

Density functional conformational analysis of 1,2-ethanediol

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Abstract

Generalized gradient approximation density functional theory calculations at BP, B3P, BLYP and B3LYP levels coupled with a series of basis sets of increasing quality are presented for the six gauche conformers of 1,2-ethanediol. The results show that the extent of the correlation effects depends on the functional and that these methods reproduce correctly the consequences of correlation. The neighboring OH group orients the other OH group and this results in a preferred orientation.

1. Introduction

Generalized gradient approximation density functional theory (GGA-DFT) and ab initio MO calculations are useful tools for predicting molecular geometries and the associated potential energy hypersurfaces (PEH). The 1,2-ethanediol molecule is the simplest saturated carbon compound with vicinal hydroxyl groups. Other polyhydroxylated compounds play an important role in biochemistry, probably the most important examples are the carbohydrates. The hydroxyl groups of these hydrophilic molecules serve as donors and acceptors in hydrogen bonds. The intra- and inter-molecular interactions of these hydroxyl groups may play a role in the molecular recognition of sugar molecules and in binding to a specific receptor site [1]. Also diols are employed as the central part of series of HIV-1 protease inhibitors [2,3]. These facts stress the importance of 1,2-ethanediol as a model compound.

There are three possible rotameric dihedral angles in the 1,2-ethanediol molecule. According to multi-

mensional conformational analysis a typical 3-fold torsion potential for the three rotameric dihedrals provides $3^3 = 27$ conformational minima. Symmetry decreases the number of unique isomers to 10. Following conventional notation, the idealized dihedral angles are designated by g, t, and g⁻ for gauche clockwise (60°), anti (180°), and gauche counterclockwise (−60°) respectively for the two C–C–O–H torsions and capital letters (G and T) are used for the corresponding idealized O–C–C–O torsions. Thus the tGg⁻ conformer is an idealized anti (180°), gauche (60°), gauche (−60°) conformation. The actual dihedral angles may differ considerably from their idealized values. It should be noted that all G⁻ conformations have a mirror image among the G conformations, consequently 4 unique T and 6 unique G conformers exist. The 6 G conformers are shown in Fig. 1. Recent theoretical studies of the 10 unique 1,2-ethanediol conformers show that the most stable conformers are the tGg⁻ and gGg⁻ conformers [4–6]. In these conformations an intramolecular O–H...O interaction is present. The comparison of

HF and MP2/6-311G(d, p) results show that the MP2 nonbonded O...H distances decrease by up to 0.19 Å relative to the corresponding HF distances [3]. The relative stability of the conformers depends on the theoretical method applied. The HF method provided that the tGg⁻ conformer is significantly more stable than the other conformers [4,5]; however MP2 and GGA-DFT results indicate that the gGg⁻ conformer has a similar stability [4–6].

The available experimental data also suggest the co-existence of two intramolecular hydrogen-bonded conformers in the gas phase [7] and in low tempera-

ture Ar matrices [8]. It should be noted that the accurate measurement of the equilibrium structure of the 1,2-ethanediol molecule is difficult because of the presence of several stable conformations and the complicated tunneling motion of the two hydroxyl hydrogens [7,8]. This fact underlines the importance of reliable theoretical studies.

In this Letter, we concentrate on the possible HO...H interactions. These interactions are present in sugars; however, they can be studied at a much higher level of theory in 1,2-ethanediol than in sugars. Theoretical studies for aldopyranohexoses show

