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The Correlation between Molecular Graph Properties and Vibrational Frequencies

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ABSTRACT

It seems that the general applicability of the quantum theory of atoms in molecules (QTAIM) on characterizing the bonded interactions is still questionable even after 30 years since its formulation. For demonstrating the generality of bonding schemes in QTAIM, C_6H_6 isomers were chosen as the model systems and the results from molecular charge density analysis and vibrational normal modes were compared to each other. It was demonstrated that the mathematical properties of the elements of molecular graph, derived from charge density analysis, have an excellent correlation with the properties of the vibrational normal modes. The excellent correlation among four different indices of chemical bond i.e. inter nuclear distances, ρ_b, QTAIM bond orders (n) and vibration frequencies was also established.

Keywords: Molecular Graph; PES; Vibrational Normal Mode

INTRODUCTION

Benzene (C_6H_6) is an outstanding example in the history of the development of bond and structure concepts. Although no theoretical justification or physical rules were supporting these two concepts at 19th century (the time of their proposal), they rapidly became the cornerstone of chemistry because of their success to provide the explanation about the fundamental experimental facts, such as combining power and chemical reactivity. By the advent of quantum chemistry these two concepts were defined in their new forms by Pauling, which are still used in chemistry [1]. By proposing the molecular orbital theory, MO, by R.J Mulliken [2] bond and structure were redefined again in consistent with their old meanings. An alternative approach was proposed after the MO theory, using the electron density as the main source of information for deducing the bond and structure. This approach is known as the quantum theory of atoms in molecules (QTAIM) [3]. The key elements in this theory are topological atoms which their properties are derived from fundamental laws of quantum mechanics. It has been established rigorously that the sum of their properties are exactly equal to the corresponding molecular properties. While

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the outcomes of QTAIM are almost consistent with classical bonding and structure schemes but in some cases like HH bonding are not. Consequently the debates about the generality of QTAIM bonding schemes started by publishing series of papers.

The Bonds in the carbon skeleton of non classical geometries of C_6H_6 found to be the good basis for investigating the general applicability of QTAIM bonding and structure schemes. Comparison of the QTAIM results with that of vibrational frequencies (as the indication of mathematical properties of the potential energy surface) is presented as a tool for illustrating this generality.

COMPUTATIONAL DETAILS

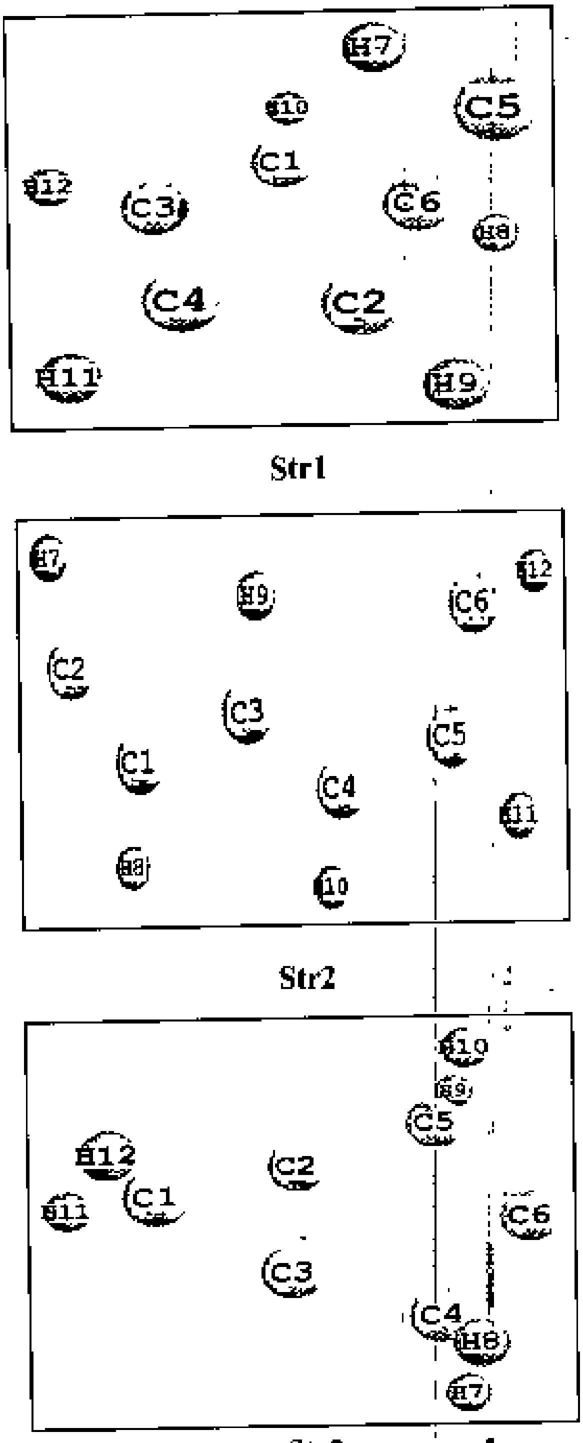
All geometry optimizations on C_6H_6 isomers were performed using RB3LYP/6-311+G(d,p) followed by frequency computations. The excellent results of B3LYP in conjunction with Pople type basis set has been well documented for studying the molecular properties of large number of organic molecules. All DFT calculations were performed by PC GAMESS7 1 package [5].

