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QTAIM study of Bonding and Structure of Pure Atomic Clusters,Part III : Nn Clusters (n= 4,6)

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ABSTRACT

DFT and QTAIM computations have been performed on numbers of pure nitrogen cluster species i.e. Nn (n = 4, 6) for investigating the structure and bonding. This study is critical since these molecules have been nominated as the good synthetic targets of High Energy Materials (HEM).On the other hand the decomposition mechanism is closely depends on the bonding pattern. This latter concept was searched via modern theory of Atoms in molecules (QTAIM) since the conventional methods were found to be incapable for describing the structure and bond in these atomic clusters.

Keywords: Nitrogen Clusters ; DFT; QTAIM ; Structure ; Bonding

INTRODUCTION

Nitrogen and its compounds are known as High Energy Materials(HEM) .From the vast verity of Nitrogen containing molecules the pure nitrogen clusters considered to be the good targets for synthesis of HEM since it has been proposed that their decomposition to N_2 with bonding energy of 228 kcal/mol releases large amounts of energy.

Thermal decomposition of white phosphorous P_4 at high temperature, to P_2, led the chemists toward its analogous N_4 molecule[1]. Although the T_d minimum geometry was found on HF/STO-3G and HF/double-ζ-STO Potential Energy Surfaces (PES) but the appropriate TS was not found so the decomposition path to N_2 remained unknown.

The computations using correlated models such as MP2/6-311G* , MP2/6-311++G* and MP4SDQ , demonstrated the existence of distorted TS geometry in D_2d form as well as minimum T_d geometry. The energy difference between them and the estimated decomposition energy to N_2, were reported to be 315 kcal/mol and 814 kcal/mol[2,3].

The unusual thermodynamic stability of Benzene was the starting point of thinking about the existence of N_6 molecule. Simply, replacing each (CH) group in Benzene with the isoelectric N atoms produce Hexaazabenzene [4].

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The planar D_6h form with NN distance of 1.288 Å has been reported as minimum geometry on HF/DZ and HF/DZ+P singlet Potential Energy Surface(PES) for the first time , while the TS geometry with NN distances of 1.178 and 1.551 Å were also found on the same PES for the decomposition of N_6 to three N_2 molecules. The low value of 10.3 kcal/mol energy difference between these geometries and the reported decrease of this value by implying the correlation effect , sounds the insufficient thermodynamic stability of N_6 under normal conditions. Subsequent computations with more advanced methods and basis sets ultimately revealed that N_6 in its D_{6h} form is minimum in HF level and second order saddle point in all Post HF levels[5,6].

All of the cited molecules have more structural isomers that could be used as HEM, the complete study of the PES of each one has been done by Bartlett group[7]. Since non of them have been observed experimentally It is the goal of this work to shed the light on the quantum mechanical structure and bonding of these clusters through searching the properties of their total electron density and provide basic information which is curial in proposing the best synthetic strategy.

METHODS OF COMPUTATION

Bartlett group has reported that B3LYP/cc-pVDZ model produce the same geometries as the very sophisticated CCSD(T)/aug-cc-pVDZ model in N_n clusters ,so because of the less computational time needed for the former model it was chosen in this work for geometry optimization, frequency computation and wave function construction. Some of their reported geometries had been optimized using the symmetry constraints, here all geometries have been optimized in C_1 space to assure the existences of true local minimum. All DFT computations were performed by **WinGAMESS** package[8]. The wave functions were analyzed by QTAIM, using **AIM2000** and **MORPHY99** softwares[9-12] to investigate the structure and Bond. The useful utilities implemented in the **ChemCraft** program[13] were optimized for handling the outputs of WinGAMESS.

