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Quantum Theory of Atoms in Molecules Analysis on the Conformational Preferences of Vinyl Alcohol and Related Ethers

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Vinyl alcohol, methyl vinyl ether, and *tert*-butyl vinyl ether were studied within the framework of the quantum theory of atoms in molecules at the B3LYP/6-311++G(2d,2p) level. Local and integrated properties of the charge density indicate that the anti conformational preference of the *tert*-butyl derivative is not due to a differing resonance contribution with regard to the less bulky vinyl ethers but to steric effects. There is a small delocalization of charge density, either total or π, between oxygen and the terminal vinyl carbon, which does not support the resonance picture of vinyl compounds.

Introduction

Experimental evidence[1] and theoretical calculations[2−4] agree on the cis conformational preference of vinyl alcohol (**1**) over the anti conformation. In a similar vein, the most stable rotamer of methyl vinyl ether (**2**) is found to possess a cis skeleton.[2−10] Several explanations for the sterically unfavored cis conformational preference of **1** and **2** have been proposed: Bernardi et al. explained the preference of **2** in terms of attractive interactions between the methyl group and the C═C bond;[7] Larson et al.[2] suggested hyperconjugative interactions between the oxygen lone pair and the C═C σ^* or C─H σ^* orbitals as a major cause for the conformational preference of **1** as well as methyl vinyl sulfide and related substances. Bond and Schleyer[4] natural bond orbital analysis found the above hyperconjugative interactions to be relatively unimportant in determining the molecular conformation of **1** and **2**; instead, they concluded that intramolecular electrostatic interactions are the dominant factor.

The energy ordering is reversed if the methyl group is replaced with the more bulky *tert*-butyl group. Experimental work on *tert*-butyl vinyl ether (**3**) yielded only a single conformer with a slightly nonplanar anti structure (170(5)°), though ab initio calculations also predict a cis stable structure around 8 kJ mol^{-1} higher in energy.[11] NMR spectra of a series of alkyl vinyl ethers[12] were employed to state that the contributions of the resonance are greater in **1** and **2** and less in **3,** accounting for the differing conformational preference.

This paper is mainly aimed at providing an interpretation of the conformational preferences of **1**, **2**, and **3** within the approach of the quantum theory of atoms in molecules (QTAIM).[13] The application of this theory, which does not rely on orbital models,[14] has shown to provide original rationalizations of similar problems where resonance forms[15] or hyperconjugative delocalizations[16] were thought to be present.

Computations

B3LYP/6-311++G(2d,2p) geometry optimizations were carried out using the Gaussian 98 program.[17] The evaluation of local properties was performed using MORPHY98,[18,19] and the integrations over the atomic basins were carried out using the AIMPAC program series[20] on the above electron distributions. The delocalization indexes (DIs) defined within the framework of the QTAIM[21] were computed by means of a program developed by our group.

The ellipticity, ϵ, was employed to get insight into the π character of bonds. The position of the maxima of the $-\nabla\rho(\mathbf{r})$ function not associated to bonds were used to represent the position of the maximum charge density of the oxygen lone pairs.[13] We also base our analysis on the electron population, $N(\Omega)$, and energy, $E(\Omega)$, of an atom, Ω.

Results and Discussion

Structures and Energies. Figure 1 shows the structures and atom numbering of the compounds and their conformers. The letters **c** and **a** were employed to indicate cis or anti conformations. Our calculations do not predict a stable gauche conformer for any of the studied compounds. Some controversy remains, however, regarding the structure of the less stable conformation of methyl vinyl ether (see ref 2 and references therein). As can be seen in Figure 2, the torsion potential energy curve of **2** is quite flat around the anti region, yielding a relative minimum at a C═C─O─C torsion of 175.5° which is only 4×10^{-3} kJ mol^{-1} more stable than the exact anti conformation. According to the calculated torsional potential curve (Figure 2), the most stable conformer of compound **3** has an exactly planar anti structure.

