



Bonding Analysis of $C_2H_4^+$

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Abstract

The present work deals with the study of different models of bonding and structure such as Lewis, VSEPR, qualitative MO and QTAIM have been applied to analyze the Bonds and structures of two equilibrium geometries (planar D_{2h} and perpendicular D_{2d}) of $C_2H_4^+$. It is shown that the cited models fail in predicting the existence of perpendicular, D_{2d} form of $C_2H_4^+$. In this regard the interpretations of significant energetic stabilization of D_{2d} form over planar isomer has also been revisited. This is attributed to the hidden effect of the Pauli Exclusion principle.

Keywords: $C_2H_4^+$, LCP, exclusion principle

1. Introduction

The remarkably large rotational barrier energy, 28.1 kcal/mol has been described by the Hyper-conjugation between two formally vacant orbitals and corresponding vicinal CH_2 group [1]. The substituted ethylene dications have also been extensively studied [2, 3] and the results were explained using descriptive tools such as π donation/conjugation, orbital diagrams, lone pairs, steric repulsion and Hyperconjugation. The energy lowering in twisted geometry of ethylene radical cation [4, 5] has also been described by the attractive interaction of a p orbital of C atom with the p-like group orbital of adjacent σ bonds [6, 7]. It is the goal of this work to reinvestigate the effect of each of these models on the final geometry of $C_2H_4^+$ individually.

2. Results and Discussion

Some differences between the results of present computations at MP2 level and those of 6-31G* and 6-31G** [1, 2] are discussed first. C-C distances which have been reported previously as 1.317 and 1.587 Å in C_2H_4 and $C_2H_4^+$ (D_{2h}) respectively [1], are 1.332 and 1.603 Å, each are 0.015 Å longer at MP2 level. In contrast, the C-C distance in $C_2H_4^+$ (D_{2d}) shrinks from 1.432 [1] to 1.393 Å, the significant shortening of 0.039 Å. The energy difference between two isomers is reported as 30.9 kcal/mol at MP2 level, in agreement with previously reported value of 28.1 kcal/mol [1, 2].

There are different chemical models predict or provide the explanation about these geometrical changes is discussed below. Here we start with basic Lewis model.

2.1 Lewis Model

In Lewis model, a planar structure composed of single bonds and can be written [8]. The formal charge of each C is +1 and that of H is zero. Simple electrostatic rule predicts that the C-C distances in planar Lewis structure should be longer than

1.5 Å, the normal C-C single bond in saturated hydrocarbons, because of the repulsion between two C atoms; each bears a positive formal charge. In this model the existence of more stable perpendicular form cannot be predicted or described.

2.2. VSEPR

The VSEPR model provides that the three single bonding pairs around each C atom should adapt the trigonal arrangement and thus the molecular geometry could be planar [8, 9]. However the model is only reliable for predicting the relative geometry around any one central atom and not the relative arrangements of the bonds around two adjacent atoms [16]. The model indicates that in both $C_2H_4^+$ isomers the vicinal HH distances are significantly longer than 2.40 Å (sum of the Van der Waals radii) so steric repulsion between them is negligible and therefore is not responsible for twisting the geometry to D_{2d} form. Therefore VSEPR together with steric repulsion model cannot predict or explain the existence of twisted $C_2H_4^+$.

2.3 Qualitative MO

Analyzing the orbital density [7, 10] is other method for tracking the geometrical changes. The densities, of HOMO and HOMO-1 for each isomer of $C_2H_4^+$. The shape of MOs in D_{2h} form support the VB picture of bonding. The HOMO and HOMO-1 of D_{2d} are degenerate and they are more delocalized than HOMO of D_{2h} . More inspection revealed that The HOMO-2 of the D_{2d} shows orbital density between C nuclei. HOMO-2 shape of D_{2d} is the same in shape to HOMO-1 in D_{2h} .

2.4 The QTAIM

In the framework of QTAIM theory, the total molecular electron density, ρ [12], is the source of chemical information about the molecule. The integration of ρ over all space is exactly equal to the total number of electrons in

the molecule [7, 12].