INTRODUCTION TO QTAIM

a-The Chemical Atoms

Based on experimental facts , it has been generally accepted that the molecules are the collections of atoms and the network of pair wise interactions which are denoted for example by lines. For example in H2O the lines are drawn between the O and each H nucleus and never between H nuclei .Therefore automatically chemists partition the molecule in to parts, call them atoms (usually they called the O nucleus as an O atom) and specify any interactions between them by assigning the number of electrons between the pairs. As any one knows the atom itself is composed of nucleus and the electrons. When O atom combines with two H atoms, what will happen?, does the O atom, similar to its free form (Nucleus + electrons), still exist in molecule. All the proposed models of bonding from the beginning till now imply the existence of atoms in molecules, but they do not give any practical information's about these objects. For example Lewis proposed that the O atom shares one electron with each H atom, therefore he implied that the free O atom (Nucleus + 8 electrons) undergoes some changes ,i.e. the number of electrons , (Nucleus + 10 electrons) , when combine with two H atoms, The same is true for H atoms. The exchange of electrons between the O and H, produce the Chemical Bond as he proposed. Ignoring the deficiencies of this model, the two basic cornerstones of model i.e. the Bond and Atom, have been kept in proposing other models. With the advent of quantum mechanics, Bader tried to find the quantitative justification for these cornerstones[14].

First it has been proved that the electronic density of molecules can be divided in to the parts in only one way. Nothing has changed about the physics of electrons, the electrons are still particles but the uncertainty principle imposes the limitations on the predication of the exact location of electrons. Therefore the total amount of electronic charge density of molecule is still equal to the total number of electrons. Now what about the exchanging of electrons , proposed by Lewis .It is proved that the exchanging still exists but not as simple as he proposed (one electron), ones has to look through the total electronic charge density which has the necessary information (probability in quantum) about the dispersion of electrons in molecule. Automatically one faces with the question that which parts exchanges the electrons with each other.

In QTAIM the molecule is divided by the mathematical surfaces in to 3 dimensional parts. Each part has a nucleus and a portion of molecular electronic charge density (you can assume the numbers of electrons).It has been established that these parts also obey the laws of quantum mechanics and no other ways exist for partitioning[15]. Therefore H2O molecule is divided to two H parts and one O part. If we call these parts, the atoms, (because they are just like the free atoms, they have nucleus and electrons), therefore the mathematical surfaces are called Interatomic surfaces, IAS (Figure 1).

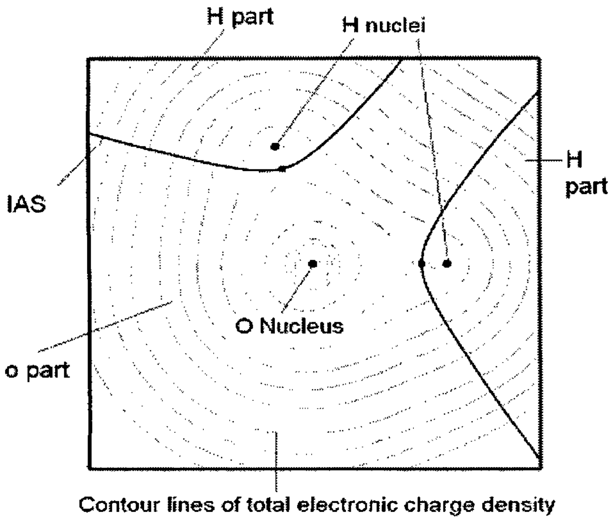


Figure 1. Contour Maps of electron density, derived from MORPHY98.

Are these parts the chemical atoms? First the sum of each atomic property among the parts is equal to the corresponding molecular value. Second, comparison to lots of experimental facts (Functional group, Enthalpy of formation, magnetic and electrical properties,...), has established that these parts are the best models of chemical atoms which quantum mechanics in its present form, presents to chemist. With these parts in hand, it is possible to calculate the amount of charge density of each atom in water molecule and compare it to the free atom. These values are gathered in the following Table

Atom	Rho a.u in Molecule	Rho a.u ,free atom	Gain(+)Loose(-)
O	9.2385	8.0000	+1.2385
H	0.3808	1.0000	-0.6192
H	0.3808	1.0000	-0.6192
Sum	10.0001	10.0000	0.0001

Comparison the amount of electron density (Rho) in a.u between the atoms in Water molecule and their free form. HF/6-31G** wave function has been used for Water.