Relative conformational energies for the compounds studied were compared with the best available previous calculations in the literature as a check on the reliability of the method. The most recent calculation on **1** is that of Bond et al.[4] at the MP2/6-31G*//3-21G level that produced a relative energy of 8.7 kJ mol^{-1}; the experimental estimate (4.5 kJ mol^{-1})[5] is in better accordance with our B3LYP/6-311++G(2d,2p)-optimized value (5.0 kJ mol^{-1}). G2 calculations[9] on **2** yielded an anti−cis energy difference of 8.0 kJ mol^{-1}, also in good accordance with our B3LYP result (7.6 kJ mol^{-1}). MP2/6-31G* calculations[11] on **3** gave an energy difference of 9.2 kJ mol^{-1}, which also compares quite favorably with the number obtained in this work (9.8 kJ mol^{-1}).

The experimental dipole moments of **1c**[22] and **2c**[6] (1.05 D and 0.96 ± 0.02 D, respectively) are also reasonably well reproduced by B3LYP charge densities, which gave the value of 1.01 D for both compounds.

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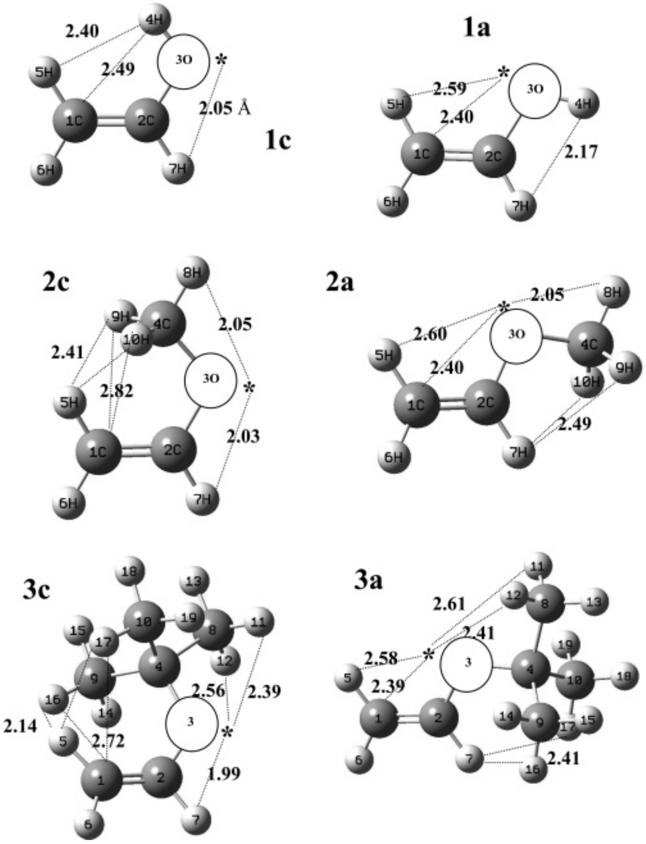

Figure 1. Structure and atom numbering of the rotational isomers of the compounds under study. An asterisk represents the lone pair if we consider it is placed at the maximum of $-\nabla^2\rho(r)$ placed over the plane of the figure. Another one is placed symmetrically down the plane of the figure. All distances are in angstroms.

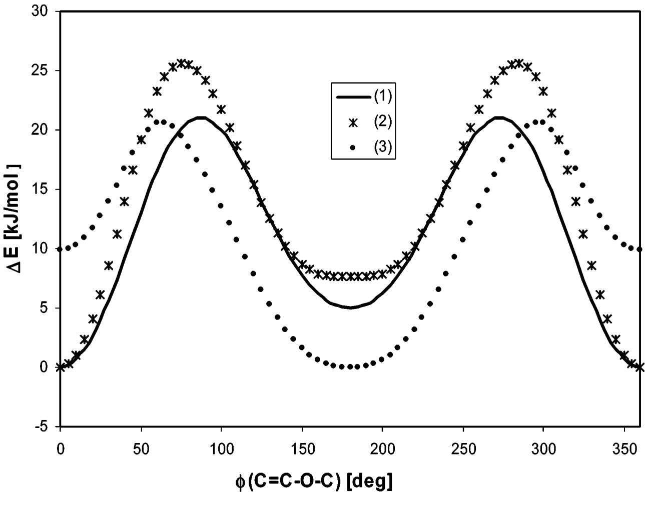

Figure 2. B3LYP/6-311++G(2d,2p) potential curve for internal rotation around the O−C (sp²) bond in **1**, **2**, and **3**.

