation. The extremely high energy of *e*(*g*′*g*) is not unusual since it is characterized with one negative frequency. The relative stabilities of the five conformations can be interpreted in terms of dipolar and anomeric interactions. These two effects seem to operate in the same direction. As expected, in the gas phase the relative energies of the conformations increase as their dipole moments increase. On the other hand, anomeric interactions also influence the relative stabilities. Although *a*(*gt*) *b*(*gg*′) and *d*(*tt*) all have two favourable anomeric interactions (the first between the C—O4 bond and the lone pair of O6 and the second between the C—O6 bond and the lone pair of O4), *b(gg′)* and *d*(*tt*) also exhibit unfavorable 1,3 steric interactions between the hydrogens on O4 and O6. Therefore, *b*(*gg*′) and *d*(*tt*) are less stable than *a*(*gt*). There is only one anomeric interaction in *c*(*tg*) and therefore it is also less stable than *a*(*gt*). No anomeric effect is present in *e*(*g*′*g*), which is responsible for its high energy.

The comparison of MP2 and 6—31G** results shows that there is an apparent increase in relative energies of *c*(*tg*) and *e*(*g*′*g*) when the electron correlation is included in the calculations. As explained above, *c*(*tg*) exhibits only one and *e*(*g*′*g*) exhibits no anomeric effect. Electron correlation treatment allows a much improved representation of non-bonded iteractions (e.g. anomeric effect or H-bonding) than HF treatent. Therefore, in MP2 calculations, the conformations with more non-bonded interactions are expected to be stabilized. As a result, the conformations with less non-bonded interactions have higher relative energies.

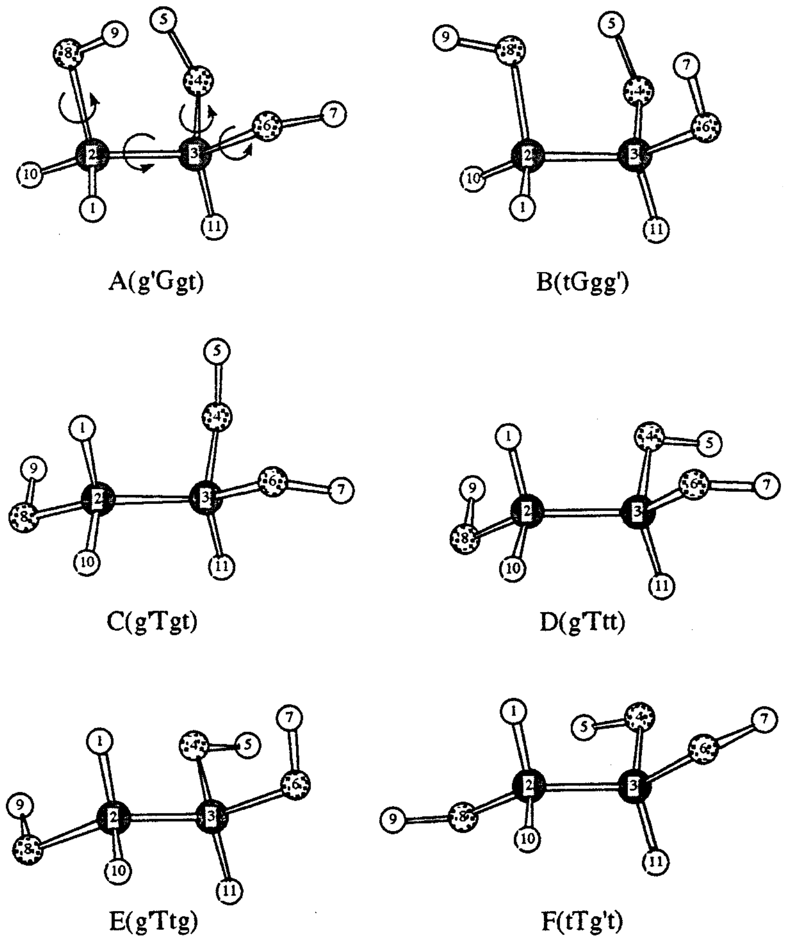
Even though split valence HF calculations are not able to evaluate non-bonded iteractions, they can accurately predict structural trends. It is known that the anomeric effect leads to the shortening of the C—O (donor oxygen) bond and a lengthening of the C—O (acceptor σ^*) bond and also an increase in the O—C—O angle.[6] Such variations are easily observed in Table 2 for *c*(*tg*), which shows one anomeric effect where the lone pair of O4 is antiperiplanar with the C—O6 bond. The O—C—O bond angle is greater in the conformers containing two anomeric effects than in *c*(*tg*) and it is the smallest in *e*(*g*′*g*], which shows no anomeric


a(gt) b(gg′)

c(tg) d(tt)

e(g′g)

Figure 3. Conformations of ethane-1,1-diol in the gas phase



A(g'Ggt) B(tGgg')

C(gTgt) D(gTtt)

E(gTtg) F(tTg't)