The above table shows that O atom gains 1.2385 a.u more electric charge in comparison to its free form and each H atoms looses 0.6192 a.u (It sounds like the number of electrons in classical view).The above table demonstrates the amount of changes in the electronic charge of each atom quantitatively, when the free atoms combine to form a molecule.

b.Chemical Bond and Theory of Structure[16]

With the chemical atoms in hand , Bader goes naturally to find the meaning of chemical bond .Chemical bond in its basic form should be a special kind of interaction between two parts, in QTAIM between the parts which are separated by IAS. Experimental evidences (X ray diffraction patterns) demonstrate the existence of higher electronic charge concentration between some nuclei. It sounds that the electron density undergoes fluctuations through the molecules. The quantum conditions which define the IASs, demonstrate that the gradient of Rho should show the fluctuations of this function better. The gradient is the vector quantity which points toward the higher value of Rho. Therefore it is better to call it the Gradient Vector Field. Small Gradient vector derived in each point of space, produced the Gradient Path (Figure 2).

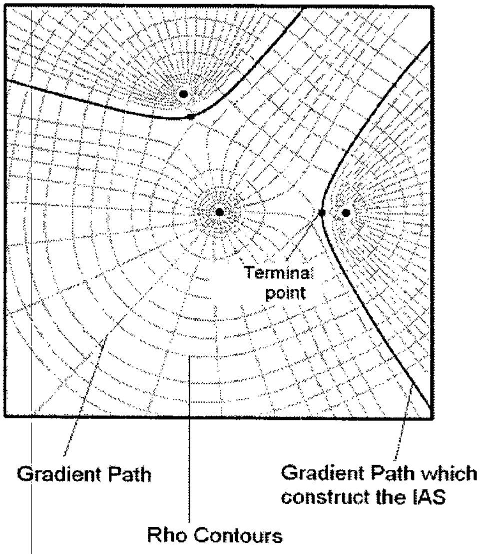


Figure 2. Gradient Vector Field of electron density , derived from MORPHY98.

Figure 2 shows that some of the gradient paths terminate at nucleus. Some of them terminate at the points between the nuclei, these Gradient paths construct the IASs therefore IASs are the bundle of Gradient paths which terminate at special point. The gradient paths have no flux across the IAS. Therefore the IAS is the zero flux surfaces. The terminal point is the point which the gradient of Rho is zero and therefore it is called the critical point. Searching the Gradient paths (GPs) between each part shows another kind of GPs. These are shown in Figure 3.

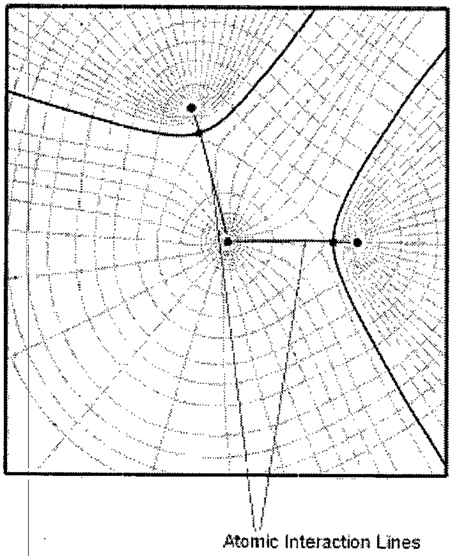


Figure 3. Interatomic surfaces and atomic interaction lines, derived from MORPHY98.

These GPs have special mathematical character. They are the only GPs which connect the Nuclei with the common IAS and the Rho value in each point of them are higher than every other neighbor GPs. They are called Atomic Interaction lines (AIL), Figure 3 .Lets go through Figure 4.

