Hybrid-DFT study and NBO interpretation of Conformational Analysis of Dihydroxymethane in relation to the Anomeric Effect

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Abstract

Introduction: The conformational behavior of dihydroxymethane has been analyzed by means of hybrid-density functional theory (B3LYP/6-311++G**) based method and NBO interpretation.

Aim: The correlation between the energy differences between the various conformations of dihydroxymethane, the anomeric effect associated with the electron delocalization, diploe-dipole interactions (i.e. the electrostatic mode) and steric repulsions have been investigated.

Results: Based on the potential energy surface obtained at the B3LYP/6-311++G** level of theory, the most stable conformation of dihydroxymethane is found to be an axial symmetrical (C2 symmetry) conformation (i.e. gauche-gauche, g.g). The calculated energy for the second lowest energy-minimum conformation, viz. gauche-gauche* (g.g*, Cs symmetry) is 2.44 kcal mol-1. Third lowest energy-minimum structure of dihydroxymethane is the unsymmetrical quasi-gauche-anti conformation (i.e. qa.g, by about 2.58 kcal mol-1 higher than g.g conformation). Based on the obtained NBO results, the calculated generalized anomeric effect (GAE) value decreases from of the g.g conformation of dihydroxymethane to its qa.g conformation but decreases from qa.g conformation to g.g* conformation. Therefore, the GAE can not explain the more stability of the g.g conformation of dihydroxymethane compared to the corresponding g.g* conformation. On the other hand, the calculated dipole moment value of the g.g conformation of dihydroxymethane is smaller than that of g.g* conformation.

Conclusion: Interestingly, these findings led to the proposal that the electrostatic model is more significant for the explanation of the conformational preference of dihydroxymethane than the GAE and steric interactions.

***Keywords**:* generalized anomeric effect, molecular modeling, ab initio, NBO, dihydroxymethane

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Introduction

Stereoelctronic effects have been recognized to influence the conformation and configuration of saturated heterocyclic compounds. The preferred geometry of the saturated heterocyclic compounds can be viewed as the result of the maximization of an interaction between the best donor lone pair and the best acceptor bond.[1-3] The most dominant conformation-controlling factor in carbohydrate compounds is known as the anomeric effect (AE).[4]

It should be noted that the *AE* is in favor of the axial conformation of a six-membered saturated ring in opposition to the steric effect which normally leads to a preference for the equatorial conformation.[5-7]

The generalized anomeric effect (*GAE*), is a generalization of this preference observable in acyclic compounds (such as dimethoxymethanes), as well as within rings.[8] In the *GAE*, the stereoelectronic effects cause a conformational preference for a gauche arrangement of the R-Y-C-X fragment, where Y is an atom bearing at least one lone pairs of electrons, LP, and X is an element more electronegative than C.[9,10] There is much published experimental and theoretical data for dimethoxymethane using this compound as a model for the *AE*.[11-22] Also, the origin of the *GAE* in methandiol and its sulfur, selenium and tellurium derivatives has been examined by ab initio calculations[23,24] and NBO[25-31] analysis.

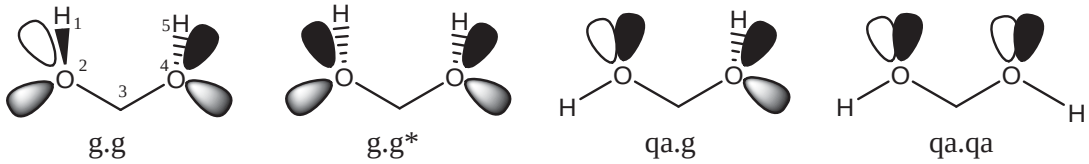
There is a stereoelectronic preference for conformations in which the best donor lone pair is antiperiplanar to the best acceptor bond,[1-3] therefore, we could stress that the generalized anomeric effect *(GAE*), observable in acyclic compounds (such as dimethoxymethanes),[8] must be considered as the difference between the *GAE* of the g.g, qa.g and g.g* conformations of dihydroxymethane:

$GAE_{qa.g-g.g} = GAE_{qa.g} - GAE_{g.g}$ (Eq. 1)

$GAE_{g.g^*-g.g} = GAE_{g.g^*} - GAE_{g.g}$ (Eq. 2)

Cramer reexamined the four stationary points of dihydroxymethane.[32] The MP2/6-31G** calculated relative energies show that the g.g conformation of dihydroxymethane is more stable than g.g* and qa.g conformations by about 3.09 and 3.77 kcal mol^{-1}. The calculations produce the structural and energetic features of the anomeric effect, in particular those expected from LP $O \rightarrow \sigma^*_{C-O}$ electron delocalization with concomitant shortening of the donor C-O bond, lengthening of the acceptor C-O bond and widening of the O-C-O bond angle.

