AL-TAHADI UNIVERSITY
FACULTY OF SCIENCE
DEPARTMENT OF CHEMISTRY
SERIT- LIBYA

AB INITIO MOLECULAR ORBITAL STUDY OF AMINOMETHANE PHOSPHINE AND THEIR HALIDES DERIVATIVES.

THIS THESIS SUBMITTED AS PARTIAL
FULLFILLMENTS FOR THE
REQUIRMENTS OF THE DEGREE OF MASTER OF SCIENCE IN
CHEMISTRY
BY
ADEL MANSOR HAMAD NAJAR
SUPERVISOR:
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2005

إن الدراسة ليست غاية في حد ذاتها
وإنما هي خلق الإنسان نموذجي الجديد

G.S.P.L.A.J.
AL - TAHDI UNIVERSITY

الرقم الإشاري : ....

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التاريخ : ....
الموافق : ....

Faculty of Science

Department of Chemistry

Title of Thesis

((AB INITIO MOLECULAR ORBITAL STUDY OF AMINO METHANE PHOSPHINE AND THEIR HALIDE DEERIVATIVES))

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بِسۡمِ ٱللَّهِ ٱلرَّحۡمَٰنِ ٱلرَّحِيمِ

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إِلَى ٱلنُّورِۖ وَٱلَّذِينَ كَفَرُوٓاْ أَوۡلِيَآؤُهُمُ ٱلطَّٰغُوتُ يُخۡرِجُونَهُم
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خَٰلِدُونَ ٢٥٧

صدق الله العظيم

سورة البقرة الآية رقم 257

DEDICATION

TO THOSE CLOSEST TO ME
PARENTRS
BROTHERS
SISTERS
CHILDREN《ALHASSAN&FATEMA》
& MY WIFE.

Abbreviation

HF = Hartree- Fock .
SCF = Self consistent field .
3-D = Three - Dimension .
STO = Slater Type Orbital .
STO$_S$ = Slater Type Orbitals.
ZDO = Zero differential orbital .
CNDO = Complete neglect of differential overlap.
INDO = Intermediate neglect of differential overlap.
MINDO = Modification neglect of differential overlap.
MO = Molecular orbital.
MO$_S$ = Molecular orbitals.
AO = Atomic orbital.
AO$_s$ = Atomic orbitals.
AM1 = Austin model 1.
PM3 = Parameterized model 3.
RHF = Restricted Hartree-Fock.
M.D.S = Molecular dynamic simulation .
L.D.S = Langevin dynamic simulation .
MOT = Molecular Orbital Theory.
GTO = Gaussian Type Orbital.
IP = Ionization potential .
HOMO = High occupied molecular orbital .
LUMO = Low unoccupied molecular orbital.
LACO = Linear combination of atomic orbital.

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ACKNOWLEDGMENT

In the name of God most Gracious most Merciful

First of all , I give my prayerful to Allah who helped me to complete this work. It's with a deep sense of gratitude that I am so grateful to my supervisor

Ass.prof. Abdul Hakeem Ahmed

For his close supervision, guidance, advice, courteous support and helpful comments throughout all stages of this work.. Without him the thesis wouldn't have been possible.

Also I wish to think **Dr. Salima Ben Guzzi.** for her help.

Above all, I am highly indebted to my parents, wife and my brother Fowzi who constantly supported me through their kindness and prayers.

Finally, my thank go to **AL-TAHADI UNIVERSTY** and the Chemistry department for offering me this opportunity to submit my **M.Sc.** thesis in Chemistry.

Adel najar

ABSTRACT

Computational methods have been extensively used in chemistry, and have shown very fascinating results. In this work we used Ab initio calculations to study the stability of some Amino methane phosphine derivatives. The hyperchem package has been used with 3-21G basis set. We calculated the following parameters: Geometries, charges electronic densities, total energies, HOMO-LUMO gap, LUMO energies, ionization energies (1^{st}, 2^{nd} and 3^{rd}) and dipole moments.

Based upon the parameters considered, our investigations proved that the most stable species is $PH_2CH_2NH_2$. The molecules PH_2CHFNH_2, $PHFCH_2NH_2$ and PH_2CH_2NHF also showed a little stability in association with their counterparts species in the classes .

الخلاصة

استخدم في هذا العمل طريقة(AB INITIO) و ذلك من خلال برنامج HyperChem. الإصدار 7.5 لحساب استقرارية الجزيء امينو ميثان فوسفين و مشتقاته الهاليدية باستخدام دالة غاوس الأساسية 3-21G لحساب المتغيرات الآتية:

1. الاشكال الهندسية (التركيبات البنائية) .
2. الشحنات .
3. الكثافات الإلكترونية .
4. الطاقات(الطاقة الكلية وطاقة المدرات بأنواعها) .
5. طاقات التأين الأولي والثانية والثالثة .
6. العزم ثنائي القطب .

وبناء علي تلك الحسابات ومن خلال النتائج المتحصل عليها استنتج بأن الجزيء امينو ميثان فوسفين هو الجزيء الأكثر استقرارا بين تلك الجزيئات العديدة التي تم أخذها في الحسبان كمدخلات في البرنامج ولذلك يمكن استخدامه كمتصلة ثنائية السن . كما أظهرت الدراسة ان الجزيئات PH_2CH_2NHF, PH_2CHFNH_2, $PHFCH_2NH_2$ اكثرها استقرارية و قريبة الي حد ما من استقرارية الجزيء $PH_2CH_2NH_2$.

CHAPTER

I

INTRODUCTION

INTRODUCTION

Phosphorus lies directly below nitrogen in the periodic table its valence shell is similar to the electron configuration of nitrogen [1], consequently one might expect that the chemistry of these two elements to be similar [2]. But beyond the similarity in stoichiometeries of compound such as NH_3,PH_3[1], it has been known that the chemistry of phosphorus and nitrogen compound showed many differences . For example, despite the fact that the similarity in stoichiometry of NH_3 and PH_3 electronically there is a clear differences in IP_S and total energies count [3].There is a little resemblance in the chemistry between P and N [1].In the comparison between NH_3, PH_3 , the P-H bond is longer than the N-H bond and therefore the electron density is less at phosphorus atoms due to its lower electronegativity than nitrogen , the electron density is concentrated nearer the hydrogen in P-H than in N-H. Both these factors mean that there is less electron density at the phosphorus atom in the P-H bond than in the case of nitrogen in NH_3 , and therefore the HPH angle in PH_3 is much more drastically reduced by the lone pair repulsion [4]. Phosphines are more pyramidal than amines, but there is considerable variation in the bond angles about phosphorus atom . Trimethyl phosphine has a <CPC angle of 99°, some what expanded from <HPH angle of 93°in phosphine itself.

Triphenyl phosphine has CPC angles of 103°.Since phosphine are analog. of amine, we expect the phosphorus lone pair show characteristic basic properties.

Phosphine do act as Lewis base,but the base strength is strongly dependent on structure, particularly on bond angle variation between the pyramidal phosphine and tetrahedral phosphonium salt. Phenyl phosphines are less basic than alkyl compounds. Tertiary phosphines also act as good donor ligand toward metals and are commonly used in the preparation of organometallic complex such as:

$[C_9H_7\ Fe\ (CO)\ (\ P(Ph)_2\text{-}CH_2\text{-}P(Ph)_2)]\ BF_4$ [5].

Bidentate phosphines with only one bridging group such as $Ph_2P(CH_2)_2PPh_2$ and $CH_3N(PF_2)_2$ tend to metal-metal interaction or bond formation because the two donor P-atoms are so close to gather, the use of chelate phosphine with many bridging groups gives long flexible chains has quite a different effect[6].

Ammonia has a pyramidal shape, The rN-H length is 1.008 Å and the HNH bond angle is 107.3° .The hybridization of nitrogen is approximately sp^3 . It forms three approximation sp^3-σ- bonds to hydrogen and has a nonbonding electron pair that occupies the other approximately sp^3- orbital. The nonbonding electron pair is important in chemistry of amines, since it is responsible for the typical basic and nucleophilic properties of these compounds .Amines that have an aryl group attached to nitrogen are characterized by somewhat large <HNH and <HNC angles; that is, the nitrogen is more nearly planar than in alkyl amine[5].

The construction of rP-C bond in organophosphours is often difficult and their preparation usually require tedious steps establishing the need for easier protocol compound[2].

The computational chemistry aims to solving chemically related problems by means of calculation, the goal for the computational chemistry is to understand and to predict chemical properties in term of electronic structure [7].

Fewer theoretical studies has been reported for Bis(diphosphino)methane. Lapper and coworker have studied the above molecule in detail both experimentally, by electron diffraction, and theoretically by an ab intio calculations.The theoretical results showed a good agreement with the experimental one. The substituted diphosphines ligand has been reacted with organometallic compound namely $[C_9H_7Fe(CO)_3]BF_4$.

The reaction of $\Phi_2PCH_2P\Phi_2$ (dppm) with $[C_9H_7Fe(CO)_3]BF_4$ resulted in three different compounds.

The $[\eta^5\text{–}C_9H_7)Fe(CO)\ \eta^2$ dppm] BF_4 ,The ^{1}H-NMR for the $-CH_2$ showed four very interesting features , which appeared as nonequivalent one proton on observed at $\delta = 5.16$ ppm as a sextet and other at $\delta=4.31$ppm also as sextet, both being split by other J= 12.09Hz and by phosphorus atom J= 10.44 Hz[8].

Chang and coworker has been investigated hydrogen bond effects of $H_2PCH_2PNH_2$ and related species using ab initio molecular orbital treatment [9].

We are going to use a similar molecules, i.e halide substitute has been constructed, $X_2PCX_2NX_2$ (where X= H, F, Cl).

Also , Hakeem and coworker previously carried out some calculations, on $X_2PMX_2PX_2$ (X= H, F, Cl), (M= C, Si) [3].

Borisenko and coworker studied the energetic and structure changes in tetramethyl diphosphines and tetrasilyl diphosphine by using ab initio MO calculation [10], Lohr and Ahrens used ab initio method for study the characterizations of P-P bonds in model diphosphours compounds in which the two directly bonded phosphours atoms are bridged by one or two urea group [11].

1.1. Atomic Orbitals:

We all know that an atom is made up of electrons, protons and neutrons. In addition, we know that the neutrons and protons are what make up the nucleus which the electrons orbital. In chemistry, we want to be able to locate and characterize the electrons. To do this we must think about the electron in three-dimensional space. Quantum numbers is a method that scientists use to describe the location of an electron. There are three quantum numbers, n, l, and m_l, which represent each of the three dimensions. All quantum numbers are always integers.

"n" is the principle quantum number and can range from 1 to infinity. This value is the best estimate of the electrons distance from the nucleus. The value of "n" also defines the electron shell. Therefore, more than one electron can have the same "n" value. "l" is the angular momentum quantum number. As "n" was used to define the electron shell, "l" is used to define the electron sub shells.

"l" values can range from 0 to "n-1," in addition, each "l" value is assigned a label or name of the sub shell which it represents. Below is a table of the first four sub shells. The first three sub shells are labeled according to the types of lines produced in the spectrum. After the fourth sub shell, the labels proceed in alphabetical order.

Last is the "m_l" which is the magnetic quantum number. This number can range from negative to positive "l" including zero. "m_l" represents the orbital within a subshell. The orbitals within a subshell are the same shape but different orientation. This brings up another point...the shapes of orbitals. Each orbital has a characteristic shape. The s, p, and d orbitals are shown below. Notice that the orbitals are not straight paths, but more like clouds. This shows us that electrons do not stay on one path around the nucleus. Instead, they move around the nucleus in a given region or "orbital." The probability of locating an electron is the greatest around the nucleus because that is where the attraction is strongest. The size of the orbital increases with the value of "n", the electron's distance from the nucleus. Also, observe the symmetry in these orbitals [12].

Value of l	**Corresponding Subshell Label**
0	s (sharp)
1	p (principal)
2	d (diffuse)
3	f (fundamental)
4	g

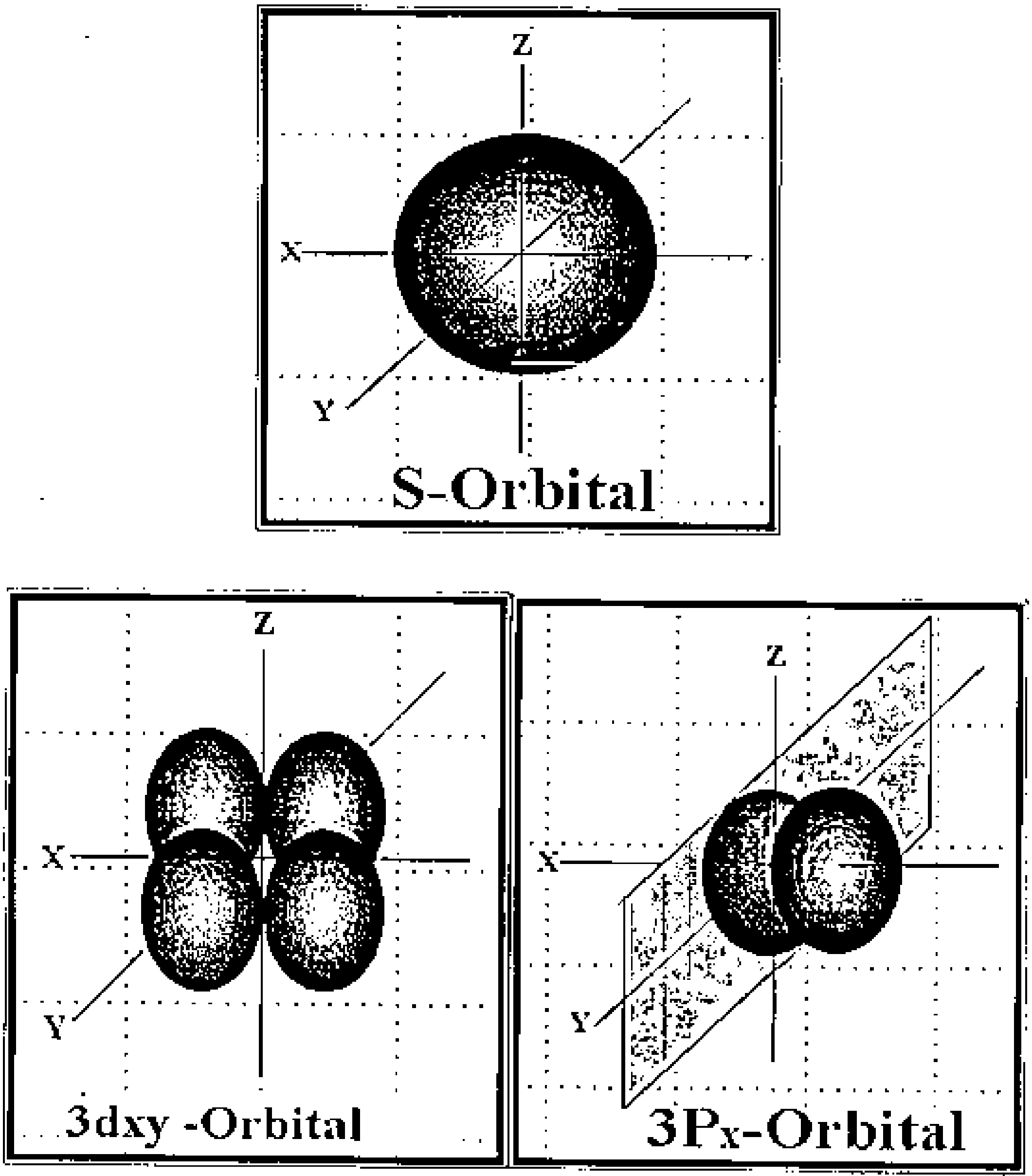


Fig.(1.1): The s, p, and d orbitals

1.1.2. Overlap of atomic orbitals:-

If two atoms approach each other closely enough for one orbital on each atom to have appreciable amplitude in a region of space common to both of them , the orbitals are said to overlap. The magnitude of the overlap may be positive, negative, or zero, according to the properties of the orbitals concerned.

Overlap has a positive sign when the superimposed regions of the two orbital have the same sign, both (+) or both (-) . Overlap has a negative sign when the superimposed regions of the two orbitals have opposite signs . precisely zero overlap results when three are precisely equal regions of overlap with opposite signs.

The physical reason for the validity of the overlap criterion is straightforward. In a region where two orbital, Φ_1 and Φ_2 ,have positive, overlap the electron density is higher than the mere sum of the electron densities of the two separate orbitals. That is, $(\Phi_1 + \Phi_2)^2$ is greater than $\Phi^2_1 + \Phi^2_2$,by $2\Phi_1\Phi_2$. More electron density is shared between the two atoms. The attraction of both nuclei for these electrons is greater than the mutual repulsion of the nuclei, and a net attractive force or bonding interaction therefore results [1].

1.1.3. MO Interactions:-

When two chemical species (atoms or molecules) come together, we can understand the new molecular orbitals(and their energies) in terms of the orbitals(and their energies)of the separated species. The interaction of an orbital of one species with an orbital of the other generates two new orbitals, one a favorable (bonding)combination, which is lower in energy than either of the separate orbitals , and the other an unfavorable (antibonding) combination, which is higher than either of the separated orbitals. The amount by which the energies shift depends on overlap and energy match between the mixing orbitals. To get an idea of the tendency of the two species (let's call them molecules A and B) to stick together, we can check the interactions of all pairs of orbitals (their overlap and energy match) and see whether there is a way to lower the total energy from that of the separated molecules. Each molecule has so many orbitals that it looks like a daunting task to consider all possible pairs of orbitals between A and B and to decide what the overall effect on energy should be of bringing A and B together. Fortunately most interactions are irrelevant, and usually it is possible to focus on just one or two orbital interactions to decide whether two molecules should react with one another.

1.1.4. HOMO-LUMO Interaction:-

Every molecule has a highest occupied molecular orbital (HOMO) and a lowest unoccupied molecular orbital (LUMO). Sometimes the HOMO is not only the highest in the molecule but is unusually high, like the one indicated in red on the near right. Sometimes the LUMO is unusually low, like the one indicated in red on the far right. Because there is reasonable energy match between this HOMO and this LUMO, there can be substantial lowering in energy. If this is enough to overcome reaction partner and an unusually low LUMO in the other. Note that in the case on the right molecule A is reactive because of its unusually high HOMO (It's LUMO is nothing special). Molecule B is reactive because of it's unusually low LUMO(It's HOMO is nothing special).

By predicting which molecules should have unusually high HOMOs and which should have unusually low LUMOs we can recognize functional groups, and predict which functional groups should react with one another. Once we learn to identify unusually high HOMOs and unusually low LUMOs we'll be in great shape[13].

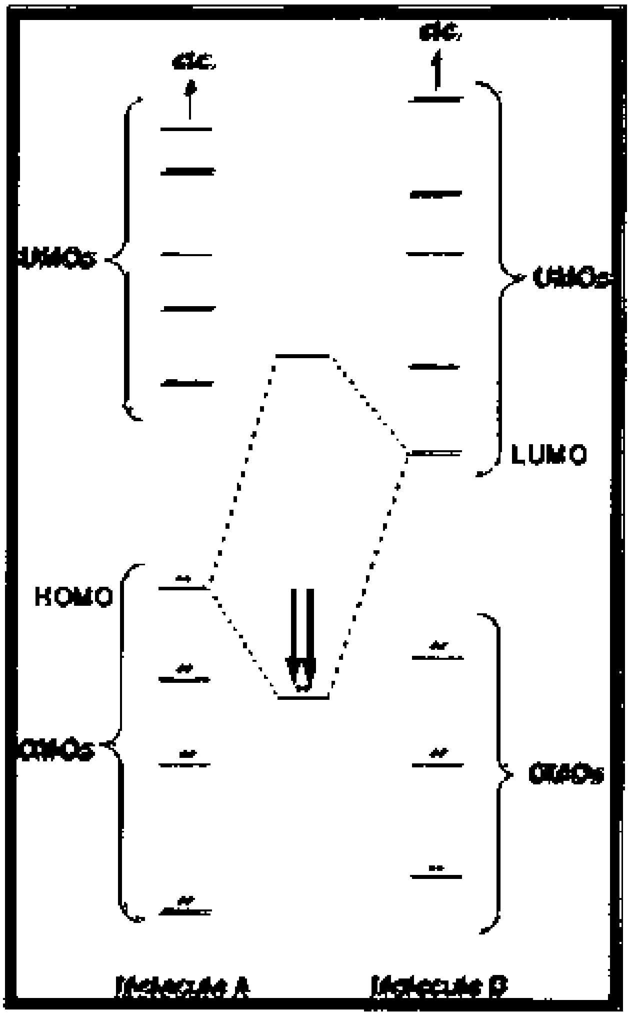


Fig.(1.2): HOMO-LUMO MO Interaction

1.2. Symmetry and structure:

Molecular symmetry and ways of specifying it with mathematical precision are important for several reasons .The most basic reason is that all molecular wave function-those governing electron distribution as well as those for vibrations, NMR spectra ,and so on-must conform, rigorously ,to certain requirements based on the symmetry of the equilibrium nuclear framework of the molecule. When the symmetry is high these restriction can be very severe. Thus from a knowledge of symmetry alone it is often possible to reach useful qualitative conclusion about molecular electronic structure and to draw inferences from spectra about molecular structure . The qualitative application of symmetry restrictions is most impressively illustrated by the crystal-field and ligand-field theories of electronic structure of transition metal complexes. A more mundane use for the concept and notation of molecular symmetry is in the precise description of a structure .One symbol ,such as D_4h, can convey precise, unequivocal structural information that would require long verbal description to duplicate.Thus if we say that the $[Ni(CN)_4]^{2-}$ ion has D_4h symmetry, we imply that (a) It's completely planar , (b)The Ni-C-N groups are all linear, (c)The C-Ni-C angles are all equal, at 90°, (d) The four CN groups are all precisely equivalent to one another, and (e) The four Ni-C bonds are precisely equivalent to on another. The use of symmetry symbol has become increasingly common in the chemical literature, and it's now necessary to be familiar with the basic concepts and rules of notation to read many of the contemporary research paper in inorganic and, indeed, also organic chemistry with full comprehension[6].