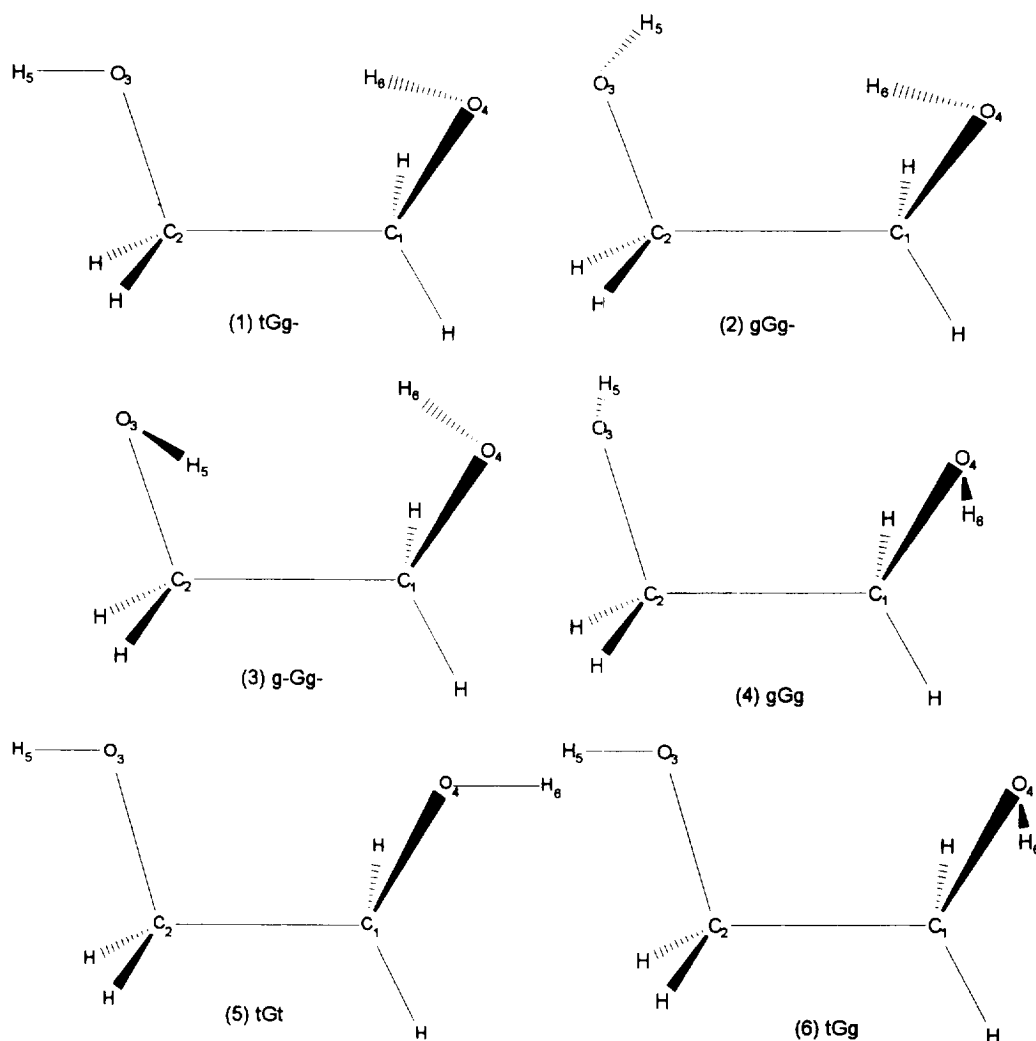


Fig. 1. Schematic representation of 6 G minimum energy conformations of 1,2-ethanediol. For (1): t is for H5-O3-C2-C1, G is for O3-C2-C1-O4 and g⁻ is for C2-C1-O4-H6 dihedral angles.

that tGg[−] type of HO...H interactions appear frequently in the most stable conformations of the pyranose rings [9–12]. We also study the performance of GGA-DFT methods with respect the energetics and equilibrium geometry of the six G conformation of 1,2-ethanediol.

2. Computational methods

We use the following combinations of the GGA-DFT functionals:

(i) BP or Becke–Perdew method, in which Becke's exchange functional [13] is combined with Perdew's correlation functional [14].

(ii) B3P is a hybrid method. It is a linear combination of various exchange and correlational functionals in the form:

$$AE_x[\text{HF}] + (1 - A)E_x[\text{S}] + B\Delta E_x[\text{B}] + E_c[\text{VWN}] + C\Delta E_c[\text{P86}],$$

where $E_x[\text{HF}]$, $E_x[\text{S}]$ and $\Delta E_x[\text{B}]$ are the HF, Slater and Becke exchange functionals; and $E_c[\text{VWN}]$ and $\Delta E_c[\text{P86}]$ are the Vosko et al. [15] and Perdew [14] correlation functionals, respectively. Note that $\Delta E_x[\text{B}]$ is a gradient correction to the S + WVN or LSDA, for exchange and $\Delta E_c[\text{P86}]$ is a gradient correction for correlation. The constants A , B and C are those determined by Becke by fitting heats of formations ($A = 0.2$, $B = 0.72$, $C = 0.81$) [16]. Note that Becke used the Perdew–Wang (PW91) functional instead of P86 [16].

