

DFT/GIAO Calculations of the Relative Contributions of Hyperconjugation to the Chemical Shifts of Ethanol

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Abstract: Our previous DFT/GIAO calculations on different types of alcohols reveal that the rotation of the hydroxyl group can affect the chemical shift of carbons and hydrogens close to the substituent in different ways. Besides the steric and electrostatic effects that have been widely studied, hyperconjugation with the lone pairs on oxygen of the hydroxyl group leads to changes in bond lengths and angles as well as to different charge distributions. As all three of these factors also affect chemical shifts, we undertook a systematic investigation of their relative contributions to the chemical shifts of ethanol, a molecule in which there is minimum interference among these factors. Calculations by the B3LYP method at the 6-31G(d) level for ethanol conformers corresponding to a rotation around the carbon-oxygen bond at 30° increments are used to show how relative contributions vary with the dihedral angle formed between the carbon-carbon and oxygen-hydrogen bonds (C-C-O-H). Largest contributions to carbon chemical shifts can be attributed to changes in bond lengths while for hydrogen chemical shifts also contribute significantly differences in charge distribution.

Resumo: Nossos cálculos DFT/GIAO anteriores de diferentes tipos de álcoois revelam que a rotação do grupo hidroxila pode afetar o deslocamento químico dos carbonos e hidrogênios próximos do substituinte de diferentes maneiras. Além dos efeitos estéricos e eletrostáticos já largamente estudados, a hiperconjugação com os pares isolados do oxigênio da hidroxila leva a mudanças no comprimento e nos ângulos das ligações bem como a diferentes distribuições de carga. Como todos os três fatores afetam também os deslocamentos químicos, fizemos uma investigação sistemática da contribuição relativa dos mesmos sobre os deslocamentos químicos do etanol, molécula na qual a interferência entre os fatores é mínima. Cálculos pelo método B3LYP no nível 6-31G(d) para os conformeros do etanol correspondentes a rotação da ligação carbono-oxigênio com incrementos de 30° são usados para mostrar como as contribuições relativas variam com o ângulo diedro formado entre a ligação carbono-carbono e oxigênio-hidrogênio (C-C-O-H). As maiores contribuições para o deslocamento químico de carbono podem ser atribuídas a mudanças no comprimento de ligação enquanto que para o deslocamento químico de hidrogênio diferenças na distribuição de carga também contribuem significativamente.

Introduction

Our previous studies on cyclic^{1,2} and acyclic³ alcohols show that rotation of the hydroxyl group can affect chemical shifts of carbon and hydrogen atoms in the neighborhood of the substituent in different ways. Besides the well-known steric and electrostatic effects, hyperconjugation with the lone pairs on the hydroxyl oxygen can lead to changes in bond lengths and angles as well as to differences in charge distribution.⁴ However, these three factors seem to contribute in a different way to the patterns observed for variations of carbon and hydrogen chemical shifts.³ In order to verify to which of these

factors the most significant contributions can be attributed in each case, we undertook a systematic investigation of chemical shifts for ethanol, a molecule in which interference among the above factors is minimum.

The present paper reports the calculations of chemical shifts for the 12 rotamers of ethanol that are generated by 30° rotations of the dihedral angle formed between the carbon-carbon and oxygen-hydrogen bonds (φ), as shown in Figure 1, followed by complete relaxation of the other structural parameters. The contribution of bond lengths, bond angles and charge distribution to carbon and

hydrogen chemical shifts may be evaluated by comparing their respective variations with this dihedral angle. As chemical shift dependence on bond angles has been thoroughly investigated elsewhere,^{5,6} only the influence of bond lengths and charge distributions is analyzed.

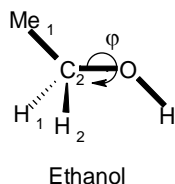


Figure 1. Ethanol (optimized at B3LYP/6-31(d) level) showing the dihedral angle φ (formed by the “bold bonds”). Me₁ denotes the methyl group containing atoms C1, H3, H4, H5.