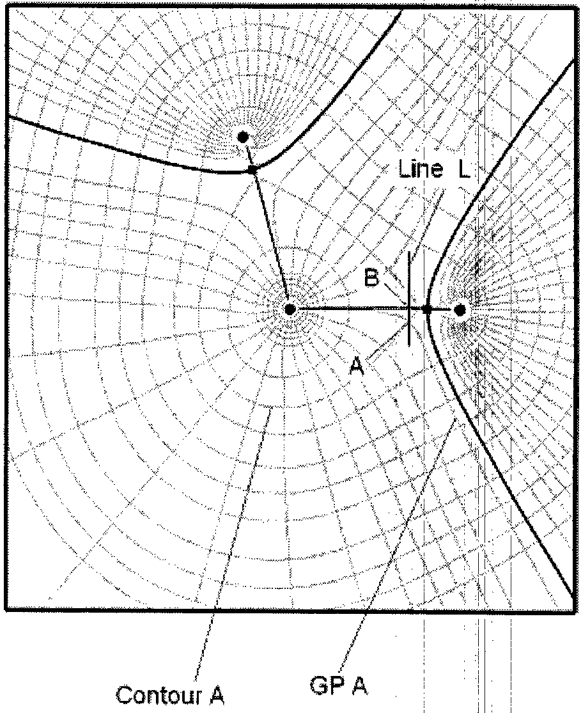


Figure 4. Gradient Paths and Atomic Interaction lines , derived from MORPHY98.

GP A, is one of the Neighbor GPs of AIL, which cross the contour A at point A on line L. Follow the line L, upward from A, we will reach to the point B on AIL. It is apparent from the figure that B locates in the inner contour than contour A and then it has the higher Rho Value.
Therefore AILs show the specific paths in space between the neighboring Nuclei which have the highest value of electron density. Therefore the second cornerstones of chemistry, i.e. specifying the pair wise interactions between the special nuclei by the network of Bonds, is nicely derived form quantum mechanics. In Equilibrium geometry the AILs are called Bond Paths[17].They are originated from a kind of critical point located in IAS , called as BCP and terminated to the corresponding nuclei .The BCPs and their corresponding bond paths construct the quantum mechanical structure of a

molecule which is called the Molecular Graph (MG) (Figure 5).

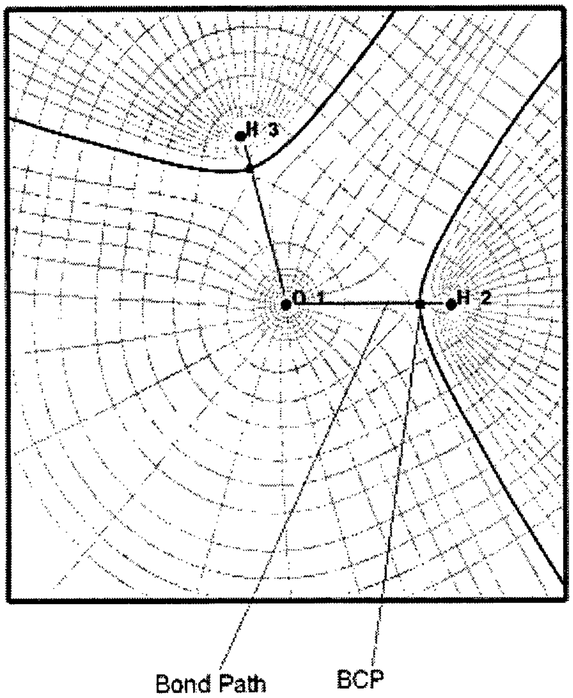


Figure 5. The Bond Path , derived form MORPHY98.

The partitioning of molecules to their constituent chemical atoms is the cornerstone of QTAIM and the concept of chemical bond and theory of structure are constructed on this base.