1.3. Computational chemistry :

Computational science (computational, physics, chemistry, biology, etc...), which is distinct from computer science, emerged in recent years as a third way of doing science, besides experimental and theoretical. It uses computer to perform extremely complex calculation or simulation, the outcome of which could never be guessed a prior even when the underlying theory is well known and the equation simple [14]. Computational science is the application of computational and numerical techniques to solve large and complex problems. Computational science takes of not only the improvements in computer hardware, but also probably more importantly, the improvements in computer algorithms and mathematical techniques. Computational science allows us to do things that were previously too difficult to do due to the complexity of the mathematics, the large number of calculations involved, or a combination of the two.Computational science also allows us to build models that allow us to make predictions of what might happen in the lab, so that we are perhaps better prepared to make good observations or to understand better what we are seeing. We can also use computational techniques to perform experiments that might be too expensive or too dangerous to do in the lab. There are many definitions of computational science most of them describe it as "an inter disciplinary approach to the solution of complex problems that uses concepts and skills from the disciplines of science, computer science, and mathematics ". Of considerable importance is your understanding that the study of computational science is not computer science computational science is a methodology that allows the study of various phenomenons. We consider computational science to be a fourth method of doing research, an addition to observational, experimental, and theoretical methods [12]:

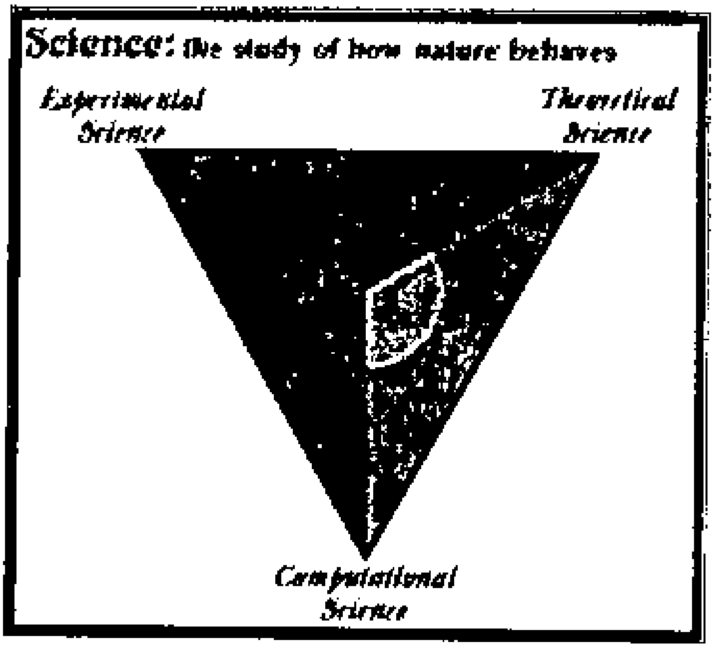


Fig.(1.3):Relations between computational , theoretical and experimental science

Computational chemistry is simply the application of,chemical mathematical and computing skills to the solution of interesting chemical problems. It uses computers to generate information such as properties of molecules or simulated experimental results. Computational chemistry has become a useful way to investigate materials that are too difficult to find or too expensive to purchase. It also helps chemists make predictions before running the actual experiments so that they can be better prepared for making observations.

The Schrödinger equation (explained in another section) is the basis for most of the computational chemistry scientist's use. This is because the Schrödinger equation models the atoms and molecules with mathematic [12]. Example is computing precise energy difference for relatively large molecules. Typically, the trial wave function and the Schrödinger equation is cast in matrix form. The matrixes involved in a typical calculation can be 200 x 200 ,some SCF calculation have been performed involving matrixes with more than a thousand rows and columns . The results can not be guessed without diagonalzing such matrixes which is clearly impossible without a powerful computer. As Computer becomes more powerful and accessible and as chemists developed better algorithms and software a larger variety of problems in chemistry can be tackled by computational methods. Not so long, computational chemistry was, almost synonymous with quantum chemistry but this is not longer true. Today computational methods are used in chemistry to study electronic structure by matrix equation and others. To predict the properties of non-existent molecules that look interesting candidates for synthesis by searching and analyzing huge databases of known molecular structure and properties [14].Currently, there are two ways to approach chemistry problems: computational quantum chemistry and non-computational quantum chemistry. Computational quantum chemistry is primarily concerned with the numerical computation of molecular electronic structures by ab initio and semi-empirical techniques and non-computational quantum chemistry deals with the formulation of analytical expressions for the properties of molecules and their reactions[12]. The real strength of computational chemistry is the ability to generate data (for example by analyzing the wave function) from which is chemist may gain insights and thereby rationalize the behavior of a large class of molecules. Such insights and rationalization are much more likely to be useful over a larger period than the raw results themselves. A good example is the concept used by organic chemistry with molecules composed of functional groups, and representing reactions by"pushing electrons".This may not be particularly accurate from a quantum mechanical point of view, but it is very effective in rationalizing large body of experimental result, and has a good predictive power [15].

1.4. What is HyperChem?

HyperChem is a sophisticated molecular modeling program that is known for it's quality ,flexibility ,and ease of use HyperChem.unites 3-D visualization and animation with quantum chemical calculation,molecular mechanics and molecular dynamic . HyperChem puts more molecular modeling tools at your fingertips than any other windows program [16].

1.4.1. Calculation methods with HyperChem.

HyperChem. Uses two types of methods in calculations: molecular mechanics and quantum mechanics. The quantum mechanics methods implemented in HyperChem include semi-empirical quantum mechanics and ab initio quantum mechanics method . The molecular mechanics and semi-empirical quantum mechanics methods have several advantages over ab initio methods. Most importantly, these methods are fast .While this may not be important for small molecules, it's certainly important for biomolecules. Another advantage is that for specific and well-parameterized molecular system, these methods can calculate values that are closer to experimental than lower level ab initio techniques.

1.4.2. Types of calculation in HyperChem :-

There are three types of calculation in HyperChem : single point, geometry optimization , and molecular dynamic

I. Single point calculation :-

A single point calculation gives the static properties of a molecule. The properties include potential energy, derivatives of the potential energy, electrostatic potential, molecular orbital energies, and the coefficients of molecular orbitals for ground or excited states.

The input molecular structure for a single point calculation usually reflects the coordinates of a stationary point on the potential energy surface, typically a minimum or transition state.

II. Geometry optimization :-

To carry out a geometry optimization, HyperChem start with a set of Cartesian coordinates for a molecule and tries to find a new set of coordinates with a minimum potential energy. You should appreciate that the potential energy surface is very complex, even for a molecule containing only a few dihedral angles.

Since minimization calculation can't cross or penetrate potential energy barriers, the molecular structure found during an optimization may be a local and not a global minimum. The minimum represents the potential energy closest to the starting structure of a molecule. Researchers frequently use minimizations to generate a structure at a stationary point for a subsequent single point calculation or to remove excessive strain in a molecule, preparing it for a molecular dynamics simulation.

III. Transition state searching :-

As mentioned earlier, a potential energy surface may contain saddle point; that is , stationary points where there are one or more directions in which the energy is at a maximum . A saddle point with one negative eigenvalue corresponds to a transition structure for chemical reaction involving separated species. Calculated transition structure may be very sensitive to the level of theory employed .Semi-empirical methods, since they are parameterized for energy minimum structures , may be less appropriate for transition state searching than ab initio methods. Transition structures are normally characterized by weak "partial "bonds, hat is , being broken or formed .In these cases UHF calculations are necessary , and sometimes even the inclusion of electron correlation effects[17].

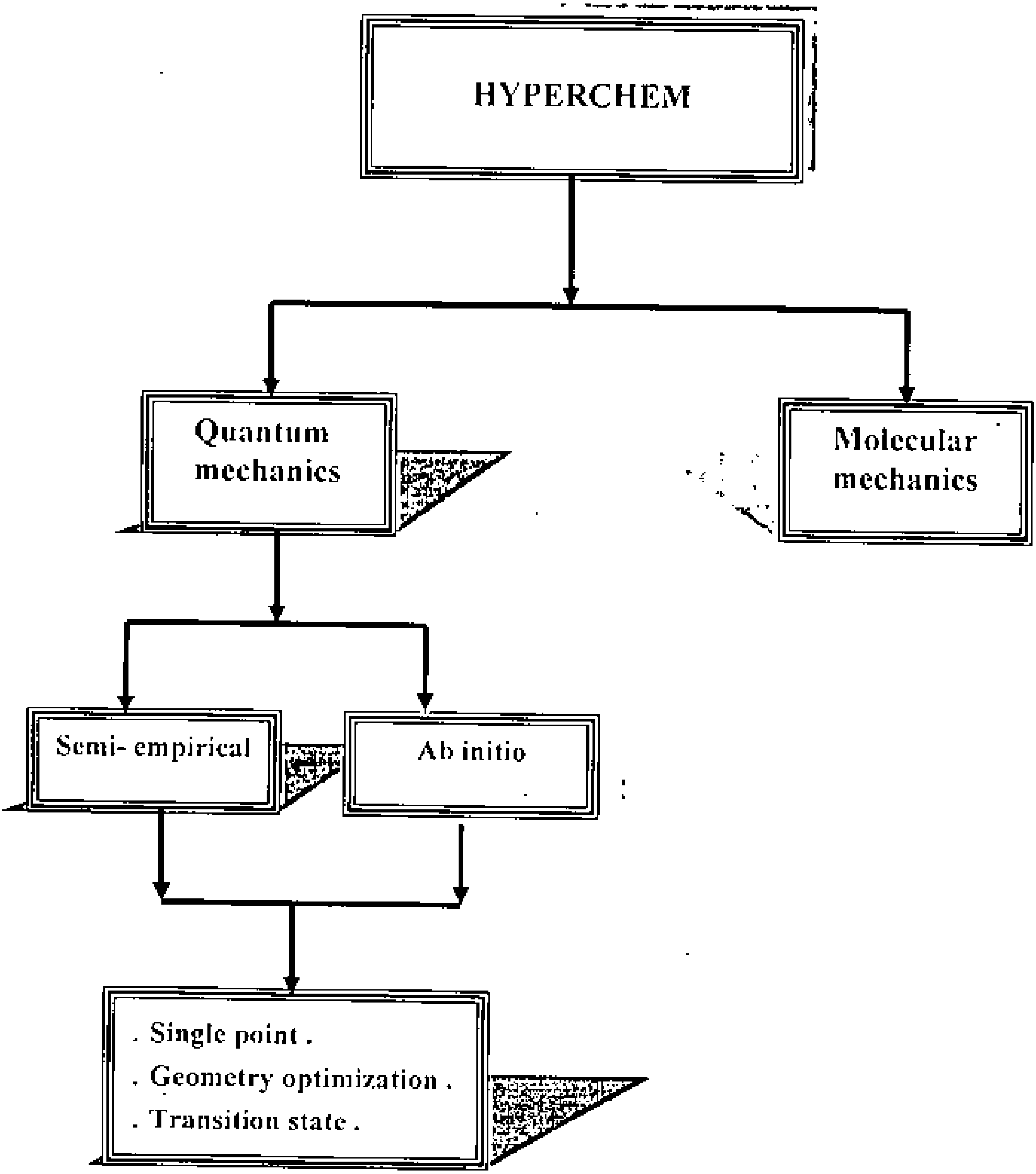


Fig. (1.4): Methods of calculation based on HyperChem.

1.5. The Schrödinger equation:

Historical note

It is interesting to note that the first systematic approach to what we now call quantum mechanics was made by Heisenberg , who began to develop his own algebra to describe that the frequencies and intensities of spectral transition . It was soon seen the new algebra is really matrix algebra .Heisenberg's function were later called wave function by Schrödinger in his independent but equivalent method . Schrödinger method is called wave mechanics and is the method most familiar to chemists. Heisenberg method is called matrix mechanics [18]. Although the two methods appear different they can be shown to be mathematically equivalent. We will consider only the Schrödinger formulation [19]. If the electron is to behave as a wave, one might expect there to be a wave equation that describe it's motion [20]. Schrödinger developed it from the classical wave equation and De Broglies ideas about matter waves , but it involves the new idea of a wave function ψ for a particle. The Schrödinger equation involves time, but we are concerned primarily with the time-independent form because many chemical application involve stationery equation states [19]. Schrödinger proposed time-independent equation that specified no discrete orbitals, but instead was an equation describing the wave associated with the electron. This equation is given below [21-23] : -

$$\hat{H}\,\Psi = E\,\Psi \qquad (1)$$

where:

Ψ = psi , the wave function

E = The energy of the system

$\hat{H}$ = The "Hamiltonian", a nasty mathematical operator. The Hamiltonian equation is shown below.

$$H^{elec} = -\frac{1}{2}\sum_{i}^{elec}\left(\frac{\partial^2}{\partial x_i^2}+\frac{\partial^2}{\partial y_i^2}+\frac{\partial^2}{\partial z_i^2}\right)-\sum_{i}^{elec}\sum_{I}^{nuclei}\left(\frac{Z_I}{|R_I-r_i|}\right)+\sum_{i}^{elec}\sum_{j>i}^{elec}\left(\frac{1}{|r_i-r_j|}\right)+\sum_{I}^{nuclei}\sum_{J>I}^{nuclei}\left(\frac{Z_I Z_J}{|R_I-R_J|}\right) \qquad (2)$$

The Hamiltonian shown in the graphic above is the Hamiltonian for the electrons. Notice that there are four terms (each term separated by a "+" or "-" sign):

1. A term to calculate the kinetic energy (k = 1/2 mv^2) of the electrons
2. A term to describe the attraction of electrons to the nuclei. The little "r" term is the radius, or distance, of the electron from the nucleus. The large "R" term is the internuclear distance.
3. A term to describe the repulsive force of an electron to another electron.
4. A term to describe the repulsive force of a nuclei with another nuclei. Schrödinger's equation is an eigenvalue equation. From it we obtain two interesting and important values: E, the energy of the system, and Ψ, (psi) the wave function. The wave function by itself has no significance. However, the square of the wave function can be used to

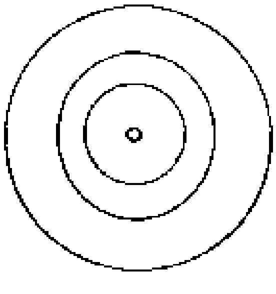
find the probability of locating an electron in an atom. To find this probability for 3-D space (x, y, and z coordinate system), you must use Schrödinger's equation with a specified radius, the squared wave function value, and multiply the wave function by $4(\pi)r^2$ (the volume of sphere)[12]. This equation is a fundamental dynamical equation of quantum theory [23],The mathematics of the Schrödinger method is more familiar to the chemist, and its usual , therefore , the Schrödinger equation is used as the basic of chemical application of quantum mechanics [25]. The importance of the Schrödinger equation lies in its validity and the agreement of calculation value with experimental facts for atoms and molecules system [26].

1.6. Quantum chemistry:

There are basically two different models of atomic structure, the Bohr model and the quantum model. In both models, we are often interested in evaluating the energy of a particular system.

Bohr Model:

Electrons are "particles" that revolve around the nucleus in orbits. These orbits are at fixed distances from the nucleus. Electrons can move between orbits, using or releasing energy in the process.



The energy needed to jump to a different orbital is given in the equation:

$$\Delta E = h \times \text{radius}\left(1/n_f^2 - 1/n_i^2 \right) \tag{3}$$

where

h = Planck's constant

n = quantum number (orbit number)

Using the Bohr model, we are able to determine exactly where each electron is on it's path around the nucleus.

Quantum Model:

The quantum model says that electrons are not particles, but have wavelike characteristics. It uses the Schrödinger's equation to calculate various properties of the electrons[12].

1.7. Quantum mechanics :-

Historical background .

Quantum theory was developed principally over a period of thirty years. The first contribution was the explanation of blackbody radiation in 1900 by Max Planck, who proposed that the energies of any harmonic oscillator, such as the atoms of a blackbody radiator, are restricted to certain values, each of which is an integral (whole number) multiple of a basic minimum value. In 1905 Albert Einstein proposed that the radiation itself is also quantized, and he used the new theory to explain the Photoelectric effect. Niels Bohr used the quantum theory in 1913 to explain both atomic structure and atomic spectra, showing the connection between the energy levels of an atom's electrons and the frequencies of light given off and absorbed by the atom. Quantum mechanics, the final mathematical formulation of the quantum theory, was developed during the 1920s. In 1924 Louis de Broglie proposed that particles exhibit wavelike properties. This hypothesis was confirmed experimentally in 1927 by Clinton J. Davisson and Lester H.Germer, who observed diffraction of a beam of electrons. Two different formulations of quantum mechanics were presented following de Broglie's suggestion. The wave mechanics of Erwin Schrödinger (1926) involves the use of a mathematical entity, the wave function, which is related to the probability of finding a particle at a given point in space. The matrix mechanics of Werner Heisenberg (1925) makes no mention of wave functions or similar concepts but was shown to be mathematically equivalent to Schrödinger's theory. Quantum mechanics was combined with the theory of relativity in the formulation of P.A.M. Dirac (1928), which also predicted the existence of antiparticles. A particularly important discovery of the quantum theory is the uncertainty principle, enunciated by Heisenberg in 1927, which places an absolute theoretical limit on the accuracy of certain measurements[27]. Quantum mechanics takes it's name from the term quantum (Latin for "how much") .The terms quantum chemistry and quantum theory are often used as synonyms of quantum mechanics. Some authors refer to"quantum mechanics"in the restricted sense of non-relativistic quantum mechanics. Quantum mechanics should however be taken to mean quantum theory in its most general sense when used in this article[28]. Quantum mechanical methods can usually be classified either as ab initio or semi-empirical. The first label, ab initio, means ``from the beginning" and implies an approach which contains no empirical parameters. The second, semi-empirical, includes methods which make serious approximations to the quantum mechanical laws and then employ a few empirical parameters to (hopefully) patch things up. These methods include the modified neglect of differential overlap (MNDO), Austin Model 1 (AM1), and many others. Density functional theory (DFT) methods are quantum mechanical approaches which are hard to categorize as ab initio or semi-empirical. Some DFT methods are free from empirical parameters, while others rely heavily on calibration with experiment.The current trend in DFT research is to employ increasing numbers of empirical factors, making recent DFT techniques semi-empirical. One of the postulates of quantum mechanics is that the wave function contains all information which is known or can be known about a molecule. Hence, quantum mechanical methods provide all possible information about a system, in principle at least. In practice, theoretical chemists have to figure out how to extract the property from the wave function, and then they have to write computer programs to perform the analysis. However, it's now fairly routine to compute the following molecular properties :

Properties Obtainable From Quantum Mechanical Methods

- Geometrical structures (rotational spectra).
- Infrared and Raman spectra.
- Electronic energy levels (UV and visible spectra).
- Quantum Mechanics + Statistical Mechanics → Thermo chemistry (ΔH, ΔS, ΔG, C_v, C_p), primarily gas phase.
- Potential energy surfaces (barrier heights, transition states); with a treatment of dynamics, this leads to reaction rates and mechanisms.
- Ionization potentials (photoelectron and X-ray spectra).
- Electron affinities.
- Franck-Condon factors(transition probabilities,vibronic intensities).
- IR and Raman intensities.
- Dipole moments.
- Polarizabilities.

- Electron density maps and population analyses.
- Magnetic shielding tensors → NMR spectra [7].

1.8. Semi empirical method :-

The following steps are typically carried out in any semi empirical MO calculation :

- Read input and set up the geometry .
- Assign the semi empirical parameters to calculate nuclear repulsion energy.
- Calculate electronic energy .

  Calculate total energy = nuclear repulsion energy+electronic energy.
- Calculate "force " or :gradient : (i.e. the first derivative of the total energy with respect to nuclear motion) and optimize the geometry of the molecule.
- Analyze the electron density .

1.8.1. Assumption of semi empirical method:-

Certain overlap integrals are small and can be neglected. Other quantities in the Schrödinger equation can be parameterized to fit the experimental.

Core orbital don't participate in bonding and in determining the physical properties of a molecule. The Born-Oppenheimer approximation is a fundamental assumption.

1.8.2. Limitation and reliability of semi empirical :-

a. Limitations : Partly based on experimental data parameters are no better than the information used to obtain them, neglect orparameterization of overlap integrals can lead to errors.

Restricted to smaller system than empirical method takes more CPU time than empirical method , omitted Core orbitals are lead to errors, electron correlation is included implicitly through Parameterization (this could be seen as a strength) and there is no systematic way to improve a semi empirical MO calculation (i.e. there is not straightforward progression of level of theory).

b. Reliability :MNDO is considerably more reliable than MINDO/3. It gives much better results for unsaturated molecules, compounds with adjacent lone pairs, the calculation of bond length and angles , the ordering of molecular orbitals. AM1 and PM3 are generally considered to be an improvement over MNDO. In addition, PM3 attempts to treat hydrogen bonding in a more realistic manner .

Overall, MNDO ,AM1and PM3 are better than empirical methods for the geometries and energies of transition structures intermediates and compounds with unusual more information about properties.

1.9. Ab initio method:-

The term ab initio means from first principles . It does not mean that we are solving the Schrödinger equation exactly . It means that we are Selecting a method that in principle can lead to reasonable approximation to the solution of the Schrödinger equation and then selecting a basis set that will implement that method in a reasonable way [29].

Ab initio MOT it makes no difference to the final out come whether one takes as a basis set , hybrid orbitals or AO', becomes hydride orbitals are themselves LCAO .In some approximate or empirical molecular there can be a difference between the two basis if some of the small overlap or Hamiltonian integrals are neglected [30].

1.9.1.Assumption of an ab initio method :-

Assume that the Born Oppenheimer approximation holds. This assumption can become invalid when two electronic states lie very close together. Assume that basis sets adequately represent MO, and assume that electron correlation is adequately included within a certain level of theory.