Figure 4. Conformations of ethane-1,1,2-triol in the gas phase

Table 1. Relative energies (E_{rel}, kcal mol^{-1}) and dipole moments (μ) for ethane-1,1-diol in the gas phase

	6–31G		E_{rel}	
Structure	E_{rel}	μ	6–31G**//6–31G	MP2/6–31G**//6–31G
a(gt)	0.00[a]	0.254	0.00[b]	0.00[c]
b(gg′)	4.95	3.541	3.90	3.81
c(tg)	3.61	2.715	3.21	3.66
d(tt)	3.93	3.136	3.33	3.34
e(g′g)	10.81	4.269	7.834	8.20

[a] Total energy of *a(gt)* = − 143605.06 kcal mol^{-1} at the 6–31G level.
[b] Total energy of *a(gt)* = − 143674.9605 kcal mol^{-1} at the 6–31G**//6–31G level.
[c] Total energy of *a(gt)* = − 144085.6104 kcal mol^{-1} at the MP2/6–31G**//6–31G level.

interaction. However, $a(gt)$, $b(gg')$ and $d(tt)$ exhibit two anomeric effects but there are no significant variations in the structural parameters of these conformers. This observation indicates that the two anomeric interactions have approximately equal but opposite effects on the C—O bond lengths.

The electronic charges given in Table 3 also reflect the anomeric effect. The O4 atom of $c(tg)$, which exhibits only one anomeric interaction between the non-bonded electrons on O4 (donor oxygen) and σ^* of C3—O6 (acceptor σ^*), possesses a low electronic charge while O6 has the highest. On the other hand, the oxygen atoms of the conformers having two anomeric interactions exhibit a medium charge which is almost equal in magnitude for O4 and O6. In latter conformers, O4 and O6 serve as both electron donors and also acceptors, and therefore the effect cancels out.

Intramolecular hydrogen bonding interactions also show a parallel behaviour with anomeric effect in terms of electronic charges. The only O—H bonding interaction seems to be present between H5 and O6 (2.3 Å) in the $c(tg)$ conformer. The other conformers, a, b and d, show very weak interactions with longer interatomic O—H distances (2.5—2.7 Å) while $e(g'g)$ shows no possibility of O—H interaction. If one classifies the oxygens as H-acceptor and H-donor, the electronic charge on H-acceptor oxygens is higher and proportional to the strength of O—H interaction.

Table 2. Optimized parameters for the conformations of ethane-1,1-diol at the 6–31G level

	$a(gt)$	$b(gg')$	$c(tg)$	$d(tt)$	$e(g'g)$
Bond distances (Å):					
H1—C2	1.082	1.081	1.081	1.081	1.084
C2—C3	1.508	1.517	1.507	1.502	1.516
C2—H9	1.084	1.088	1.081	1.081	1.081
C2—H10	1.081	1.081	1.084	1.081	1.084
C3—O4	1.419	1.418	1.405	1.420	1.414
C3—O6	1.418	1.419	1.430	1.420	1.414
C3—H8	1.078	1.072	1.085	1.085	1.087
O4—H5	0.953	0.952	0.952	0.951	0.950
O6—H7	0.952	0.952	0.950	0.951	0.950
Bond angles (°)					
H1—C2—C3	110.1	110.4	110.1	110.1	111.0
H1—C2—H9	109.2	108.2	108.9	109.0	109.0
H1—C2—H10	109.3	109.1	108.6	109.6	108.0
C3—C2—H9	109.9	110.7	109.2	108.9	108.9
C3—C2—H10	110.3	110.3	110.9	110.1	111.0
H9—C2—H10	108.0	108.1	109.3	109.0	109.0
C2—C3—O4	112.7	111.4	108.2	107.4	111.1
C2—C3—O6	107.0	111.3	112.5	107.4	111.1
C2—C3—H8	111.9	112.0	111.4	111.8	110.9
O4—C3—O6	110.5	112.2	106.1	112.1	104.3
O4—C3—H8	104.1	104.8	109.9	109.1	109.6
O6—C3—H8	110.6	104.7	108.6	109.1	109.6
C3—O4—H5	112.9	114.6	112.2	114.9	113.7
C3—O6—H7	113.0	114.5	114.7	114.9	113.7
Tortional angles (°)					
H1—C2—C3—O4	56.7	56.7	58.5	56.0	62.2
H1—C2—C3—O6	178.5	− 177.2	175.5	180.0	177.8
H1—C2—C3—H8	− 60.2	− 60.3	− 62.3	− 60.6	− 60.1
H9—C2—C3—O4	− 63.6	− 63.0	− 60.9	− 60.5	− 57.8
H9—C2—C3—O6	58.1	63.1	56.1	60.3	57.8
H9—C2—C3—H8	179.7	180.0	178.3	180.0	180.0
H10—C2—C3—O4	177.4	177.3	178.7	− 180.0	− 177.8
H10—C2—C3—O6	− 60.9	− 56.6	− 64.4	− 59.1	− 62.2
H10 − C2—C3—H8	60.5	60.3	57.8	60.5	60.1
C2—C3—O4—H5	55.7	51.2	157.7	− 173.8	− 74.8
O6—C3—O4—H5	− 64.0	− 74.4	36.7	68.4	165.4
H8—C3—O4—H5	177.2	172.6	− 80.6	− 52.5	48.1
C2—C3—O6—H7	178.2	− 55.0	64.9	172.7	74.9
O4—C3—O6—H7	− 58.7	70.6	− 176.9	− 69.5	− 165.4
H8—C3—O6—H7	56.0	− 176.3	− 58.8	51.4	− 48.1