RESULT AND DISCUSSION

The geometrical parameters of the cited Nitrogen clusters are depicted in Figure 6.The NN inter nuclear distances in set of molecules i.e. N_2 , N_2H_2 and N_2H_4 , with the well known classical bonding schemes at the same level of computations are 1.105 , 1.243 and 1.437Å. The inter nuclear distance range is between 1.539 and 1.248 Å in Figure 6, so it is not possible to assign the bond and structure to each of the clusters clearly by comparing their NN distances to the standard values. On the other hand the NNN angles in Figure6 are outside the range of classical behavior. One apparent example is the planar geometry of N_4.While the conventional bonding models could predict the geometry of T_d with the normal tetrahedron bonds, the existence of planar rectangular geometry with the same energy is strange. Why the concept such as electron pair effect could be applicable in T_d but not in planar form?.

It is found that there is no unambiguous answers to these questions in traditional chemistry. So we switched to QTAIM approach to find out the structure and bonding patterns. The QTAIM analysis began by searching the bond critical points(BCPs) of electron density. The mathematical characters of them are gathered in Table 1. In all cases the nitrogen clusters are compose of networks of shared interactions since all the Lapalacians are negative in the location of BCPs. Although the internuclear distances are not match exactly to the standard values (as mentioned before) but the properties of electron density at BCPs are comparable.For example the ρ_b values of NN interactions in $N_4(T_d)$ are equal to that of N_2H_4 with the same sign of Lapalcians. It has to be mention that the sign and magnitude of $\nabla^2\rho_b$ is controlled by potential and kinetic energy densities which will be discussed in subsequent manuscript.The structures of cited molecules were searched via their molecular graphs(Figure7).

Bond Orders

This concept was first proposed by Dr.Popelier ,based on the mathematical properties of BCPs,in QTAIM framework. He showed that this bond order , recovers the traditional one in known molecules and produces the acceptable values in complex systems where the orbital analysis are failed. QTAIM ties the classical bond orders to their corresponding values in quantum mechanics. In this regard the NN classical bond orders in N_2 , N_2H_4 and N_2H_2 were taken as the standard ones(Table 2) to find the parameters A and B in the following equation where n is the QTAIM bond order:

$$n=\exp[A(\rho_b-B)] \quad \text{Eq.1}$$

A and B were found to be 2.738 and 0.2529 respectively.With these parameters in hand all bond orders have been computed and gathered in Table 3.The values derived from Lowdin analysis i,e, orbital analysis [18], have also been given in this table for comparison. A glance at Table3 reveals that the bond orders from orbital analysis are all nonsense. In $N_6(C_{2h})$, negative values bond orders have been obtained.

CONCLUSIONS

The structure and bonding of class of High energy density materials, i.e. Pure Nitrogen clusters,N_n(n=4,6),have been studied theoretically.Since the traditional approaches were unable to describe the two cited cornerstone of chemistry for the ab initio obtained geometries, the independent theory (based on the properties of total electron density) known as QTAIM was applied for this purpose. The connected atoms have been depicted via molecular graphs which construct the modern meaning of Structure.

The existence of Bond Path between two atoms implies the existence of bonded interaction or simply the chemical bond. A useful chemical concept is the Bond order which enables us to compare the strength of these interactions in similar situations. Modern definition of this concept has been introduced and compared with that of orbital analysis. It has been demonstrated that while the orbital analysis produce reasonable results in simple carbon containing molecules they are not reliable in other simple species such as Pure Nitrogen Clusters.