Bond Properties. Ethene and ethanol wave functions were obtained at the current theoretical level to assess the applicability of resonance structures in these compounds. C═C bond length in ethene is ca. 1.355 Å and C─O bond length in ethanol is ca. 1.431 Å. Preferably, these values should be compared with those of **1**. As can be seen in Table 1, C─O bond lengths are considerably shortened in comparison with ethanol (0.068 Å), which could be related to the participation of H_2C^-─CH═O^+R resonance forms. Nevertheless, C═C bond is shortened compared to ethene.

TABLE 1: Selected Bond Lengths (in Angstroms)

	1c	1a	2c	2a	3a	3c
C_1═C_2	1.328	1.325	1.332	1.328	1.329	1.333
C_1─H_5	1.083	1.083	1.078	1.080	1.080	1.076
C_1─H_6	1.078	1.078	1.079	1.078	1.078	1.079
C_2─O_3	1.363	1.369	1.355	1.360	1.356	1.353
C_2─H_7	1.081	1.084	1.082	1.086	1.083	1.083
O_3─X_4	0.963	0.959	1.422	1.423	1.457	1.461

TABLE 2: Bond Ellipticities[a]

	1c	1a	2c	2a	3a	3c
C_1═C_2	36.8	36.7	35.8	36.1	36.3	36.7
C_2─O_3	0.9	3.1	2.7	3.5	2.8	1.8
O_3─X_4	1.9	2.2	1.5	1.7	0.6	0.3
C_1─H_5	2.4	2.0	2.4	2.1	2.3	2.7
C_1─H_6	2.9	2.5	2.7	2.6	2.8	3.1
C_2─H_7	3.9	3.9	4.1	4.0	3.8	4.0
C_4─X_8			4.3	4.4	3.6	3.7
C_4─X_9			4.3	4.5	3.2	3.1
C_4─X_{10}			4.3	4.5	3.2	3.1

[a] Values multiplied by 10^2.

Bond ellipticities of 0.296 and 0.029 were obtained for the C═C bond in ethene and the C─O bond in ethanol, respectively. The comparison of these numbers with those of **1c** (Table 2) indicates that there seems to be no significant loss/enhancement of the double character of C═C/C─O bonds in the studied methyl vinyl compounds

It is also remarkable that the ellipticity of the C_1═C_2 bond is nearly equal in the three compounds, regardless the rotational conformer (Table 2). This, coupled with the moderate variation of the C_1═C_2 bond distance (the largest variation is that of 0.005 Å in **3c** with respect to **1c**) could be viewed as indicating that the contribution of the H_2C^-─CH═O^+R resonance form is nearly constant in the three molecules. According to this, resonance effects would not be responsible for the differing conformational preference of **3**, as was previously concluded.[12] The variations in C_2─O_3 ellipticities are larger, both between compounds and conformers of a given compound. Nevertheless, they are not conclusive because the significant displacements experienced by the position of bond critical points of these bonds preclude comparison of so similar ϵ values.

The existence of intramolecular hydrogen bonding was also checked for compound **3**. The QTAIM theory provides straightforward criteria to track hydrogen bonding: if hydrogen bonding is present, there must be atomic interaction lines connecting donor and acceptor atoms, along with the concomitant critical points.[23,24] Instead of “conventional” hydrogen bonding, the topological analysis has yielded H···H atomic interaction lines connecting H_5 with both H_{16} and H_{17} in **3c**, at a distance of 2.145 Å (appreciably lesser than 2.4 Å, the double of the van der Waals radius of hydrogen). Matta et al. have coined the term H···H bonding for these interactions and concluded that they fall in the class of van der Waals interactions,[27] such as the Cl−Cl bonding present in solid chlorine.[28] The total energy density at the corresponding critical point, H_c, which has proven to be an adequate index to gauge the type of interaction,[25] has a positive value (1.4×10^{-3} au), indicating a closed-shell interaction.[26] RHF, MP2, and QCISD charge densities (Supporting Information, Table S1) also confirm the existence of the above interactions.