1.9.2.Limitations,strengths and reliability of ab initio method :-

a. **Limitations**: The method limitation appear because it requires more CPU time than empirical or semi empirical method, can treat smaller molecules than empirical and semi empirical methods, calculations are more complex .

b. **Strengths** : The method strength is appeared because it has no experimental , can improve a calculation in a logical manner(basis sets, level of theory), provides information on intermediate species , including spectroscopic data. Can calculate novel structure (no experimental data is required) and can calculate any electronic state.

c. **Reliability** : The method reliability is clear because the mean deviation between experimental and theory for the heavy atom bond lengths in two heavy atom hydrides drops from 0.082A for the RHF/STO-3G level of theory to just 0.019A for MP2/6.31G(d). Heats of hydrogenation of range of saturated and unsaturated system are calculated sufficiently well at the Hartree Fock level of theory with a moderate basis set(increasing the basis set from 6.31/G(d) to 6-31G(d, p) has little effect on the accuracy of these numbers).Inclusion of electron correlation is mandatory in order to get good agreement between experiment and theory for bond dissociation energies (MP2/6-31G(d ,p) does very well for the one heavy atom hydrides) [29].

1.9.3.Ab initio implementation of HF-MO :-

The fundamental assumption of HF theory that each electron sees all of the other as an average field , allows for tremendous progress to be made in carrying out particle MO calculation. However, neglect of electron correlation can have profound chemical consequences when it co comes to determining accurate wave function and properties derived therefore, the development of semi-empirical theories was motivated in part by the hope that judicious parameterization efforts could composite for this feature of HF theory. While such compensation has no rigorous foundation, to the extent it permits one to make accurate chemical presentation , it may have great practical utility [31].

1.10. Molecular mechanics :

Molecular mechanical force fields use the equations of classical mechanics to describe the potential energy surface and physical properties of molecules . A molecule is described as a collection of atoms that interact with each other by simple analytical functions .

This description is called a force field. One component of a force field is the energy arising from compression and stretching a bond.

This component is approximated as a harmonic oscillator and can be calculated using Hook's low.

$$V_{spring} = 1/2\ K(r-r_0)^2 \qquad (4)$$

The bonding between two atoms is analogous to a spring connecting two masses . Using this analogy , equation(4) gives the potential energy of the system of masses ,V_{spring} and the force constant of the spring ,K_r. The equilibrium and displaced distances of the atoms in bond are r_0 and r. Both K_r and r_0 are constants for as specific pair of atoms connected by a certain spring.K_r and r_0 force field parameters.

The potential energy of a molecular system in force field is the sum of individual components of the potential , such as bond ,angle, and van der Walls potentials (equation 5).The energies of the individual bonding components (bonds, angles, and dihedrals) are function of the deviation of a molecule from a hypothetical compound that has bonded interactions at minimum values.

$$E_{Total} = term_1 + term_2 + \ldots\ldots.. + term_n \qquad (5)$$

The absolute energy of a molecule in molecular mechanics has no intrinsic physical meaning: E_{Total} values are useful only for comparisons between molecules . Energies from single point calculations are related to the enthalpies of the molecules .However ,they are not enthalpies because thermal motion and temperature dependent contributions are absent from the energy terms (equation 5).

Unlike quantum mechanics , molecular mechanics doesn't treat electron explicitly. Molecular mechanics calculation can't describe bond formation, bond breaking, or system in which electronic delocalization or molecular orbital interactions play a major role in determining geometry or properties[17].

Method Type	Advantages	Disadvantages	Best for	
olecular echanics	uses classical physics .relies on force-field with embedded empirical parameters	.Computationally least intensive - fast and useful with limited computer resources .can be used for molecules as large as enzymes	.particular force field applicable only for a limited class of molecules .does not calculate electronic properties .requires experimental data (or data from *ab initio*) for parameters	.large systems (thousands of atoms) .systems or processes with no breaking or forming of bonds
mi- ipirical	.uses quantum physics .uses experimentally derived empirical parameters .uses approximation extensively	.less demanding computationally than *ab initio* methods .capable of calculating transition states and excited states	.requires experimental data (or data from *ab initio*) for parameters .less rigorous than *ab initio*) methods	.medium-sized systems (hundreds of atoms) .systems involving electronic transitions
ı Initio	.uses quantum physics .mathematically rigorous, no empirical parameters .uses approximation extensively	.useful for a broad range of systems .does not depend on experimental data .capable of calculating transition states and excited states	Computationally expensive	.small systems (tens of atoms) .systems involving electronic transitions .molecules or systems without available experimental data ("new" chemistry) systems requiring rigorous accuracy

ble(1.1): Comparing between molecular mechanics,ab intio,semi-empirical methods

1.11. Approximate solution :-

We have said that the Schrödinger equation for molecules cann't be solved exactly .That is because the exact equation is not separable. One strategy is to make assumption that permit us to write approximate forms of the Schrödinger equation for molecules and ultimately to separate the new and approximate equations. There is then a choice as to how to solve the separated equation. The Hartree Fock method is one possibility. the Born-Oppenheimer method is the another.

Three major approximation are made to separate the Schrödinger equation into a set of smaller equation.

1. Hartree Fock (HF) method.
2. Bron-Oppenheimer Approximation.
3. Hückel method [18] .

1.12. HF method

When the calculation is carried out with combination which ensure that the pauli exclusion principle is obeyed , the orbitals are said to be Hartree Fock orbitals . The HF gives the best possible description of the wave function for atom with the orbital description , i.e. with the wave function for the atom described the orbitals , each orbital being a function of the coordinates of a single electron [32]. The essential idea of the Hartree-Fock or molecular orbital method is that, for a closed shell system, the electrons are assigned two at a time to a set of molecular orbitals. For an eight electron system this can be represented by the simple picture:

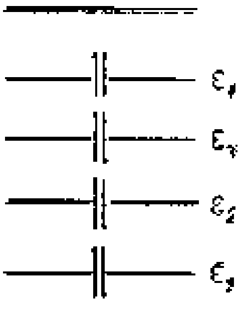


Fig.(1.5) : System of electrons occupying the MO.

This gives the following determinantal wave function:-

$$\psi=\frac{1}{\sqrt{8!}}\begin{vmatrix}
\phi_1(1)\alpha(1) & \phi_1(1)\beta(1) & \phi_2(1)\alpha(1) & \phi_2(1)\beta(1) & \phi_3(1)\alpha(1) & \phi_3(1)\beta(1) & \phi_4(1)\alpha(1) & \phi_4(1)\beta(1)\\
\phi_1(2)\alpha(2) & \phi_1(2)\beta(2) & \phi_2(2)\alpha(2) & \phi_2(2)\beta(2) & \phi_3(2)\alpha(2) & \phi_3(2)\beta(2) & \phi_4(2)\alpha(2) & \phi_4(2)\beta(2)\\
\phi_1(3)\alpha(3) & \phi_1(3)\beta(3) & \phi_2(3)\alpha(3) & \phi_2(3)\beta(3) & \phi_3(3)\alpha(3) & \phi_3(3)\beta(3) & \phi_4(3)\alpha(3) & \phi_4(3)\beta(3)\\
\phi_1(4)\alpha(4) & \phi_1(4)\beta(4) & \phi_2(4)\alpha(4) & \phi_2(4)\beta(4) & \phi_3(4)\alpha(4) & \phi_3(4)\beta(4) & \phi_4(4)\alpha(4) & \phi_4(4)\beta(4)\\
\phi_1(5)\alpha(5) & \phi_1(5)\beta(5) & \phi_2(5)\alpha(5) & \phi_2(5)\beta(5) & \phi_3(5)\alpha(5) & \phi_3(5)\beta(5) & \phi_4(5)\alpha(5) & \phi_4(5)\beta(5)\\
\phi_1(6)\alpha(6) & \phi_1(6)\beta(6) & \phi_2(6)\alpha(6) & \phi_2(6)\beta(6) & \phi_3(6)\alpha(6) & \phi_3(6)\beta(6) & \phi_4(6)\alpha(6) & \phi_4(6)\beta(6)\\
\phi_1(7)\alpha(7) & \phi_1(7)\beta(7) & \phi_2(7)\alpha(7) & \phi_2(7)\beta(7) & \phi_3(7)\alpha(7) & \phi_3(7)\beta(7) & \phi_4(7)\alpha(7) & \phi_4(7)\beta(7)\\
\phi_1(8)\alpha(8) & \phi_1(8)\beta(8) & \phi_2(8)\alpha(8) & \phi_2(8)\beta(8) & \phi_3(8)\alpha(8) & \phi_3(8)\beta(8) & \phi_4(8)\alpha(8) & \phi_4(8)\beta(8)
\end{vmatrix}$$

This is usually abbreviated to:-

$$\psi=\det\{\phi_1(1)\alpha(1)\ \phi_1(2)\beta(2)\ \phi_2(3)\alpha(3)\ \phi_2(4)\beta(4)\ \phi_3(5)\alpha(5)\ \phi_3(6)\beta(6)\ \phi_4(7)\alpha(7)\ \phi_4(8)\beta(8)\} \qquad (6)$$

This is often further abbreviated to:-

$$\psi=\det\{\phi_1(1)\ \bar{\phi}_1(2)\ \phi_2(3)\ \bar{\phi}_2(4)\ \phi_3(5)\ \bar{\phi}_3(6)\ \phi_4(7)\ \bar{\phi}_4(8)\} \qquad (7)$$

where the bar over the molecular orbital (MO) indicates β spin associated with that MO and the absence of a bar over the MO indicates α spin associated with that MO.

To give us freedom to vary the molecular orbitals to best suit the molecule in question, we expand each molecular orbital in terms of a set of basis functions which are normally centred on the atoms in the molecule. This gives:-

$$\psi_i = \sum_{\mu=1}^{n} C_{\mu i}\phi_\mu \qquad (8)$$

Here each molecular orbital Φ_i is now expanded as a linear combination of basis functions, χ_μ: Our aim is to find the value of the coefficients $C_{\mu i}$ that gives the best molecular orbitals. The sum is over *n* basis functions. n is the number of basis functions choosen for the system. We call this "the basis set size"[29].

1.12.1. The HF approximation

The starting point for any molecular electronic problem is the electronic Schrödinger equation :

$$\hat{H}\,\psi(1,2,3\ldots,N) = E\,\psi(1,2,3,\ldots,N) \qquad (9)$$

The HF method , or Self Consist field (SCF) method , approximates $\psi(1,2,3\ldots,N)$ by expressing it solely in term of function each of which contains the coordinates of just one electron; these functions are called molecular orbitals (MOs) .This is an approximation because in readily the position of one electron is always correlated with the position of the others , so that the function which describes a given electron can't be independent of the function describing the other electron . For this reason the error in the electronic energy in the HF approximation is called the correlation energy[33].

1.13. Basis set:

The basis set is the set of mathematical function from which the wave function is constructed[29].The essential idea as you have seen is that the molecular orbital are expanded as a linear combination of atomic orbitals as they are now more correctly called " basis function ".

There are two general categories of basis sets:

Minimal basis sets

A basis set that describes only the most basic aspects of the orbitals.

Extended basis sets

A basis set with a much more detailed description .

The general expression for a basis function is given as:

$$\textbf{Basis Function} = \mathbf{N} * e^{(\text{-alpha} * r)} \tag{10}$$

where: N =normalization constant

Alpha = orbital exponent

r = radius in Angstroms

This expression given as a Slater Type Orbital (STO) equation is:

$$STO = \frac{\zeta^3}{\pi^{0.5}} e^{(-\zeta r)} \tag{11}$$

Now it is important to remember that STO is a very tedious calculation. Notice that the difference between the STO and GTO is in the "r." The GTO squares the "r" so that the product of the gaussian "primitives" (original gaussian equations) is another gaussian. By doing this, we have equation we can work with and so the equation is much easier. However, the price we pay is loss of accuracy. To compensate for this loss, we find that the more gaussian equations we combine, the more accurate our equation all basis set equations in the form STO-NG (where N represents the number of GTOs combined to approximate the STO) are considered to be "minimal" basis sets. (Remember our definition of minimal.) The "extended" basis sets, then, are the ones that consider the higher orbitals of the molecule and account for size and shape of molecular charge distributions. There are several types of extended basis sets:

- Double-Zeta, Triple-Zeta, Quadruple-Zeta
- Split-Valence
- Polarized Sets
- Diffuse Sets

Double-Zeta, Triple-Zeta, Quadruple-Zeta

Previously with the minimal basis sets, we approximated all orbitals to be of the same shape. However, we know this is not true. The double-zeta basis set is important to us because it allows us to treat each orbital separately when we conduct the Hartree-Fock calculation. This gives us a more accurate representation of each orbital. In order to do this, each atomic orbital is expressed as the sum of two Slater-type orbitals (STOs).The two equations are the same except for the value of ζ (zeta). The zeta value accounts for how diffuse (large) the orbital is. The two STOs are then added in some proportion. The constant 'd' determines how much each STO will count towards the final orbital. Thus, the size of the atomic orbital can range anywhere between the value of either of the two STOs. For example, let's look at the following example of a 2s orbital:

$$\Phi_{2s}(r) = \underbrace{\Phi_{2s}^{STO}(r,\zeta_1)}_{\text{Slater Orbital 1}} + \underset{\substack{\uparrow \\ \text{Constant}}}{d}\underbrace{\Phi_{2s}^{STO}(r,\zeta_2)}_{\text{Slater Orbital 2}} \tag{12}$$

In this case, each STO represents a different sized orbital because the zetas are different. The 'd' accounts for the percentage of the second STO to add in. The linear combination then gives us the atomic orbital. Since each of the two equations are the same, the symmetry remains constant. The triple and quadruple-zeta basis sets work the same way, except use three and four Slater equations instead of two. The typical trade-off applies here as well, better accuracy...more time/work.

Split-Valence

Often it takes too much effort to calculate a double-zeta for every orbital. Instead, many scientists simplify matters by calculating a double-zeta only for the valence orbital. Since the inner-shell electrons aren't as vital to the calculation, they are described with a single Slater Orbital. This method is called a split-valence basis set. A few examples of common split-valence basis sets are 3-21G, 4-31G, and 6-31G .

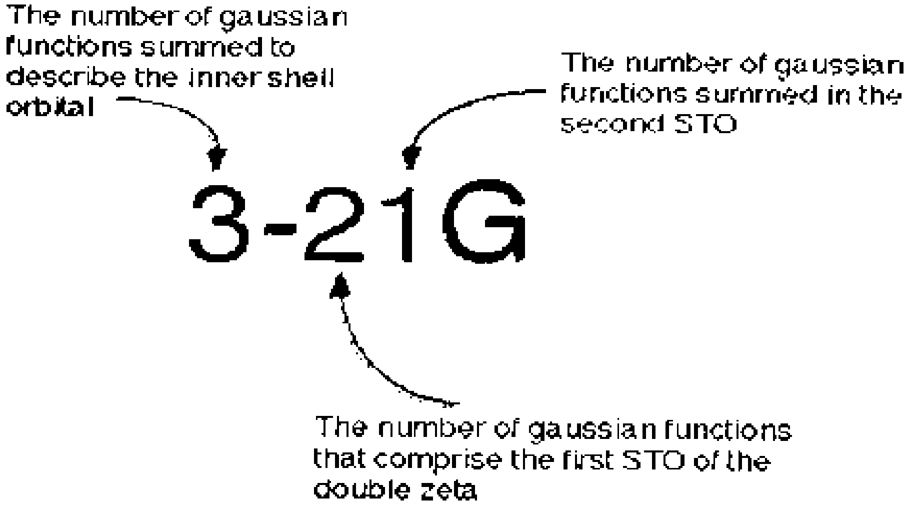


Fig.(1.6): Split-valence 3-21G basis sets

Polarized Sets :-

In the previous basis sets we have looked at, we treated atomic orbitals as existing only as 's', 'p', 'd', 'f' etc. Although those basis sets are good approximations, a better approximation is to acknowledge and account for the fact that sometimes orbitals share qualities of 's' and 'p' orbitals or 'p' and 'd', etc. and not necessarily have characteristics of only one or the other.As atoms are brought close together,their charge distribution causes a polarization effect (the positive charge is drawn to one side while the negative charge is drawn to the other) which distorts the shape of the atomic orbitals. In this case, 's' orbitals begin to have a little of the 'p' flavor and 'p' orbitals begin to have a little of the 'd' flavor. One asterisk (*) at the end of a basis set denotes that polarization has been taken into account in the 'p' orbitals. Notice in the graphics below the difference between the representation of the 'p' orbital for the 6-31G and the 6-31G* basis sets. The polarized basis set represents the orbital as more than just 'p', by adding a little 'd'.

Original 'p' orbital

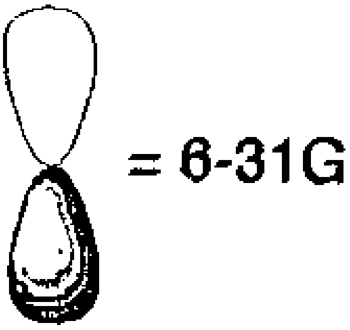


Fig.(1.7): P-orbital for 6-31G bases set

Modified 'p' orbital

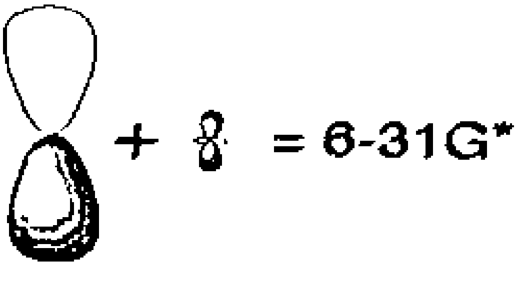


Fig.(1.8): P-orbital for 6-31G* bases set

Two asterisks (**) means that polarization has taken into account the 's' orbitals in addition to the 'p' orbitals. Below is another illustration of the difference of the two methods.

Original 's' orbital

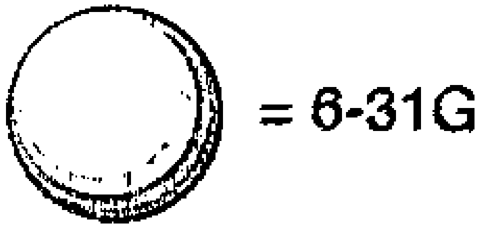


Fig.(1.9): Original 's' orbital for 6-31G bases set

Modified 's' orbital

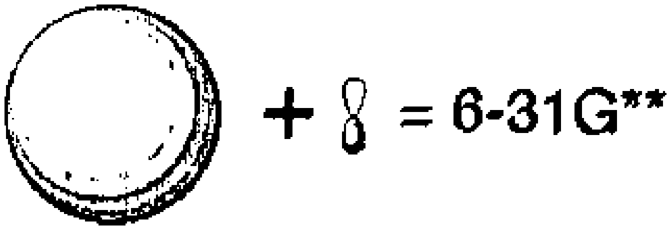


Fig.(1.10): Modified 's' orbital for 6-31G** bases set

There are two ways in which we can think about the basis functions , and as you progress to using more advanced basis function you will probably move your thinking from the first way to the second . The first and simplest way, is to think of basis functions as the atomic orbitals the study of the qualitative molecular orbital part of these modules . This certainly applies to the minimum basis set that are still very popular , although they are known to have significant defects. This idea can still be used in part for spilt valence and double zeta basis set, which can be thought of as orbital that have been scaled to a different size .The second way is just think of basis functions as a set of mathematical function, which are designed to give the maximum flexibility (subject to the costs of doing the calculation) to the MO. This leads to what are are often called extended basis set .We can add almost anything we like since the coefficients of the basis function in the final molecular orbitals are selected by the variation function to minimize the energy , if we make a bad guess for some basis function , they will simply appear with small or zero coefficients. However we must include basis function that really do count for something and we must exclude poor basis function since they increasing the cost for normal gain[29]

1.5.9. The Born-Oppenheimer Approximation

We know that if a Hamiltonian is separated into two or more terms , then the total eigenfunction are product of the individual eigenfunction of the separated Hamilton terms and the total eigenvalues are sums of individual eigenvalue of the separated Hamiltonian terms [34-36]

Consider, for example, a Hamiltonian which is separable into two terms , one involving coordinate q_1 and the other involving coordinate q_2

$$\hat{H} = \hat{H}_1(q_1) + \hat{H}_2(q_2) \tag{13}$$

With the overall Schrödinger equation being

$$\hat{H}\,\psi(q_1, q_2) = E\,\psi(q_1, q_2) \tag{14}$$

What do this equation mean ? The equation mean that the total wave function of a molecule can be separated into an electronic and a nuclear part . The electronic wave function is obtained for various fixed position of the nuclei by solving equation (14) [37].

CHAPTER

II

EXPERIMENTAL METHOD

2. Experimental methods used .

1. Machines

LG. PC. System with Intel Pentium IV , 1600 MHz , with 256 MB of RAM Storage disk space of 20 GB of all disk space .

2. Operating system.

WINDOWS XP.

3. HyperChem 7.5.

4. ChemOffice ultra 7.0.

5. Office XP.

2.2. Molecular modeling with HyperChem :-

HyperChem is a powerful program that enables us to do high quality molecular calculations. Using HyperChem you can: Draw simple and complex molecular structures, Including crystals, carbohydrates, peptides and nucleic acid sequences, display these structures in various different renderings including ball , stick and space filling structures.