There is insufficient published experimental and theoretical information about dihydroxymethane[32-34], there is no published experimental or quantitative theoretical data about the donor-acceptor electron delocalization and steric effects on the conformational behaviors of dihydroxymethane. In this work, the impacts of the stereoelectronic interactions associated with the generalized anomeric effect (*GAE*), electrostatic interactions and total steric exchange energies (*TSEE*) on the conformational and structural properties of dihydroxymethane have been investigated computationally using hybrid-DFT based method and natural bond orbital (NBO) analysis (scheme 1).[35-40]



Scheme 1- Schematic representation of the various conformations of dihydroxymethane.

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Computational details

Hybrid DFT calculations were carried out using the B3LYP/6-311++G** level of theory with the GAUSSIAN 03 package of programs.[22] The most stable conformations of dihydroxymethane were found by changing and scanning the dihedral angles H_1-O_2-C_3-O_4 at the B3LYP/6-311++G** level of theory (Fig. 1).

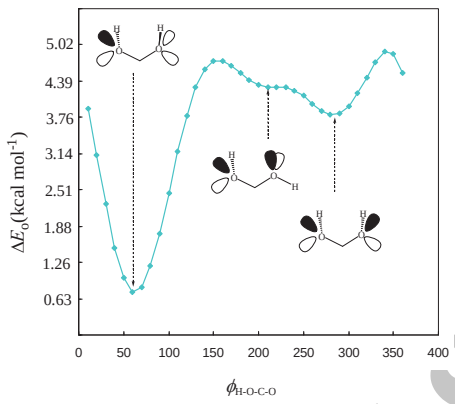

Fig. 1- Energy profile calculated for the rotations about O_2-C_3 bond in dihydroxymethane at the B3LYP/6-311+G** level of theory.

In order to estimate quantitatively the magnitude of the plausible donor-acceptor hyperconjugative interactions in dihydroxymethane, we conducted NBO analyses for the most stable conformations by the NBO 5.G program contained in the PC-GAMESS interface.[27] In the NBO analysis the electronic wavefunctions are interpreted in terms of a set of occupied Lewis and a set of unoccupied non-Lewis localized orbitals. The delocalization effects (or donor–acceptor charge transfers) can be estimated from the presence of off-diagonal elements of the Fock matrix in the NBO basis. The NBO program searches for an optimal natural Lewis structure, which has the maximum occupancy of its occupied NBOs, and in general agrees with the pattern of bonds and lone pairs of the standard structural Lewis formula. Therefore, the new orbitals are more stable than pure Lewis orbitals, stabilizing the wave function and giving a set of molecular orbitals equivalent to canonical molecular orbitals.

The bonding and antibonding orbital occupancies in the global and local minimum strucrures of dihydroxymethane**,** and also the stabilization energies associated with electron delocalizations were calculated using NBO analysis. The stabilization energies associated with donor-acceptor electron delocalizations are proportional to $S^2/\Delta E$ where S is the orbital overlap and ΔE is the energy differences between the LP and σ* orbitals.[1,41] The stabilization energy (E_2) associated with $i \rightarrow j$ delocalization, is explicitly estimated by the following equation:

$$E_2 = q_i \frac{F^2(i,j)}{\varepsilon_j - \varepsilon_i}$$

where q_i is the ith donor orbital occupancy, ε_i, ε_j are diagonal elements (orbital energies) and F(i,j) off-diagonal elements, respectively, associated with the NBO Fock matrix. Therefore, there is a direct relationship between F(i,j) off-diagonal elements and the orbital overlap (S).