Table 3. Electronic charges on oxygen atoms (hydrogen's charge summed into oxygens) of ethane-1,1-diol in the gas phase and in acetonitrile from 6—31G calculations

	In gas phase		In acetonitrile	
Structure	O4	O6	O4	O6
a(*gt*)	− 0.340	− 0.335	− 0.352	− 0.345
b(*gg*′)	− 0.339	− 0.338	− 0.350	− 0.350
c(*tg*)	− 0.319	− 0.359	− 0.338	− 0.358
d(*tt*)	− 0.341	− 0.341	− 0.350	− 0.350

As a result, O6 of *c*(*tg*) exhibits the highest charge, as seen in Table 3.

A smaller molecule, methanediol, was also studied at the MP2/6—311++G** level as a model system for carbohydrates by Woods *et al.*[4b] Methanediol exhibits the same conformation-controlling interactions, such as anomeric effect, dipolar interaction and 1,3-hydrogen repulsions, as ethane-1,1-diol. Our results for ethane-1,1-diol showed the same trends as methanediol in terms of both relative energies and geometric parameters.

Calculations is solution at the 6—31G level (Table 4) show that the conformer with the larger dipole moment is better solvated in acetonitrile, as expected. As a result, *b*(*gg*′) is the best solvated conformer and *a*(*gt*) is the least solvated. Since the solvent effect is larger on *b*(*gg*′), *c*(*tg*) and *d*(*tt*), the order of relative stabilities in solution is changed in comparison with the gas phase. However, this effect is not sufficient to make *b*(*gg*′), *d*(*tt*) and *c*(*tg*) more stable in solution than *a*(*gt*).

It has been observed that the geometic parameters are not much affected by the solvent. On the other hand, electronic charges are solvent dependent. In a polar solvent, acetonitrile, the negative charge on oxygens increases in general, as expected. However, the charge on O6 in *c*(*tg*) is almost unchanged or even slightly lower. This can be attributed to the H5—O6 hydrogen bonding interaction or the anomeric interaction between lone pairs of O4 and σ^* of the C3—O6 bond which are already present in the gas phase.

Table 4. Relative energies (E_{rel}, kcal mol^{-1}), solvation energies ($^{a}E_{solv}$, kcal mol^{-1}) and dipole moments (μ) for ethane-1,1-diol in acetonitrile

	6—31G		
Structure	$^{a}E_{solv}$	E_{rel}	μ
a(*gt*)	− 5.58	0.00[b]	0.312
b(*gg*′)	− 8.51	2.02	4.266
c(*tg*)	− 6.86	2.34	3.794
d(*tt*)	− 8.38	1.15	3.830

[a] Energy in solution − energy in gas phase.
[b] Total energy of *a*(*gt*) = − 143610.6395 kcal mol^{-1}.

Ethane-1,1,2-triol

In Figure 4, six conformational minima located by 6—31G calculations are given. Relative energies and dipole moments in the phase are listed in Table 5. All six conformers exhibit two anomeric effects except *F*(*tTg*′*t*), which has only one anomeric interaction, between the lone pair of O6 and the C—O4 bond. On the other hand, *B*(*tGgg*′) and *D*(*g*′*Ttt*) have 1,3-hydrogen repulsions between H5 and H7. They also exhibit high dipole moments, leading to unfavourable dipolar interactions in the gas phase. As a result, they are the least stable among all the conformers. However, *B*(*tGgg*′) is more stable than *D*(*g*′*Ttt*) even though its dipole moment is higher than that of *D*(*g*′*Ttt*). It appears that intramolecular H-bonding plays an important role in predicting the stabilities of *B*(*tGgg*′) and *D*(*g*′*Ttt*) because *B*(*tGgg*′) seems to have stronger O—H interactions than *D*(*g*′*Ttt*) in Table 6. The relative energy of *F*(*tTg*′*t*) is higher than those of *C*(*g*′*Tgt*) and *E*(*g*′*Ttg*′) although its dipole moment is smaller. This destabilization of *F*(*tTg*′*t*) is due to a smaller number of anomeric interactions with respect to *C*(*g*′*Tgt*) and *E*(*g*′*Ttg*′).