The QTAIM computations were dane on the appropriate wave function derived from DFT computation in selected number of molecules. All these computations were performed using AIM2000 software [6].

RESULTS AND DISCUSSION

Among the 15 computed geometries three local minima with non classical structure were found. They are depicted in Figure 1.

Inter nuclear distances, bond orders derived from Mulliken-Lowdin (ML) population analysis and total energies for each geometry are gathered in Table 1. Although ML analysis predicted the bond order scheme in consistent with internuclear distances it produced unacceptable results in structure 1(**Str1**). Although the C2-C4 and C5-C6 distances are almost the same (1.5Å) in **Str1** but their corresponding ML bond orders are markedly different (Table 1). The C5-C6 bond order is 0.345 dramatically below 1.000 (normal value for single covalent bonds).



Str1

Str2

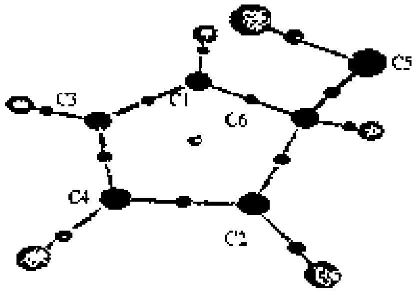
Str3

Fig.1. The optimized geometries of three C_6H_6 isomers

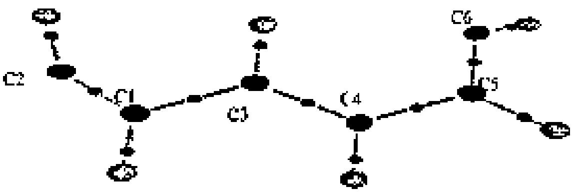
For investigating the QTAIM bonding scheme in these molecules the topology of their electron density were searched via their molecular graphs [3]. The molecular graphs are depicted in Figure 2. The mathematical properties of BCPs used to

Table 1. Inter molecular distances, Mulliken-Lowdin bond order and molecular energies

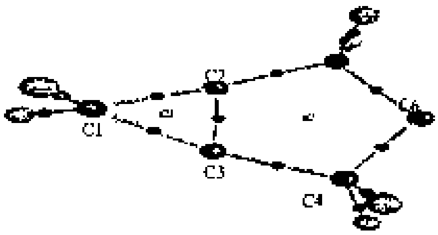
Molecule	Carbon nuclei numbering	Inter nuclear distances (Å)	Mulliken-Lowdin bond order	Total Energy (a.u.)
Str1				
	1,3	1.365	1.822	-232.13091
	1,6	1.487	0.991	
	3,4	1.371	1.754	
	2,4	1.507	0.999	
	2,6	1.438	1.360	
	5,6	1.501	0.345	
Str2				
	1,2	1.336	1.731	-232.02404
	1,3	1.438	1.195	
	3,4	1.370	1.859	
	4,5	1.443	1.123	
	5,6	1.338	1.800	
Str3				
	1,2	1.512	1.060	-232.04416
	1,3	1.512	1.060	
	2,3	1.314	1.842	
	2,5	1.515	0.728	
	3,4	1.515	0.728	
	4,6	1.506	1.083	
	5,6	1.506	1.083	



Str1



Str2



Str3

Fig.1. The Molecular graphs at RB3LYP/6-311+G(d,p).

characterize the nature of bonded interactions between two atoms are gathered in Table 2. The ρ_b>0.1 au and $\nabla^2\rho_b$<0 clearly show that each molecule is composed of shared interactions (The analogous terminology for covalent bond). Contrary to what was predicted by ML analysis, the similar values of the ρ_b and $\nabla^2\rho_b$ at the position of BCPs between C2-C4 and C5-C6 nuclei in **str1** is seen. Traditionally the covalent bonds are characterized by their bond orders in chemistry, the QTAIM formula for obtaining the bond orders n is defined by equ1[3,7].

$$n = \exp[A(\rho_b - B)] \qquad (1)$$

For evaluating the constants A and B, the accepted value of C..C bond orders and their ρ_b values at the BCPs between C nuclei in C_2H_6 (single bond), C_2H_4 (Double bond) and C_2H_2 (triple bond) molecules at RB3YP/6-311+G(d,p) have been used (Table 3). A and B were adjusted by non linear fitting procedures of n to ρ_b values. The obtained values are A=6.2432 and B=0.2346 respectively

The calculated bond orders based on equation 1 have been gathered in Table 2. Equation 1 is a bridge between old concept of bond order and electron density value at BCP. These new bond orders i.e. 1.7 for C2-C4 and 1.1 C5-C6 clearly removed the observed discrepancy in ML bond orders in **str1**. For providing more evidences of the generality of the QTAIM bonding and structure schemes, all the vibration normal modes of each isomer have been analyzed carefully. The assigned values of frequencies for each pair of nuclei are also gathered in the last column of Table 2. These values are found to have excellent correlation with other bond indices (QTAIM bond orders, internuclear distances, ρ_b and $\nabla^2\rho_b$). All presented data supported the general trend i.e. stronger frequencies are characterized by the greater bond orders and ρ_b values and shorter inter nuclear distances.