Calculations

The DFT B3LYP functional approach⁷ with the 6-31G(d) basis set was employed for geometry optimization and for chemical shift calculations of the rotamers. B3LYP is based on the exchange functional of Becke⁸ and the correlation functional of Lee, Yang and Parr.⁹ Magnetic shielding tensors were calculated using the GIAO method.^{10,11} Chemical shift values were obtained relative to the isotropic shielding of TMS (32.18 ppm for hydrogen and 189.70 ppm for carbon-13), as calculated by that method at the same level. All calculations were carried out with the Gaussian 98W package of molecular orbital programs.¹² Results for the contribution variation with φ dihedral angle are shown in Figures 2-9

Results and Discussion

The relative energies of the rotamers that were calculated are shown in Figure 2. As expected, minima are found at conformations that correspond to staggered geometries, minimizing the interactions between the hydrogen of the hydroxyl group and C1 (180°) or the hydrogens on C2 (60° and 300°). Chemical shifts observed for ethanol should thus reflect the relative populations of these conformers.

The most favorable situation for hyperconjugation of the lone pair on oxygen with other bonds in its neighborhood⁴ can be verified by recourse to Figure 3. As expected, hyperconjugation

with the C1-C2 bond is favored at 90 and 270°, with the C1-H1 bond at 30 and 210°, and with the C1-H2 bond at 150 and 330°, as reflected by orbital interaction energy.¹³ These positions correspond to the geometry that is best suited for maximum overlap between the occupied p-orbital on oxygen and the unoccupied anti-bonding π orbitals on each bond of the neighboring group. For the three bonds that are capable of participating in hyperconjugation an intermediate position, which maximizes concomitant participation of two of them will be favored.

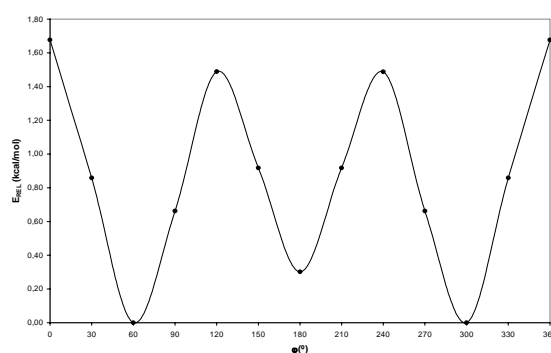


Figure 2. Variation of the relative energy (E_{REL}) with the dihedral angle (φ).

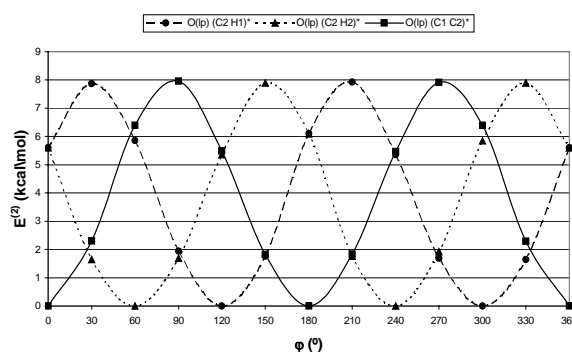


Figure 3. Variation of the energies of the second-order perturbation analysis of the Fock matrix elements with the dihedral angle (φ).

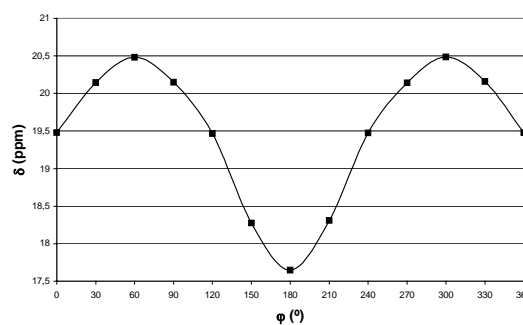


Figure 4. Variation of C1 chemical shift with the dihedral angle (φ).

The relative contribution of the factors that are responsible for carbon chemical shifts may be verified by comparing Figure 4 with Figure 5 and Figure 6. It is quite clear that maxima and minima for chemical shifts coincide with those of C-C bond lengths.

