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Ab initio study of the conformational equilibrium of ethylene glycol

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Summary. The conformational equilibrium of ethylene glycol (CH_2OHCH_2OH) has been examined by performing geometry optimizations at the 6-31G*, MP2/6-31G* and 6-31G** levels. Final energies have been calculated at the MP3 level with the optimized geometries. The two most stable conformers are a *tGg′* and *gGg′* but it is verified that the inclusion of electronic correlations reduces their energy difference of 0.6 kcal/mol at the HF level to less than 0.2 kcal/mol. The possible coexistence of the two most stable conformers is in agreement with some previous studies of Frei et al. For the *tXg′* conformer a detailed analysis of the intramolecular potential as a function of rotation around the C–C bond is also reported.

Key words: *Ab initio* – Intramolecular interactions – Electronic correlation effects – Conformational equilibrium – Ethylene glycol

1. Introduction

Studies on the conformational equilibrium of ethylene glycol (ETG) are important for the discussion of hydrogen bonding [1] and for the understanding of intramolecular interactions of complex molecular systems. Several theoretical [2–7, 11] and experimental [4, 6–12] studies on the conformational equilibrium of ETG have been reported.

Some of the more recent *ab initio* MO (molecular orbital) theory [13–15] studies have involved a significant number of conformers [13] and employed relatively large basis sets for a protonated form of ETG [15]. However, some specific questions related to the conformational equilibrium of ETG merit some attention. Firstly, to our knowledge, *ab initio* intramolecular potential functions for ETG have not been reported and their construction is of importance for a global view of the conformational equilibrium as well as for computer simulations. Furthermore, an investigation of the role played by electronic correlation effects in determining the conformational barriers of ETG is essential for comparison with experimental data and such an approach seems to be still lacking.

In this work we report an *ab initio* MO study [16] of the conformational equilibrium of ETG. Geometries have been fully optimized by gradient methods at the 6-31G*, MP2/6-31G* and 6-31G** [16] levels. Correlation effects were studied with the Møller–Plesset perturbation theory at the MP3/6-31G** level with the optimized geometries. In order to construct an intramolecular potential related to rotation around the C–C bond, a series of ten rotamers for each of the two most stable conformers were investigated. Finally, a fitted Fourier expansion for the intramolecular potential function as a function of the rotation around the C–C has been proposed.

2. Computational method

Three ETG conformers defined by the relative orientations of the O–H group around the C–C–O plane are shown in the Fig. 1. They are represented by *tXt*, *tXg'* or *gXg'*, respectively a *trans* (t) and two gauche (g, g') conformers. X is C, G or T denoting a *cis* ($0° \leqslant \phi < 60°$), gauche ($60° \leqslant \phi < 120°$) or *trans* ($120° \leqslant \phi \leqslant 180°$) conformer with respect to the C–C bond. Full optimizations have been carried out by gradient methods at the 6-31G*, MP2/6-31G* and 6-31G** levels for the three conformers. For the construction of the intramolecular potential for the rotation around the C–C bond, ten rotamers (defined by the angle ϕ (0, 20, ..., 180) around the C–C bond) for the two most stable conformers have been further investigated. The energy values at $\phi = 0, 20, \ldots, 180$ for the optimized geometries allowed the construction of an intramolecular potential $V(\phi)$ for the internal rotation around the C–C bond.