The most stable conformer is *A*(*g*′*Ggt*) because it has two anomeric interactions with no 1,3-H repulsions; it has the lowest dipole moment and three possible internal long-range O—H interactions. Intramolecular O—H interactions are more important in ethane-1,1,2-triol than in ethane-1,1-diol since the substitution on C2 by a third OH group enhances the possibility of H-bonding. Table 6 shows all intratomic O—H distances in ethane-1,1,2-triol. Intramolecular hydrogen bonding interactions with various strengths can be observed in the table.

The stability of *A*(*g*′*Ggt*) relative to the other conformers is enhanced when the electron correlation is included in the calculations at the MP2 level (Table 5). This leads us to suggest that non-bonded interactions (intramolecular H-bonding or anomeric interactions) are stronger or they are larger in number in *A(g*′*Ggt)* than in the other conformers. The second important effect of MP2 treatment is that *F(tTg*′*t)* becomes the least stable conformer. The striking increase in the relative energy of *F*(*tTg*′*t*) can be attributed to the presence of only one anomeric interaction in this conformer while the others have two such favourable interactions. The increase of relative energies of *B*(*tGgg*′),

Table 5. Relative energies (E_{rel}, kcal mol^{-1}) and dipole moments (μ) for ethane-1,1,2-triol in the gas phase

	6—31G		E_{rel}	
Structure	E_{rel}	μ	6—31G**//6—31G	MP2/6—31G**//6—31G
A(*g′Ggt*)	0.00[a]	1.640	0.00[b]	0.00[c]
B(*tGgg′*)	3.52	4.686	3.31	3.63
C(*g′Tgt*)	2.94	2.539	2.20	3.06
D(*g′Ttt*)	4.87	3.972	4.32	5.36
E(*g′Ttg′*)	2.07	2.303	1.57	2.36
F(*tTg′t*)	3.24	2.165	3.89	5.61

[a] Total energy of *A*(*g′Ggt*) = − 190555.8473 kcal mol^{-1} at the 6—31G level.
[b] Total energy of *A*(*g′Ggt*) = − 190647.4396 kcal mol^{-1} at the 6—31G**//6—31G level.
[c] Total energy of *A*(*g′Ggt*) = − 191167.7843 kcal mol^{-1} at the MP2/6—31G**//6—31G level.

C(*g′Tgt*), *D*(*g′Ttt*) and *E*(*g′Ttg′*) is smaller, probably because of the smaller number of O—H interactions or weaker O—H interactions in these conformers in comparison with *A*(*g′Ggt*), as seen in Table 6.

Geometric parameters are also influenced by intramolecular O—H interactions. Table 7 shows that there are some variations in C—O bond lengths depending on the type of oxygen. One can classify the oxygens involved in hydrogen bonding as H-donor, H-aceptor and both H-donor and -acceptor. As expected, the C—O distances are shorter for the oxygen donating the proton and longer for the oxygen accepting the proton. For instance, in *B*(*tGgg′*), O8 acts as a proton acceptor from both H5 and H7 and therefore the C2—O8 bond is the longest whereas the C3—O4 and C3—O6 bonds are short because O4 and O6 are proton donors. Similarly, for *A*(*g′Ggt*), the C2—O8 length is long whereas the C3—04 bond is short. For *F*(*tTg′t*), the C2—O8 bond is long whereas the C3—O6 bond is short and the C3—O4 bond of medium length since O4 gives its proton to O8 and also accepts the proton of O6.

The electronic charges on the oxygen atoms also show variations. Although the variations are small, there is a systematic trend. The negative charge on the oxygen increases as the H-acceptor property of the oxygen increases and the charge is small for the oxygen donating its proton. An oxygen which has both H-donor and H-acceptor properties exhibits a medium charge. Table 8 shows that the charges on O8 of *B(tGgg′)* and *F*(*tTg′t*) are the highest because O8 is a relatively strong H-acceptor in *B*(*tGgg′*) and *F*(*tTg′t*). On the other hand, the charges on O4 and O6 of *B*(*tGgg′*) and O4 of *A*(*g′Ggt*) are the smallest because these are the H-donor oxygens.

The tendency mentioned above is reversed in solution. In acetonitrile, the charge on H-acceptor oxygens decreases because their charge distribution is already disturbed in the gas phase by the approaching hydrogen through an internal O—H interaction. As a result, polarization of the charge density by the solvent is not so effective. In parallel with this, the interatomic O—H distances (between an H-acceptor oxygen and the hydrogen of an H-donor oxygen) have been observed to be 0.03—0.04 Å shorter in acetonitrile than in the gas phase. On the other hand, the charge on H-donor oxygens increases in acetonitrile since such oxygens are much more polarizable by the solvent.