(iii) BLYP method, in which Becke's exchange functional [13] is combined with the correlation functional of Lee et al. [17].

(iv) B3LYP is a hybrid method. This functional was not published before the implementation into the GAUSSIAN 92/DFT [18]. It is a logical extension of Becke's three parameter concept using different correlational functionals (e.g. LYP) in the form:

$$AE_x[\text{HF}] + (1 - A)E_x[\text{S}] + BE_x[\text{B}] + (1 - C)E_c[\text{VWN}] + CE_c[\text{LYP}].$$

The constants A , B and C are selected to be equal to those determined by Becke for the B3P method [16].

The geometries were optimized with a normal grid (50 radial shells, 194 angular points per shell,

pruned to about 3000 points per atom). The HF and GGA-DFT calculations were carried out using 6-31G(d), 6-31G(d, p) and 6-311G(d) and 6-311G(d, p) basis sets [19]. All calculations were performed on Silicon Graphics workstations.

3. Results and discussion

3.1. Geometry

Table 1 shows the calculated geometrical parameters for the 3 lowest energy (Table 2) gauche conformers of 1,2-ethanediol. In the first two conformers H–O...H interaction is possible. In the third conformation this interaction is hardly present. Comparison of two sets of HF results in Table 1 indicates that using more extended basis set causes C–C, C–O and O–H bond shortening. This observation is in agreement with earlier results [20]. The bond shortening is caused by the underestimated electron correlation effects in the HF method. This deficiency results an increased electron density in the bonding regions, to which polarization functions contribute considerably [21]. Because of the increased electron density in the bonding regions nearby bonds repel each other more as the basis set size increases, so the bond angles become larger, and the dihedral angles change toward their idealized values (Table 1).

The correlation corrections redistribute the electron density by decreasing it in the bonding regions and increasing it elsewhere (near the nuclei and in the far regions) [22]. The MP2/6-311G(d, p) optimizations lengthen the C–O and O–H bond lengths by 0.016–0.020 Å, shrink the C–C–O bond angles and turn dihedral angles generally farther from their idealized trans or gauche value [3]. It should be noted that the C–C bond length changes only slightly upon inclusion of the electron correlation because the bond lengthening effect is balanced by the smaller repulsion of dihedral bond centers. The GGA-DFT results in Table 1 show that these methods reproduce the geometrical consequences of correlation effects correctly, although the extent of the correlation effects varies with the functional applied. The results are in agreement with our earlier observation, that the correlation effect for the structural parameters