The stabilization energies (E_2) associated with LP_1 $O_2 \rightarrow \sigma^*_{C3-O4}$, LP_2 $O_2 \rightarrow \sigma^*_{C3-O4}$, LP_1 $O_4 \rightarrow \sigma^*_{C3-O2}$ and LP_2 $O_4 \rightarrow \sigma^*_{C3-O2}$ electron delocalizations, total steric exchange energies (*TSEE*) and their influences on the conformational properties of dihydroxymethane were

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investigated quantitatively by the NBO analysis.[40] It has to be noted that the NBO analysis is a sufficient approach to investigate the stereoelctronic interactions on the reactivity and dynamic behaviors of chemical compounds.[42]

Results and Discussion

Conformation preference

Hybrid-DFT based method (B3LYP/6-311++G**) calculated thermodynamic functions *H*, *S*, *G* and the Δ*G*, Δ*S* and Δ*H* parameters for the global and local minimum structures of dihydroxymethane are given in Table 1. The absolute values of the thermodynamic properties certainly can not be calculated at the accuracy level shown in this table, the correction for anharmonicity in a C-H bond may alone be on the order of 0.2 kcal $mole^{-1}$ (the value in the C-H radical). However, the quantities of interest here are the relative values of the thermodynamic functions for different conformations of the same molecule. We expect that the errors in such differences will be very small and that even the corresponding errors between the different closely related compounds will be minimal. The smooth variation among the calculated values supports this expectation.

Table 1- B3LYP/6-311++G** calculated thermodynamic functions [H, G, S] and parameters [ΔH, ΔG (in: hartree) and ΔS (in: cal $mol^{-1}K^{-1}$)] for the various conformations of dihydroxymethane.

Geometries	*H*	*S*	*G*	Δ*H*[a]	Δ*S*[a]	Δ*G*[a]
g.g	-190.957871	62.317	-190.987480	0.000000 (0.00)[b]	0.000	0.000000 (0.00)[b]
qa.g	-190.952703	64.535	-190.983365	0.005168 (3.24)[b]	2.218	0.004115 (2.58)[b]
g.g*	-190.953294	63.779	-190.983598	0.004577 (2.87)[b]	1.462	0.003882 (2.44)[b]

[a] relative to the most stable conformation. b Numbers in parenthesis are in kcal mol^{-1}.

The B3LYP/6-311++G** results showed that the axial symmetrical (C_2 symmetry) g.g conformation of dihydroxymethane is more stable than qa.g and g.g* conformations by about 2.58 and 2.44 kcal mol^{-1}, respectively. The more stability of the g.g conformation of dihydroxymethane compared to the qa.g and g.g* conformations can be attributed to its lower total dipole moment value and also the *GAE* associated with the electron delocalization. Therefore, these factors are examined.

Stabilization energies and GAE

The g.g, qa.g and g.g* conformations of dihydroxymethane benefit from the stabilization energies associated with the donor-acceptor electron delocalizations. Based on the ground state geometries optimized at the B3LYP/6-311++G** level of theory, the NBO analysis of donor-acceptor (bond-antibond) interactions showed that the stabilization energies associated with $LP_2O_2 \rightarrow \sigma^*_{C3\text{-}O4}$ electron delocalizations for the g.g, qa.g and g.g* conformations of dihydroxymethane are 12.87, 11.51 and 14.54 kcal mol^{-1}, respectively. Also, the stabilization energies associated with $LP_1O_2 \rightarrow \sigma^*_{C3\text{-}O4}$ electron delocalizations for the qa.g conformation of dihydroxymethane is 0.67 kcal mol^{-1}, there is no $LP_1O_2 \rightarrow \sigma^*_{C3\text{-}O4}$ electron delocalization for the g.g and g.g* conformations of dihydroxymethane (Table 2).

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Table 2- NBO calculated stabilization energies (E_2, in kcal mol^{-1}), generalized anomeric effect (*GAE*, in kcal mol^{-1}), off-diagonal elements (F_{ij}, in a.u.), orbital energies (in a.u.) and orbital occupancies, bond orders (Wiberg Bond Index, *WBI*), total steric exchange energies (*TSEE*, in kcal mol^{-1}), based on the calculated geometries at the B3LYP/6-311++G** level of theory for the various conformations of dihydroxymethane.