Table 9 shows that the solvent effect in acetonitrile produces an overall decrease in the energy of the conformers. On the other hand, the conformers with large dipole moments, *B(tGgg′)* and *D*(*g′Ttt*), gives rise to more negative solvation energies than the conformers having smaller dipole moments. As a result, these two conformers are the most solvated and there is an apparent decrease in their relative energies in solution. An anomeric effect is also

Table 6. Interatomic O—H distances (Å) obtained from 6—31G calculations in ethane-1,1,2-triol

Structure	H9—O6	H9—O4	H7—O8	H7—O4	H5—O8	H5—O6
A(*g′Ggt*)	2.485	3.168	3.573	2.515	2.360	2.680
B(*tGgg′*)	3.617	3.615	2.363	2.673	2.364	2.762
C(*g′Tgt*)	3.869	2.478	4.368	2.652	3.287	2.489
D(*g′Ttt*)	3.897	2.447	4.380	2.681	3.518	2.783
E(*g′Ttg′*)	3.920	2.404	3.975	2.562	3.579	2.636
F(*tTg′t*)	4.331	3.605	4.256	2.351	2.329	3.120

evident in solution. *F*(*tTg′t*) exhibits only one anomeric interaction whereas all the others have two such interactions. The relative energies in Table 9 demonstrate that, in acetonitrile, *F*(*tTg′t*) is still less stable than *C*(*g′Tgt*) and *E*(*g′Ttg′*) although these three conformers have comparable dipole moments.

Structural comparison of ethane-1,1-diol and ethane-1,1,2-triol

The main consequence of introducing a third hydroxy group in ethane-1,1-diol is the increase in the number of hydrogen bonding interactions, which also influences the structural

Table 7. Optimized parameters for the conformational energy minima of ethane-1,1,2-triol at the 6—31G level

	A(*g′Ggt*)	*B*(*tGgg′*)	*C*(*g′Tgt*)	*D*(*g′Ttt*)	*E*(*g′Ttg′*)	*F*(*tTg′t*)
Bond distances (Å):						
H1—C2	1.081	1.081	1.084	1.081	1.085	1.081
C2—C3	1.510	1.515	1.510	1.506	1.511	1.506
C2—O8	1.431	1.441	1.424	1.423	1.421	1.436
C2—H10	1.077	1.081	1.076	1.076	1.077	1.081
C3—O4	1.407	1.411	1.424	1.421	1.420	1.417
C3—O6	1.423	1.411	1.409	1.410	1.411	1.404
C3—H11	1.077	1.073	1.077	1.083	1.076	1.082
O4—H5	0.955	0.954	0.954	0.950	0.951	0.953
O6—H7	0.952	0.954	0.951	0.951	0.953	0.952
O8—H9	0.953	0.949	0.952	0.952	0.952	0.949
Bond angles (°)						
H1—C2—C3	110.3	110.4	109.3	108.3	109.1	108.9
H1—C2—O8	111.4	110.7	111.6	111.9	111.1	111.2
H1—C2—H10	109.6	110.0	108.6	109.3	109.1	109.7
C3—C2—O8	108.9	104.3	110.2	110.3	110.7	104.9
C3—C2—H10	110.4	110.4	110.4	110.1	111.0	110.4
O8—C2—H10	106.3	110.8	106.7	106.9	106.9	111.5
C2—C3—O4	111.5	109.8	110.7	106.3	105.7	111.1
C2—C3—O6	105.4	109.9	107.1	106.7	112.3	107.3
C2—C3—H11	112.4	111.9	111.1	111.1	111.4	110.5
O4—C3—O6	110.9	112.9	111.0	112.6	111.3	107.9
O4—C3—H11	106.1	106.1	104.7	109.4	111.0	109.3
O6—C3—H11	110.7	106.2	112.3	110.6	105.4	110.7
C3—O4—H5	111.8	112.4	112.5	115.6	114.1	112.4
C3—O6—H7	113.1	112.4	114.2	115.4	113.4	112.4
C2—O8—H9	111.7	115.1	112.5	111.6	111.6	114.7
Tortional angles (°)						
H1—C2—C3—O4	−179.2	178.7	−63.3	−63.0	−63.3	−61.3
H1—C2—C3—O6	−58.8	−56.7	57.9	57.4	58.2	56.4
H1—C2—C3—H11	61.9	61.0	−179.2	178.1	176.1	177.2
O8—C2—C3—O4	−56.8	−62.4	59.6	59.8	59.3	57.9
O8—C2—C3—O6	63.6	62.3	−179.2	−180.0	−179.3	175.6
O8—C2—C3—H11	−175.7	180.0	−56.2	−59.2	−61.3	−63.6
H10—C2—C3—O4	59.6	56.7	177.3	177.6	177.2	178.1
H10—C2—C3—O6	180.0	−178.7	−61.5	−62.0	−61.4	−64.1
H10 − C2—C3—H11	−59.4	−60.9	61.4	58.6	56.6	56.7
H1—C2—O8—H9	54.1	−61.4	69.3	57.8	63.6	−62.5
C3—C2—O8—H9	−67.7	180.0	−56.3	−62.8	−57.8	180.0
H10—C2—O8—H9	173.4	61.0	−172.2	177.5	−177.6	60.3
C2—C3—O4—H5	39.8	51.4	71.7	−161.7	−171.7	−48.4
O6—C3—O4—H5	−77.3	−71.5	−47.1	81.9	66.3	−165.8
H11—C3—O4—H5	162.4	172.6	−168.5	−41.6	−50.8	73.7
C2—C3—O6—H7	−171.7	−51.3	169.9	176.3	−61.1	−155.9
O4—C3—O6—H7	−50.9	71.6	−69.1	−67.5	57.0	−36.1
H11—C3—O6—H7	66.5	−172.5	47.7	55.2	177.5	83.5

