



COMPARISON OF COMPUTATIONAL STUDIES AND X-RAY CRYSTALLOGRAPHIC STUDIES OF SOME SCHIFF BASES

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Abstract: Recent years have seen an increase in the number of people doing theoretical chemistry. This increase has been facilitated by the development of computer software which is increasingly easy to use. Computational chemistry is used when a mathematical method is sufficiently well developed that it can be automated for implementation on a computer. Very few aspects of chemistry can be computed exactly, but almost every aspect of chemistry has been described in qualitative or approximate quantitative computational scheme. Often a qualitative or approximate computation can give useful insight into chemistry if we understand what it tells us and what it doesn't. In this study, Geometric optimization of some Schiff bases was done using computational methods – Molecular mechanics (MM+) and semi empirical methods (PM3). The software used is HYPERCHEM. The geometric parameters were calculated and the results thus obtained were compared with x-ray crystallographic results. The parameters were comparable.

Index Terms – Computational methods, molecular mechanics, semi-empirical, Schiff Bases

1. INTRODUCTION

Computational chemistry is a branch of chemistry that use the product of theoretical chemistry that is translated into computational program to calculate molecular properties and its changes and also to perform simulation to macromolecules system and apply the program to the real chemical system. The molecular properties that are calculated are structures, energy and deviation energy, charges, dipole moments, reactivity, wave frequency and other spectroscopic measurements. Simulation to macromolecules and large system can include the study of molecule conformation and its change, phase change and also prediction of macroscopic properties based on properties in atomic level and molecules.

The term of computational chemistry sometimes also used for interdisciplinary studies between computer science and chemistry. Theoretical chemistry can be defined as mathematical description of chemistry. While computational chemistry usually used when mathematics methods are developed well to be used in computer program. Computational chemist usually tries to solve the Schrodinger equation non relativistic with the addition of relativistic correlation. But in its practical term,

it is impossible except for the system that is very small. Therefore, a big number of approximation methods were developed to reach best compromise between the accuracy of calculation and computational cost.

Computational studies can be carried out in order to find a starting point of laboratory synthesis, or to assist in understanding experimental data, such as the position and source of spectroscopic peaks. Computational studies can be used to predict the possibility of so far entirely unknown molecules or to explore reaction mechanism. Computational approaches help in the efficient synthesis of compounds. Computational chemistry approaches are used to design molecules that interact in specific ways with other molecules (Ex: - Drug design).

II. REVIEW OF LITERATURE

Molecular modelling involves the development of mathematical models of molecules that can be used to predict and interpret their properties. There are two types of molecular modelling – molecular mechanics and quantum mechanics.

Molecular mechanics is a classical mechanical model that represents a molecule as a group of atoms held together by elastic bonds. Molecular mechanics methods give predictions of molecular geometrics and heats of formation. Molecular mechanics looks at the bond as springs. Interaction between non bonded atoms is considered. The sum of all these forces is called force field of the molecule. As molecular mechanics look at molecules as set of springs, they cannot be used to predict electronic properties of molecules. To make predictions about the electronic properties of a molecule, quantum mechanical models are used.

Quantum mechanical model of the electronic structure of a molecule involves solving Schrodinger equation. They are used to predict electronic properties of molecules, such as dipole moments and spectroscopy it is easy to solve Schrodinger equation for H atom. In more complicated situations; ex, the presence of an external electric and magnetic fields, in case of heavy elements, other terms are required in the Hamiltonian. Solving the Schrodinger equation is very difficult problem and cannot be done without making approximations. Two types of approximations are the Born- Oppenheimer approximation and the independent electron approximation.

Because of the large number of particles in a molecule, computer programs are used to do the calculations necessary for the solution of the Schrodinger equation. These calculations involve an enormous number of difficult integrals for large molecules. Ab initio computational methods solve all of these integrals without approximation. Ab initio methods are reliable for small and medium-sized molecules, but are prohibitively time consuming for large molecules. For large molecules, semi empirical methods have been developed which ignore or approximate some of the integrals used in Ab initio methods. To compensate for neglecting the integrals, the semi empirical methods introduce parameters based on molecular data. Commercial software packages are available for both ab initio and semi empirical calculations.