	g.g	**qa.g**	**g.g***
E_2			
$LP_1\ O_2 \rightarrow \sigma^*_{C3-\ O4}$	---	0.67	---
$LP_2\ O_2 \rightarrow \sigma^*_{C3-\ O4}$	12.87	11.51	14.54
$LP_1\ O_4 \rightarrow \sigma^*_{C3-\ O2}$	---	1.39	---
$LP_2\ O_4 \rightarrow \sigma^*_{C3-\ O2}$	12.44	5.21	14.65
$\sum$	25.31	18.87	29.19
$GAE_{qa.g-g.g}$		-6.44	
$GAE_{g.g^*-g.g}$		3.88	
Orbital energy			
$LP_1\ O_2$	-0.62305	-0.61351	-0.61634
$LP_2\ O_2$	-0.32317	-0.31820	-0.32136
$\sigma^*_{C3-\ X4}$	-0.62150	-0.61045	-0.61701
$LP_1\ O_4$	-0.32331	-0.34104	-0.32118
$LP_2\ O_4$	0.29143	0.27595	0.28995
$\sigma^*_{C3-\ O2}$	0.29125	0.30664	0.29037
F_{ij}			
$LP_1\ O_2 \rightarrow \sigma^*_{C3-\ O4}$	---	0.022	---
$LP_2\ O_2 \rightarrow \sigma^*_{C3-\ O4}$	0.080	0.074	0.085
$LP_1\ O_4 \rightarrow \sigma^*_{C3-\ O2}$	---	0.032	---
$LP_2\ O_4 \rightarrow \sigma^*_{C3-\ O2}$	0.078	0.052	0.085
Dipole moment			
μ(debye)	0.1027	2.7581	2.9766
$\Delta\mu_{qa.g-g.g}$		2.6554	
$\Delta\mu_{g.g^*-g.g}$		2.8739	
$\Delta\mu_{g.g^*-qa.g}$		0.2185	
TSEE	52.37	53.78	52.79
$\Delta(TSEE)_{qa.g-g.g}$		1.41	
$\Delta(TSEE)_{g.g^*-g.g}$		0.42	

The *GAE* associated with the stabilization energies (E_2) associated with $LP_1O_2 \rightarrow \sigma^*_{C3-O4}$, $LP_2O_2 \rightarrow \sigma^*_{C3-\ O4}$, $LP_1O_4 \rightarrow \sigma^*_{C3-\ O2}$ and $LP_2O_4 \rightarrow \sigma^*_{C3-O2}$ electron delocalizations for the g.g, qa.g and g.g* conformations of dihydroxymethane are 25.31, 18.87 and 29.19 kcal mol^{-1}, respectively. The *GAE* decreases from the g.g conformation to the qa.g conformation and increases from the qa.g conformation to the g.g* conformation. Therefore, the trend observed for the variation of the GAE is the same with the trend observed for the calculated ΔG values. It has to be noted that the GAE for the g.g* conformation of dihydroxymethane is greater than that of g.g conformation. Based on equations 1 and 2, the calculated $GAE_{qa.g-g.g}$ and $GAE_{g.g^*-g.g}$ values are -6.44 and 3.88 kcal mol^{-1}, respectively. Consequently, the calculated *GAE* values explain the more stability of the g.g conformation compared to the qa.g conformation but fails

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in accounting for the more stability of the g.g conformation compared to the g.g* conformation.

Orbital energies and off-diagonal elements

The stabilization energies associated with donor-acceptor electron delocalizations are proportional to $S^2/\Delta E$ where S is the orbital overlap and ΔE is the energy differences between the donor and acceptor orbitals. Therefore, the stereoelectronic orbital interactions are anticipated to be more effective for the *anti* rather than the *syn* or *gauche* arrangement between the donor and acceptor orbitals, and the stabilization should increase as the acceptor orbital energy decreases and the donor orbital energy increases.