Working with HyperChem :-

To start working with HyperChem after install to our system ,click on the start button, then programs , in program files there is a green icon labeled as below click on to start HyperChem version 7.5. There should be a HyperChem 7.5 icon on your Windows desktop. Double click on this icon with the left mouse button to start the program and open HyperChem screen . Across the top of the HyperChem are various menus that you will use. Clicking on any of these opens additional submenus. Try this for several of the menus. (Remember that menu items that are grayed-out are not available at that time) . (If the background in your screen is not white, or whatever color you wish select preferences under the file menu and change it to that color.) Also, make sure that the choices explicit hydrogen's and allow arbitrary valence are checked under the build menu. Otherwise HyperChem will add hydrogen atoms to your structure as you build it, and you may end up with something other than what you were setting out to build. In addition, you would be unable to work with expanded octet systems below the menus are some tools that you can use to affect what is on the screen or to manipulate files.The eight tools to the left side are used to manipulate the display. The left-most tool, which I call the cross hair, is used to construct molecules. Double clicking on this tool brings up a periodic table from which you can select atoms. Holding down the left mouse button and dragging it between two atoms draws a bond. Clicking the mouse any place on the screen adds another atom, whether you want one or not. I suggest that as soon as you have your molecule on the screen, you click on the second tool from the left, the bagel, which will not allow you to add any additional atoms. The bagel, also called the build tool, has several uses. Double clicking (left button) on the bagel, while a molecule is on the screen, applies simple (idealized) VSEPR rules to the molecule. You can also click on atoms with the bagel. If you click on two atoms you get the distance between them, three atoms gives you the bond angle, and four the torsion angle(all assuming that atoms and multiple selections are chosen from the select menu . This information about distances and angles is displayed at the bottom left portion of the screen. Note that atoms and bonds turn green after clicking with the bagel. If on click with the right mouse button, you unselect the atoms and bonds you have selected. The third tool you will use frequently is the third one from the left, which I call the hook. Holding down the left mouse button and dragging the mouse across the screen, with the hook selected, allows you to rotate the molecule or 3-D surface on the screen .

Building a molecule and optimizing its structure:

Open the periodic table and select carbon, nitrogen , and phosphorus. Go to the display menu and under labels select symbol.

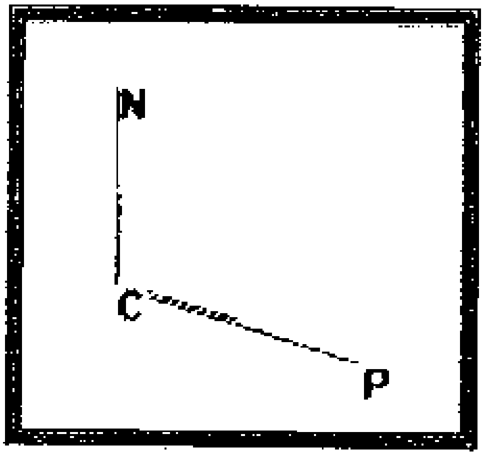


Fig.(2.1): Structure of Amino methane phosphine without hydrogen.

there are no hydrogen's yet. (A second caution about the crosshair. Any left mouse clicks while the cross hair is chosen will add additional atoms to the screen and any right clicks will delete atoms or bonds, if the cursor is on such, or whole structures. I suggest changing to the bagel as soon as you have drawn your atoms and bonds.) go to the build menu and select add hydrogen's and then model build. If you double click the bagel, you will generate a structure based on simple valence rules. If you chose the combined action above, hydrogen's are added and the model is built at the same time. Here is my structure at this point:

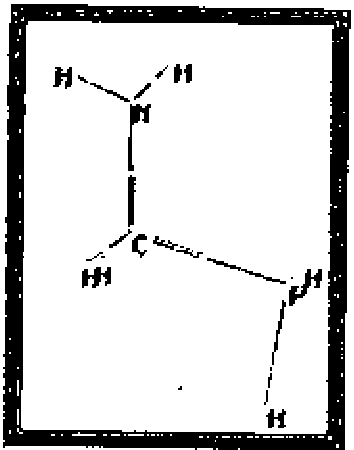


Fig.(2.2) : Structure of Amino methane phosphine with hydrogen

Now select the bagel and do some bond length and bond angle measurements. Clicking on one atom gives its coordinates at the bottom of the screen. Clicking a second atom gives the bond length, a third atom the bond angle. Right clicking an atom unselects it, while clicking outside of the molecule either selects (left click) or unselects (right click) the whole molecule. Use the rotate tool (the third tool down on the vertical toolbar the hook) to look at your idealized structure from different perspectives. Go to the rendering choice under the display menu and try several options on your molecule. Repeat this for choices under labels (note that some of these choices only apply to biological molecules).Now go to the setup menu and choose ab initio. (ab initio calculations apply sets of rules to the atoms in molecules which affect bond lengths and angles in order to determine the geometry which minimizes the molecular energy.) from here, choose a set of parameters (start with 3.21 G) to be used to minimize the energy of the structure. Go to the compute menu and choose geometry optimization In the RMS gradient box enter 0.0001, and click on OK. Select a calculation method (or for this case accept the default values) and start the process. The progress of the calculation is shown at the bottom of the screen. When the process is completed, check some bond angles and lengths to see what, if anything, has changed. Performing a molecular orbital calculation: Your molecule should still be on the screen. Under setup, choose ab initio this menu gives you a list of calculation options, roughly in increasing order of sophistication. When the calculation converges, choose orbitals under calculate and look at the orbital diagram. Click on the labels box to see the energies and the electrons. You can zoom in on particular regions of the orbital diagram. Click on any of the orbitals (it will turn red) and then on OK to leave the box. This will give you a 2D or 3D-plot of the orbital (or the orbital squared if you have clicked on that box in the orbital dialog).Look at plots of various orbitals (the one shown here is not the one in red in the previous figure) .

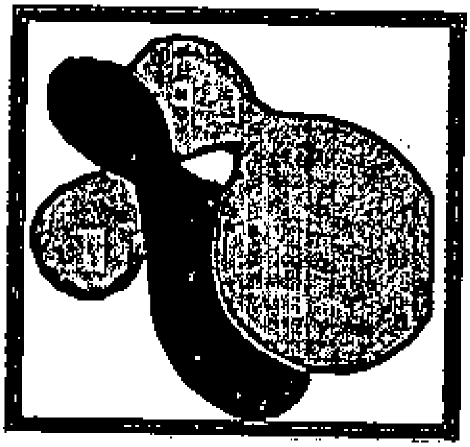
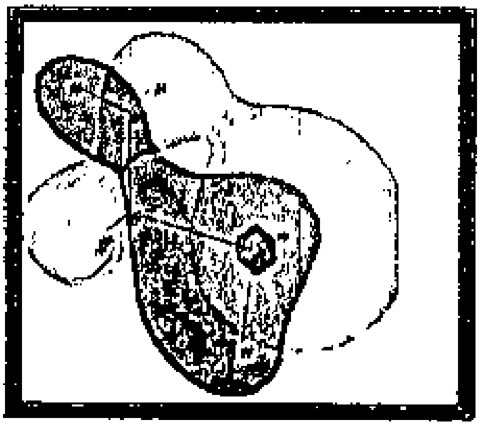


Fig.(2.3) : The 3D-plot of Amino methane phosphine orbital .

There are many options available for customizing the way that the orbital is displayed. These are found by clicking the options button on the orbitals screen. You may also use choices from the rendering option in the display menu. Here are several other views of the orbital shown above.



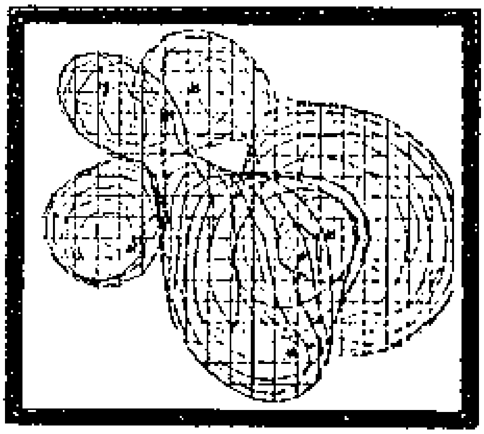


Fig.(2.5):Amino methane phosphine orbital . Fig.(2.4):Amino methane phosphine orbital .

If you return rendering to sticks, and turn off the display of the surface (found under display) and choose charge under labels (which is also under display) you will see the computed charges on the various atoms.

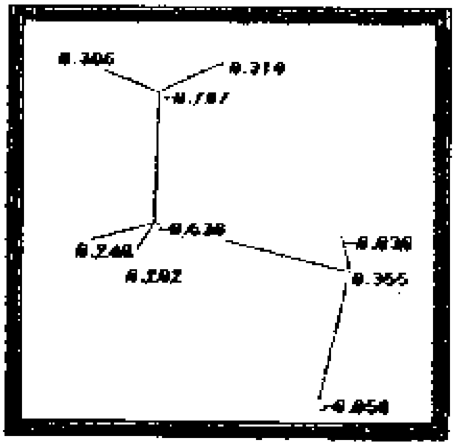


Fig.(2.6):Amino methane phosphine charges of atoms .

One of the choices in the file menu is start log file. A log file is a text file That contains the results of the molecular orbital calculations. depending on choices that have been made in the setup of the program, various information from the calculation will be reported in the log file[38].

Using on help :

Wherever you want more information about how to use HyperChem , you can access on – line help in the following ways : L-click help on the menu bar , L click on the menu or menu item if you want information on and press F1.

Clearing the HyperChem work space:

To clear the workspace: Select new on the file menu , windows appears asking if you want to save the current change , choose no or yes . HyperChem Clear the remaining atom and bonds from the HyperChem screen.

Exit from HyperChem

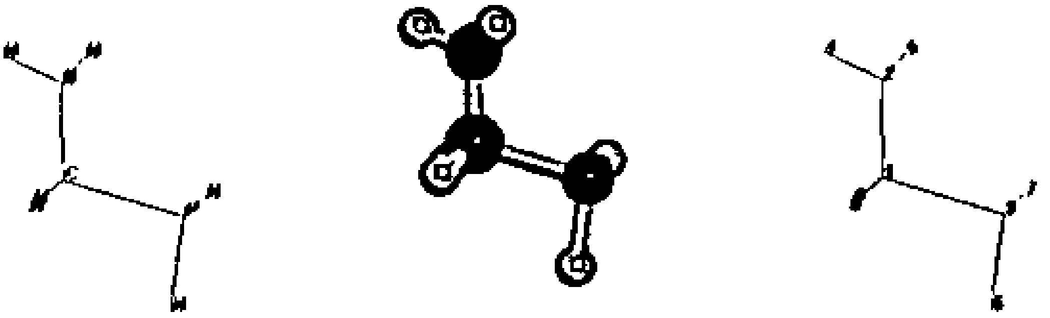
To exit from HyperChem and return to windows , select file menu choose exit icon from the menu . HyperChem exit from the screen .There are numerous other application of HyperChem that have not been mentioned.

2.3. CHEMOFFICE

Its that software which used in our work for named the compound .

Table (3.1) :Abbreviation , structure and name of compounds,(Class I)

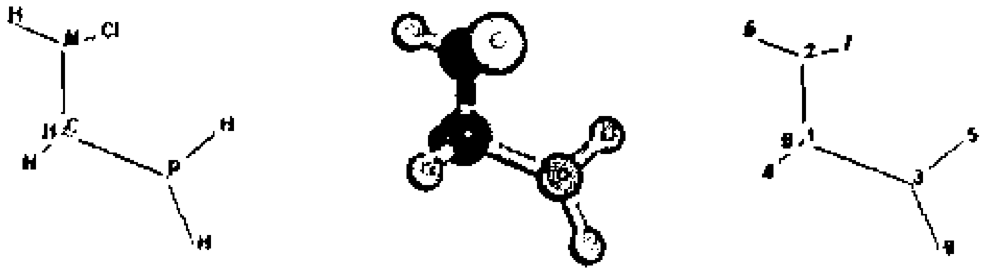
Abbreviation	Structure	Name
AMP	$PH_2CH_2NH_2$	Amino methane phosphine



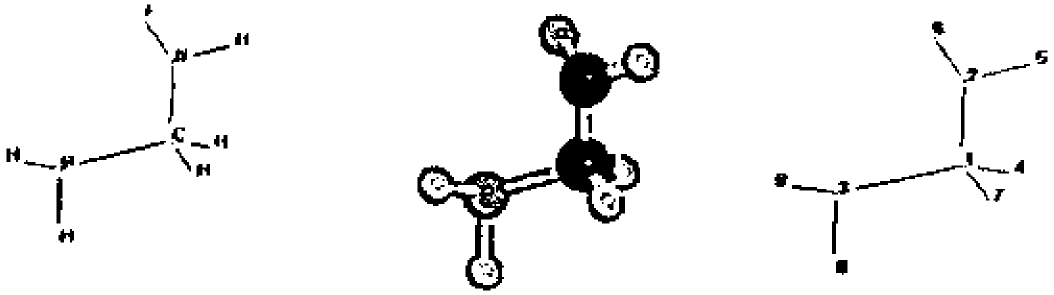
$PH_2CH_2NH_2$

Fig.(3.1): Structure of compound (Class I) ble (3.1): Cont. (Class II)

bbreviation	Structure	Name
2AMP	PH_2CH_2NHCl	N-Chloro -C- phosphanyl methyl amine
2AMP	PH_2CH_2NHF	N-Flouro -C- *phosphanyl methyl amine*
3AMP	$PHClCH_2NH_2$	P-Chloro -C- phosphanyl methyl amine
3AMP	$PHFCH_2NH_2$	P-Flouro -C- phosphanyl methyl amine
FAMP	$PH_2CH_2NF_2$	N- Di Flouro -C- phosphanyl methyl amine
CAMP	$PH_2CH_2NCl_2$	N- Di Chloro -C- phosphanyl methyl amine
2F2AMP	PH_2CH_2NFCl	N-Flouro-N-Chloro-C-phosphanyl methyl amine
C3AMP	$PCl_2CH_2NH_2$	P-P-DiChloro- C-phosphanyl methyl amine
F3AMP	$PF_2CH_2NH_2$	P-P-DiFlouro -C-phosphanyl methyl amine
FAMP	$PFClCH_2NH_2$	P-Flouro-P-Chloro-C-phosphanyl methyl amine
FAMP	$PHFCH_2NHF$	N-Chloro-P-Flouro-C-phosphanyl methyl amine
CAMP	PHClCH2NHCl	N-Chloro-P-Chloro -C-phosphanyl methylamine
3F2AMP	$PHClCH_2NHF$	N- Flour -P-Chloro-C-phosphanyl methyl amine
CAMP	$PHFCH_2NHCl$	N-Chloro-P-Flouro-C-phosphanylmethyl amine

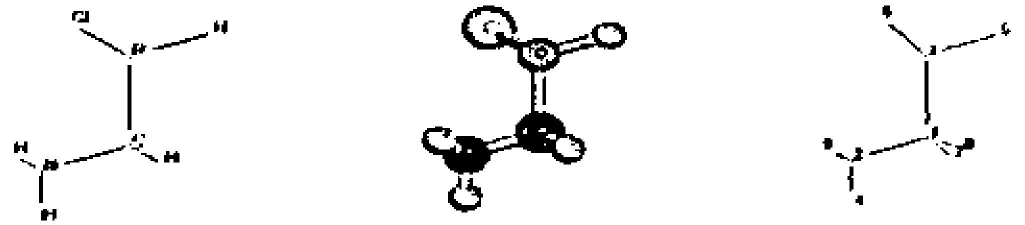


PH_2CH_2NHCl

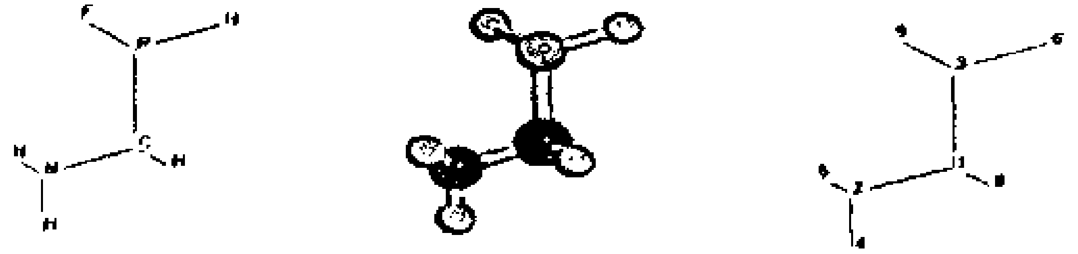


PH_2CH_2NHF

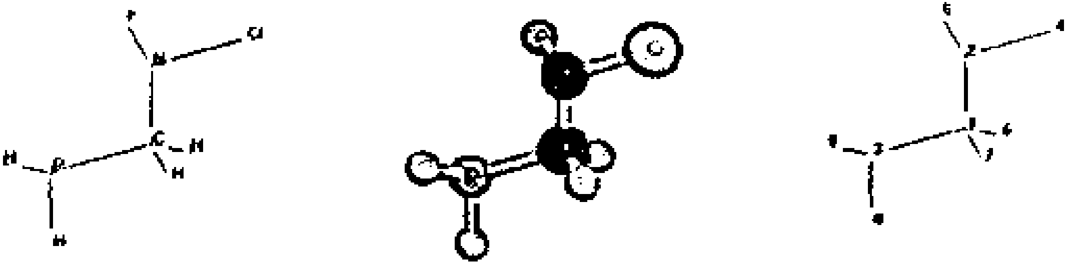
Fig. (3.2): Structures of compounds (Class II)



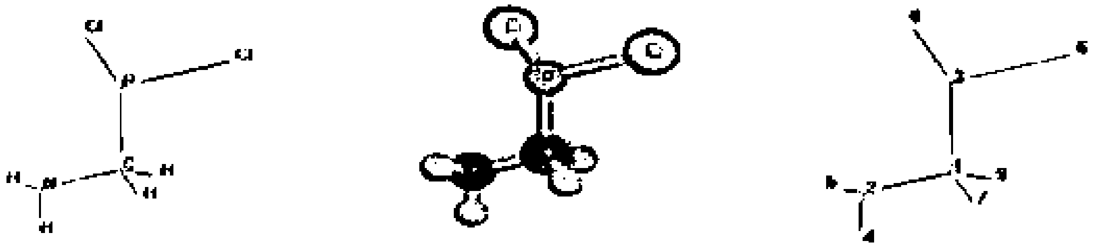
$PHClCH_2NH_2$



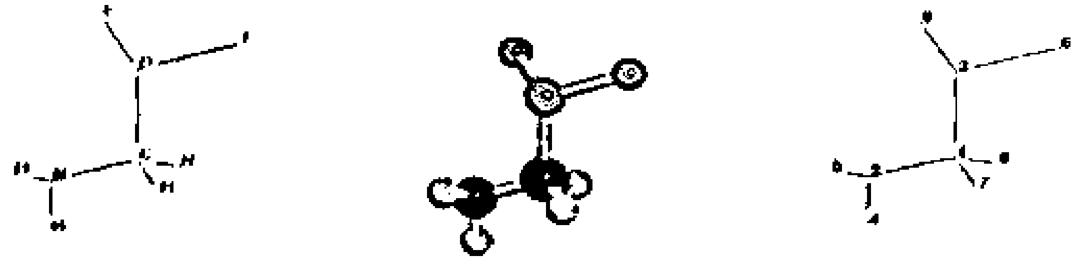
$PHFCH_2NH_2$



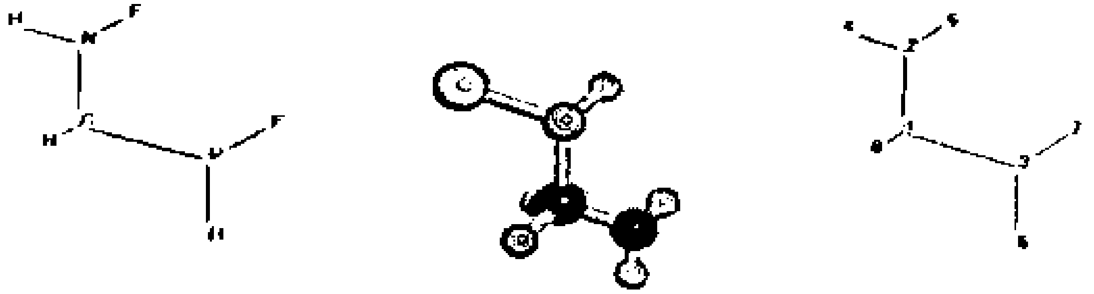
PH_2CH_2NFCl



$PCl_2CH_2NH_2$

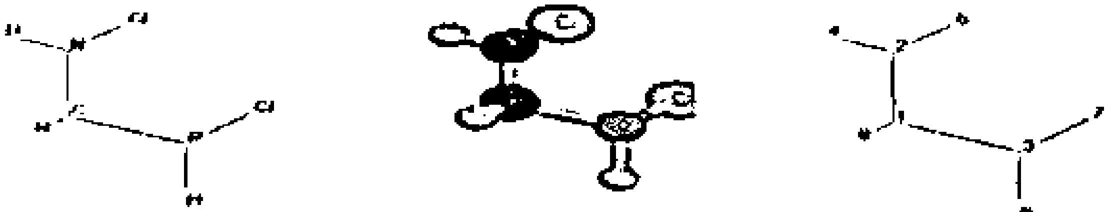


$PF_2CH_2NH_2$

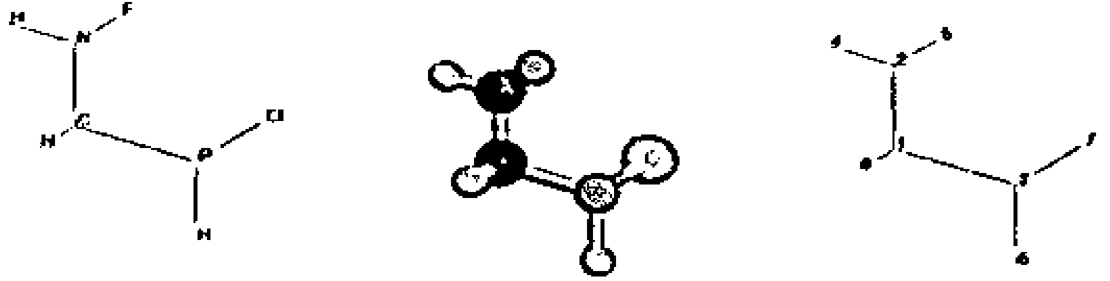


$PHFCH_2NHF$

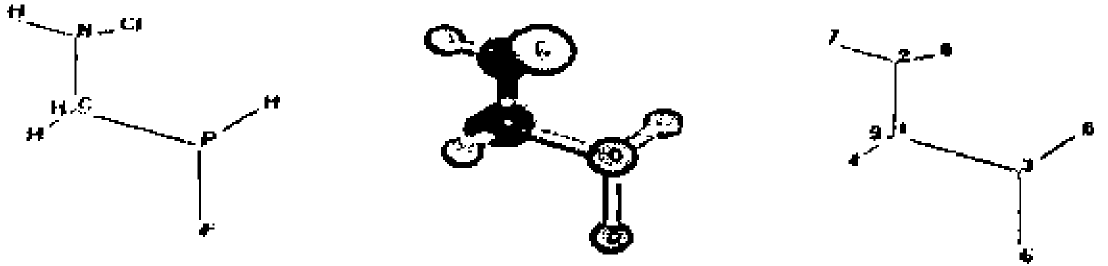
Fig.(3.2)Cont.