Optimized geometric parameters for C_6H_6 and C_6D_6 complexes: C_6H_6												
PM3	HF	3-21G	HF ^b 6-311G (d, p)	MP2 ^b 6-311G (d, p)	B3P 6-31G(d)	B3P 6-311G (d, p)	B3LYP 6-31G(d)	B3LYP 6-311G (d, p)	BP 6-31G(d)	BP 6-311G(d)	BLYP 6-31G(d)	BLYP 6-311G (d, p)
C_6H_6												
	1.537	1.520	1.512	1.512	1.514	1.510	1.521	1.517	1.527	1.526	1.532	1.528
C1-C2												
C2-O3	1.409	1.449	1.408	1.427	1.422	1.423	1.430	1.432	1.440	1.440	1.449	1.452
C1-O4	1.401	1.435	1.397	1.414	1.408	1.410	1.417	1.418	1.425	1.425	1.434	1.436
O3-H	0.947	0.965	0.940	0.959	0.966	0.959	0.968	0.961	0.977	0.974	0.979	0.971
O4-H	0.949	0.968	0.942	0.962	0.971	0.963	0.972	0.964	0.984	0.980	0.984	0.975
O3...H	2.661	2.172	2.380	2.260	2.224	2.230	2.287	2.291	2.217	2.220	2.258	2.264
C1-C2-O3	107.6	103.8	107.1	105.9	105.8	106.0	106.0	106.1	105.5	105.6	105.7	105.9
C2-C1-O4	113.1	108.9	111.6	110.6	110.7	111.0	111.1	111.3	110.7	110.7	111.2	111.4
C2-O3-H	106.7	111.8			108.7	108.8	108.6	108.8	107.8	107.8	107.8	108.1
C1-O4-H	107.3	106.9			104.7	105.2	105.1	105.6	103.5	103.5	104.1	104.7
O3-C2-	75.0	56.5	61.3	60.9	58.6	59.7	59.7	60.7	58.6	58.8	60.2	61.1
C1-O4												
C1-C2-	185.3	188.0	189.7	198.2	195.5	195.4	195.0	195.0	198.8	198.9	196.8	196.8
O3-H												
C2-C1-	-61.6	-48.4	-53.9	-49.8	-48.1	-49.3	-49.5	-50.7	-47.1	-47.1	-49.1	-50.6
O4-H												
C_6D_6												
C1-C2			1.515	1.515	1.519	1.515			1.531		1.527	
C2-O3			1.408	1.427	1.424	1.424			1.443		1.444	
C1-O4			1.397	1.413	1.407	1.408			1.422		1.425	
O3-H			0.941	0.961	0.968	0.961			0.981		0.973	
O4-H			0.942	0.963	0.972	0.965			0.986		0.977	
O3...H			2.390	2.260	2.189	2.239			2.181		2.230	

C1–C2–O3	110.9	110.0	109.9	110.1	109.7	110.0	
C2–C1–O4	111.4	110.5	110.2	110.6	110.1	110.5	
C2–O3–H	109.6		107.6	107.9	106.6	106.9	
C1–O4–H	108.1		104.6	105.2	103.4	104.1	
O3–C2–C1	58.8	57.0	53.1	54.6	52.6	53.9	
C1–O4							
C1–C2–O3–H	74.7	68.8	72.5	71.9	71.3	71.0	
C2–C1–O4–H	46.8	–43.1	–39.5	–40.6	–39.3	–40.2	
g^-Gg^-							
C1–C2	1.539	1.520	1.516	1.517	1.519	1.526	1.523
C2–O3	1.402	1.446	1.405	1.423	1.419	1.427	1.428
C1–O4	1.402	1.446	1.405	1.423	1.419	1.427	1.428
O3–H	0.949	0.966	0.940	0.960	0.967	0.964	0.962
O4–H	0.949	0.966	0.940	0.960	0.967	0.964	0.962
O3...H	2.809	2.606	2.710	2.600	2.588	2.609	2.669
C1–C2–O3	112.9	109.0	111.4	110.7	110.8	111.0	111.2
C2–C1–O4	112.9	109.0	111.4	110.7	110.8	111.0	111.2
C2–O3–H	107.4	109.1			106.1	106.2	106.9
C1–O4–H	107.4	109.1			106.1	106.2	106.9
O3–C2–C1	71.2	54.4	58.3	56.8	54.6	55.2	58.0
C1–O4							
C1–C2–O3–H	73.0	–81.2	–81.5	–76.0	–76.8	–76.4	–78.2
C2–C1–O4–H	–73.2	–81.4	–81.5	–76.0	–76.9	–76.4	78.2

^a Bond lengths in Å, bond angles in deg. ^b Ref. [3].

increase in the following order: B3P, B3LYP, BP and BLYP [23]. The results in Table 1 suggest the following relations for C–O and O–H bond lengths: $r(\text{HF}) < r(\text{B3P}) < r(\text{MP2}) < r(\text{B3LYP}) < r(\text{BP}) < r(\text{BLYP})$ (all methods are supplemented with 6-311G(d, p) basis set). There is a rather small difference between the B3P, MP2 and B3LYP results. For bond and dihedral angles the BP method shows very good agreement with MP2 results.