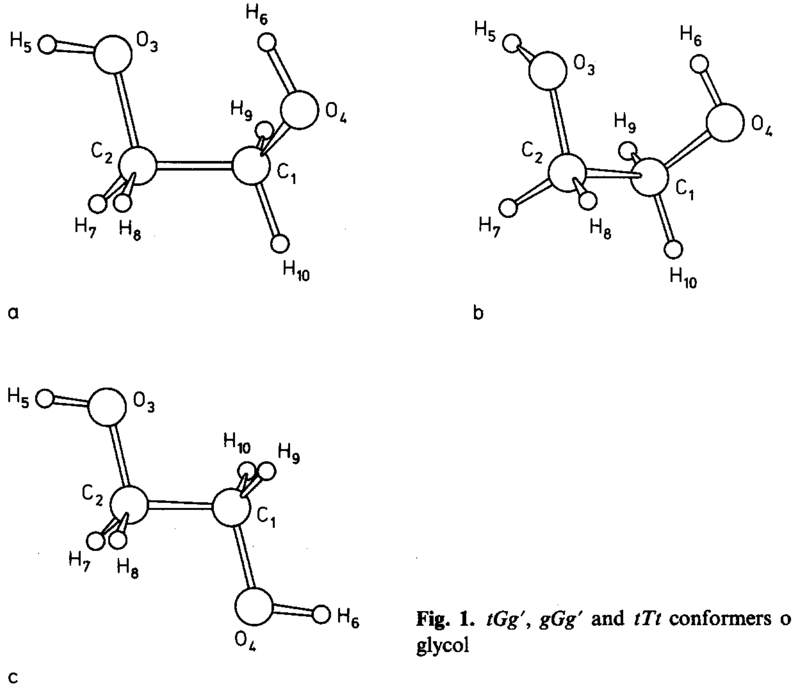

Fig. 1. *tGg'*, *gGg'* and *tTt* conformers of ethylene glycol

The set of values has been fitted to a Fourier expansion in the form:

$$V(\phi) = V_0 + \tfrac{1}{2} \sum_{i=1}^{k} V_i(1 \pm \cos i\phi), \quad k = 4. \tag{1}$$

The *ab initio* MO calculations have been done with GAUSSIAN-82 [17] on a VAX system and with GAUSSIAN-88 [18] on a Convex-C220 supercomputer.

3. Optimized geometries and energies

The optimized geometries for the conformers *tGg′* and *gGg′* are reported in Table 1. Comparison between the geometries optimized at the MP2/6-31G* and 6-31G* levels suggests that correlations effects increase the O–H (R46 and R35) bond lengths by ~0.3 Å and reduce the valence angles related to the O–H orientation (A235 and A146) by 3.0°. The two torsional angles ∠(H–O–C–C) related to the intramolecular hydrogen bonding (T2146 and T1235) are also different in the 6-31G* and MP2/6-31G* geometries. The most important aspect

Table 1. Ethylene-glycol 6-31G*, MP2/6-31G* and 6-31G** optimized geometries

	tGg′			*gGg′*		
	6-31G*	MP2/6-31G*	6-31G**	6-31G*	MP2/6-31G*	6-31G**
Bond distances (Å)						
R21	1.514	1.511	1.513	1.517	1.515	1.516
R23	1.407	1.432	1.406	1.408	1.434	1.407
R14	1.397	1.419	1.396	1.396	1.417	1.395
R28	1.088	1.098	1.089	1.087	1.098	1.088
R27	1.087	1.097	1.087	1.081	1.091	1.082
R110	1.083	1.093	1.084	1.083	1.093	1.084
R19	1.088	1.099	1.089	1.091	1.028	1.092
R35	0.946	0.971	0.942	0.947	0.973	0.943
R46	0.948	0.947	0.944	0.949	0.975	0.945
Valence angles (degrees)						
A123	106.7	105.2	106.8	110.5	109.6	110.6
A214	111.3	110.4	111.3	111.1	110.0	111.2
A128	110.2	110.9	110.1	110.8	111.7	110.6
A127	109.4	109.2	109.4	109.7	109.7	109.6
A2110	109.9	110.5	109.8	110.3	111.0	110.1
A219	109.1	109.0	109.0	109.6	109.4	109.5
A235	110.2	108.3	110.4	109.6	107.2	109.8
A146	107.7	104.6	107.8	107.9	104.6	108.1
Torsion angles (degrees)						
T3214	60.7	60.0	60.7	57.9	55.4	57.8
T3128	120.6	120.6	120.7	123.7	124.1	123.8
T3127	−119.9	−119.2	−120.0	−116.6	−115.1	−116.8
T42110	118.6	118.2	118.8	118.9	118.7	119.1
T4219	−122.9	−122.7	−122.9	−122.8	−122.5	−122.9
T1235	189.9	193.4	189.9	75.7	73.4	76.2
T2146	−53.9	−50.3	−53.8	−45.7	−42.1	−45.6