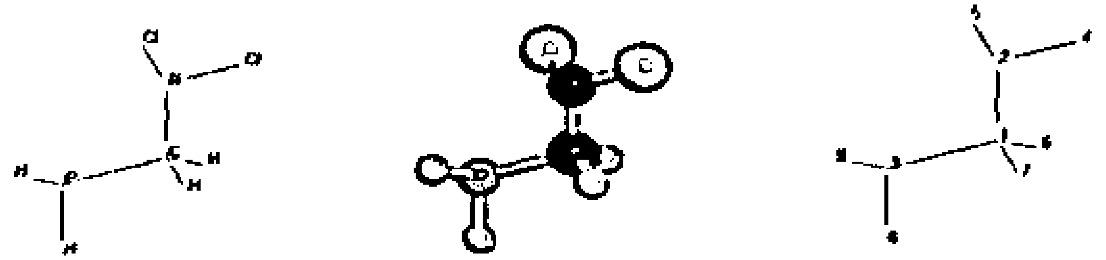
PHClCH$_2$NHCl



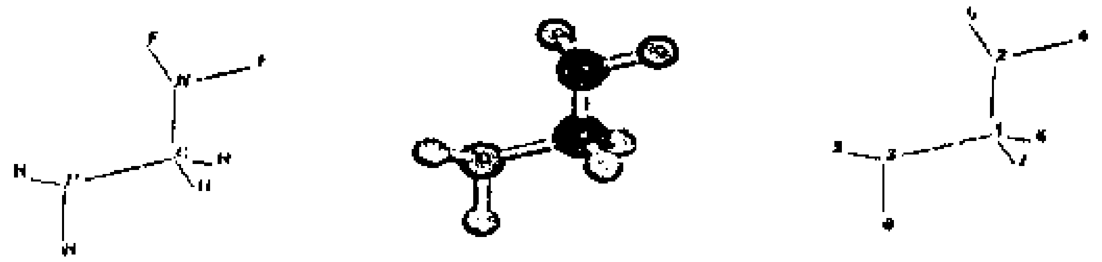
PHClCH$_2$NHF



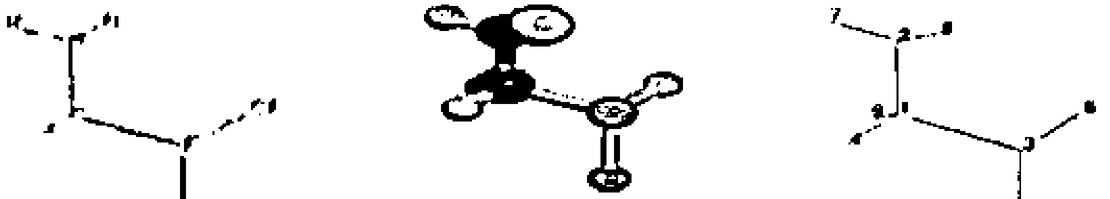
PHFCH$_2$NHCl



PH$_2$CH$_2$NCl2



PH$_2$CH$_2$NF$_2$

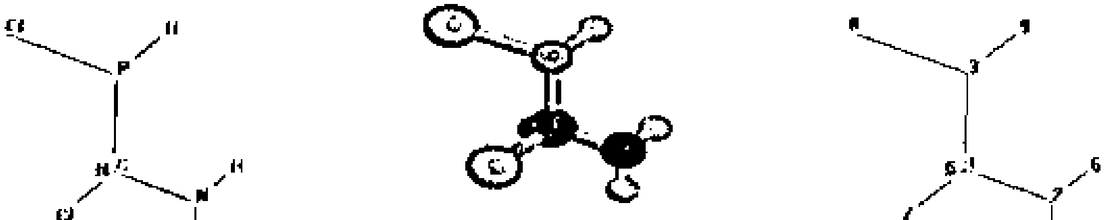


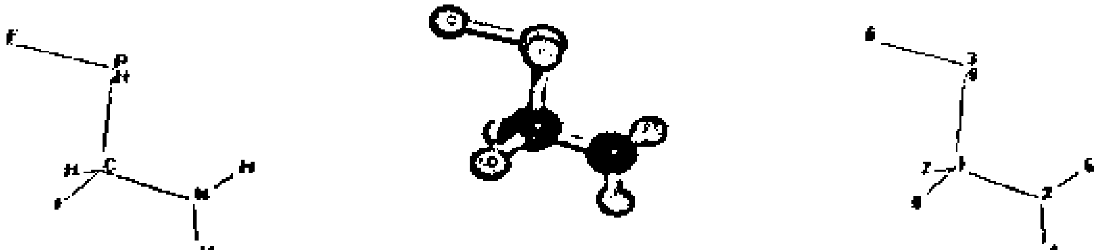
PClFCH$_2$NH$_2$

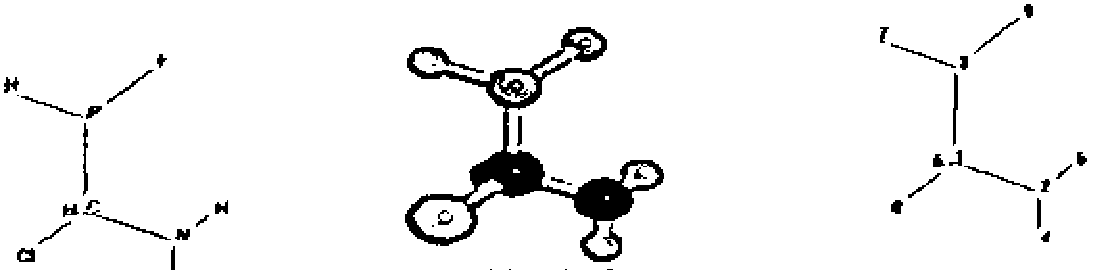
Fig.(3.2)Cont.

ie (3.1) cont. : (Class III)

breviation	Structure	Name
'MP	$PH_2CHClNH_2$	C-Chloro -C- Phosphanyl- methyl amine
MP	PH_2CHFNH_2	C-flouro -C- Phosphanyl- methyl amine
CMP	$PH_2CCl_2NH_2$	C-Dichloro -C- phosphanyl- methyl amine
FMP	$PH_2CF_2NH_2$	C-Diflouro -C- phosphanyl- methyl amine
FMP	$PH_2CClFNH_2$	C-Chloro-C-flouro-C-phosphanyl-methyl amine
MCP	$PHClCHClNH_2$	P-Chloro-C-Chloro-C-phosphanyl-methyl amine
MFP	$PHFCHFNH_2$	P-Flouro-C-flouro-C-phosphanyl-methyl amine
'MFP	$PHFCHClNH_2$	P-Flouro-C-Chloro-C-phosphanyl-methyl amine
MCP	$PHClCHFNH_2$	P-Chloro-C-flouro -C-phosphanyl-methyl amine


$PHClCHClNH_2$


$PHFCHFNH_2$


$PHFCHClNH_2$

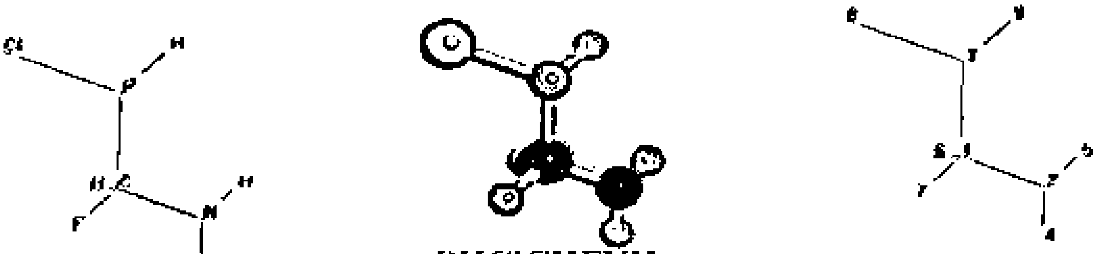
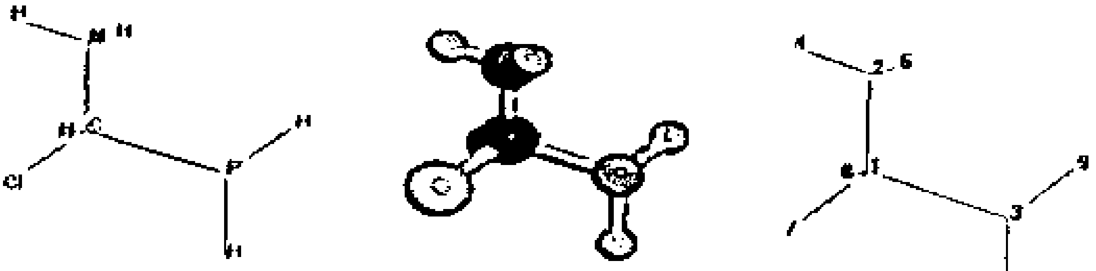
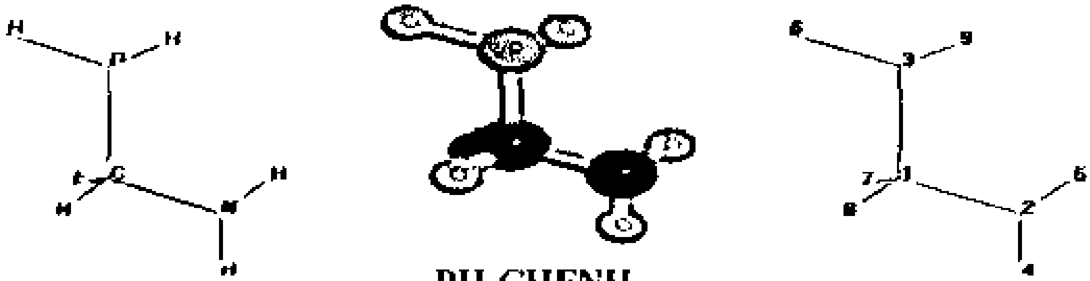

$PHClCHFNH_2$

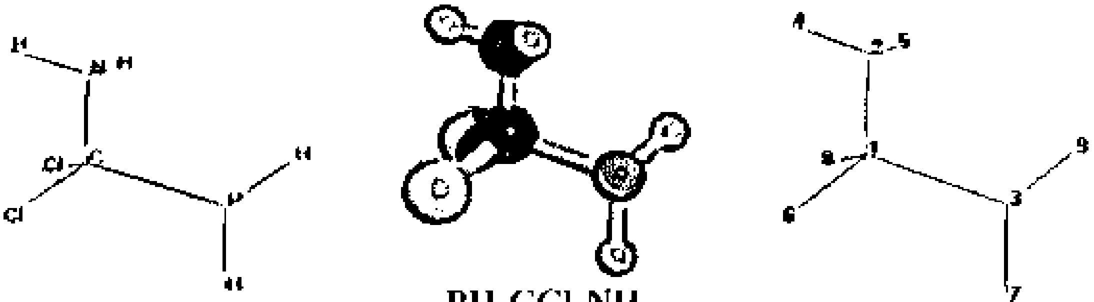
Fig.(3.3): Structures of compounds (Class III)



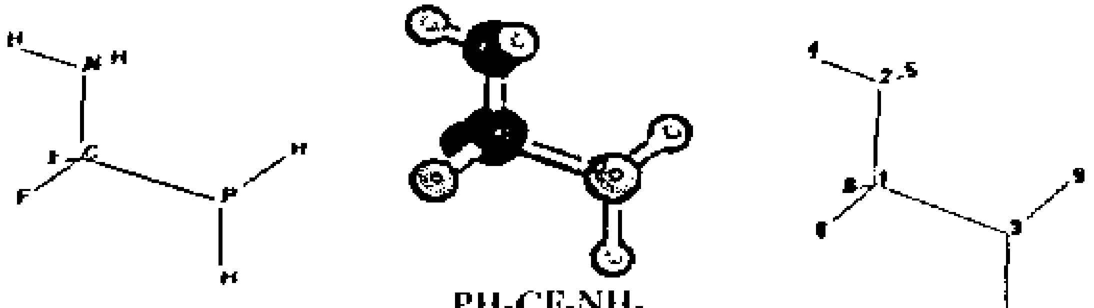
PH$_2$CHClNH$_2$



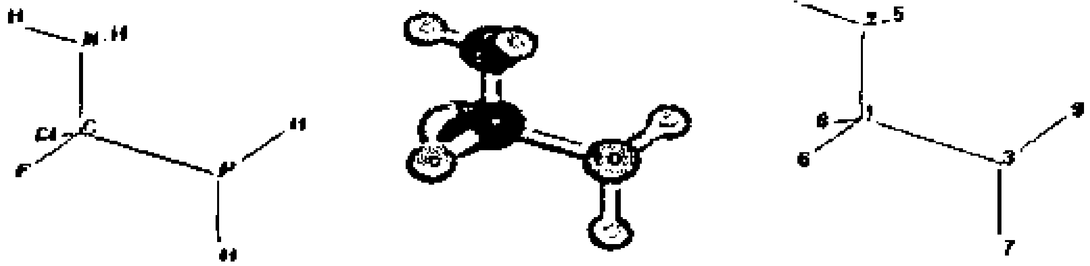
PH$_2$CHFNH$_2$



PH$_2$CCl$_2$NH$_2$



PH$_2$CF$_2$NH$_2$

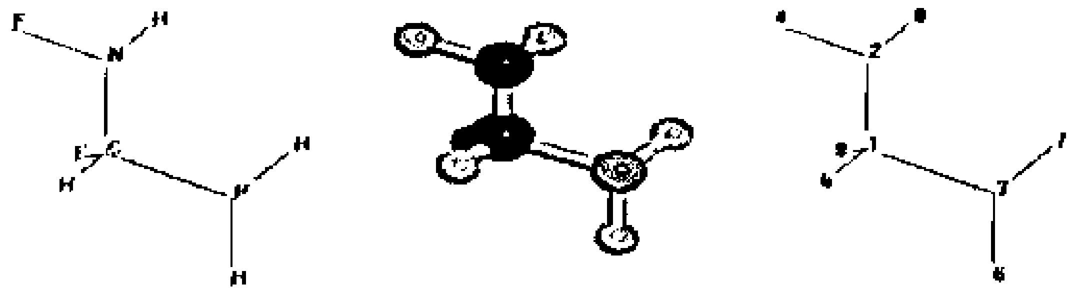


PH$_2$CFClNH$_2$

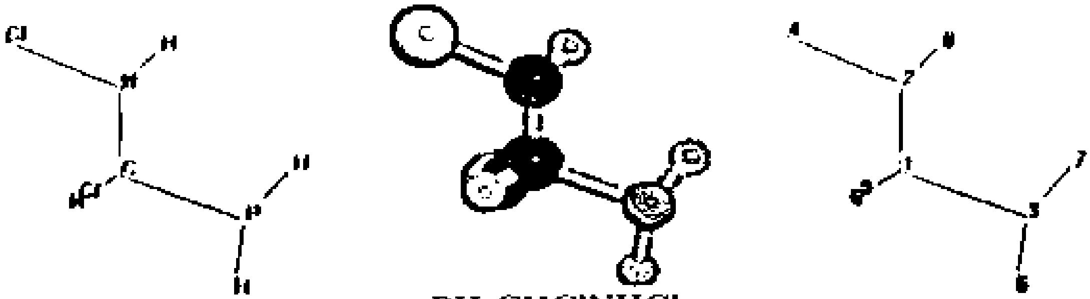
Fig.(3.3) Cont.

able (3.1) Cont.: (Class IV)

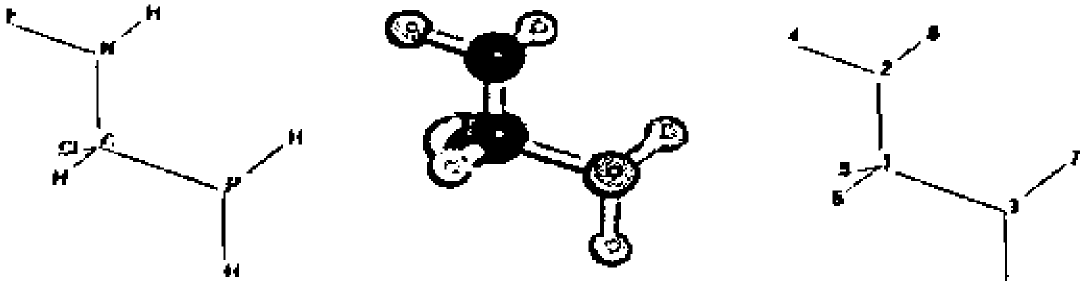
bbreviation	Structure	Name
AFMP	PH$_2$CHFNHF	N-Flouro-C-Flouro-C-phosphanyl methyl amine
2ACMP	PH$_2$CHClNHCl	N-Chloro-C-Chloro -C-phosphanyl methyl amine
ACMP	PH$_2$CHClNHF	N-Flouro-C-Chloro -C-phosphanyl methyl amine
AFMP	PH$_2$CHFNHCl	N-Chloro-C-Flouro -C-phosphanyl methyl amine



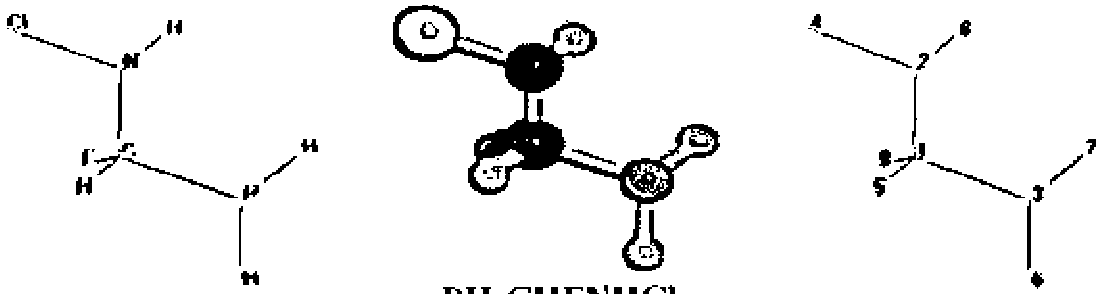
PH$_2$CHFNHF



PH$_2$CHClNHCl



PH$_2$CHClNHF



PH$_2$CHFNHCl

Fig.(3.4): Structures of compounds (Class IV)

CHAPTER

III

RESULTS

&

DISCUSSION

Table (3.2): The bond length(Å) and bond angles (°) of compounds.

Class I	P-H	P-C	N-C	C-H	N-H	NCP
$NH_2CH_2PH_2$	1.4206	1.9121		1.08711	1.0036	106.87
	1.4283	-	-	1.07978	1.0038	-
Class II						
PH_2CH_2NHCl	1.4285	1.9108	1.48186	1.0822	1.0091	108.69
	1.4214	-	-	1.0826	-	-
PH_2CH_2NHF	1.4288	1.9134	1.47882	1.0796	1.0109	107.79
	1.4221	-	-	1.0816	-	-
$PHClCH_2NH_2$	1.4158	1.8926	1.46854	1.0783	1.0006	100.19
	-	-	-	1.0798	1.0008	-
$PHFCH_2NH_2$	1.4251	1.8823	1.43469	1.0894	1.0024	108.44
	-	-	-	1.0816	1.0027	-
$PH_2CH_2NF_2$	1.4248	1.9160	1.48259	1.0765	-	108.27
	1.4228	-	-	1.0774	-	-
$PH_2CH_2NCl_2$	1.4275	1.9183	1.49276	1.0783	-	107.38
	1.4208	-	-	1.0805	-	-
PH_2CH_2NFCl	1.4274	1.9195	1.48714	1.0767	-	106.66
	1.4219	-	-	1.0787	-	-
$PCl_2CH_2NH_2$	-	1.8939	1.45056	1.0811	0.9987	103.32
	-	-	-	1.0806	0.9994	-
$PF_2CH_2NH_2$	-	1.8582	1.46657	1.0845	1.0002	105.24
	-	-	-	1.0820	1.0012	-
$PFClCH_2NH_2$	-	1.8660	1.46636	107876	1.003	100.16
	-	-	-	1.0820	1.0013	--
$PHFCH_2NHF$	1.4250	1.8837	1.47671	1.0811	1.0104	108.42
	-	-	-	1.0828	-	-
$PHClCH_2NHCl$	1.4233	1.8993	1.47323	1.0852	1.0081	108.48
	-	-	-	1.0816	-	-
$PHClCH_2NHF$	1.4238	1.8966	1.47222	1.0789	1.0206	107.67
	-	-	-	1.0839	-	-
$PHFCH_2NHCl$	1.4174	1.8910	1.47644	1.0819	1.0079	106.79
	-	-	-	1.0827	-	-

Table (3.2) cont. :

Class III	P-H	P-C	N-C	C-H	N-H	NCP
$PH_2CHClNH_2$	1.41665	1.9040	1.3727	1.07119	1.0000	112.39
	1.42621	-	-	-	0.9998	-
PH_2CHFNH_2	1.42193	1.9087	1.4079	1.0759	1.0011	109.54
	1.42059	-	-	-	1.0012	-
$PH_2CCl_2NH_2$	1.41366	1.9072	1.3746	-	1.0004	111.89
	1.41953	-	-	-	1.0001	-
$PH_2CF_2NH_2$	1.41745	1.9026	1.3865	-	0.9971	111.89
	1.41672	-	-	-	1.0007	-
$PH_2CClFNH_2$	1.41546	1.9041	1.3802	-	0.9995	112.05
	1.4141	-	-	-	0.9993	-
$PHClCHClNH_2$	1.41816	1.9008	1.4053	1.07263	1.0013	106.54
		-	-	-	1.0009	-
$PHFCHFNH_2$	1.41034	1.8883	1.4351	1.0828	1.0022	105.73
	-	-	-	-	1.0001	-
$PHFCHClNH_2$	1.4094	1.8913	1.3556	1.07119	0.9993	115.14
	-	-	-	-	0.9988	-
$PHClCHFNH_2$	1.4193	1.9057	1.4182	1.0744	1.0022	104.91
		-	-	-	1.0014	-
Class IV						
$PH_2CHFNHF$	1.42317	1.91095	1.43519	1.0726	1.0097	108.30
	1.42098	-	-	-	-	-
$PH_2CHClNHCl$	1.42169	1.91164	1.41034	1.0719	1.0050	108.85
	1.41801	-	-	-	-	-
$PH_2CHClNHF$	1.41744	1.90673	1.4251	1.0714	1.0079	109.52
	1.42147	-	-	-	-	-
$PH_2CHFNHCl$	1.4239	1.91548	1.42914	1.0736	1.0071	107.73
	1.4216	-	-	-	-	-

Table(3.3):Bond length which compared with the package value. [39]

Type of bond	Experimental value (Å)
C-H	1.09
P-H	1.42
P-C	1.85
N-C	1.46
C-Cl	1.79
C-F	1.39
P-Cl	2.04
P-F	1.57
N-F	1.37
N-Cl	1.90
N-H	1.02

able (3-4) : The charges of compounds.