For the nonbonded interactions it is expected that the inclusion of the electron correlation provides an improved representation. As the HF/6-311G(d, p) method over-concentrate the electrons in bonding

centers, the optimized covalent bond lengths become too short and the nonbonded O3...H6 distance is too long (Table 1). The MP2 optimizations with the same basis set provided longer O–H bond lengths, smaller bond angles. The combined effect of these changes was to decrease the O3...H6 distance by ≈ 0.12 Å compared to HF/6-311G(d, p) distance. The GGA-DFT results in Table 1 show similar (slightly larger or smaller) decrease in the O3...H6 distance. The GGA-DFT results also show a moderate basis set dependence (except the BP method).

The HF/3-21G geometries in Table 1 show that this basis set provides geometrical parameters which

Table 2

Total energy of tGg[−] conformer and calculated relative energies for 6 gauche conformers of 1,2-ethanediol ^a

Method	Total energy tGg [−]	Relative energies					
		OH...H interaction		no OH...H interaction			
		tGg [−]	gGg [−]	g [−] Gg [−]	gGg	tGt	tGg
HF/3-21G	−227.65731	0.00		2.68		6.15	6.59
HF/4-21G ^b	−228.39443	0.00	0.88	2.28	4.30	5.39	6.44
HF/6-31G(d, p) ^c	−228.94501	0.00	0.64	1.28			
HF/cc-pVDZ ^c	−228.95339	0.00	0.56	1.53	3.22	3.61	3.94
HF/6-311G(d, p) ^b	−229.00277	0.00	0.72	1.50	3.29	3.50	4.02
MP2/6-31G(d, p) // HF/6-31G(d, p) ^b	−229.59648	0.00	0.20	1.22			
MP2/cc-pVDZ ^c	−229.61337	0.00	−0.04	1.58	3.27	4.34	4.33
CCSD(T)/cc-pVDZ // MP2/cc-pVDZ ^c	−229.66885	0.00	−0.12	1.39	3.03	4.27	4.28
MP4/6-311G(d, p) // MP2/6-31G(d, p) ^d	not reported	0.00	−0.09	1.49		4.24	
BP/TZVP // BP/DZVP2 ^d	not reported	0.00	−0.01	1.02	2.70	3.60	3.68
MP2/6-311G(d, p) ^b	−229.79756	0.00	0.06	1.71	3.17	4.15	4.40
MP2/cc-pVTZ // MP2/cc-pVDZ ^c	−229.86044	0.00	0.31	1.20	3.22	3.48	3.81
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BP/6-31G(d)	−230.23806	0.00	−0.54	0.82	2.80	4.57	4.11
BP/6-31G(d, p)	−230.25365	0.00		0.83		4.46	4.02
BP/6-311G(d)	−230.30236	0.00		1.35		4.64	4.49
BP/6-311G(d, p)	−230.32056	0.00	−0.32	1.14	2.83	4.42	4.13
B3P/6-31G(d)	−230.85275	0.00	−0.15	1.10	3.01	4.58	4.31
B3P/6-31G(d, p)	−230.86892	0.00		1.10		4.47	4.21
B3P/6-311G(d)	−230.91332	0.00		1.61		4.63	4.66
B3P/6-311G(d, p)	−230.93201	0.00	0.00	1.39	3.02	4.39	4.26
BLYP/6-31G(d)	−230.15946	0.00		0.63		4.35	3.93
BLYP/6-31G(d, p)	−230.17541	0.00		0.64		4.25	3.85
BLYP/6-311G(d)	−230.22870	0.00		1.15		4.45	4.38
BLYP/6-311G(d, p)	−230.24649	0.00		0.95		4.26	4.05
B3LYP/6-31G(d)	−230.24093	0.00		0.95		4.37	4.13
B3LYP/6-31G(d, p)	−230.25735	0.00		0.95		4.27	4.04
B3LYP/6-311G(d)	−230.30494	0.00		1.46		4.44	4.53
B3LYP/6-311G(dy, p)	−230.32325	0.00		1.24		4.23	4.15
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ZPE ^c	0.09188	0.00	0.05	−0.37	−0.53	−0.51	−0.43

^a Total energies are in hartrees, relative energies are in kcal/mol. ^b Ref. [3]. ^c Ref. [4] and references therein. ^d Ref. [5].

are closer to the MP2/6-311G(d, p) results than to the corresponding HF/6-311G(d, p) results, however it provides rather poor C–O–H bond angles and short O3...H6 distances. The poor performance of the PM3 method for the nonbonded interactions and dihedral angles should also be noticed from the results in Table 1.