This clearly demonstrates that electron density properties at BCP have an excellent correlation with vibration frequencies derived from PES of polyatomic molecules. This consistency does not exist when arbitrary population analysis like ML is used for bond order assignment. The correlation was also found when the assigned frequencies to each CC pairs were compared to that of experimental values of C-C, C=C and C≡C bond stretching values. The experimental values are (650-1550 cm^{-1}), (1550-1650 cm^{-1}) and (2000-2500 cm^{-1}) for C-C, C=C and C≡C respectively [8]. Table 2 shows that all the assigned frequencies are in the range of experimental frequencies for single and double bonds. In traditional chemical language the carbon skeleton of all isomers in this work are just composed of single and double CC bonds. One of the interesting values in Table 2 is the 2.2 bond order between C2-C3 in **Str3**. This is the greatest value of bond order in this molecule. The 1689 cm^{-1} of its frequency is slightly greater than the upper limit of experimental double bond frequency(1650 cm^{-1}) which is also compatible with its QTAIM bond order value 2.2 (slightly more than 2.0) .This bond order of 2.2 does not have any classical analogous.

Table 2. AIM based bond order and normal mode, the mathematical characteristic (ρ_b and $\nabla^2\rho_b$) at bond critical point (BCP) at RB3LYP/6-311+G(d,p)

	Carbon nuclei numbering	ρ_b (a.u.)	$\frac{1}{4}\nabla^2\rho_b$	QTAIM bond order (n)	Normal mode (cm^{-1})
Str1					
	1,3	0.325	-0.23	1.8	1439
	1,6	0.262	-0.16	1.2	1318,1225
	3,4	0.286	-0.19	1.4	1418
	2,4	0.323	-0.23	1.7	1439
	2,6	0.243	-0.13	1.1	1318, 1225
	6,5	0.247	-0.13	1.1	1058
Str2					
	1,2	0.334	-0.25	1.9	1525
	1,3	0.279	-0.18	1.3	1168
	3,4	0.320	-0.23	1.7	1584
	4,5	0.278	-0.19	1.3	1063,1449
	5,6	0.343	-0.26	2.0	1584,1449
Str3					
	1,2	0.224	-0.10	0.9	1108
	1,3	0.224	-0.10	0.9	1108
	2,3	0.362	-0.27	2.2	1689
	2,5	0.237	-0.12	1.0	1162
	3,4	0.237	-0.13	1.0	1162
	4,6	0.261	-0.16	1.2	1228,1250
	5,6	0.261	-0.16	1.2	1228,1250

Table 3. Relationship of ρ_b in bond critical point (BCP) and bond order at RB3LYP/6-311+G(d,p)

	ρ_b (a.u.)	Bond order
C_2H_6	0.237	1
C_2H_4	0.344	2
C_2H_2	0.411	3

CONCLUSIONS

The correlation among four different indices of chemical bond i.e. inter nuclear distances, ρ_b, QTAIM bond orders (n) and vibration frequencies were found. The advantages of using the new definition of bond order based on topological properties of molecular electron density, ρ_b and $\nabla^2\rho_b$, have been well established by applying to non classical geometries of C_6H_6. The failures of old definition of bond order based on the Mulliken-Lowdin population analysis were addressed and the good correlation of QTAIM bond orders with inter nuclear distances was demonstrated. All $\nabla^2\rho_b$ values in were found to be negative, which precisely showed the existence of shared interaction between each pair of carbon nuclei. As a direct tool for deducing the bonded interactions between two nuclei (like what has been done in diatomic molecules) [10], vibration normal modes have been analyzed carefully. The normal modes with major contribution from motion of each pair of nuclei were found by precise inspection of all molecular normal modes. These values were found to be in excellent correlation with QTAIM bond orders and inter nuclear distances too. The observed correlation demonstrates the validity and advantages of using the topological properties of molecular electron density for establishing the chemical bond in anomalous molecules.

The interesting point is that the assigned values of bond orders and frequencies were comparable to the well known experimental stretching frequencies of C-C and C=C bonds. No C ≡ C bond have been observed in C_6H_6 isomers in this analysis. As have been previously reported in Nitrogen Clusters [9], the traditional population analysis has great deficiencies in calculating the bond orders and establishing the chemical bond between two nuclei. These kinds of orbital analysis aren't consistent with computed vibrational frequencies, which are the reliable and direct evidences of existence of chemical bond in quantum mechanical approach.

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