Class I	C	H	H	P	N	H_P	H_P	H_N	H_N
$PH_2CH_2NH_2$	-0.538	0.201	0.239	0.355	-0.786	-0.058	-0.029	0.355	0.306
Class II									
PH_2CH_2NHCl	-0.578	0.262	0.243	0.414	-0.648	-0.025	-0.050	0.355	-
PH_2CH_2NHF	-0.590	0.253	0.240	0.408	-0.297	-0.020	-0.053	0.342	-
$PHClCH_2NH_2$	-0.573	0.730	0.747	0.637	-0.816	-	-0.031	0.325	0.317
$PHFCH_2NH_2$	-0.636	0.261	0.201	0.987	-0.783	-	-0.139	0.308	0.313
$PH_2CH_2NF_2$	-0.587	0.282	0.281	0.405	0.172	-0.013	-0.033	-	-
$PH_2CH_2NCl_2$	-0.585	0.293	0.265	0.415	-0.570	-0.012	-0.034	-	-
PH_2CH_2NFCl	-0.595	0.275	0.282	0.421	-0.188	-0.014	-0.030	-	-
$PCl_2CH_2NH_2$	-0.572	0.273	0.288	0.825	-0.822	--	-	0.350	0.340
$PF_2CH_2NH_2$	-0.715	0.229	0.270	1.433	-0.808	-0.131	-	0.327	0.316
$PFClCH_2NH_2$	-0.657	0.264	0.273	1.219	-0.817	-0.021	-	0.336	0.340
$PHFCH_2NHF$	-0.683	0.244	0.274	1.044	-0.290	-0.027	-0.131	0.345	-
$HClCH_2NHCl$	-0.611	0.254	0.306	0.670	-0.648	-0.102	-0.021	0.366	-
$PHClCH_2NHF$	-0.626	0.255	0.255	0.676	-0.285	-	-0.021	0.351	-
$PHFCH_2NHCl$	-0.662	0.277	0.257	1.019	-0.670	-	-0.102	0.365	-
Class III									
$PH_2CHClNH_2$	-0.336	0.309	-	0.441	0.805	-0.003	-0.031	0.357	0.362
PH_2CHFNH_2	0.043	0.239	-	0.381	-0.851	-0.037	-0.032	0.331	0.338
$PH_2CCl_2NH_2$	-0.383	-	-	0.473	0.790	0.012	-0.002	0.372	0.375
$PH_2CF_2NH_2$	0.632	-	-	0.387	0.904	-0.011	-0.008	0.356	0.354
$PH_2CClFNH_2$	0.221	-	-	0.430	0.853	-0.002	0.004	0.369	0.365
$HClCHClNH_2$	-0.458	-	0.327	0.668	-0.798	-	0.005	0.349	0.358
$PHFCHFNH_2$	-0.006	0.221	-	0.960	-0.859	-	-0.077	0.339	0.329
$PHFCHClNH_2$	-0.370	0.322	-	1.041	-0.804	-0.075	-	0.369	0.370
$PHClCHFNH_2$	0.042	-	0.261	0.614	-0.852		-0.008	0.339	0.348
CLASS IV									
$PH_2CHFNHF$	0.006	-	0.282	0.343	-0.343	-0.026	-0.099	0.357	-
$H_2CHClNHCl$	-0.441	-	0.335	-0.460	-0.706	-0.017	-0.001	0.384	-
$PH_2CHClNHF$	-0.492	-	0.345	0.451	-0.294	-0.015	-0.000	0.369	-
$PH_2CHFNHCl$	0.021	-	0.276	0.077	-0.720	-0.009	-0.026	0.369	-

Table (3.5) : The energy ,HOMO-LUMO gap and LUMO energy(ev) for compounds

Class I	Energy	H/L gap	LUMO energy
$PH_2CH_2NH_2$	-434.2401466	14.60768	4.9640
Class II			
PH_2CH_2NHCl	-890.9188545	13.5404	3.5460
PH_2CH_2NHF	-532.4937392	14.7447	4.7363
$PHClCH_2NH_2$	-890.9834817	11.8278	1.7598
$PHFCH_2NH_2$	-532.5832506	14.3716	4.4606
$PH_2CH_2NF_2$	-630.7559042	14.8541	4.1974
$PH_2CH_2NCl_2$	-1347.5922209	12.1081	1.6370
PH_2CH_2NFCl	-989.1727216	12.9849	2.4097
$PCl_2CH_2NH_2$	-1347.7318467	11.6595	1.0314
$PF_2CH_2NH_2$	-630.9541565	14.7630	4.6411
$PFClCH_2NH_2$	-989.3409060	12.6971	2.0501
$PHFCH_2NHF$	-630.8374163	14.6447	4.1450
$PHClCH_2NHCl$	-1347.6610159	12.0614	1.3891
$PHClCH_2NHF$	-989.2361736	12.2015	1.4275
$PHFCH_2NHCl$	-989.2647248	13.4379	3.0896
Class III			
$PH_2CHClNH_2$	890.971795740	13.9494	3.5537
PH_2CHFNH_2	532.569329780	14.6558	4.5414
$PH_2CCl_2NH_2$	-1347.6737976	13.1925	2.4828
$PH_2CF_2NH_2$	-630.90281167	14.7726	4.2094
$PH_2CClFNH_2$	-989.28207613	13.7355	3.2260
$PHClCHClNH_2$	-1347.7053496	12.1062	1.4578
$PHFCHFNH_2$	-630.9005480	14.3375	4.0051
$PHFCHClNH_2$	-989.3158595	13.5804	3.0706
$PHClCHFNH_2$	-989.3081660	12.4280	1.7163
Class IV			
$PH_2CHFNHF$	-630.8118464	14.8859	4.0965
$PH_2CHClNHCl$	-1347.6391717	13.2533	2.7630
$PH_2CHClNHF$	-989.2101881	13.5775	2.9149
$PH_2CHFNHCl$	-989.2415667	13.6716	2.9333

Table(3.6) : The 1st , 2nd and 3rd ionization energies for compounds

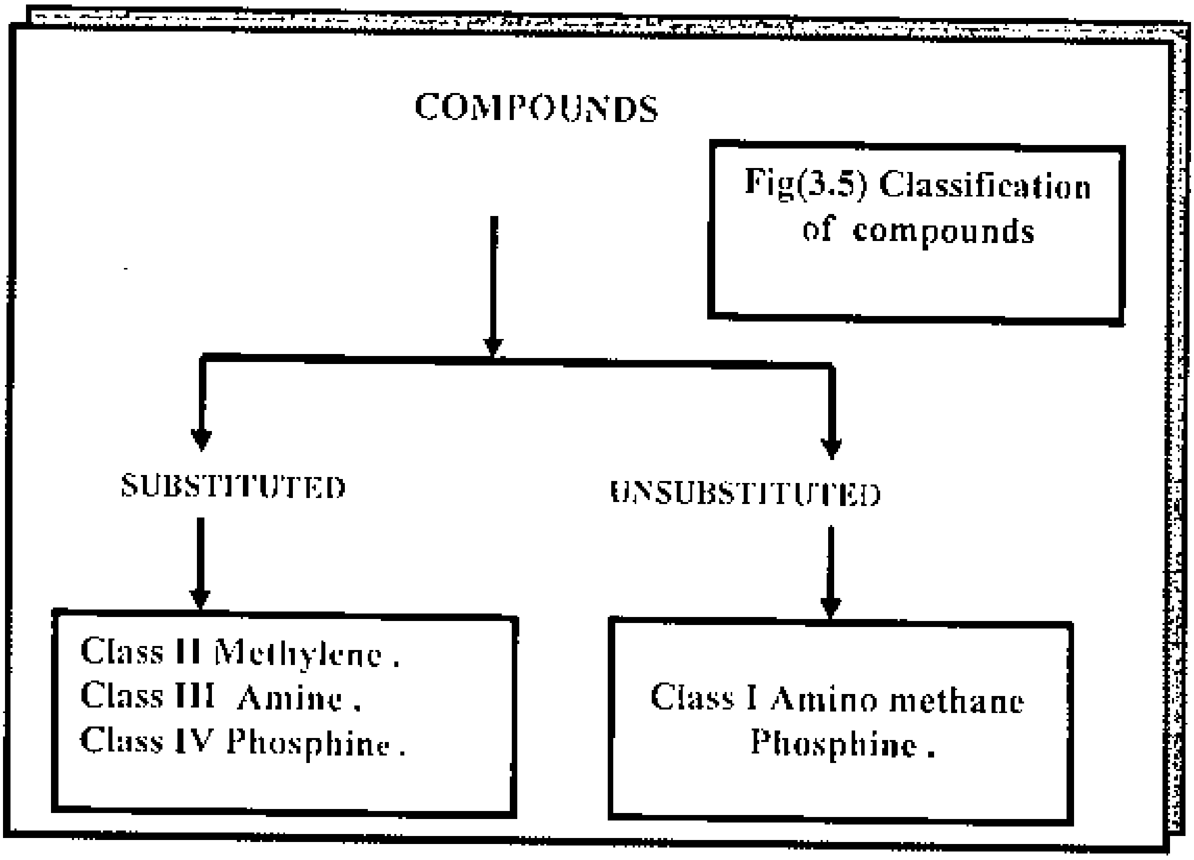
Class I	First	Second	Third
$PH_2CH_2NH_2$	9.6436	15.243	23.2565
Class II			
PH_2CH_2NHCl	9.9943	15.206	22.9726
PH_2CH_2NHF	10.0087	16.993	23.5316
$PHClCH_2NH_2$	10.0681	14.170	22.3755
$PHFCH_2NH_2$	9.9109	15.820	23.7666
$PH_2CH_2NF_2$	10.6567	16.070	24.0048
$PH_2CH_2NCl_2$	10.4712	15.461	22.5886
PH_2CH_2NFCl	10.5752	15.423	23.3670
$PCl_2CH_2NH_2$	10.6281	14.902	21.799
$PF_2CH_2NH_2$	10.1217	16.513	24.6086
$PFClCH_2NH_2$	10.6469	16.329	23.0196
$PHFCH_2NHF$	10.4997	17.201	24.0993
$PHClCH_2NHCl$	10.6723	14.222	22.2246
$PHClCH_2NHF$	10.7740	15.886	22.6186
$PHFCH_2NHCl$	10.3482	15.722	23.2837
Class III			
$PH_2CHClNH_2$	10.3951	15.7783	22.58731
PH_2CHFNH_2	10.1143	15.6534	23.58648
$PH_2CCl_2NH_2$	10.7096	16.0482	22.23183
$PH_2CF_2NH_2$	10.5631	14.1735	24.10934
$PH_2CClFNH_2$	10.5095	16.5751	22.72508
$PHClCHClNH_2$	10.6483	14.3985	22.02342
$PHFCHFNH_2$	10.3324	16.1351	24.01438
$PHFCHClNH_2$	10.5097	13.9788	23.01664
$PHClCHFNH_2$	10.7116	15.7428	22.44859
Class IV			
$PH_2CHFNHF$	10.5752	15.4233	23.36705
$PH_2CHClNHCl$	10.4903	15.3927	22.15563
$PH_2CHClNHF$	10.6627	15.6544	22.62948
$PH_2CHFNHCl$	10.7383	15.7741	23.37019

Table (3.7): lists point group and dipole moment of compounds.

Class I	Point Group	Dipole Moment(D)
$PH_2CH_2NH_2$	C_1	2.0911
Class II		
PH_2CH_2NHCl	C_1	3.7537
PH_2CH_2NHF	C_1	3.5958
$PHClCH_2NH_2$	C_1	5.1356
$PHFCH_2NH_2$	C_1	3.5956
$PH_2CH_2NF_2$	C_1	3.4316
$PH_2CH_2NCl_2$	C_1	3.1489
PH_2CH_2NFCl	C_1	3.4683
$PCl_2CH_2NH_2$	C_1	5.6386
$PF_2CH_2NH_2$	C_1	3.8798
$PFClCH_2NH_2$	C_1	5.2125
$PHFCH_2NHF$	C_1	3.8420
$PHClCH_2NHCl$	C_1	4.7591
$PHClCH_2NHF$	C_1	4.9703
$PHFCH_2NHCl$	C_1	2.6459
Class III		
$PH_2CHClNH_2$	C_1	4.0386
PH_2CHFNH_2	C_1	2.0388
$PH_2CCl_2NH_2$	C_1	3.0639
$PH_2CF_2NH_2$	C_1	1.8935
$PH_2CClFNH_2$	C_1	2.6438
$PHClCHClNH_2$	C_1	5.2032
$PHFCHFNH_2$	C_1	3.3605
$PHFCHClNH_2$	C_1	2.8180
$PHClCHFNH_2$	C_1	5.2149
Class IV		
$PH_2CHFNHF$	C_1	1.9855
$PH_2CHClNHCl$	C_1	2.0389
$PH_2CHClNHF$	C_1	2.4626
$PH_2CHFNHCl$	C_1	1.7541

Compounds :-

Compounds under investigation are listed in table (3.1) and figures (3.1) ,(3.2),(3.3)and (3.4). The species are classified into four classes based upon the site of hydrogen's substitute . Therefore class I is containing only one molecule namely PH_2-CH_2-NH_2. Class II consist of fourteen species in all of them CH_2 group remained unsubstituted .So for simplicity we named classII methylene class. When NH_2 group remained unsubstituted in contrast to CH_2 and PH_2 groups , we deduced nine species which named as amine class (class III). Finally there are four species which are named as phosphine class (class IV) , because PH_2 remain unchanged in all species also in this class there are $PH_2CX_2NX_2$ (X= H, C l, F) sites substitutes .



Fig(3.5) Classification of compounds

Geometries :-

One of the most important and widespread applications of energy derivative is geometry optimization .[40]

The geometries optimizations has been adapted throughout the calculation geometries optimizations, using the software that change the geometry (bond angle , bond length) based on the calculation inputs . After many cycles, the optimization achieved which means the molecule with lowest energy is constructed.

The geometries of the species (bond angles and bond length) are listed in table (3.3) and figure (3.3) . For class I the $CNPH_6$ molecules show that the rP-C being highest 1.92Å and the rC-H being average at 1.085 the lowest bond lengths . The<NCP angle is as expected at 106.9°.for typical tetrahedral. on comparing the symmetry between $CNPH_6$ and CP_2H_6 the two molecules are different , the CH_2 group are perpendicular to one of PH_2 and in plane with the other in CP_2H_6, so the two hydrogen attached to carbon atom are lies in the same distance from lone pairs of each phosphorus . In contrast to $CNPH_6$ the two hydrogen atoms attached to carbon are lies in different position from nitrogen and phosphorus lone pairs one is nearer to nitrogen and other nearer to phosphorus lone pairs ,

all the symmetry difference results in the unequivalent bond length for example rC-H which noted at 1.087Å and 1.079Å while r C-H for CP_2H_6 are identical [2].

For class II species the geometries showed the r P-H ranged from 1.415Å assign for $PHClCH_2NH_2$ to 1.428Å assign for PH_2CH_2NHF also monohalid substituted species . The rN-H range from 0.998Å to 1.010Å assign for $PCl_2CH_2NH_2$ and $PHFCH_2NHF$ respectively.

For class III species the geometries showed the rP-H ranged from 1.409Å assign for $PHFCHClNH_2$ to 1.426Å assign for $PH_2CHClNH_2$ also monohalid substituted species . The rN-H range from 0.998Å to 1.0014Å assign for $PHFCHClNH_2$ and $PHClCHFNH_2$ respectively.

The rP-C is appeared at 1.88Å which the lowest value while the highest rP-C value is at 1.908Å assign for $PHFCFHNH_2$ and PH_2CHFNH_2 respectively. Finally for class III , the <NCP is ranged between 104.912° and 115.149° assigned for $PHClCHFNH_2$ and $PHFCHClNH_2$ respectively.

For class IV species the geometries showed the rP-H ranged from 1.417Å assign for $PH_2CHClNHF$ to 1.4239Å assign for PH_2CH_2NHCl also monohalid substituted species . The rN-H range from 1.005Å to 1.009Å assign for $PH_2CHClNHCl$ and $PH_2CHFNHF$ respectively.

The rP-C is appeared at 1.906Å which the lowest value while the highest rP-C value is at 1.915Å assign for $PH_2CHClNHF$ and $PH_2CHFNHCl$ respectively. Finally for class IV , the <NCP is ranged between 107.733° and 109.52° assigned for $PH_2CHFNHCl$ and $PH_2CHClNHF$respectively

The rP-C is appeared at 1.858Å which the lowest value while the highest rP-C value is at 1.918Å assign for $PF_2CH_2NH_2$ and $PH_2CH_2NCl_2$ respectively. Finally for class II , the <NCP is ranged between 100.16° and 108.69° assigned for $PFClCH_2NH_2$ and PH_2CH_2NHCl respectively.

Charges :-

The charges are summarized in table (3.4). Charges and geometries are so related and followed the same pattern and arrangement for geometry discussion in (c.f.page 50) . The charges recorded for $PH_2CH_2NH_2$ is as expected q_p is equal to 0.355 , q_c equal to -0.538 and q_N equal to-0.786. The difference in phosphours hydrogen charges is equal to 0.028

This huge difference is due to their orientation of hydrogen . the highest q_{HP} is equal to 0.0580 and the other is equal to 0.0299. The nitrogen hydrogen charges are centered at 0.335. finally the carbon hydrogen are also close and they centered at 0.220.

The classII species have the changes of phosphors ranged from 0.405 to 1.434 which assigned for $PH_2CH_2NF_2$ and $PF_2CH_2NH_2$, respectively. The nitrogen charges are ranged from 0.172 to -0.822 which are attributed to $PH_2CH_2NF_2$ and $PCl_2CH_2NH_2$. The carbon charges are ranged from -0.572 to -0.715 which are attributed for $PCl_2CH_2NH_2$ and $PF_2CH_2NH_2$ respectively . The hydrogen charges followed the same pattern . The above results showed that the most negative charges are achieved when the fluorine substitution take place which in good agreement with previous study[2].

The class III charges the carbon charge are markely changed between species in this class due to the substitution which take place on it . The lowest charge is appeared at -0.458 which assigned for $PHClCHClNH_2$ and the highest value is appeared at 0.632 recorded for $PH_2CF_2NH_2$, which is the highest value recorded in all classes . The nitrogen charge are ranged from -0.790 to -0.904 assign for $PH_2CCl_2NH_2$ and $PH_2CF_2NH_2$ respectively. The phosphorus charges are positive in the class and ranged from 0.381 to 1.041 which are attributed to PH_2CHFNH_2 and $PHFCHClNH_2$,respectively. The hydrogen charges did not showed any deviation from expected trend. The class four species showed a carbon charges to be the highest at 0.0218 assign for $PH_2CHFNHCl$ and the lower charges at -0.492 is attributed to $PH_2CHClNHF$. The nitrogen charges are ranged from -0.294 to -0.720 assign for $PH_2CHClNHF$ and $PH_2CHFNHCl$, respectively .Finally the phosphorus charge is equal to 0.460 assign for $PH_2CHClNHCl$ and the lowest one is appeared at 0.077 attributed for $PH_2CHFNHCl$. Again the hydrogen charges remain normal and followed the expected trend.

Energies (Total energy,H/L gap and LUMO energy):-

The energies are listed in table (3.5).

1. Monosubstitution on N- atom and P-atom is higher in energy than flouro case.
2. Dihalogen substitution on N and P atoms is higher than the monosubstitution as expected.
3. Diflouro substitution is lower than dichloro substitution.