3.2. Relative stability

In Table 2, the calculated total energies and the relative energies are summarized for the tGg[−] and for the 5 other G conformers. The theoretical predictions are consistent with the experimental observations; in that, there exists two conformers which are nearly equally stable [7,8]. Our GGA-DFT results are in agreement with the earlier correlated results in Table 2. It should be noted that there is a rather good agreement between the MP2/6-311G(d, p), MP2/cc-pVDZ and B3P/6-311G(d, p) results. The B3P/6-311G(d) method shows only a slightly worse agreement with the MP2 results than the B3P/6-311G(d, p) method, and it agrees well with the CCSD(T) and MP4 results in Table 2. The tGt

conformers are not stable conformations according to GGA-DFT calculations. The GGA-DFT results differ in this respect from the earlier HF and MP2 results [4,5]. The HF/3-21G results in Table 2 show that this method exaggerate the stability of the tGg[−] conformation relative to the tGt and tGg conformations. This is probably because of the too short O3...H6 distance, which is a sign of an exaggerated interaction resulting an overstated stability for the tGg[−] conformation. An MM2 study of the energy surface showed that the MM2 method largely underestimates the energetic differences between the conformers, and fails to reproduce the stability of the gGg[−] conformer.

3.3. Potential energy curves

For a more detailed insight we provide a potential energy curve (PEC) for the C1–C2–O3–H5 torsion. In these geometry optimizations all geometrical parameters were allowed to relax except the C1–C2–O3–H5 torsion. The initial C2–C1–O4–H6 dihedral angle was always set to its g[−] value (−60°). This PEC in the Fig. 2 includes the 3 lowest energy

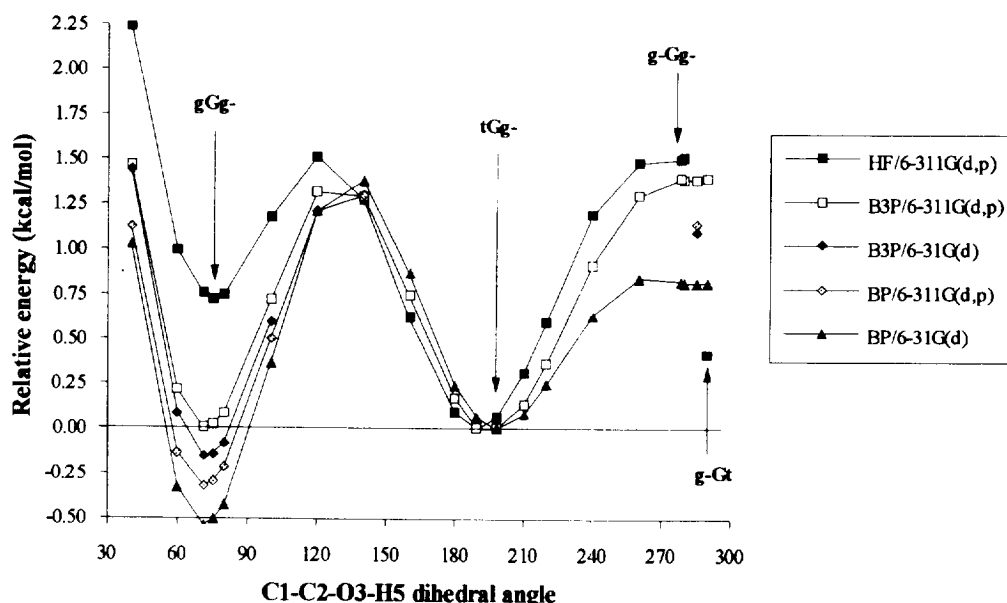


Fig. 2. The calculated relative energies and the C2–C1–O4–H6 dihedral angles (deg) as a function of the C1–C2–O3–H5 dihedral angle (deg) for 1,2-ethanediol. The legend shows the theoretical methods applied. The labeled arrows point to the positions of a specific equilibrium conformation.