Table 2. Ethylene-glycol: total energies (hartrees)

	tGg′	*gGg′*	*tTt*
HF/6-31G*[a]	−228.92572	−228.92466	
HF/6-31G**[b]	−228.94500	−228.94398	−228.94156
MP2/6-31G*[c]	−229.55798	−229.55770	−229.55225
HF/6-31G**[d]	−228.94496	−228.94393	
MP2/6-31G**[d]	−229.59683	−229.59653	
MP3/6-31G**[d]	−229.62393	−229.62353	
MP2/6-31G**[e]	−229.59648	−229.59615	
MP3/6-31G**[e]	−229.62365	−229.62322	
HF/6-31G**[f]	−228.94176	−228.94061	
MP2/6-31G**[f]	−229.59878	−229.59806	
MP3/6-31G**[f]	−229.62454	−229.62418	

[a–c] Geometry optimized

[d–f] Calculated with the corresponding optimized geometries a–c

in the comparison between the 6-31G* and MP2/6-31G* basis set structures seems to be that for the *gGg′* conformer, the torsional angle associated with the trans O–H bond increases at the MP2/6-31G* by ~3.0°, while for the gauche O–H bond it is reduced by ~2.0°. The reinforcement of the internal hydrogen bonding by the introduction of correlation effects at the MP2/6-31G* level is also suggested by the reduction of the dihedral angle, T3214, of the oxygen atoms with respect to the C–C bond for the *gGg′* conformer (60.0° for *tGg′* and 55.4° for *gGg′*). The geometries optimized at the 6-31G* basis set level seem not to be significantly modified by the introduction of polarization functions (2*s*, 2*p*) for hydrogen atoms, suggesting that they would not differ significantly if they were optimized at the MP2/6-31G** level, although this assumption is based on a separation between basis set improvement and correlation effects. This is equivalent to assuming that the effect on the structure of the basis set improvement (inclusion of polarization functions on hydrogens) would be the same as the HF and MP2 levels.

Total energies for the two most stable conformers are reported in Table 2. The *tGg′* conformer is the most stable one, in agreement with the results reported by van Alsenoy et al. [13]. However, we observe that some studies using standard experimental geometries [2, 5] or performing only partial optimizations [3, 4] predicted that the conformer with two internal hydrogen bonds (*gGg′*) is the most stable one. It can be verified that although the energy difference between the two conformers at the HF/6-31G* level is 0.66 kcal/mol, it is reduced to 0.17 kcal/mol at the MP2/6-31G* level. Comparison between energies calculated at higher levels of the theory (6-31G** basis set or MP3//6-31G** Møller–Plesset contribution) with the optimized geometries shows the same tendency as the MP3/6-31G**//MP2/6-31G* calculations where the energy difference is increased to 0.22 kcal/mol. Thus, it appears that for ETG, correlation effects at the MP2/6-31G* level, induce some changes in the rotational barriers. This conclusion is in agreement with the study of Ikuta and Nomura [15] for protonated ethylene glycol, although their geometry optimizations have been performed at 6-31G* and MP2/3-21G levels which makes an independent discussion of basis set and correlation effects difficult.

The *tGg′* and *gGg′* coexistence has been pointed out by Frei et al. [4]. They reported an *ab initio* HF energy difference of 0.19 kcal/mol between the two conformers and observed that experimental results suggested the simultaneous presence of both conformers. We note that their *ab initio* calculations were based on experimental geometries of methanol and 2-chloroethanol and have optimized only the O–H distances and the C–C torsional angle. Thus, the agreement with the present calculation (0.17 kcal/mol) is not necessarily significant. Other experimental data on the conformational barriers of ETG in the liquid phase (0.6 kcal/mol), have been reported by Pachler and Wessels and by Pruettiangkura et al. [11]. However, a direct comparison with the present results is difficult as a consequence of solvent effects.