Table 8. Electronic charges on oxygen atoms (hydrogen's charge summed into oxygens) of ethane-1,1,2-triol in the gas phase and in acetonitrile from 6—31G calculations

	In gas phase			In acetonitrile		
Structure	O4	O6	O8	O4	O6	O8
A(*g′Ggt*)	− 0.321	− 0.345	− 0.336	− 0.340	− 0.344	− 0.353
B(*tGgg′*)	− 0.322	− 0.322	− 0.371	− 0.342	− 0.342	− 0.363
C(*g′Tgt*)	− 0.342	− 0.333	− 0.338	− 0.345	− 0.337	− 0.358
D(*g′Ttt*)	− 0.350	− 0.337	− 0.341	− 0.346	− 0.341	− 0.361
E/*g′Ttg′*)	− 0.346	− 0.333	− 0.329	− 0.340	− 0.341	− 0.354
F(*tTg′t*)	− 0.340	− 0.332	− 0.368	− 0.353	− 0.339	− 0.359

parameters. A structural comparison of ethane-1,1diol and ethane-1,1,2-triol has been made so that *a*(*gt*) corresponds to *A*(*g′Ggt*) and *C*(*g′Tgt*), *b*(*gg′*) to *B*(*tGgg′*) and *d*(*tt*) to *D*(*g′Ttt*). Based on this comparison, it was observed (Tables 2 and 7) that the C2—C3 bond length in ethane-1,1,2-triol is 0.002—0.004 Å longer thant that in ethane-1,1-diol, as expected, except for *B*(*tGgg′*), which has a shorter bond length than *b*(*gg′*) by 0.002 Å. The shortening of the C2—C3 bond in *B*(*tGgg′*) can be rationalized in terms of two relatively strong O—H interactions between H5 and O8 and also between H7 and O8. The same effect can also be observed in comparing the C3—C2—O angle in ethane-1,1,2-triol in Table 7 with the C3—C2—H9 angle in ethane-1,1-diol in Table 2. The C3—C2—O8 angle is 6.4° and 1° smaller in the hydrogen-bonded conformers *B*(*tGgg′*) and *A*(*g′Ggt*), respectively, than those in *b*(*gg′*) and *g*(*gt*) because the favourable O—H interactions are expected to push O8 towards H5 or H7. However, for *C*(*g′Tgt*) and *D*(*g′Ttt*) the C3—C2—O8 angle is larger than that in the corresponding conformers of ethane-1,1-diol since internal O—H interactions between O8 and the protons of O4 and O6 are negligible in *C*(*g′Tgt*) and *D*(*g′Ttt*).

The structural variations of the O—C—O fragment can be interpreted in terms of steric and electronic factors rather than O—H interactions, which are more favourable in the O—C—C—O fragment. Tables 2 and 7 show that the O4—C3—O6 angles in ethane-1,1,2-triol are about 0.5° larger whereas the 04—C3—C2 and O6—C3—C2 angles are smaller than those in ethane-1,1–diol.

Table 9. Relative energies (E_{rel}, kcal mol^{-1}), solvation energies ($^{a}E_{solv}$, kcal mol^{-1}) and dipole moments (μ) for ethane-1,1,2-triol in acetonitrile

	6—31G		
Structure	$^{a}E_{solv}$	E_{rel}	μ
A(*g′Ggt*)	− 6.52	0.00[b]	2.222
B(*tGgg′*)	− 8.99	1.05	5.628
C(*g′Tgt*)	− 8.07	1.38	2.856
D(*g′Ttt*)	− 9.92	1.46	4.750
E(*g′Ttg′*)	− 7.56	1.03	2.599
F(*tTg′t*)	− 7.02	2.74	2.667

[a] Energy in solution − energy in gas phase.

[b] Total energy of *A*(*g′Ggt*) = − 190562.3658 kcal mol^{-1}.