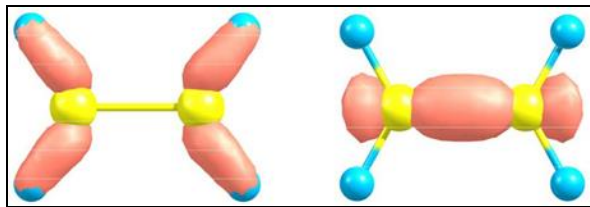


Fig 1: q_{Mulliken} (C = 0.362 H = 0.319)

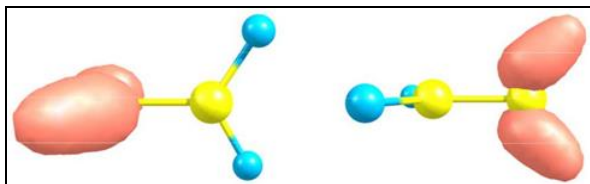


Fig 2: q_{Mulliken} (C = 0.342 H = 0.329)

2.5 The RHF orbital density (Ψ^2_{MO}) of the HOMO (a, c), HOMO-1 (b, d) and Mulliken atomic charges in planar (a, b) and perpendicular (c, d) forms of $\text{C}_2\text{H}_4^{2+}$.

At MP2 level the ρ values at the chosen points in D_{2h} are 0.232, 0.345 a.u., in D_{2d} are 0.343, 0.316 a.u. respectively. These numbers nicely represent the correct picture of

distribution of electronic charge from C-H regions to C-C region when the geometry is changed from D_{2h} to D_{2d} . The accumulation of charge density between C nuclei in twisted form, result in the decrease of positive charge on C atoms and the marked decrease of C-C length [13]. Because of this transferring of negative charge, the H atoms bear more positive charge in D_{2d} . While the ρ between C-C changes by 0.111 a.u. from D_{2h} to D_{2d} , the corresponding value in each CH region is only 0.029 a.u. This explains why C-H distances remain al-most the unchanged between two isomers. Does the ρ provide the explanation for why the D_{2d} isomer is the lowest energy isomer? The quantum theory of atoms in molecules has provided the physical basis for the LCP and VSEPR models based on the arrangement of maxima in the Laplacian map of ρ around the central atom [14]. Instead of electron pairs, the concept of elec-tron domains is used when using LCP or VSEPR in their new forms [8]. It is expected that at least three maxima be found around each C atom. The Laplacian maps of the two $\text{C}_2\text{H}_4^{2+}$ isomers are essentially the same. It is not clear yet why $\text{C}_2\text{H}_4^{2+}$ preferred geometry is the D_{2d} isomer. Finally we present the full QTAIM analysis [8, 11-13 15], Atomic basin charge and energy values in Table 1. Energy analysis demonstrates that each C basin is stabilized by 68.15 kcal/mol but each H basin is destabilized by 26.36 kcal/mol, from D_{2h} to D_{2d} .

Table 1: The Atomic properties (in atomic units) from QTAIM analysis at MP2/cc-p VTZ

	Q_{\pm}^{\dagger}	$E(\Omega)^{**}$	$V(\Omega)^*$
$\text{C}_2\text{H}_4(D_{2h})$			
C1	-0.0750	-37.5776	97.69
C2	-0.0850	-37.7776	
H3	0.0377	-0.6116	47.75
H4	0.0328	-0.7116	
H5	0.0328	-0.7116	
H6	0.0327	-0.6116	
$ (AIM-Ab\ initio) $	0.0008	0.2 kcal/mol	
$\text{C}_2\text{H}_4^{2+}(D_{2d})$			
C1	0.0914	-37.8837	83.97
C2	0.0984	-37.9837	
H3	0.4563	-0.3904	27.00
H4	0.4783	-0.3564	
H5	0.4453	-0.3454	
H6	0.4556	-0.3444	
$ (AIM-Ab\ initio) $	0.0000	0.002 kcal/mol	
$\text{C}_2\text{H}_4^{2+}(D_{2h})$			
C1	0.2012	-37.7751	85.13
C2	0.2012	-37.7751	
H3	0.3994	-0.4404	26.01
H4	0.3994	-0.4404	
H5	0.3994	-0.4404	
H6	0.3994	-0.4404	
$ (AIM-Ab\ initio) $	0.0002	0.1 kcal/mol	

3. Conclusion

In 1954 Lennard- Jones published the paper, the distribution functions of neutral fermionic particles with same spin

moving in the closed ring and Surface of sphere [16]. The orientation of maxima of probability of finding the particles on the ring or sphere, were demonstrated mathematically as

180° for two particles, 120° for three particles and tetrahedral arrangement for four particles moving on the surface of sphere.

4. References

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