conformations, namely gGg^- , tGg^- and g^-Gg^- . The curves show a considerable difference between the various methods concerning the relative stability of these three conformers. It is also clear that the B3P provide a PEC which is between the HF and BP curves. All methods agree with each other in that the gGg^- and tGg^- conformers are stable because of the considerable barriers on the both sides of the minima. However, the third g^-Gg^- minimum is a very shallow one, and this symmetric conformation may easily be transformed to tGg^- or g^-Gt conformations (two equivalent conformations). For the HF method Fig. 2 shows that as the $C1-C2-O3-H5$ dihedral angle is fixed at 290° the $C2-C1-O4-H6$ dihedral angle rotates from its starting value of -80 to -165° yielding a low energy point. Here the $C2-C1-O4-H6$ dihedral angle is closer to the idealized t position. This separate point may be characterized as t (trans) for the $C2-C1-O4-H6$ dihedral angle and it is shown by an arrow labeled as g^-Gt in Fig. 2.

The $C2-C1-O4-H6$ dihedral angle changes con-

siderably as the $C1-C2-O3-H5$ is rotated from 40 to 290° (Fig. 3). At small values of $C1-C2-O3-H5$ angle the $C2-C1-O4-H6$ angle has a small absolute value and deviates considerably from the idealized -60° value. In GGA-DFT calculations this deviation is larger than in HF calculations, because of the stronger $O3...H6$ interaction (in agreement with MP2 results [4]). The GGA-DFT results are nearly functional and basis set independent in this respect. As the $C1-C2-O3-H5$ dihedral angle is rotated towards larger values the $C2-C1-O4-H6$ angle slowly decreases towards its idealized value as the $H6$ atom follows the turning $O3$ lone pair. However, an interesting change can be seen in Fig. 3 above 160° of the $C1-C2-O3-H5$ angle: the $C2-C1-O4-H6$ angle starts to deviate again considerably from its idealized value, because the $H6$ atom starts to follow the another $O3$ lone pair.

Van den Enden et al. [24] classified the $O...H$ nonbonded interactions into three major groupings: sp^3 -, π -, or σ -type interactions. The idealized values for the out-of-plane angles between an $O3...H6$