HOW COMPUTATIONAL CHEMISTRY IS USED

Computational chemistry is used in a number of different ways. One way is to model a molecular system prior to synthesizing that molecule in the laboratory. Although computational models may not be perfect, they are often good enough to rule out 90% of possible compounds as being unsuitable for their intended use. This is very useful information because synthesizing a single compound could require months of labour and raw materials and generate toxic waste.

Another use is in understanding a problem more completely. There are some properties of a molecule that can be obtained computationally easier than by experiment means. Thus, many experimental chemists are now using computational modeling to gain additional understanding of the compounds examined in the laboratory.

As computational chemistry has become easier to use, professional computational chemists have shifted their attention to more difficult modelling problems. No matter how easy computational chemistry becomes, there will always be problems so difficult that only an expert in the field can tackle them.

III. METHODS USED IN COMPUTATIONAL CHEMISTRY

Mainly used methods are: -

- Ab initio methods
- Density functional methods
- Semi empirical methods
- Molecular mechanics

1. AB INITIO METHODS

The programs used in computational chemistry are based on quantum chemical methods. They solve Schrodinger equation associated with the molecular Hamiltonian. Methods that do not include any empirical or semi-empirical parameters in their equations – being derived directly from theoretical principles, with no inclusion of experimental data are called ab initio methods. They are approximate quantum mechanical calculations.

The simplest type of ab-initio electronic structure calculation is the Hartree-Fock Scheme, an extension of molecular orbital theory. Fock scheme, and extension of molecular orbital theory, in which correlated electron – electron repulsion is not taken into account, only its average effect is included in calculation. In all of these approaches, it is necessary to choose a basis set. Ab-initio methods need to define a level of theory and a basis set.

Ab-initio method solve a Schrodinger equation for a molecule and gives us the energy and a wave function. From the electron distribution we can tell things like how polar the molecule is and which parts of it are likely to be attacked by nucleophiles and electrophiles.

Ab-initio calculations are relatively slow; the geometry and IR spectra of propane can be calculated at a reasonably high level in minutes on a PC, but a fairly large molecule, like steroid, could perhaps take days.

In general, Ab-initio calculations give very good qualitative results and can yield increasingly accurate quantitative results. The advantage of Ab-initio methods is that they eventually converge to the exact solution once all the approximations are made sufficiently small in magnitude.

The disadvantage of Ab-initio methods is that they are expensive. These methods often take enormous amounts of computer CPU time, memory and disk space. In practice, extremely accurate calculations are obtained when the molecule contains a dozen of electrons or less. However, results with an accuracy rivalling that of many experimental techniques can be obtained for moderate size organic molecules.

2. DENSITY FUNCTIONAL METHODS

Density functional theory (DFT) is a quantum mechanical modeling method used in chemistry to investigate the electronic structure of many-body systems. With this theory, the properties of a many electrons system can be determined by using functionals; which use parameters derived from empirical data.

Density functional methods are like Ab-initio methods. In this type of calculation, there is an approximate Hamiltonian and an approximate expression for the total electron density. DFT methods can be very accurate for little computational cost.

DFT calculations must use a basis set and most DFT calculations today are being done with HF-optimized GTO basis sets. The accuracy of results from DFT calculations can be poor or fairly good, depending on the choice of basis set and density functional. The B3LYP hybrid functional is most widely used for organic molecules.

DFT is newer than other Ab-initio methods; DFT's recent heavy usage has been due to optimal accuracy versus CPU time.

3. SEMI EMPIRICAL METHODS

Semi empirical quantum chemistry methods are based on the Hartree – Fock Formalism, but make many approximations and obtain some parameters from empirical data. They are very important in computational chemistry for treating large molecules. The user of empirical parameters appears to allow some inclusion of electron correlation effects into methods.