Table 1. Mathematical Characters of CPs in the Rho(r) functions at B3LYP/aug-cc-pVDZ

	CP's number	Type of CP	ρ_b **a.u**	$\nabla^2\rho_b$	Connected Atoms
$N_2(D_{\infty h})$					
	1	BCP	0.66	-2.0	**N,N**
$N_2H_2(S_2)$					
	1	BCP	0.47	-1.1	**N,N**
$N_2H_4(C_2)$					
	1	BCP	0.30	-0.6	**N,N**
$N_4(T_d)$					
	1	BCP	0.29	-0.3	**N1,N2**
	2	BCP	0.29	-0.3	**N1,N3**
	3	BCP	0.29	-0.3	**N1,N4**
	4	BCP	0.29	-0.3	**N2,N3**
	5	BCP	0.29	-0.3	**N2,N4**
	6	BCP	0.29	-0.3	**N3,N4**
$N_4(D_{2h})$					
	1	BCP	0.26	-0.5	**N1,N2**
	2	BCP	0.26	-0.5	**N4,N3**
	3	BCP	0.48	-1.2	**N1,N4**
	4	BCP	0.48	-1.2	**N2,N3**

Table 1. Continued

$N_6(D_{3h})$					
	1	BCP	0.28	-0.4	**N1,N2**
	2	BCP	0.28	-0.4	**N1,N3**
	3	BCP	0.28	-0.4	**N5,N4**
	4	BCP	0.27	-0.5	**N5,N1**
	5	BCP	0.28	-0.4	**N5,N6**
	6	BCP	0.28	-0.4	**N3,N2**
	7	BCP	0.27	-0.5	**N4,N2**
	8	BCP	0.27	-0.5	**N6,N3**
	9	BCP	0.28	-0.4	**N6,N4**
$N_6(C_2)$					
	1	BCP	0.29	-0.5	**N1,N2**
	2	BCP	0.26	-0.6	**N1,N4**
	3	BCP	0.29	-0.5	**N5,N1**
	4	BCP	0.48	-1.2	**N2,N3**
	5	BCP	0.29	-0.5	**N4,N3**
	6	BCP	0.29	-0.5	**N6,N4**
	7	BCP	0.48	-1.2	**N5,N6**
$N_6(C_{2h})$					
	1	BCP	0.56	-1.4	**N1,N2**
	2	BCP	0.43	-0.9	**N2,N3**
	3	BCP	0.29	-0.5	**N3,N4**
	4	BCP	0.43	-0.9	**N4,N5**
	5	BCP	0.56	-1.4	**N5,N6**
$N_6(D_2)$					
	1	BCP	0.4	-0.9	**N1,N2**
	2	BCP	0.4	-0.9	**N2,N3**
	3	BCP	0.4	-0.9	**N6,N1**
	4	BCP	0.4	-0.9	**N3,N4**
	5	BCP	0.4	-0.9	**N4,N5**
	6	BCP	0.4	-0.9	**N5,N6**

Table 2. The assigned values of NN bond orders and their corresponding ρ_b values, At B3LYP/aug-cc-pVD level

Molecule	$\rho_{b\ a.u}$	Assigned bond orders
N2	0.66005	3
N2H2	0.47382	2
N2H4	0.30101	1

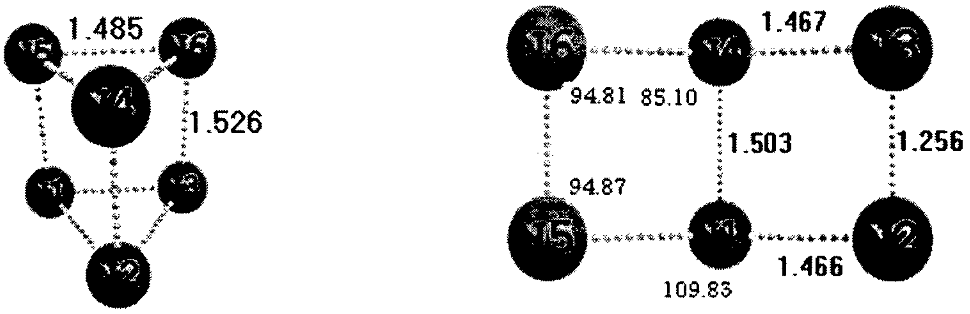
Table 3. Bond orders(BO) from QTAIM and Lowdin orbital analysis.