The introduction of polarization functions on the hydrogens does not modify the energy difference between the conformers (0.64 kcal/mol). This is in accord with the effect of polarization functions on the structure and suggests that for this system it is to assume some additivity of basis set improvement and correlation effects on the calculated energy differences [16]. The energy difference between the two most stable conformers at the MP3//6-31G** level is reduced to 0.27 kcal/mol.

The dipole moments for both *tGg′* and *gGg′* conformers are about 2.8 D at 6-31G*, MP2/6-31G* and 6-31G** levels, reflecting approximate independence of this property from the improvement of basis set and the inclusion of correlation effects at this level of the theory. The experimental value of the dipole moment for ETG in the gas phase and in some solvents is 2.3 ± 0.1 D [6], but the experimental value for the neat liquid is 3.5–4.0 D [8].

4. Intramolecular potential function

One of the purposes of this study was to construct an intramolecular potential function for the rotation of the the most stable ETG conformer around the C–C bond. We intend to use this function in Monte Carlo simulations [20] to model the solvation of ETG in methanol. In order to construct this function we used a simplified approach which is partially based on the results reported in Sect. 3. Thus, the geometries are not fully optimized and the final energies are based on single-point SCF (self consistent field) calculations at the MP2//6-31G* level. While the absence of polarization functions for hydrogens can be justified on the basis of the results of Sect. 3, we expect that a partial optimization is required for the construction of the intramolecular function. We expect that a partial optimization is a reasonable compromise between full and no optimization for the 20 different rotamers which were investigated since the whole field of chemistry is based essentially on energy differences.

The optimized geometries for the *tGg′*, *gGg′* and *tTt* conformers are reported in the Table 3. We call attention to the point that the dihedral angle T3214 (ϕ) is now set to 60.0° for the most stable *tGg′* and *gGg′* conformers. This is not a problem for the *tGg′* conformer, but it is not exact for the *gGg′* one (see Table 1). Furthermore, with this set of optimized parameters the *tTt* conformer is, by symmetry, fully optimized.

The analysis of the different geometries at the 6-31G*, MP2/6-31G* and 6-31G** levels closely follows that reported in the Sect. 3. The same conclusions about the importance of the MP2/6-31G* correlation energies to the relative energies of the *tGg′* and *gGg′* conformers can be obtained from Table 4. Thus,

Table 3. Ethylene-glycol HF/6-31G*, MP2/6-31G*, and HF/6-31G** optimized geometries

	tGg′			*gGg′*			*tTt*		
	6-31G*	MP2/6-31G*	6-31G**	6-31G*	MP2/6-31G*	6-31G**	6-31G*	MP2/6-31G*	6-31G**
Bond distances (Å)									
R21	1.514	1.510	1.513	1.517	1.514	1.516	1.513	1.510	1.513
R23	1.404	1.427	1.404	1.404	1.427	1.405	1.405	1.428	1.513
R28	1.086	1.096	1.087	1.085	1.096	1.086	1.086	1.096	1.087
R35	0.948	0.970	0.942	0.947	0.971	0.943	0.946	0.970	0.942
R46	0.946	0.974	0.944	0.949	0.975	0.945	0.946	0.970	0.942
Valence angles (degrees)									
A123	108.9	107.9	108.9	110.6	110.0	110.6	106.8	105.9	106.8
A128	109.7	109.9	109.7	110.2	110.4	110.1	109.4	109.3	109.4
A235	107.2	108.0	110.1	109.3	106.9	109.5	109.7	107.7	109.9
A146	109.8	103.7	107.3	107.5	104.3	107.7	109.7	107.7	109.9
Torsion angles (degrees)									
T1235	190.5	196.5	191.8	75.6	71.7	75.6	180.0	180.0	180.0
T2146	−52.9	−49.3	−52.8	−45.9	−43.9	−45.9	180.0	180.0	180.0
T3214[a]	60.0	60.0	60.0	60.0	60.0	60.0	180.0	180.0	190.0