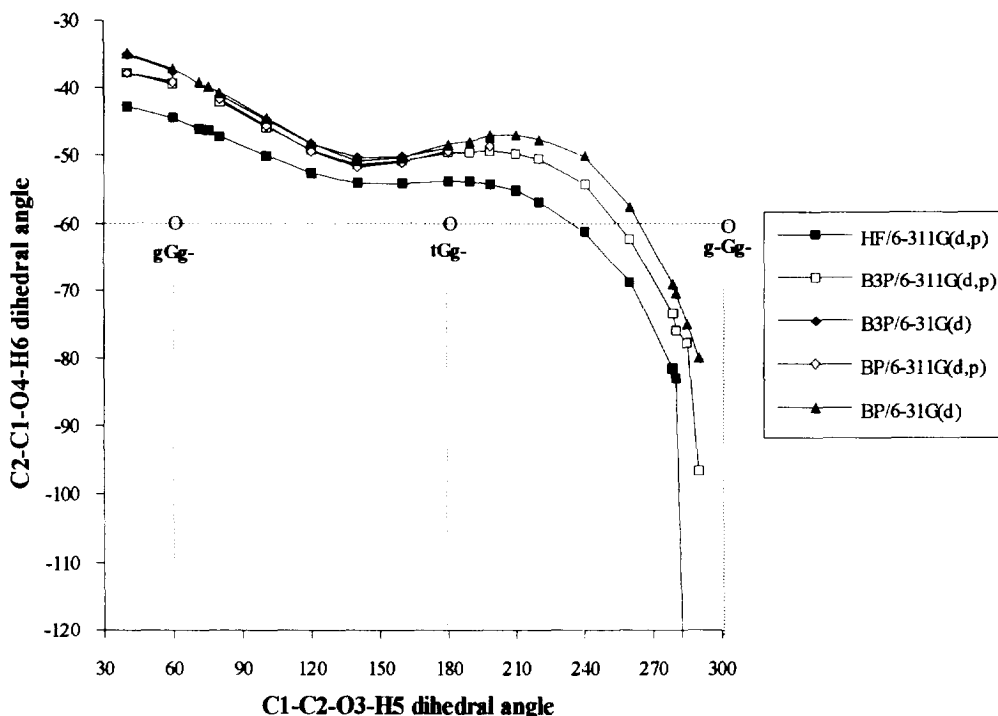


Fig. 3. The calculated $C2-C1-O4-H6$ dihedral angles (deg) as a function of the $C1-C2-O3-H5$ dihedral angle (deg) for 1,2-ethanediol. The legend shows the theoretical methods applied. The labeled circles show the positions of idealized conformers.

vector and the C2–O3–H5 plane would be 55, 90 and 180°, respectively. The sp^3 type of interaction seems to be energetically favorable, and the H6 atom is trying to keep the 55° angle as much as possible. The two sp^3 -type regions are separated by a σ region (at 140–160° of the C2–C1–O3–H angle), where the interaction seems to be weaker (Fig. 3).

The PECs of the rotation of the C2–C1–O4–H6 dihedral angle are dominated by the minima at tGg^- and gGg^- conformations. All the other possible conformations are less stable at least by 3 kcal/mol (Table 2). The lowest energy minimum at g^- position for the C2–C1–O4–H6 dihedral angle provides a very important consequence for vicinally polyhydroxylated compounds. The field of the neighboring OH group orients the other OH group and this results in a preferred gGg^- or tGg^- orientations for the gauche (G) O–C–C–O chains. A good example is the β -D-glucose with four vicinal OH groups in equatorial position. In the energetically most stable conformations the tGg^- OH patterns dominate [12]. For axial OH groups the 1,3 interactions provide similar possibilities; however, this is outside the realm of this study.

4. Conclusions

The following conclusions can be drawn from the above discussion:

(1) The GGA-DFT results show that these methods reproduce the geometrical consequences of correlation effects correctly for 1,2-ethanediol, however the extent of the correlation effects varies with the functional. For C–O and O–H bond lengths the order is the following: $r(HF) < r(B3P) < r(MP2) < r(B3LYP) < r(BP) < r(BLYP)$. The GGA-DFT and MP2 methods agree with each other in the O3...H6 distance too. The HF/3-21G method provides geometrical parameters for the tGg^- conformation of 1,2-ethanediol which are closer to the MP2/6-311G(d, p) results than to the corresponding HF/6-311G(d, p) results; however, the C–O–H bond angles are too large and the O3...H6 distance is too short. The PM3 method fails to reproduce the dihedral angles correctly.

(2) The theoretical predictions are consistent with the experimental observations. There exist two con-

formers (gGg^- and tGg^-) which are nearly equally stable. In this respect the GGA-DFT results, especially B3P/6-311G(d, p), are in good agreement with the MP2/6-311G(d, p), MP2/cc-pVDZ results. The B3P/6-311G(d) results are close to the CCSD(T)/cc-pVDZ//MP2/cc-pVDZ and MP4/6-311G(d, p)//MP2/6-311G(d, p) results. The HF/3-21G method provides an exaggerated stability for the tGg^- conformation compared to the tGt and tGg rotamers.

(3) The PEC studies yielded that the gGg^- and tGg^- conformations are separated by a 1.5 kcal/mol barrier. The g^-Gg^- conformation is in a shallow minimum. The PEC studies for the C2–C1–O4–H6 dihedral angle yielded that the preferred position for this dihedral angle is the g^- position. The important consequence of this is that the field of the neighboring OH group orients the other OH group and this results in a preferred gGg^- or tGg^- orientation for the gauche (G) O–C–C–O chains. The H6 atom follows the turning O3 lone pair in order to keep the O3...H6 interaction as strong as possible thus the C2–C1–O4–H6 dihedral angle deviates considerably from its idealized value (-60°).

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