	Connected Atoms	BO_{Qtaim}	BO_{lowdin}
$N_4(T_d)$			
	N1,N2	1.10	0.45
	N1,N3	1.10	0.45
	N1,N4	1.10	0.45
	N2,N3	1.10	0.45
	N2,N4	1.10	0.45
	N3,N4	1.10	0.45
$N_4(D_{2h})$			
	N1,N2	1.03	0.49
	N4,N3	1.03	0.49
	N1,N4	1.85	1.03
	N2,N3	1.85	1.03
$N_6(D_{3h})$			
	N1,N2	1.08	0.44
	N1,N3	1.08	0.44
	N5,N4	1.08	0.43
	N5,N1	1.08	0.54
	N5,N6	1.08	0.44
	N3,N2	1.08	0.43
	N4,N2	1.08	0.54
	N6,N3	1.08	0.54
	N6,N4	1.08	0.44
$N_6(C_2)$			
	N1,N2	1.12	0.57
	N1,N4	1.10	0.51
	N5,N1	1.12	0.57
	N2,N3	1.86	0.93
	N4,N3	1.12	0.57
	N6,N4	1.12	0.57
	N5,N6	1.86	0.94
$N_6(C_{2h})$			
	N1,N2	2.31	-0.7
	N2,N3	1.63	0.07
	N3,N4	1.12	0.65
	N4,N5	1.63	0.06
	N5,N6	2.31	-1.3

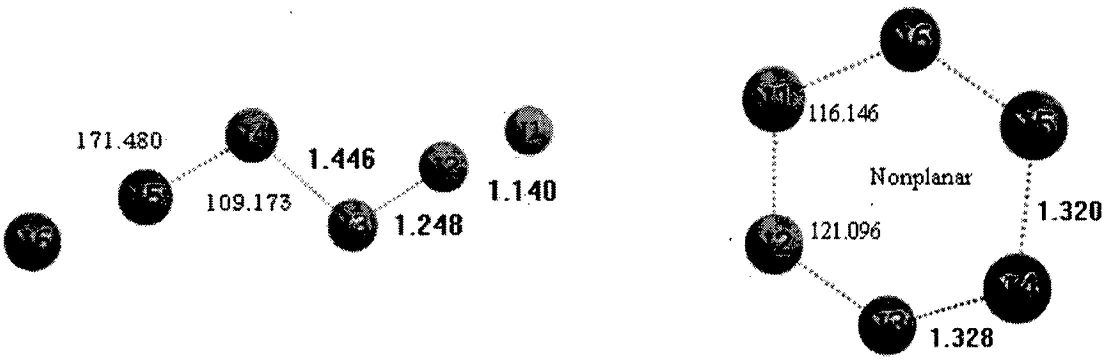
Table 3. Continued

$N_6(D_2)$			
	N1,N2	1.50	0.67
	N2,N3	1.50	0.65
	N6,N1	1.50	0.5
	N3,N4	1.50	0.5
	N4,N5	1.50	0.65
	N5,N6	1.50	0.66

1) -218.7058 a.u (T_d) 2) -218.7079 a.u (D_{2h})



3) -327.9931 a.u (D_{3h}) 4)-328.12932 a.u (C_2)



5) -328.2253 a.u (C_{2h}) 6) -328.1861 a.u (D_2)

Figure 6. Geometrical parameters,Distances(Å), Angles(°) and total energies of N_n(n=4,6) clusters at B3LYP/aug-cc-pVDZ.