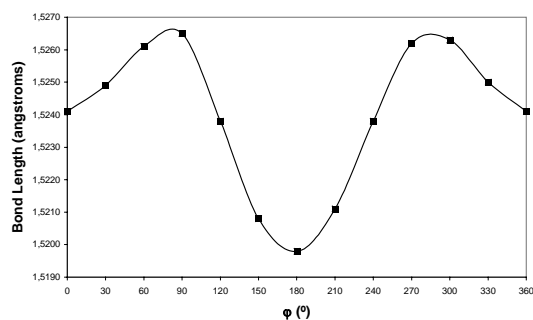


Figure 5. Variation of the C1-C2 bond length with the dihedral angle

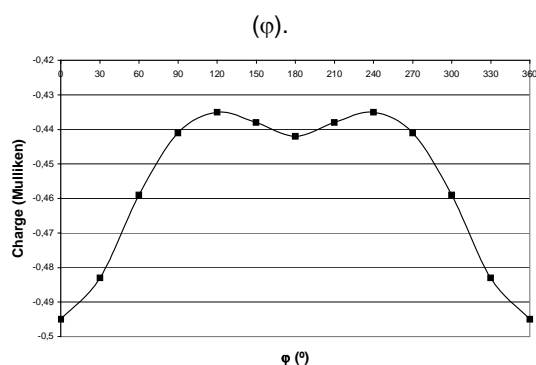


Figure 6. Variation of the charge distribution (Mulliken) on C1 with the dihedral angle (φ).

A similar approach to hydrogen chemical shifts, Figure 7, Figure 8 and Figure 9 reveals that, in the case of hydrogen, when the hydroxyl hydrogen is on the opposite side ($30^\circ < \varphi < 180^\circ$ for H1 and $180^\circ < \varphi < 330^\circ$ for H2), chemical shifts are mainly affected by bond lengths, but as the hydroxyl hydrogen approaches H1 or H2, electrostatic interactions become important and may dominate contributions to chemical shifts. It is noteworthy that variations in hydrogen chemical shifts for ethanol are much smaller than those observed for norbornesols.² This must be owing to the fact that the particular geometry of the bicyclic compound leads to situations in which those two nuclei are closer in space.³ Charge plays a much more significant role in determining chemical shifts. Comparing these results to Figure 3 reveals that charge distribution

on the hydrogen atoms must be mostly due to electrostatic interactions rather than hyperconjugation.

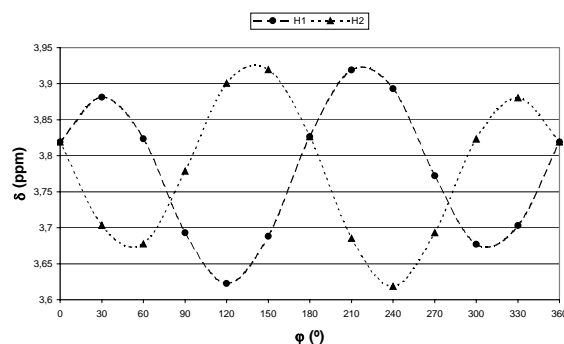


Figure 7. Variation of the H1 and H2 chemical shifts with the dihedral angle (φ).

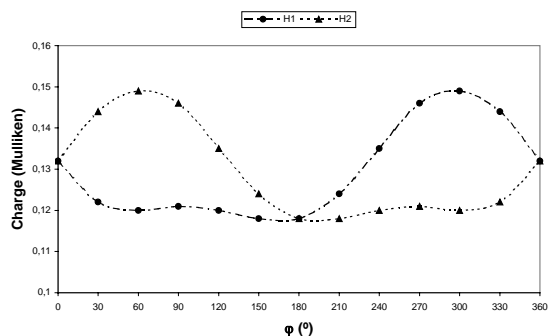


Figure 8. Variation of the charge distribution on H1 and H2 chemical shifts with the dihedral angle (φ).

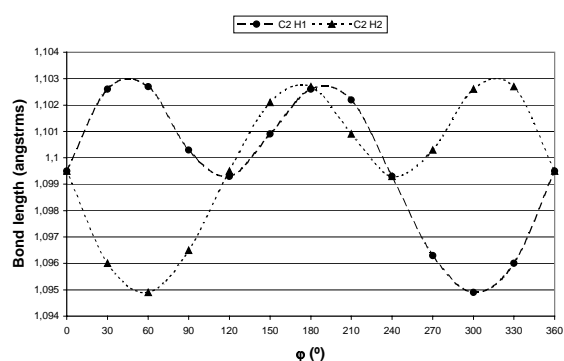


Figure 9. Variation of the C2-H1 and C2-H2 bond lengths with the dihedral angle (φ).

Conclusions

These results are in agreement with our previous calculations of conformational effects on alcohols.³ Carbon chemical shifts respond strongly to variations in bond lengths due to hyperconjugation while hydrogen chemical shifts are

not so sensitive to this factor, responding rather to charge distribution and electrostatic interactions.

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