Comparison of ethane-1,1-diol and ethane-1,1,2-triol with findings for ethane-1,2-diol

The conformational space of ethane-1,2-diol was characterized with 10 unique conformational minima in the literature.[3c,e—h] Among these, the two *gauche* conformations, *tGg′* and *gGg′*, are the most stable and the next most stable conformers, respectively, as supported by experimental measurements.[2a—d] The stability of *tGg′* and *gGg′* was explained in terms of internal H-bonding. Both conformers form an intramolecularly H-bonded five-membered ring indicated by the calculated –HO—HO– interatomic distance. This distance varies between 2.093 and 2.362 Å depending on different *ab initio* and DFT calculations.[3c,e] The same type of intramolecular O—H interactions were also observed in ethane-1,1,2-triol (Table 6) between H7 and O8 and between H5 and O8 for *B*(*tGgg′*) and only between H5 and O8 in *A*(*g′Ggt*). In addition to H5—O8 interaction, *A*(*g′Ggt*), which is the most stable conformer, exhibits the possibility of other weaker O—H interactions between H9 and O6 and between H7 and O4. On the other hand, *F*(*tTg′*), which contains one less anomeric effect than the others, has two shorter O—H distances but its relative energy is fairly high. This indicates that the energy lowering gained by H-bonding does not compensate for the lack of one anomeric interaction.

In ethane-1,2-diol, there are four pairs of *gauche—trans* forms with respect to the C—C bond. In the pair *gTg′*—*gGg′*, where the *gauche* preference is attributed to the intramolcular H-bonding, *gGg′* is more stable by 1.79—3.91 kcal mol^{-1} (1 kcal = 4.184 kJ) depending on the method used.[3c] According to our calculations on ethane-1,1,2-triol, the energy difference between *A*(*g′Ggt*) and *C*(*g′Tgt*) is 2.94 kcal mol^{-1}, *A*(*g′Ggt*) being more stable. This energy difference corresponds to the presence of two *gauche* O—O iteractions in *A*(*g′Ggt*) but one *gauche* and one *trans* O—O interaction in *C*(*g′Tgt*). The intramolecular O—H interaction is also expected to contribute to this energy lowering since such interactions are stronger in $A(g'Ggt)$, as seen in Table 6.

CONCLUSION

We found that the conformational minima of ethane-1,1-diol and ethane-1,1,2-triol lie within 4.9 kcal mol at the 6—31G level. For ethane-1,2-diol, 10 minima were reported to be within 4.5 kcal mol^{-1} with different calculation methods.[3a—c] These small energy differences found among the conformers suggest that there can be numerous low-energy conformers of large biomolecules containing polyhydroxyethane units, which may play important roles in bioactive conformation. The results obtained in this work showed the importance of the anomeric effect, H-bonding and *gauche* interactions in determining the molecular conformations of small model molecules and their large analogues.

In ethane-1,1-diol, the anomeric effect is the determining factor, whereas in ethane-1,1,2-triol, H-bonding and the *gauche* effect also play important roles in addition to the anomeric effect. The *a*(*gt*) conformer was found to be the lowest energy conformer for ethane-1,1-diol. The stability of the *gt* arrangement of the O/C—O fragment was also observed in ethane-1,1,2–triol and methanediol.[4b] Similarly, the stability of the *tGg′* arrangement in the O—C—C—O unit is common to both ethane-1,1-diol and ethane-1,1,2-triol.

The comparison of the geometric parameters of ethane-1,1,2-triol and ethane-1,1-diol indicated the predominance of hydrogen bonding interactions in ethane-1,1,2-triol.

Solvent effect calculations with the SCRF method emphasized the role of the solvent in conformational analysis. The energies of all the conformers decrease in solution but the conformers with larger dipole moments become more stable than those having smaller dipole moments. As a result, a change in the order of relative stabilities is observed. The examination of electronic charges for solvated molecules confirmed that special effects such as intramolecular O—H interactions and anomeric interactions are also important in solution.