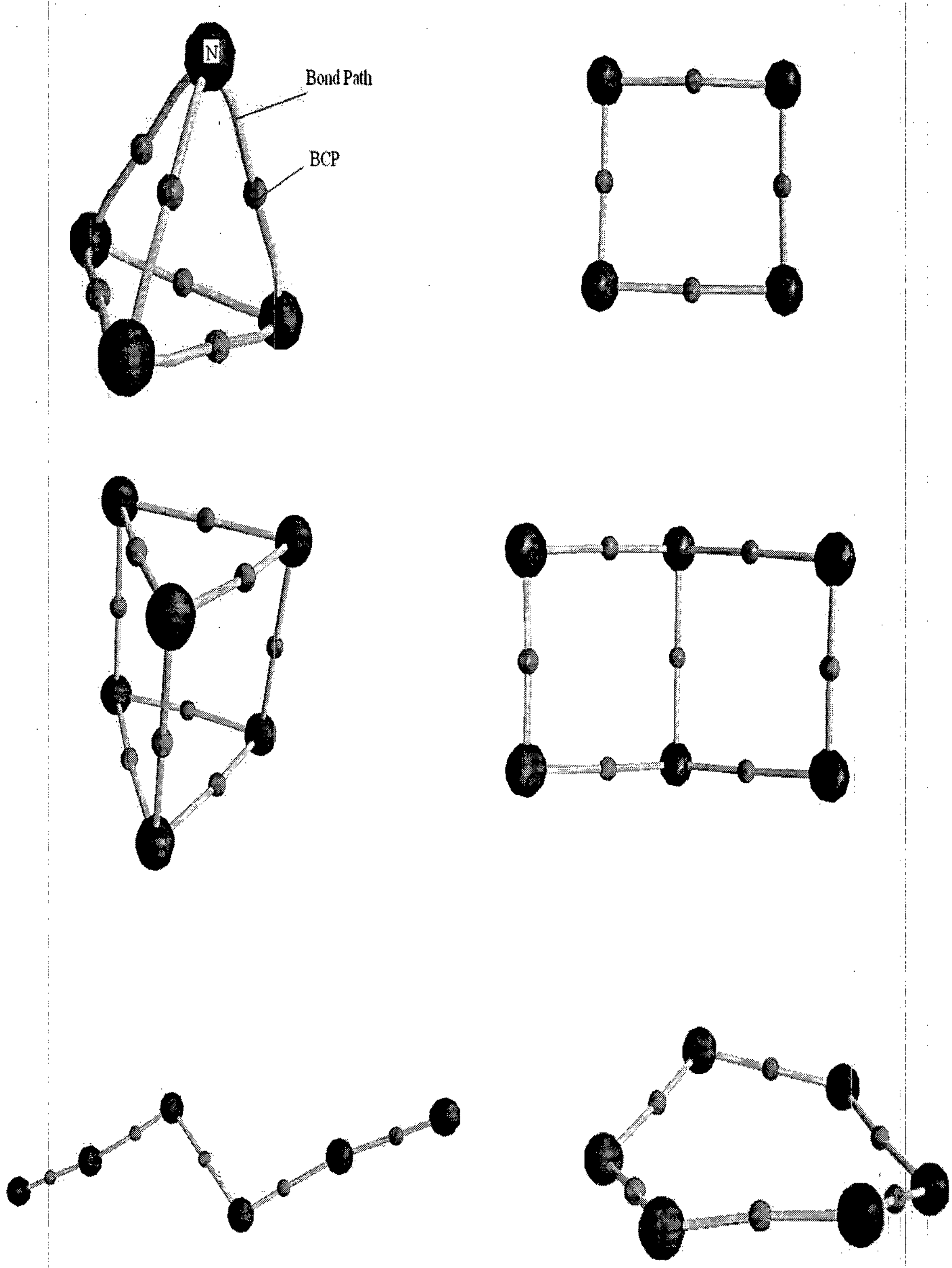


Figure 7. Molecular Graphs of N_n(n=4,6) from AIM2000 at B3LYP/aug-cc-pVDZ .Large circles are the Nitrogen nuclie Dark small circles are BCPs,lines are Bond Paths.

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