Atomic Properties and Delocalization Indexes. Similar to the ellipticities, QTAIM DIs for **1c** are not in keeping with the traditional picture of the resonance model discussed above. Figure 3 shows the values of electron delocalization indexes as a fraction of the atomic population of the reference atom. For

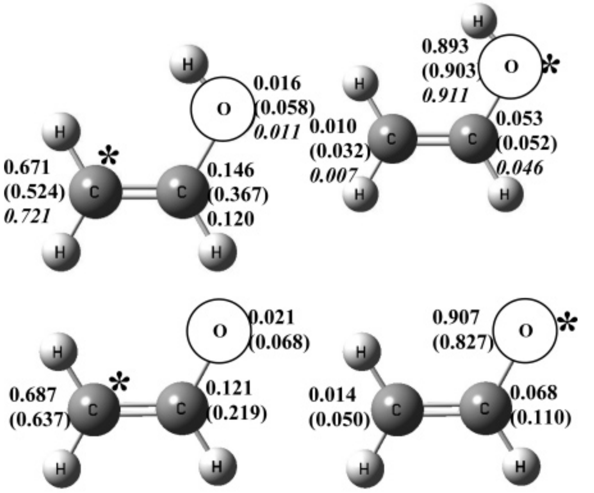

Figure 3. Total and π (in brackets) DIs of the electron population in **1c** and enolate molecule as a fraction of the reference population. An asterisk is employed to indicate the reference atom. Values in italics correspond to the total delocalization at the MP2 level (also expressed as a fraction of the reference population).

TABLE 3: Total and π Electron Populations (in au) of Enolate Relative to the Corresponding Values in 1c

	ΔN	ΔN^{π}	ΔN^{σ}
C_1	0.219	0.244	0.005
C_2	−0.292	−0.127	−0.165
H_4	−0.436	−0.015	−0.421
H_5	0.077	0.025	0.052
H_6	0.115	0.031	0.084
H_7	0.162	0.007	0.155
O_3	0.153	-0.164	0.317

instance, only 1.0% of the oxygen charge density is delocalized into C_1, and 1.6% of C_1 electron density is delocalized into O_3. The charge of the oxygen is essentially localized within its atomic basin, whereas that of C_1 is appreciably delocalized into C_2, as expected from the $C_1{=}C_2$ double-bond character. The reliability of this result, which strikingly departs from deeply established ideas of structural organic chemistry, deserves further comments. First, we note that, in this connection, similar values and conclusions were reported by Laidig and Cameron regarding resonance in formamide and thioformamide.[29] Also, Wiberg and Laidig obtained that the electron population of C_1 is lower in conjugated than in "unconjugated" conformations of vinyl alcohol and vinylamine.[30] Second, as a refusal to the possibility of nonsignificance of QTAIM DIs, we remind here that they recover the also well-accepted π delocalization of benzene and butadiene.[31] Finally, as a check on the reliability of the calculations, we note that the corresponding MP2/6-311++G-(2d,2p) results also yielded values in accordance with those provided by the B3LYP electron density (Figure 3).

Looking for further evidences about the small contribution of resonance effects in these systems, we have compared the charge distributions of molecule **1** and the corresponding enolate. Table 3 shows that though the electron population of C_1 and O_3 increases in the enolate of **1** (in accordande with the resonance described by forms $H_2C{=}CH{-}O^-$ and $H_2C^-{-}CH{=}O$), there is also an important decrease of $N(C_2)$ and a significant increase of the electron population of the remaining hydrogens (that amounts to ca. 0.354 au), which is not predicted by the resonance model. Also, Table 3 indicates that σ charge reorganization exceeds the π one if we exclude C_1. So, once more, a chemical process that has been traditionally explained using resonance forms obtained by concerted movements of π electron pairs is much more related to σ-charge reorganization, as previously found for the anomeric effect[16] and diverse protonations.[15,32,33] The notable role played by hydrogens is also in accordance with their importance in several chemical phenomena.[15,33−36]