The mixed disubstitution on N and P atoms are approximately the same. The H/L gap have been used as a good reference for measuring the stability of many species [41] . If the H/L gap is large then the stability of molecule is greater and Vice versa, for class I the H/L gap appeared at 14.607eV. The class II their H/L gap ranged from 11.659 eV to 14.854 eV , which have been assign for $PCl_2CH_2NH_2$ and $PH_2CH_2NF_2$ respectively LUMO energy for class II has been ranged from 1.031eV to 4.736eV assign for PH_2CH_2NHF and $PCl_2CH_2NH_2$ respectively .From the energy point view the most stable specie has been found to be PH_2CH_2NHF.For classIII in which the Amino group remain unsubstituted , the total electronic energy is ranged from 532.569 a.u to 1347.705 a.u .

The H/L gap values has been lower at 12.106 eV which assign for $PHClCHClNH_2$ and the highest value has been appeared at 14.772 eV assign for $PH_2CF_2NH_2$.

The LUMO energy which appeared at 1.457eV is the lower value which assign for $PHClCHClNH_2$.The highest value at 4.541eV is assign for the most stable species for the most stable species in this class which is PH_2CHFNH_2.

Finally , the remaining four species which have been classified as the lowest energy , H/L gap and LUMO energy for $PH_2CHFNHF$ as expected agreed to be the most stable species , whereas the $PH_2CHClNHCl$ is the most unstable species with the highest total electronic energy.

Ionization energy :

The energy necessary to remove the electron from its highest occupied state is called the 1st ionization energy . similarly , there can be second , third or fourth .etc .We have seen that the ionization energy of a multi electron atom is much lower than what one would expect due to nuclear charge because of the inter electronic repulsion [42].

The table (3.6) showed the 1st ,2nd and 3rd ionization energy for all species . the 1st , 2nd and 3rd IE for $PH_2CH_2NH_2$ is appeared at 9.645 eV ,15.24 and 23.26 respectively , which is in good agreement with previous related study [2].As expected the 1st two IE differ little but the 3rd is far from the two previous values .

The class II species showed the lowest 1st IE is at 9.91 eV and the highest is at 10.77 eV assign for $PHFCH_2NH_2$ and $PHClCH_2NHF$ respectively , the 2nd IE for class II ranged from 14.170 eV to 17.20 which are assign for $PHClCH_2NH_2$ and $PHFCH_2NHF$,respectively . the 3rd IE for this class is also ranged from 21.799 to 24.608 which are attributed for $PCl_2CH_2NH_2$ and $PF_2CH_2NH_2$ respectively .

For class III showed that the lowest 1st IE is at 10.114 assign for PH_2CHFNH_2 and the highest at 10.711 assign for $PHClCHFNH_2$. The 2nd IE for this species are ranged from 13.978 to 16.575 which are assign for $PHFCHClNH_2$ and $PH_2CClF\ NH_2$ respectively . Finally the 3rd IE is also ranged from 22.02 to 24.109 attributed to $PHClCHClNH_2$ and $PH_2CF_2NH_2$ respectively.

Finally classIV the 1st ,2nd and 3rd IE for class IV show that $PH_2CHClNHCl$ species possesses the lowest 1st , 2nd and 3rd IE in which $PH_2CHFNHCl$ possesses the highest 1st 2nd and 3rd IE.

Dipole moment

The values of dipole moment is summarized in table (3.7). Actually the dipole moment rises from the difference in electronegativety between atoms which forms the bond. Therefore every bond should have dipole moment associated with it [43].

It is noted previously that the values of the dipole moment is always positive [44]. The dipole moment for $PH_2CH_2NH_2$ is appeared at 2.091. The class II species showed huge difference in dipole moment which is recorded at 5.63, the highest value assign to $PCl_2CH_2NH_2$ and the lowest value is appeared for $PHFCH_2NH_2$ 2.64. The class III species their dipole moment ranged from 5.21 to 1.89 assign for $PHClCHFNH_2$ and $PH_2CF_2NH_2$ respectively. Finally class IV showed the highest dipole moment at 2.46 assign for $PH_2CHClNHF$ and the lowest value is appeared at 1.75 assign for $PH_2CHFNHCl$. It is worth noting that the dipole moment measurements did not show the expected trend as far as the electronegativety concern. The main factor seems to influence the dipole moment is the geometry rather than the electronegativety

CHAPTER

IV

CONCLUSION

Conclusion

The investigation of twenty-eight molecules constructed from amino methane phosphine showed the following facts based on the parameters calculated. First, the stability of the molecules are related directly to the geometries despite the fact that the molecules possesses a C_1 symmetry which is arise from the bent angle PCN. Second, The most stable molecule is $PH_2CH_2NH_2$ which is appeared in class I. The molecules $PHFCH_2NH_2$, PH_2CHFNH_2 and PH_2CH_2NHF are also showed a little stability in association with their counterpart's species in the classes. Third, the PCN angle (bite angle) which is important in coordination chemistry. The bite angle PCN when it acts as bidentate ligand through P and N atoms. The magnitude of bite angles showed to be increasing as the distance between the substituted halogen decreases. Thus the methane class showed the lowest bite angle whereas the amino class showed the highest 100.1° to 115.2° respectively.

APPENDIX

Appendix will gives some calculations of the compounds under investigation .

Table (a) .Bond angle in degree (°) .
Table (b) .Bond length in Angstrom (Å) .
Table (c) .Energies .
Table (d) .Charges and Electron density .

Table(1): (PH$_2$CH$_2$NH$_2$) ,C$_1$

Table (a)

Angle	Value	Angle	Value
H5N2H4	111.722	H7P3H6	96.3596
H5N2C1	113.633	H7P3C1	97.4738
H4N2C1	113.978	H6P3C1	98.4048
N2C1H9	108.641	P3C1H9	109.793
N2C1H8	114.979	P3C1N2	106.874
H9C1H8	108.43	P3C1H8	108.055

Table (b)

Bond	Value	Bond	Value
P3-H7	1.42063	C1-H8	1.08711
P3-H6	1.42833	C1-H9	1.07978
P3-C1	1.91217	N2-H5	1.00362
C1-N2	1.46843	N2-H4	1.00385

Table(c)

ENERGY	eV
Ionization energy(1st)	9.643659
(2nd)	15.243
(3rd)	23.25657
LUMO energy	4.96397
HOMO-LUMO gap	14.607652
E(RHF) a.u	-434.240146605

Table(d)

Atom	Charge	Electron density
C1	-0.538379	1.538379
N2	-0.786606	1.786606
P3	0.355260	0.64474
H4	0.306078	0.693922
H5	0.310105	0.689895
H6	-0.058204	1.058204
H7	-0.029960	1.02996
H8	0.201782	0.798218
H9	0.239926	0.760074

Table(2): (PH_2CH_2NHCl) ,C_1

Table (a)

Angle	Value	Angle	Value
Cl7-N2-H6	103.595	H4-C1-H8	109.394
H6-N2-C1	112.559	H4-C1-P3	109.626
Cl7-N2-C1	111.182	H8-C1-P3	110.178
N2-C1-H4	113.481	H5-P3-H9	95.9517
N2-C1-H8	105.501	C1-P3-H5	96.1256
C1-P3-H9	96.3048	N2-C1-P3	108.576

Table (b)

Bond	Value	Bond	Value
Cl7-N2	1.82701	C1-H	1.08267
H6-N2	1.00911	C1-H8	1.08223
C1-N2	1.48186	C1-P3	1.9108
P3-H5	1.42853	P3-H9	1.42141

Table(c)

ENERGY	eV
Ionization energy(1st)	9.994342
(2nd)	15.20624
(3rd)	22.97267
LUMO energy	3.546068
HOMO-LUMO gap	13.54041
E(RHF) a.u	-890.91885

Table(d)

Atom	Charge	Electron density
C1	-0.578630	1.57863
N2	-0.648403	1.648403
P3	0.414656	0.585344
H4	0.243648	0.756352
H5	-0.025843	1.025843
H6	0.355077	0.644923
Cl7	0.027687	0.972313
H8	0.262311	0.737689
H9	-0.050503	1.050503

Table(3): (PH_2CH_2NHF), C_1

Table (a)

Angle	Value	Angle	Value
H5-N2-F6	101.541	H7-C1-P3	110.946
H5-N2-C1	111.506	N2-C1-P3	107.796
F6-N2-C1	104.551	C1-P3-H8	96.325
N2-C1-H7	106.428	C1-P3-H9	95.9158
N2-C1-H4	112.351	H9-P3-H8	95.825
H4-C1-P3	108.984	H4-C1-H7	110.305

Table (b)

Bond	Value	Bond	Value
N2-H5	1.01099	C1-H7	1.07969
N2-F6	1.4474	C1-P3	1.91343
N2-C1	1.47882	P3-H8	1.42881
C1-H4	1.08165	P3-H9	1.42215

Table(c)

ENERGY	eV
Ionization energy(1st)	10.008451
(2^{nd})	16.99387
(3^{rd})	23.53167
LUMO energy	4.736346
HOMO-LUMO gap	14.744797
E(RHF) a.u	-532.493739265

Table(d)

Atom	Charge	Electron density
C1	-0.590123	1.590123
N2	-0.297739	1.297739
P3	0.408871	0.591129
H4	0.240198	0.759802
H5	0.342767	0.657233
F6	-0.283587	1.283587
H7	0.253582	0.746418
H8	-0.053723	1.053723
H9	-0.020245	1.020245

Table(4): $(PHClCH_2NH_2)$, C_1

Table (a)

Angle	Value	Angle	Value
Cl6-P3-H5	94.1958	C1-N2-H4	115.769
H5-P3-C1	96.8756	H4-N2-H9	113.714
Cl6-P3-C1	97.9864	H8-C1-N2	109.474
P3-C1-H7	106.483	H7-C1-N2	115.267
P3-C1-H8	108.325	P3-C1-N2	108.694
H9-N2-C1	116.013	H7-C1-H8	108.374

Table (b)

Bond	Value	Bond	Value
P3-H5	1.42422	C1-H8	1.07941
P3-Cl6	2.26576	C1-N2	1.45262
P3-C1	1.90391	N2-H4	1.0
C1-H7	1.08989	N2-H9	1.00041

Table(c)

ENERGY	eV
Ionization energy(1^{st})	10.068110
(2^{nd})	14.17098
(3^{rd})	22.3755
LUMO energy	1.759882
HOMO-LUMO gap	11.827832
E(RHF) a.u	-890.983481728

Table(d)

Atom	Charge	Electron density
C1	-0.556462	1.556462
N2	-0.794911	1.794911
P3	0.615206	0.384794
H4	0.325770	0.67423
H5	-0.031847	1.031847
Cl6	-0.369232	1.369232
H7	0.214840	0.78516
H8	0.279198	0.720802
H9	0.317439	0.682561

Table(5): $(PHFCH_2NH_2),C_1$

Table (a)

Angle	Value	Angle	Value
H6-P3-F9	98.5988	F9-P3-C1	99.8152
H7-C1-H8	108.308	H6-P3-C1	95.9502
H4-N2-H5	112.195	F9-P3-C1	99.8152
P3-C1-N2	108.441	H8-C1-N2	108.654
P3-C1-H7	108.03	H7-C1-N2	115.126
H5-N2-C1	114.483	C1-N2-H4	114.509

Table (b)

Bond	Value	Bond	Value
H6-P3	1.4251	C1-H8	1.08163
F9-P3	1.65317	C1-N2	1.46537
P3-C1	1.8823	N2-H4	1.00243
C1-H7	1.08945	N2-H5	1.00279

Table(c)

ENERGY	eV
Ionization energy(1st)	9.910951
(2nd)	15.8203
(3rd)	23.76663
LUMO energy	4.460651
HOMO-LUMO gap	14.371653
E(RHF) a.u	532.583250642

Table(d)

Atom	Charge	Electron density
C1	-0.636961	1.636961
N2	-0.783604	1.783604
P3	0.987637	0.012363
H4	0.313426	0.686574
H5	0.308583	0.691417
H6	-0.139090	1.13909
H7	0.201943	0.798057
H8	0.261965	0.738035
F9	-0.513901	1.513901

Table(6): $(PH_2CH_2NF_2)$, C_1

Table (a)

Angle	Value	Angle	Value
F4-N2- F5	101.386	H9-P3-H8	95.5623
F4-N2-C1	103.61	H6-C1-H7	110.931
N2-C1-H7	105.762	F5-N2-C1	102.949
N2-C1-P3	108.276	N2-C1-H6	105.974
C1-P3-H8	95.2888	H6-C1-P3	109.806
C1-P3-H9	96.3261	H7-C1-P3	113.507

Table (b)

Bond	Value	Bond	Value
N2-F4	1.42588	C1-H7	1.07656
N2-F5	1.42476	C1-P3	1.91601
N2-C1	1.48259	P3-H8	1.42484
C1-H6	1.07743	P3-H9	1.42282

Table(c)

ENERGY	eV
Ionization energy(1st)	10.656779
(2nd)	16.07088
(3rd)	24.0048
LUMO energy	4.1974
HOMO-LUMO gap	14.85414
E(RHF) a.u	-630.755904252

Table(d)

Atom	Charge	Electron density
C1	-0.587023	1.587023
N2	0.172081	0.827919
P3	0.405978	0.594022
F4	-0.255810	1.25581
F5	-0.252427	1.252427
H6	0.281628	0.71837
H7	0.282897	0.717103
H8	-0.033354	1.033354
H9	-0.013970	1.013970

Table(7): $(PH_2CH_2NCl_2)$, C_1

Table (a)

Angle	Value	Angle	Value
Cl4-N2-Cl5	107.676	H6-C1-P3	110.52
Cl4-N2-C1	109.477	H7-C1-P3	110.501
Cl5-N2-C1	110.541	C1-P3-H8	94.8793
N2-C1-H6	112.565	C1-P3-H9	96.1523
N2-C1-H7	105.601	H8-P3-H9	96.0117
N2-C1-P3	107.38	H7-C1-H6	110.141

Table (b)

Bond	Value	Bond	Value
N2-Cl4	1.82942	C1-H7	1.07836
N2-Cl5	1.82348	C1-P3	1.91832
N2-C1	1.49276	P3-H8	1.42752
C1-H6	1.08052	P3-H9	1.42089

Table(c)

ENERGY	eV
Ionization energy(1^{st})	10.471207
(2^{nd})	15.46166
(3^{rd})	22.58868
LUMO energy	1.637029
HOMO-LUMO gap	12.108169
E(RHF) a. u	-1347.592220921

Table(d)

Atom	Charge	Electron density
C1	- 0.585272	1.585272
N2	-0.570508	1.570508
P3	0.415406	0.584594
Cl4	0.104919	0.895081
Cl5	0.123539	0.876461
H6	0.265206	0.734794
H7	0.293114	0.706886
H8	-0.034199	1.034199
H9	-0.012205	1.012205

Table(8): $(PH_2CH_2NFCl),C_1$

Table (a)

Angle	Value	Angle	Value
F5-N2-Cl4	102.814	H3-C1-P3	110.018
Cl4-N2-C1	109.533	H7-C1-P3	111.723
F5-N2-C1	103.943	C1-P3-H9	96.0748
N2-C1-H6	110.893	C1-P3-H8	95.0277
N2-C1-H7	106.455	H9-P3-H8	95.7415
H6-C1-H7	111.007	N2-C1-P3	106.669

Table (b)

Bond	Value	Bond	Value
Cl4-N2	1.83331	C1-H7	1.07673
F5-N2	1.43082	C1-P3	1.9195
N2-C1	1.48714	P3-H8	1.42744
C1-H6	1.07878	P3-H9	1.42193

Table(c)

ENERGY	e.V
Ionization energy(1st)	11.575221
(2nd)	15.42334
(3rd)	23.36705
LUMO energy	2.409
HOMO-LUMO gap	12.984907
E(RHF) a. u	-989.172721624

Table(d)

Atom	Charge	Electron density
C1	-0.595243	1.595243
N2	-0.188462	1.188462
P3	0.421837	0.578163
Cl4	0.091728	0.908272
F5	-0.237904	1.237904
H6	0.275612	0.724388
H7	0.282129	0.717871
H8	-0.035064	1.035064
H9	-0.014641	1.014641

Table(9): ($PCl_2CH_2NH_2$) C_1

Table (a)

Angle	Value	Angle	Value
Cl8-P3-Cl6	98.7694	Cl8-P3-C1	95.1902
H9-C1-H7	109.375	H4-N2-C1	116.293
H4-N2-H5	114.779	H5-N2-C1	117.069
P3-C1-N2	103.329	P3-C1-H7	107.185
H9-C1-P3	109.891	H9-C1-N2	115.263
Cl6-P3-C1	97.3407	H7-C1-N2	111.358

Table (b)

Bond	Value	Bond	Value
P3-Cl6	2.26302	C1-H7	1.08118
P3-Cl8	2.25203	C1-N2	1.45056
P3-C1	1.89391	N2-H5	0.998742
C1-H9	1.08066	N2-H4	0.999423

Table(c)

ENERGY	eV
Ionization energy(1st)	10.628169
(2nd)	14.90252
(3rd)	21.7993
LUMO energy	1.031404
HOMO-LUMO gap	11.659594
E(RHF) a.u	-1347.731846721

Table(d)

Atom	Charge	Electron density
C1	-0.572161	1.572161
N2	-0.822051	1.822051
P3	0.825496	0.174504
H4	0.350024	0.649976
H5	0.340286	0.659714
Cl6	-0.354399	1.354399
H7	0.273076	0.726924
Cl8	-0.328661	1.328661
H9	0.288388	0.711612

Table(10): ($PF_2CH_2NH_2$) C_1

Table (a)

Angle	Value	Angle	Value
F6-P3-F8	96.0291	H4-N2-C1	115.321
F6-P3-C1	97.5629	H5-N2-C1	115.3
F8-P3-C1	97.427	N2-C1-P3	105.242
H9-C1-H7	108.186	H9-C1-N2	109.912
H9-C1-P3	108.057	H7-C1-N2	114.761
H4-N2-H5	112.619	H7-C1-P3	110.589

Table (b)

Bond	Value	Bond	Value
P3-F6	1.63769	C1-H7	1.08452
P3-F8	1.63271	C1-N2	1.46657
P3-C1	1.85823	N2-H4	1.00029
C1-H9	1.08203	N2-H5	1.00122

Table(c)

ENERGY	(eV)
Ionization energy(1st)	10.121748
(2nd)	16.51343
(3rd)	24.60863
LUMO energy	4.641191
HOMO-LUMO gap	14.763001
E(RHF) a.u	-630.954156526

Table(d)

Atom	Charge	Electron density
C1	-0.715431	1.715431
N2	-0.808396	1.808396
P3	1.433900	0.4339
H4	0.327395	0.672605
H5	0.316914	0.683086
F6	-0.532488	1.532488
H7	0.229493	0.770507
F8	-0.522139	1.522139
H9	0.270750	0.72925

Table(11): $(PFClCH_2NH_2),C_1$

Table (a)

Angle	Value	Angle	Value
Cl4-P3-F8	98.7266	H9-C1-N2	110.661
Cl4-P3-C1	97.8571	H6-C1-N2	115.144
F8-P3-C1	95.0262	C1-N2-H5	115.233
P3-C1-H9	109.286	C1-N2-H7	114.451
P3-C1-H6	111.455	H5-N2-H7	113.646
P3-C1-N2	100.164	H9-C1-H6	109.72

Table (b)

Bond	Value	Bond	Value
P3-Cl4	2.28562	C1-H6	1.08209
P3-F8	1.63789	C1-N2	1.46636
P3-C1	1.86608	N2-H5	1.003
C1-H9	1.07876	N2-H7	1.00132

Table(c)

ENERGY	eV
Ionization energy(1^{st})	10.646987
(2^{nd})	16.3295
(3^{rd})	23.01961
LUMO energy	2.050119
HOMO-LUMO gap	12.697106
E(RHF) a.u	-989.340906055

Table(d)

Atom	Charge	Electron density
C1	-0.657469	1.657469
N2	-0.817165	1.817165
P3	1.219309	-0.219309
Cl4	-0.458359	1.458359
H5	0.336010	0.66399
H6	0.273482	0.726518
H7	0.340168	0.659832
F8	-0.500069	1.500069
H9	0.264093	0.7359

Table(12): ($PHFCH_2NHF$) , C_1

Table (a)

Angle	Value	Angle	Value
F7-P3-H6	98.4182	F5-N2-C1	103.701
F5-N2-H4	101.779	H4-N2-C1	111.846
H9-C1-H8	110.404	H8-C1-P3	109.45
P3-C1-N2	108.426	H9-C1-P3	109.217
H6-P3-C1	94.2468	H9-C1-N2	107.387
F7-P3-C1	98.2607	H8-C1-N2	111.889

Table (b)

Bond	Value	Bond	Value
N2-F5	1.44749	C1-H8	1.0828
N2-H4	1.01041	C1-P3	1.88373
N2-C1	1.47671	P3-F7	1.65311
C1-H9	1.08117	P3-H6	1.42504

Table(c)

ENERGY	eV
Ionization energy(1st)	10.499701
(2nd)	17.20121
(3rd)	24.09934
LUMO energy	4.145066
HOMO-LUMO gap	14.644796
E(RHF) a.u	-630.837416329

Table(d)

Atom	Charge	Electron density
C1	-0.683692	1.683692
N2	-0.290039	1.290039
P3	1.044181	-0.044181
H4	0.345893	0.654107
F5	-0.287811	1.287811
H6	-0.131107	1.131107
F7	-0.515669	1.515669
H8	0.244178	0.755822
H9	0.274065	0.725935

Table(13): (PHClCH$_2$NHCl) ,C_1

Table (a)

Angle	Value	Angle	Value
Cl7-P3-H6	93.8858	H8-C1-N2	113.889
Cl5-N2-H4	104.707	H9-C1-N2	106.941
H9-C1-H8	109.651	H4-N2-C1	113.532
P3-C1-N2	108.489	Cl5-N2-C1	110.878
Cl7-P3-C1	97.1137	H9-C1-P3	108.933
H6-P3-C1	95.1407	H8-C1-P3	108.831

Table (b)

Bond	Value	Bond	Value
N2-Cl5	1.82202	C1-H8	1.08522
N2-H4	1.0081	C1-P3	1.89933
N2-C1	1.47323	P3-H6	1.42339
C1-H9	1.08165	P3-Cl7	2.2671

