



APPLICATION OF AB INITIO MOLECULAR-ORBITAL CALCULATIONS TO THE STRUCTURAL OF MINOMETHANEPHOSPHINE

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Abstract

Ab initio RHF/3-21G molecular-orbital calculations have been performed on Amionmethane phosphine as bidentate ligand. The results give a value of -434.24014 kJ/mol for total energy, 14.60768 eV for HOMO/LUMO gap and 4.9640 for LUMO energy. The calculations also predicate the symmetry point group and dipole moment (D) of molecule which were C₁ and 2.0911 respectively. However, the angles and bond length were calculated as well. The charges and ionization energy for molecules were calculated; the results give a values of 1st ; 9.645 , 2nd ; 15.24 and 3rd ; 23.26 eV .

Key works: Ab initio, molecular geometry, total energy calculations.



Introduction

Synthesis and characterization of chemical materials for whatever purpose of use is a tedious expensive and hazardous process.¹ It may be possible to consider its chemical and physical properties by computer simulation which provide researchers by: accelerate research and development of such materials, reduce the costs of synthesis. These characterization of target materials depend upon properties as molecular structure and reaction energy that predicted with computational chemistry techniques which use molecular orbital modelling. The methods of techniques can be classified to: (a) *Ab initio* method; (b) semi-empirical method; (c) molecular mechanics method. All of these computational techniques based on theoretical and mathematical postulates which applied and calculated within computer.² However, *ab initio* or 'first principles' electronic structure methods one of the most important molecular models; *ab initio* method is based upon the principle of quantum mechanics and very computer-intensive.³ Using *ab initio* molecular orbitals methods some of the molecules and reactions properties can be predicted. Heat of formations; bond and reactions energies; vibrational frequency (IR and Raman spectra); electronic transitions (UV / Visible spectra); magnetic shielding effects (NMR spectra of chemical shift)⁴ all of these properties and more can be possibly predicted using the *ab initio* calculation. The advantages for calculations have many applications such as studies of synthesis pathway, reaction product, initiation mechanisms, and exhaust plume signature. *Ab initio*-electronic structure methods has ability to consistent predications with high accuracy (± 20 kJ/mol) due to they provide the best mathematical approximation to the actual system. Many efforts have been done to solve Schrödinger equation as the basis of this kind of calculation. Density functional theory (DFT) was established in 1980s as convenient method to solve the Schrödinger equation which became one of the standard tools in quantum chemistry and are particularly widespread in computational science.³

Experimental section

Computer Acer with special characterizations.

Windows XP.

Hyperchem 7.0 software.

Chemoffice Ultra 7.0.

Office XP.

Results and discussion

The Molecular orbital calculations. Closed-shell, restricted Hartree-Fock theory was used with a 3-21G basis set for the energy calculations shown in Table I. The calculations were made on Acer computer, using HYPERCHEM 7.0.⁵ Structure of molecule in Figure 1 was built up using hyperchem 7.0 .

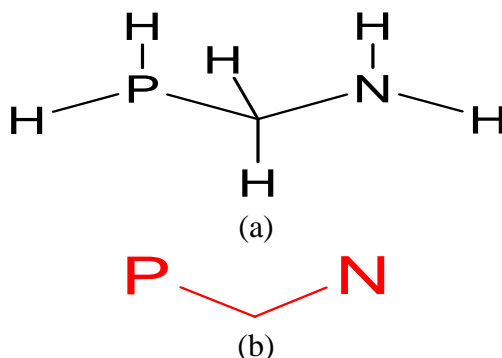


Figure 1.(a)Structure of molecule with H-atoms;(b) Structure of molecule without H-atoms.

The calculations were performed with optimization by means of point-by-point energy calculations. These results are shown in Table 1. The calculations were performed with standard bond and tetrahedral valence angles NCP 106.87 which agreed with the typical tetrahedral geometry which shows the two H-atoms attached to carbon are lies in different position from N-atom and P-atom lone pairs one is nearer to nitrogen and other nearer to phosphorus lone pair; the methylene groups are perpendicular to one of phosphine group; the two hydrogen atoms of CH₂ are lies in different position form lone pairs of Nitrogen and phosphorus which is one lone pair nearer to N-lone pair and other nearer to P-lone pair.

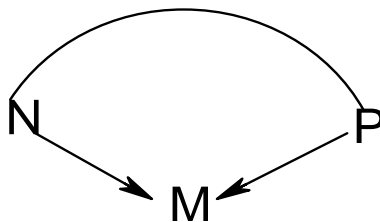


Figure 2. The bite angle of molecule.

The charges of the atoms are listed in Table 2. Charges and geometries are so related. Charges of target molecule is as expected . the difference between P-charge and H-charge is 0.028.The H/L gap have been used as a good reference for measuring the stability of many species. The total energy and H/L, LUMO energy are listed in Table 3. The 1st , 2nd and 3rd ionization energy for PH₂CH₂NH₂ listed in table 4 is appeared at 9.645 eV, 15.24 and 23.26 respectively.

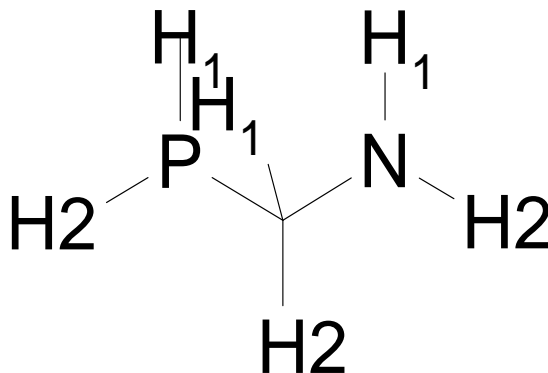


Figure 3. The charges labels of atoms.



The designed molecule $\text{PH}_2\text{CH}_2\text{NH}_2$; may be used as ligand coordinate with different kind of metal ions which its both steric bite angle effect and the electronic bite angle could effects its ability to form stable complex.⁶ The steric bite angle effect involves the steric interactions between ligands or between a ligand and a metal ions. The electronic bite angle effect, on the other hand, relates to the electronic changes that occur when the bite angle is modified. This effect is sensitive to the hybridization of metal orbitals.⁷ This flexibility range accounts for the different conformations of the ligand with energies slightly above the strain energy of the natural bite angle.

Table (1). The bond length(Å) and bond angles (°).

	P-H	P-C	N-C	C-H	N-H	NCP
$\text{NH}_2\text{CH}_2\text{PH}_2$	1.4206	1.9121	1.48182	1.08711	1.0036	106.87
	1.4283	-	-	1.07978	1.0038	-

Table (2). The charges of atoms.

C	H _{C1}	H _{C2}	P	N	H _{P1}	H _{P2}	H _{N1}	H _{N2}
-0.538	0.201	0.239	0.355	-0.786	-0.058	-0.029	0.355	0.306

Table (3). The energy, HOMO-LUMO gap and LUMO energy (ev).

Energy	H/L gap	LUMO energy
-434.24014	14.60768	4.9640

Table (4). The 1st, 2nd and 3rd ionization energies.

1 st	2 nd	3 rd
9.6436	15.243	23.2565

Table (5). The point group and dipole moment .

Point group	Dipole moment (D)
C ₁	2.0911

Conclusion

Electronic structure calculations provide useful estimates of the energetic properties of the designed ligand, including its ability as bidentate ligand to bite the metal ion under specific bite angle.

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