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REFERENCES

1. (a) K. Siam, S. Q. Newton and L. Schafer, *J. Mol. Struct. (Theochem)* **236**, 1—13 (1991); (b) S. Tsuzuki, T. Uchimaru and K. Tanabe, *J. Phys. Chem.* **97**, 1346—1350 (1993); (c) K. B. Wiberg and M. A. Murcko, *J. Phys. Chem.* **91**, 3616—3620 (1987); (d) J. M. Martell and R. J. Boyd, *J. Phys. Chem.* **96**, 6287–6290 (1992); (e) S. Ikuta and O. Nomura, *Chem. Phys. Lett.* **154**, 71–76 (1989); (f) N. Russo, E. Sicilia and M. Toscano, *J. Mol. Struct. (Theochem)* **257**, 485–490 (1992); (g) Y. Chen, S. J. Paddison and E. Tschuikow-Roux, *J. Phys. Chem.* **98**, 1100–1108 (1994); (h) J. R. Durig, J. Liu and T. S. Little, *J. Phys. Chem.* **96**, 8224–9233 (1992); (i) D. A. Dixon, N. Matsuzawa and S. C. Walker, *J. Phys. Chem.* **96**, 10740–10746 (1992); (j) V. Aviyente, T. Varnalı and M. F. Ruiz-Lopez, *J. Phys. Org. Chem.* **9**, 119–127 (1996); (k) K. B. Wiberg, M. A. Murcko and K. E. Laidig, *J. Phys. Chem.* **94**, 6956–6959 (1990).
2. (a) W. Caminati and G. Corbelli, *J. Mol. Spectrosc.* **90**, 572–578 (1981); (b) P. E. Kristiansen, K. M. Marstokk and H. Møllendal, *Acta. Chem. Scand., Ser. A.* **41**, 403–414 (1987); (c) H. Matsuura, K. Fukuhara and H. Tamoaki, *J. Mol. Struct.* **156**, 293–301 (1987); (d) F. A. J. Singelenberg, E. T. G. Lutz and J. H. van der Maas, *J. Mol. Struct.* **245**, 173–182 (1991).
3. (a) P. I. Nagy, W. J. Dunn III, G. Alagona and C. Ghio, *J. Am. Chem. Chem. Soc.* **113**, 6719–6729 (1991); (b) M. A. Murcko and R. A. DiPaola, *J. Am. Chem. Soc.* **114**, 10010–10018 (1992); (c) T. Oie, I. A. Topol and S. K. Burt, *J. Phys. Chem.* **98**, 1121–1128 (1994); (d) G. Alagona and C. Ghio, *J. Mol. Struct. (Theochem)* **254**, 287–300 (1992); (e) B. J. Teppen, M. Cao, R. F. Frey, C. van Alensoy, D. M. Miller and L. Schafer, *J. Mol. Struct. (Theochem)* **314**, 169–190 (1994); (f) S. A. Vazguez, M. A. Rios and L. Carballeira, *J. Comput. Chem.* **13**, 851–859 (1992); (h) C. J. Cramer and D. G. Truhlar, *J. Am. Chem. Soc.* **116**, 3892–3900 (1994); (g) T. S. Yeh, Y. P. Chang, T. M. Su and I. Chao, *J. Phys. Chem.* **98**, 8921–8929 (1994).
4. (a) I. Carmichael, D. M. Chipman, C. A. Podlasek and A. S. Serianni *J. Am. Chem. Soc.* **115**, 10863–10870 (1993); (b) R. J. Woods, W. A. Szarek and V. H. Smith, Jr, *J. Chem. Soc., Chem. Commun.* 334–337 (1991); (c) S. Reiling, M. Schienkrich and J. Brickmann, *J. Comput. Chem.* **17**, 450–468 (1996).
5. (a) E. Juaristi and G. Cuevas, *Tetrahedron* **48**, 5019–5087 (1992); (b) R. W. Franck, *Tetrahedron* **39**, 3251–3252 (1983).
6. (a) B. M. Pinto, H. B. Schlegel and S. Wolfe, *Can. J. Chem.* **65**, 1658–1662 (1987); (b) M. C. Krol, C. J. Huige and C. Altona, *J. Comput. Chem.* **11**, 765–790 (1990); (c) L. Nørskov-Lauritsen and N. L. Allinger, *J. Comput. Chem.* **5**, 326–335 (1984); (d) U. Salzner and P. G. Schleyer, *J. Am. Chem. Soc.* **115**, 10231–10236 (1993).
7. G. R. Runtz, R. F. W. Bader, R. R. Messer, *Can. J. Chem.* **55**, 3040–3045 (1977).
8. M. J. Frisch, G. W. Trucks, M. Head-Gordon, P. M. W. Gill, M. W. Wong, J. B. Foresman, B. G. Johnson, H. B. Schlegel, M. A. Robb, E. S. Replogle, R. Gomperts, J. L. Andres, K. Raghavachari, J. S. Binkley, C. Gonzalez, R. L. Martin, D. J. Fox, D. J. DeFrees, J. Baker, J. J. P. Stewart and J. A. Pople, *Gaussian 92.* Gaussian, Pittsburg, PA (1992).
9. J. L. Rivail, B. Terryn, D. Rinaldi and M. F. Ruiz-Lopez, *J. Mol. Struct. (Theochem)* **120**, 387–400 (1985); (b) J. L. Rivail and D. Rinaldi, *Chem. Phys.* **18**, 233–242 (1976); (c) D.

Rinaldi, M. F. Ruiz-Lopez and J. L. Rivail, *J. Chem. Phys.* **78**, 834–838 (1983).

10. D. Rinaldi, R. R. Pappalardo, *QCPE 622*. Indiana University, Bloomington, IN (1992).
11. (a) S. S. Erdem, T. Varnalı, V. Aviyente and M. F. Ruiz-Lopez, *Can. J. Chem.* **73**, 703–709 (1995); (b) G. Apaydın, T. Varnalı, V. Aviyente and M. F. Ruiz-Lopez, *J. Mol. Struct. (Theochem)* **287**, 185–191 (1993); (c) S. S. Erdem, T. Varnalı and V. Aviyente, *Turk. J. Chem.* in press; (d) V. Aviyente, T. Varnalı and M. F. Ruiz-Lopez, *J. Phys. Org. Chem.* **9**, 119–127 (1996).
12. V. Dillet, D. Rinaldi and J. L. Rivail, *J. Phys. Chem.* **98**, 5034–5039 (1994).