O–C ≡ R23 = R14; C–H ≡ R28 = R27 = R110 = R19

O–C–C ≡ A123 = A214; H–C–C ≡ A128 ≡ A127 = A219 = A2110

H5–O3–C2–C1 ≡ T1235 ≡ θ_1; H6–O4–C1–C2 ≡ T2146 = θ_2

O–C–C–O ≡ T3214 ≡ ϕ

O–C–C–H ≡ T3128 = T42110 = 120.0 T3127 = T4219 = −120.0

[a] Fixed parameter

Table 4. Ethylene glycol rotamers- 6-31G* and MP2//6-31G* calculations

tXg' ϕ	E_t		θ_1	θ_2	μ (D)
	6-31G*	MP2//6-31G*			
0	−228.91373	−229.52799	180	0	3.66
20	−228.91655	−229.53085	−180.6	−27.5	3.48
40	−228.92202	−229.53677	188.7	−40.2	3.12
60	−228.92470	−229.53943	190.5	−52.9	2.68
80	−228.92210	−229.53643	188.0	−62.5	2.26
100	−228.91745	−229.53131	183.6	−70.5	1.94
120	−228.91491	−229.52835	177.0	−72.8	1.83
140	−228.91609	−229.52931	171.7	−73.5	1.89
160	−228.91927	−229.53240	170.7	−75.5	1.93
180	−228.92082	−229.53395	176.1	−79.2	2.21
gXg'					
0	−228.91613	−229.53131	53.4	53.4	1.2
20	−228.91651	−229.53160	43.0	43.0	1.4
40	−228.92158	−229.53736	82.2	−30.7	2.9
60	−228.92372	−229.53911	75.6	−45.9	2.6
80	−228.92093	−229.53569	71.3	−57.1	2.3
100	−228.91645	−229.53067	70.6	−64.4	1.9
120	−228.91411	−229.52797	72.0	−68.2	1.6
140	−228.91537	−229.52907	74.2	−70.2	1.1
160	−228.91868	−229.53316	76.0	−72.9	0.6
180	−228.92045	−229.53409	75.2	−75.2	0.0
tXt					
180	−228.92223	−229.53508	180	−180	0.0

the energy difference between the two most stable *tGg'* and *gGg'* conformers are 0.61 kcal/mol and 0.19 kcal/mol at the 6-31G** and MP2/6-31G** levels respectively. These values are not significantly different from those calculated with complete geometry optimization. We observe that this result supports the validity of our simplified approach for the construction of the intramolecular potential.

The energies, torsional angles (T1235 $\equiv \theta_1$ and T2146 $\equiv \theta_2$) and dipole moments as a function of the rotation angle around the C–C bond (T3214 $\equiv \phi$) are presented in the Table 4. Our results show that the most important dipole moment for these rotamers corresponds to a *tXg'* conformer (3.67 D) in good agreement with the experimental value for liquid ETG (3.5–4.0 D). Thus, if we assume that electrostatic interactions are important for the conformational equilibrium [19], we could expect an enhancement of the *tXg'* conformers of ETG in condensed phases, which would be in agreement with results of Pachler and Wessels [8] which suggest that intermolecular hydrogen bonds occur in liquid ETG.

The set of coefficients for the internal rotation potential around the C–C bond for the *tGg'* conformer is reported in Table 5. The potential is shown in

Table 5. 6-31G* and MP2//6-31G* rotational potentials (kcal/mol) for *tXg′* ETG

ϕ	E_r		$V(\phi)$	
	6-31G*	MP2//6-31G*	6-31G*	MP2//6-31G*
0	6.8	7.1	6.8	7.1
20	5.1	5.3	5.1	5.3
40	1.6	1.6	1.6	1.6
60	0.0	0.0	0.0	0.0
80	1.6	1.8	1.5	1.8
100	4.5	5.1	4.5	5.1
120	6.1	6.9	6.1	6.9
140	5.3	6.3	5.3	6.2
160	3.4	4.4	3.4	4.4
180	2.4	3.4	2.4	3.4
Coefficients for the Fourier expansion (1)				
V_0	2.43	3.45		
V_1	−1.148	−2.143		
V_2	−1.567	−1.834		
V_3	5.58	5.89		
V_4	−0.503	−0.582		