Table(c)

ENERGY	eV
Ionization energy(1st)	10.672307
(2nd)	14.22265
(3rd)	22.22464
LUMO energy	1.389158
HOMO-LUMO gap	12.061498
E(RHF) a.u	-1347.661015953

Table(d)

Atom	Charge	Electron density
C1	-0.611679	1.611679
N2	-0.648062	1.648062
P3	0.670406	0.329594
H4	0.366021	0.633979
Cl5	0.041763	0.958237
H6	-0.021345	1.021345
Cl7	-0.357979	1.357979
H8	0.254813	0.745187
H9	0.306060	0.69394

Table(14): $(PHClCH_2NHF)$,C_1

Table (a)

Angle	Value	Angle	Value
F5-N2-H4	102.076	H8-C1-P3	108.248
Cl7-P3-H6	93.7149	H9-C1-P3	109.987
P3-C1-N2	107.672	F5-N2-C1	103.44
H9-C1-H8	110.595	H4-N2-C1	111.998
Cl7-P3-C1	97.1649	N2-C1-H9	108.248
H6-P3-C1	94.9931	N2-C1-H8	112.043

Table (b)

Bond	Value	Bond	Value
F5-N2	1.44669	C1-H8	1.08392
N2-H4	1.02065	C1-P3	1.8966
N2-C1	1.47222	P3-H6	1.4238
C1-H9	1.07894	P3-Cl7	2.27016

Table(c)

ENERGY	eV
Ionization energy(1st)	10.774037
(2nd)	15.88645
(3rd)	22.61864
LUMO energy	1.427515
HOMO-LUMO gap	12.201575
E(RHF) a.u	-989.236173688

Table(d)

Atom	Charge	Electron density
C1	-0.626467	1.626467
N2	-0.285327	1.285327
P3	0.676310	0.32369
H4	0.351476	0.648524
F5	-0.283906	1.283906
H6	-0.021390	1.02139
Cl7	-0.361620	1.36162
H8	0.255343	0.744657
H9	0.295582	0.704418

Table(15): ($PHFCH_2NHCl$), C_1

Table (a)

Angle	Value	Angle	Value
H6-P3-F5	99.1806	H4-C1-N2	114.103
F5-P3-C1	96.1107	P3-C1-N2	106.792
H6-P3-C1	95.0471	H9-C1-N2	106.845
P3-C1-H4	110.779	C1-N2-Cl8	111.147
P3-C1-H9	109.104	C1-N2-H7	113.533
H4-C1-H9	109.049	Cl8-N2-H7	104.162

Table (b)

Bond	Value	Bond	Value
P3-H6	1.41745	C1-H9	1.08276
P3-F5	1.65673	C1-N2	1.47644
P3-C1	1.89106	N2-Cl8	1.82506
C1-H4	1.08196	N2-H7	1.00797

Table(c)

ENERGY	eV
Ionization energy(1st)	10.348233
(2nd)	15.72219
(3rd)	23.28373
LUMO energy	3.089616
HOMO-LUMO gap	13.437916
E(RHF) a.u	-989.264724841

Table(d)

Atom	Charge	Electron density
C1	-0.662404	1.662404
N2	-0.670071	1.670071
P3	1.019939	0.019939-
H4	0.257262	0.742738
F5	-0.522118	1.522118
H6	-0.102384	1.102384
H7	0.365324	0.634676
Cl8	0.036592	0.963408
H9	0.277858	0.722142

Table(16): $(PH_2CHClNH_2)$, C_1

Table (a)

Angle	Value	Angle	Value
H5-N2-H4	115.095	C1-P3-H6	97.5317
H5-N2-C1	118.126	H9-P3-H6	96.5721
H4-N2-C1	118425	N2-C1-P3	112.394
N2-C1-H8	113.318	Cl7-C1-H8	98.117
N2-C1-Cl7	112.358	Cl7-C1-P3	103.202
C1-P3-H9	95.6329	P3-C1-H8	116.056

Table (b)

Bond	Value	Bond	Value
N2-H5	1.00007	C1-Cl7	2.03811
N2-H4	0.99986	C1-P3	1.90406
N2-C1	1.37273	P3-H6	1.41665
C1-H8	1.07119	P3-H9	1.42621

Table(c)

ENERGY	eV
Ionization energy(1st)	10.395176
(2nd)	15.77833
(3rd)	22.58731
LUMO energy	3.55371
HOMO-LUMO gap	13.94941
E(RHF) a.u	-890.971795740

Table(d)

Atom	Charge	Electron density
C1	- 0.336116	1.336116
N2	-0.805737	1.805737
P3	0.441146	0.558854
H4	0.357880	0.64212
H5	0.362858	0.637142
H6	-0.003979	1.003979
Cl7	-0.294743	1.294743
H8	0.309280	0.69072
H9	-0.030589	1.030589

Table(17): (PH_2CHFNH_2) , C_1

Table (a)

Angle	Value	Angle	Value
H5-N2-H4	113.769	C1-P3-H6	97.3152
H5-N2-C1	116.565	C1-P3-H9	97.4368
H4-N2-C1	117.046	H6-P3-H9	96.5703
N2-C2-P3	109.564	F7-C1-P3	104.351
N2-C1-F7	114.203	H8-C1-P3	112.348
N2-C1-H8	109.759	H8-C1-F7	106.557

Table (b)

Bond	Value	Bond	Value
P3-H9	1.42193	C1-H8	1.0759
P3-H6	1.42059	C1-N2	1.4079
P3-C1	1.90879	N2-H5	1.00119
C1-F7	1.42194	N2-H4	1.00122

Table(c)

ENERGY	eV
Ionization energy(1st)	10.114349
(2nd)	15.65345
(3rd)	23.58648
LUMO energy	4.541482
HOMO-LUMO gap	14.655831
E(RHF) a.u	-532.569329780

Table(d)

Atom	Charge	Electron density
C1	0.043196	0.956804
N2	-0.851549	1.851549
P3	0.381915	0.618085
H4	0.331814	0.668186
H5	0.338681	0.661319
H6	-0.031857	1.031857
F7	-0.413300	1.4133
H8	0.239062	0.760938
H9	-0.037963	1.037963

Table(18): ($PH_2CCl_2NH_2$),C_1

Table (a)

Angle	Value	Angle	Value
H9-P3-H7	97.1047	H5-N2-C1	117.736
H5-N2-H4	116.291	H4-N2-C1	118.291
Cl8-C1-Cl6	103.972	Cl6-C1-P3	105.288
P3-C1-N2	111.819	Cl8-C1-P3	114.086
H7-P3-C1	97.3514	N2-C1-Cl8	108.811
H9-P3-C1	96.1944	N2-C1-Cl6	112.637

Table (b)

Bond	Value	Bond	Value
H4-N2	1.00019	C1-Cl6	1.95724
H5-N2	1.0004	C1-P3	1.90732
N2-C1	1.37463	P3-H9	1.41953
C1-Cl8	1.87165	P3-H7	1.41366

Table(c)

ENERGY	eV
Ionization energy(1st)	10.709642
(2nd)	16.04821
(3rd)	22.23183
LUMO energy	2.48281
HOMO-LUMO gap	13.1925
E(RHF) a.u	-1347.673797638

Table(d)

Atom	Charge	Electron density
C1	-0.383185	1.383185
N2	-0.790299	1.790299
P3	0.473687	0.526313
H4	0.375834	0.624166
H5	0.372261	0.627739
Cl6	-0.107063	1.107063
H7	0.012001	0.987999
Cl8	0.048754	0.951246
H9	-0.001992	1.001992

Table(19): $(PH_2CF_2NH_2)$,C_1

Table (a)

Angle	Value	Angle	Value
H5-N2-H4	116.484	H5-N2-C1	118.526
H9-P3-H7	97.16	H4-N2-C1	117.169
F6-C1-F8	104.517	N2-C1-F8	108.617
P3-C1-N2	111.893	N2-C1-F6	113.802
H9-P3-C1	96.3802	F6-C1-P3	106
H7-P3-C1	96.2489	F8-C1-P3	111.814

Table (b)

Bond	Value	Bond	Value
P3-H9	1.41745	C1-F8	1.37534
P3-H7	1.41672	C1-N2	1.38654
P3-C1	1.90261	N2-H5	0.997155
C1-F6	1.39323	N2-H4	1.00072

Table(c)

ENERGY	eV
Ionization energy(1st)	10.563194
(2nd)	14.17356
(3rd)	24.10934
LUMO energy	4.209452
HOMO-LUMO gap	14.772672
E(RHF) a.u	-630.902811672

Table(d)

Atom	Charge	Electron density
C1	0.632682	0.367318
N2	-0.904064	1.904064
P3	0.387747	0.612253
H4	0.354304	0.645696
H5	0.356242	0.643758
F6	-0.406310	1.40631
H7	-0.008210	1.00821
F8	-0.400841	1.400841
H9	-0.011552	1.011552

Table(20): (PH2CClFNH2),C_1

Table(a)

Angle	Value	Angle	Value
H9-P3-H7	97.3255	H7-P3-C1	96.8148
H5-N2-H4	116.809	P3-C1-F6	106.16
Cl8-C1-F6	102.771	P3-C1-Cl8	112.84
H9-P3-C1	97.6506	Cl8-C1-N2	107.594
P3-C1-N2	112.059	H5-N2-C1	118.428
H4-N2-C1	118.589	N -C1-F6	115.177

Table (b)

Bond	Value	Bond	Value
N2-H5	0.999582	C1-F6	1.39283
N2-H4	0.999343	C1-P3	1.90417
N2-C1	1.3802	P3-H9	1.41546
C1-Cl8	1.90787	P3-H7	1.4141

Table(c)

ENERGY	eV
Ionization energy(1^{st})	10.509506
(2^{nd})	16.57512
(3^{rd})	22.72508
LUMO energy	3.226033
HOMO-LUMO gap	13.735553
E(RHF) a.u	-989.282076130

Table(d)

Atom	Charge	Electron density
C1	0.122684	0.877316
N2	-0.853445	1.853445
P3	0.430882	0.569118
H4	0.369503	0.630497
H5	0.365193	0.634807
F6	-0.374133	1.374133
H7	0.003708	0.996292
Cl8	-0.062206	1.062206
H9	-0.002186	1.002186

Table(21): $(PHClCHClNH_2)$,C_1

Table (a)

Angle	Value	Angle	Value
Cl5-P3-H9	95.6323	P3-C1-N2	106.545
Cl5-P3-C1	101.606	C1-N2-H8	117.046
H9-P3-C1	95.697	C1-N2-H6	116.862
P3-C1-H7	110.427	H8-N2-H6	113.529
P3-C1-Cl4	112.959	Cl4-C1-N2	112.187
H7-C1-Cl4	103.018	H7-C1-N2	111.814

Table (b)

Bond	Value	Bond	Value
P3-Cl5	2.24675	C1-H7	1.07263
H9-P3	1.41816	C1-N2	1.40534
P3-C1	1.9008	N2-H6	1.00094
C1-Cl4	1.93637	N2-H8	1.00133

Table(c)

ENERGY	eV
Ionization energy(1st)	10.648372
(2nd)	14.3985
(3rd)	22.02342
LUMO energy	1.457876
HOMO-LUMO gap	12.106248
E(RHF) a.u	-1347.705349640

Table(d)

Atom	Charge	Electron density
C1	-0.458203	1.458203
N2	-0.798862	1.798862
P3	0.668466	0.331534
Cl4	-0.116537	1.116537
Cl5	-0.334818	1.334818
H6	0.358353	0.641647
H7	0.327000	0.673
H8	0.349752	0.650248
H9	0.004851	0.995149

Table(22): ($PHFCHFNH_2$) C_1

Table (a)

Angle	Value	Angle	Value
F6-P3-H9	100.029	P3-C1-N2	105.737
H9-P3-C1	94.4719	F6-P3-C1	98.8871
H9-C1-H7	138.405	P3-C1-F8	109.575
H7-C1-F8	106.539	P3-C1-H7	110.775
H5-N2-H4	114.205	F8-C1-N2	107.725
H5-N2-C1	116.633	H7-C1-N2	116.365

Table (b)

Bond	Value	Bond	Value
F6-P3	1.6527	C1-H7	1.0828
P3-H9	1.41034	C1-F8	1.40173
P3-C1	1.88836	C1-N2	1.43469
N2-H4	1.00224	N2-H5	1.00012

Table(c)

ENERGY	eV
Ionization energy(1st)	10.332415
(2nd)	16.1351
(3rd)	24.01438
LUMO energy	4.005174
HOMO-LUMO gap	14.337584
E(RHF) a.u	630.900548026

Table(d)

Atom	Charge	Electron density
C1	-0.005968	1.005968
N2	-0.859785	1.859785
P3	0.960945	0.039055
H4	0.339527	0.660473
H5	0.329651	0.70349
F6	-0.512475	1.512475
H7	0.221592	0.778408
F8	-0.396246	1.396246
H9	-0.077241	1.077241

Table(23): (PHFCHClNH_2),C_1

Table (a)

Angle	Value	Angle	Value
H5-N2-H4	115.873	Cl7-C1-P3	96.8743
F9-P3-H6	98.6458	F9-P3-C1	98.5528
Cl7-C1-H8	98.0629	H6-P3-C1	95.4491
P3-C1-N2	115.149	C1-N2-H4	119.544
H5-N2-C1	119.669	Cl7-C1-N2	112.61
N2-C1-H8	114.018	P3-C1-H8	117.17

Table (b)

Bond	Value	Bond	Value
P3-F9	1.65306	C1-H8	1.07119
P3-H6	1.40948	C1-N2	1.35568
P3-C1	1.89138	N2-H5	0.999345
C1-Cl7	2.08034	N2-H4	0.998833

Table(c)

ENERGY	eV
Ionization energy(1st)	10.509727
(2nd)	13.97885
(3rd)	23.01664
LUMO energy	3.070686
HOMO-LUMO gap	13.580413
E(RHF) a.u	-989.315859555

Table(d)

Atom	Charge	Electron density
C1	-0.370366	1.370366
N2	-0.804951	1.804951
P3	1.041378	-0.041378
H4	0.370419	0.629581
H5	0.369957	0.630043
H6	-0.075518	1.075518
Cl7	-0.341148	1.341148
H8	0.322001	0.677999
F9	-0.511770	1.51177

Table(24): ($PHClCHFNH_2$)C_1

Table (a)

Angle	Value	Angle	Value
H9-P3-Cl5	95.0191	P3-C1-N2	104.912
H9-P3-C1	94.5592	C1-N2-H6	117.021
Cl5-P3-C1	99.5253	C1-N2-H8	116.234
P3-C1-F4	110.301	H8-N2-H6	113.149
P3-C1-H7	109.067	F4-C1-N2	113.932
H7-C1-F4	108.582	H7-C1-N2	109.934

Table (b)

Bond	Value	Bond	Value
P3-Cl5	2.26072	C1-H7	1.0744
P3-H9	1.41934	C1-N2	1.41825
P3-C1	1.90578	N2-H8	1.00225
C1-F4	1.39984	N2-H6	1.00147

Table(c)

ENERGY	eV
Ionization energy(1st)	10.711692
(2nd)	15.74284
(3rd)	22.44859
LUMO energy	1.716327
HOMO-LUMO gap	12.428019
E(RHF) a.u	-989.308166038

Table(d)

Atom	Charge	Electron density
C1	0.042129	0.957871
N2	-0.852934	1.852934
P3	0.614074	0.385926
F4	-0.387998	1.387998
Cl5	-0.357220	1.35722
H6	0.348479	0.651521
H7	0.261903	0.738097
H8	0.339892	0.660108
H9	-0.008323	1.008323

Table(25): $(PH_2CHFNHF)$,C_1

Table(a)

Angle	Value	Angle	Value
H6-P3-H7	95.8187	P3-C1-F9	109.793
H7-P3-C1	95.9674	H5-C1-N2	107.434
H6-P3-C1	95.3428	F7-C1-N2	112.099
P3-C1-N2	108.305	C1-N2-H8	112.618
H9-C1-F9	108.919	C1-N2-F4	106.162
P3-C1-H5	120.538	H8-N2-F4	102.684

Table (b)

Bond	Value	Bond	Value
N2-H8	1.00977	C1-H5	1.07263
N2-F4	1.44255	C1-P3	1.91095
N2-C1	1.43519	P3-H7	1.42317
F9-C1	1.40266	P3-H6	1.42098

Table(c)

ENERGY	eV
Ionization energy(1st)	10.789419
(2nd)	17.48326
(3rd)	24.02298
LUMO energy	4.0965
HOMO-LUMO gap	14.885
E(RHF) a.u	-630.811846451

Table(d)

Atom	Charge	Electron density
C1	0.005967	0.994033
N2	-0.343632	1.343632
P3	0.396642	0.603358
F4	-0.267213	1.267213
H5	0.282677	0.717323
H6	-0.009919	1.009919
H7	-0.026425	1.026425
H8	0.357091	0.642909
F9	-0.395189	1.395189

Table(26): $(PH_2CHClNHCl)$,C_1

Table (a)

Angle	Value	Angle	Value
H7-P3-H6	96.0849	Cl9-C1-N2	112.056
H7-P3-C1	96.2652	C1-N2-H8	116.681
H6-P3-C1	97.1358	C1-N2-H4	115.167
P3-C1-N2	108.859	H8-N2-H4	107.403
Cl9-C1-H5	102.544	H5-C1-P3	110.962
H5-C1-N2	111.071	Cl9-C1-P3	111.271

Table (b)

Bond	Value	Bond	Value
N2-H8	1.00501	C1-H5	1.07198
N2-Cl4	1.79661	C1-P3	1.91164
N2-C1	1.41034	P3-H7	1.42169
C1-Cl9	1.94519	P3-H6	1.41801

Table(c)

ENERGY	eV
Ionization energy(1st)	10.490356
(2nd)	15.39279
(3rd)	22.15563
LUMO energy	2.763035
HOMO-LUMO gap	13.253395
E(RHF) a.u	-1347.639171734

Table(d)

Atom	Charge	Electron density
C1	-0.441935	1.441935
N2	-0.706757	1.706757
P3	0.460143	0.539857
Cl4	0.129402	0.870598
H5	0.335519	0.664481
H6	-0.000938	1.000938
H7	-0.017114	1.017114
H8	0.384297	0.615703
Cl9	-0.142616	1.142616

Table(27): $(PH_2CHClNHF)$,C_1

Table (a)

Angle	Value	Angle	Value
H7-P3-H6	95.995	H5-C1-Cl9	103.433
H6-P3-C1	96.6008	H5-C1-N2	108.732
H7-P3-C1	96.5401	Cl9-C1-N2	111.269
P3-C1-H5	111383	C1-N2-H8	114.404
P3-C1-Cl9	112.34	C1-N2-F4	107.075
P3-C1-N2	109.52	H8-N2-F4	103.451

Table (b)

Bond	Value	Bond	Value
N2-H8	1.00796	C1-H5	1.07143
N2-F4	1.434	C1-P3	1.90673
N2-C1	1.4251	P3-H6	1.41744
C1-Cl9	1.92464	P3-H7	1.42147

Table(c)

ENERGY	eV
Ionization energy(1st)	10.66264
(2nd)	15.65448
(3rd)	22.62948
LUMO energy	2.914930
HOMO-LUMO gap	13.57757
E(RHF) a.u	-989.210188198

Table(d)

Atom	Charge	Electron density
C1	-0.492527	1.492527
N2	-0.294259	1.294259
P3	0.451049	0.548951
F4	-0.254442	1.254442
H5	0.345233	0.654767
H6	-0.000038	1.000038
H7	-0.015080	1.01508
H8	0.369779	0.630221
Cl9	-0.109716	1.109716

Table(28):($PH_2CHFNHCl$) , C_1

Table (a)

Angle	Value	Angle	Value
H8-N2-H4	105.465	F9-C1-H5	108.362
H8-N2-C1	114.933	F9-C1-P3	109.523
H4-N2-C1	112.876	H5-C1-P3	109.6
N2-C1-P3	107.733	C1-P3-H7	95.7281
N2-C1-F9	112.618	C1-P3-H6	95.3496
N2-C1-H5	108.977	H6-P3-H7	95.8147

Table (b)

Bond	Value	Bond	Value
N2-H8	1.00716	C1-H5	1.07361
N2-Cl4	1.8139	C1-P3	1.91548
N2-C1	1.42914	P3-H7	1.4239
C1-F9	1.4033	P3-H6	1.4216

Table(c)

ENERGY	eV
Ionization energy(1st)	10.73865
(2nd)	15.77415
(3rd)	23.37019
LUMO energy	2.933321
HOMO-LUMO gap	13.671651
E(RHF) a.u	-989.241566778

Table(d)

Atom	Charge	Electron density
C1	0.021815	0.978185
N2	-0.021815	1.021815
P3	0.406481	0.593519
Cl4	-0.576723	1.576723
H5	0.276593	0.723407
H6	-0.009893	1.009893
H7	-0.026938	1.026938
H8	0.369905	0.630095
F9	-0.395795	1.395795

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الرقم الاشاري : ....

كليــــة العلـــــوم
قسم الكيمياء

عنـــــوان البحـــــث

((دراسة أبيشو للمدارات الجزيئية للمركب أميوميثان فوسفين ومشتقاته الهاليدية))

ســـــرت / ليبيــــا

مقدمـــــة مــن الطـــــالب

عادل منصـــور حمـــد النجـــار

**لجنـــــة المناقشـــــــة

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7/24

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قسم الكيمــياء
سرت – ليبيا

دراسة إبيبنيشيو للمدارات الجزينية للمركب أمينو ميثان فوسفين ومشتقاته الهاليدية

هذا البحث مقدم لاستكمال نيل درجة الماجستير في العلوم – علم الكيمياء

من الطالب / عادل منصور حمد النجار

تحت إشراف

الدكتور / عبد الحكيم بالقاسم أحمد

2005