The NBO analysis showed that the energy differences between donor (E_{LP2O2}) and acceptor ($E\sigma^*_{C3\text{-}O4}$) orbitals [i.e. $\Delta(E\sigma^*_{C3\text{-}O4} - E_{LP2O2})$] for the g.g, qa.g and g.g* conformations of dihydroxymethane are 0.61442, 0.62484 and 0.61173 a.u., respectively. Based on the results obtained, the energy difference between donor (E_{LP2O2}) and acceptor ($E\sigma^*_{C3\text{-}O4}$) orbitals [i.e. $\Delta(E\sigma^*_{C3\text{-}O4} - E_{LP2O2})$] increases from the g.g conformation to the qa.g conformation but decreases from the qa.g conformation to the g.g conformation. Since the second order perturbation energy (E_2) is related to the F_{ij}, and $\Delta(E_{acceptor} - E_{donor})$, therefore, the $\Delta(E\sigma^*_{C3\text{-}O4} - E_{LP2O2})$ can affect the order of the stabilization energies associated with $LP_2O_2 \rightarrow \sigma^*_{C3\text{-}O4}$ electron delocalizations. In addition, the off-diagonal element (F_{ij}) [there is a direct relationship between the F_{ij} and orbital overlap matrix (S_{ij})] associated with $LP_2O_2 \rightarrow \sigma^*_{C3\text{-}O4}$ electron delocalization decreases from the g.g conformation to the qa.g conformation but increases from the qa.g conformation to the g.g* conformation. Consequently, there is no conflict between the impacts of the off-diagonal element (F_{ij}) and the energy differences between donor (E_{LP2O2}) and acceptor ($E\sigma^*_{C3\text{-}O4}$) orbitals [i.e. $\Delta(E\sigma^*_{C3\text{-}O4} - E_{LP2O2})$] on the stabilization energies associated with $LP_2O_2 \rightarrow \sigma^*_{C3\text{-}O4}$ electron delocalizations in the g.g, qa.g and g.g* conformations of dihydroxymethane.

Dipole moments

The dipole-dipole interactions may have significant impact on the conformational properties of chemical compounds. In the gas phase it is generally found that the conformation with the larger dipole moment has the larger electrostatic energy and therefore an increased overall energy,[43] therefore, there is a preference for the conformation with the smallest resultant dipole moment.

Based on the B3LYP/6-311++G** results, dipole moments of the g.g, qa.g and g.g* conformations of dihydroxymethane are 0.1027, 2.7581 and 2.9766 D, respectively. The results obtained showed that the calculated dipole moment values increase from the g.g conformation to the g.g* conformation. Therefore, the variations of the calculated dipole moment values are not in the same trend observed for the calculated ΔG values (see Tables 1 and 2). Consequently, the electrostatic model can not explain the variations of the calculated ΔG values for the g.g, qa.g and g.g* conformations of dihydroxymethane.

***Total steric exchange energies* (*TSEE*)**

The steric effects have impact on the stability of the g.g, qa.g and g.g* conformations of dihydroxymethane. The calculated total steric exchange energy (*TSEE*) value increases from the g.g conformation to the qa.g conformation but decreases from the qa.g conformation to the g.g* conformation (Table 2). The differences between the *TSEE* values of the g.g, qa.g and g.g* conformations, $\Delta(TSEE_{qa.g\text{-}g.g})$ and $\Delta(TSEE_{g.g^*\text{-}g.g})$, are 1.41 and 0.42 kcal mol^{-1}, respectively. Interestingly, the variations of the calculated $\Delta(TSEE_{qa.g\text{-}g.g})$ and $\Delta(TSEE_{g.g^*\text{-}g.g})$ parameters for dihydroxymethane are in accordance with the variations of the energy differences between its g.g, qa.g and g.g* conformations. Baesd on the results obtained, the *TSEE* and *GAE* have significant impacts on the conformational preference of dihydroxymethane.

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Conclusion

The B3LYP/6-311++G** calculations reported above and NBO analysis provided a reasonable picture from structural, energetic, bonding and stereoelectronic points of view for the conformational behavior in dihydroxymethane. Effectively, B3LYP/6-311++G** results revealed that the g.g conformation of dihydroxymethane is more stable than its qa.g and g.g* conformations.

Based on the NBO analysis, the *GAE* associated with the electron delocalization can not explain the more stability of the g.g conformation of dihydroxymethane compared to the corresponding g.g* conformation. Contrary to the trend observed for the *GAE*, the electrostatic model is more significant for the explanation of the conformational preference of dihydroxymethane. It has to be noted that the variations of the calculated $\Delta(TSEE_{qa.g\text{-}g.g})$ and $\Delta(TSEE_{g.g^*\text{-}g.g})$ parameters for dihydroxymethane are in accordance with the variations of the energy differences between its g.g, qa.g and g.g* conformations.

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