Fig. 2 and the quality of the fit is excellent. From this potential for the most stable conformer we have derived $S(\phi)$ (Fig. 3), which represents the distribution of rotamers as a function of the angle ϕ around the C–C bond and is defined by

$$S(\phi) = \exp(-\beta V(\phi)) \Big/ \int \exp(-\beta V(\phi))\, d\phi \tag{2}$$

where β is $1/\kappa_B T$ and κ_B the Boltzmann's constant. From $S(\phi)$ the *trans* population in ETG at $T = 25°\mathrm{C}$ is less than 2.5%, indicating a clear predominance of the *gauche* conformer. Experimental data concerning the isomerization from the *tGg′* and *gGg′* conformers to the all-trans *tTt* conformer of ETG in an

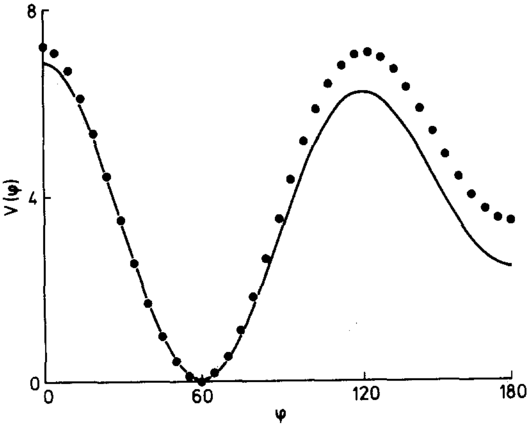

Fig. 2. Intramolecular potential $V(\phi)$ (kcal/mol) related to the rotation around the C–C bond. (———) HF//6-31G* and MP2//6-31G* (••••) potentials

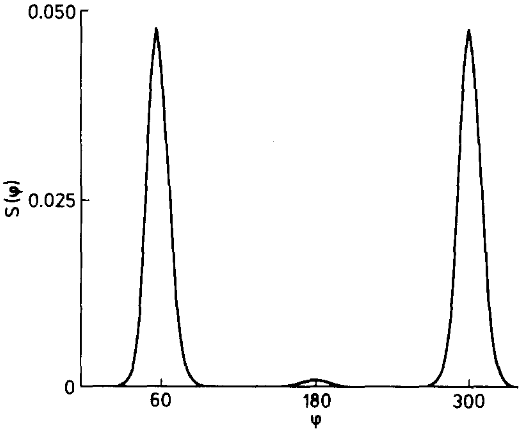

Fig. 3. Distribution of conformers $S(\phi)$ (fraction of molecules) as a function of ϕ for $T = 25°C$

argon matrix have been reported by Takeuchi and Tasumi [21]. They observed that this process is induced by radiation in the 3600–3950 cm^{-1} range. These values suggest an upper bound of ~10 kcal/mol for the rotational barrier around the C–C bond. From Table 1 we predict a value of 3.6 kcal/mol in good agreement with Frei et al. (~ 3.0 kcal/mol) [4]. However, comparison of these values with the experimental data of Takeuchi and Tasumi is difficult because it is expected that the interactions with the argon matrix change the barriers and also the isomerization path [21].

5. Conclusions

Extensive *ab initio* MO calculations have pointed out some important features related to the conformational equilibrium of ETG and enabled a discussion about the possible coexistence of a *tGg′* conformer with a *gGg′* one. In particular, inclusion of electron correlation effects at the MP2/6-31G* level results in some significant changes from the predicted 6-31G* structures, and at the MP2/6-31G** level of the theory, the energy difference between the two most stable conformers of ETG is less than 0.2 kcal/mol. This result, in agreement with theoretical and experimental data of Frei et al. [4] suggests the possibility of frequent interconversions between *tGg′* and *gGg′* conformers in the gas phase.

The construction of an intermolecular potential function related to the rotation around the C–C bond for the most stable conformer (*tXg′*) shows a strong predominance of the *gauche* rotamer in the gas phase.

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