TABLE 4: Relative δ Indexes (Multiplied by 10^3)[a]

1a	C1	O3	H4
O3	−8		
H5			−5
H7		11	−7

2a	C1	O3	X4	H5	H7
C4	−13				
H5			−17		
H7		6	5		
H9	−13			−10	6
H10	−13			−10	6

3c	C1	C2	O3	X4	H5	H6	H7
O3	−5						
H5			−8				
H7				6			
C9	10				10		−11
C10	10				10		−11
H16	19	−6			20		−17
H17	19	−6			20		−17

[a] Values in the range $(-5, +5) \times 10^{-3}$ au, autodelocalization indexes, and those corresponding to bonded atoms are not shown.

The weight of the aforementioned C_1/O_3 charge delocalization increases on going from vinyl ethers to the enolate. This increase of the delocalization from one tail of the molecule to the other is accompanied by longer C=C and shorter C−O bond distances (compare $R(1,2) = 1.381$ Å and $R(2,3) = 1.267$ Å for this compound with the corresponding values in Table 2). This fact also lends confidence to the reliability of QTAIM DIs. It is also important to notice that both the C_1/O_3 total and π DIs (Supporting Information, Table S2) remain nearly constant in the three vinyl compounds here studied.

The comparison of DIs calculated for cis and anti conformers confirms there is no significant change in electron delocalization between these conformers (Table 4). In fact no DI varies by more than 0.02 au because of the conformational change. Even more, the main variations correspond to couples of nonbonded atoms that are involved in an important steric interaction in one conformer but not in the other (Figure 1). Thus, these variations seem to be more related to geometry variations (which alter interatomic distances significantly inducing DIs variations) than to resonance effects. In fact, only $\delta(O_3,H_7)$, $\delta(C_1,O_3)$, and $\delta(O_3,H_5)$ are the unique DIs directly related to expected resonance delocalizations that experience noticeable variations in some of the molecules here studied, but they never exceed 0.011 au (Table 4).

Another central point of this work is to explain why **3** prefers the anti conformation unlike the less bulky vinyl ethers, **1** and **2**. We analyzed this conformational fact using atomic populations and energies (Table 5). It can be observed that the variations experienced by the atomic populations of the vinyl region upon the conformational change are quite similar in the three compounds. Thus, the electronic charge moves away from H_5 and C_1 (between 0.037 au in **3** and 0.049 au in **1**) when going from the cis to the anti conformer, whereas $N(C_2)$ and $N(H_7)$ increase significantly (Table 5). This trend can be explained considering the balance between the repulsions experienced by these atoms in each conformer (Figure 1). Thus, C_1 and H_5 experience repulsions with the two lone pairs, Lps,

TABLE 5: Relative Atomic Electron Populations, $\Delta N(\Omega)$, Electron Populations Variations Due to Delocalizations over Other Atoms, $\Delta N^d(\Omega)$, and Atomic Energies, $\Delta E(\Omega)$[a]

	1a	2a	3a	1a	2a	3a
	$\Delta N(\Omega)$	$\Delta N(\Omega)$	$\Delta N(\Omega)$	$\Delta E(\Omega)$	$\Delta E(\Omega)$	$\Delta E(\Omega)$
C_1	−22	−28	−16	8.1	10.7	13.8
C_2	20	23	23	−23.4	−37.0	−57.5
O_3	4	−2	−4	18.1	15.3	−7.3
X_4	−7	−9	−11	3.1	17.4	1.3
H_5	−27	−18	−21	24.0	27.0	46.8
H_6	5	2	1	−6.2	−1.6	−0.3
H_7	24	20	18	−20.8	−10.8	−18.7
X_8		−2	1		3.1	3.9
X_9		7	2		−7.9	−3.0
X_{10}		7	2		−7.9	−2.6
H_{11}-H_{13}			−4			5.5
H_{14}−H_{16}[b]			6			4.5
H_{17}−H_{19}[b]			6			4.5

[a] Atomic populations are in au and multiplied by 10^3, and atomic energies are in kJ mol^{-1}. [b] H_{16} and H_{17} experience the only significant variations with $\Delta N = 0.010$ au each. In contrast, their ΔE is only −1 kJ mol^{-1} each.

of O_3 (4 au) in conformer **1a** that clearly exceed those established with the scarce electron population of the hydroxylic hydrogen H_4 (0.436 au) in **1c** despite the fact that the H_5−Lp distance is slightly longer in **1a** than the H_5−H_4 distance in **1c**. Also, the repulsions between H_7 and the oxygen Lps in **1a** are expected to be larger than those with H_4 in **1c**, favoring more the movement of electron charge from H_5 and C_1 to C_2 and H_7 on going from **1c** to **1a**. The loss of electron population destabilizes C_1 and H_5 in **1a**, whereas $E(C_2)$, $E(H_7)$, and $E(H_6)$ become more negative in this conformer. All these atoms follow a general rule that relates atomic stabilization with increased electron population. In contrast, the variations of electron population and energy in O_3, $\Delta N(O_3)$ and $\Delta E(O_3)$, respectively, are both positive (Table 5). The QTAIM partitioning of the energy reveals this fact is a result of the larger repulsions experienced by O_3 in **1a**. Thus, though the attractions experienced by the electron charge of O_3 increase by 233 kJ mol^{-1} in **1a** with regard to **1c**, the corresponding repulsions increase by 269 kJ mol^{-1}. It has to be stressed that the relative destabilization of O_3 in **1a** is deciding for the conformational preference, favoring **1c** over **1a**.

The effects described above are combined in molecule **2** with the repulsions between the methyl group and the oxygen lone pairs. Nevertheless these repulsions are expected to be practically equivalent in both conformers (see distances shown in Figure 1). Therefore, the sequence of conformational stabilities remains unchanged in **2** with regard to **1**.

Finally, the repulsions between the lone pairs of O_3 and the hydrogens of the *tert*-butyl group are larger in **3c** than in **3a**. Distances to the lone pairs are shorter in **3c** (Figure 1), and the atomic populations of the hydrogens are larger in the *tert*-butyl group (between 1.004 and 1.020 au) than in the methyl group (0.978 to 1.001 au), where the proximity to the oxygen atom reduces N(H). In this case, O_3 is stabilized in **3a** in spite of the fact that $\Delta N(O_3)$ is negative. The reason is the evolution from the cis to the anti conformer in **3** allows to increase more the attractions over the oxygen electron charge (by 1611 kJ mol^{-1}) than the repulsions (by 1595 kJ mol^{-1}). The final consequence is the stabilization of **3a** with regard to **3c**.

In a study of Table 5, we observe that O_3 is the unique atom that is common to the three molecules where the sign of $\Delta E(\Omega)$ changes along the series of molecules, being positive when the anti conformer is not favored (molecules **1** and **2**) and negative in **3**. In contrast we observe that both the summation of $\Delta E(\Omega)$ for the vinyl group and the summation of $\Delta E(\Omega)$ for the group attached to O_3 display the same sign in the three molecules (negative for the former and positive for the latter). This fact confirms the importance of O_3 interactions for the stability sequence.

Conclusions

Bond and atomic properties indicate that the anti conformational preference of the *tert*-butyl derivative is not due to a differing resonance contribution with regard to the less bulky vinyl ethers. The balance between steric repulsions favors the cis conformer in vinyl alcohol and methyl vinyl ether and conformer anti in the *tert*-butyl derivative. The small delocalization of oxygen charge density into the terminal carbon keeps in line with previous findings about the evolution of the electron population during the internal rotation of vinyl alcohol,[30] providing strong support against the traditional picture of vinyl ethers employing $R{-}O^+{=}CH{-}^-CH_2$ resonance forms.

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Supporting Information Available: Tables showing H−H distances, electron density local properties at $H_{16}/H_{17}\cdots H_5$ bond critical points for **3c**, and O_3/C_1 total and π DIs for all the conformers. This material is available free of charge via the Internet at http://pubs.acs.org.

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