In semi empirical calculations the core electrons are not included in the calculation and only a minimal basis set is used. Also, some of the two electron integrals are omitted. In order to correct for the errors introduced by omitting part of the calculation, the method is parameterized. Parameters to estimate the omitted values are obtained by fitting the results to experimental data or Ab initio calculations. Often, these parameters replace some of the integrals that are excluded.

The advantage of semi empirical calculation is that they are much faster than Ab initio calculations. The disadvantage of semi empirical calculations is that the results can be erratic and fewer properties can be predicted reliably. If the molecule being computed is similar to molecules in the database used to parameterize the method, then the results may be very good. If the molecule being computed is significantly different from anything in the parameterization set, the answer may be poor.

Semi empirical methods are parameterized to reproduce various results. Most often, geometry and energy (usually the heat of formation) are used. Some researchers have extended this by including dipole moments, heats of reaction, and ionization potentials in the parameterization set. A few methods have been parameterized to reproduce a specific property, such as electronic spectra or NMR chemical shifts. Semi empirical calculations can be used to compute properties other than those in the parameterization set. Many semi-empirical methods compute energies as heats of formation. The researcher should not add zero-point corrections to these energies because the thermodynamic corrections are implicit in the parameterization. Semi empirical calculations have been very useful in the description of organic chemistry, where there are only a few elements used extensively and the molecules are of moderate size. Some empirical methods have been devised specifically for the description of inorganic chemistry as well. The following are some of the most commonly used semi empirical methods.

3.1 HUCKEL

The Huckel method and is one of the earliest and simplest semi empirical methods. A Huckel calculation models only the pi-valence electrons in a planar conjugated hydrocarbon. A parameter is used to describe the interaction between bonded atoms. There are no second atom effects. Huckel calculations do reflect orbital symmetry and qualitatively predict orbital coefficients. Huckel calculations can give crude quantitative information or qualitative insight into conjugated compounds, but are seldom used today. The primary use of Huckel calculations now is as a class exercise because it is a calculation that can be done by hand.

3.2 CNDO

The complete neglect of differential overlap (CNDO) method is the simplest of the neglect of differential overlap methods (NDO). This method models valence orbital's only using a minimal basis set of Slater type orbitals. The CNDO method has proven useful for some hydrocarbon results but little else. CNDO is still sometimes used to generate the initial guess for Ab initio calculations on hydrocarbons.

Practically all CNDO calculations are actually performed using the CNDO/2 method, which is an improved parameterization over the original CNDO/1 method. There is a CNDO/s method that is parameterized to reproduce electronic spectra. The CNDO/s method does yield improved prediction of excitation energies, but at the expense of the poorer prediction of molecular geometry. There have also been extensions of the CNDO/2 method to include elements with occupied and orbitals. These techniques have not seen widespread use due to the limited accuracy of results.

3.3 MINDO

There are three modified intermediate neglect of differential overlap (MINDO) methods. MINDO/1, MINDO/2, MINDO/3. The MINDO/3 method is by far the most reliable of these. This method has yielded qualitative results for organic molecules. However, its use today has been superseded by that of more accurate methods such as Austin model 1 (AM1) and parameterization method 3 (PM3). MINDO/3 is still sometimes used to obtain an initial guess for Ab initio calculations.

3.4 ZINDO

The Zerner's INDO method (ZINDO) is also called spectroscopic INDO (INDO/S). This is a reparameterization of the INDO method specifically for the purpose of reproducing electronic spectra. ZINDO is also used for modeling transition metal systems since it is one of the few methods parameterized for metals. It predicts UV transition well, with the exception of metals with unpaired electrons. However, its use is generally limited to the type of results for which it was parameterized. ZINDO often gives poor results when used for geometry optimization.

3.5 SINDO 1

The symmetrically orthogonalized intermediate neglect of differential overlap method (SINDO 1) is both a semi empirical method and a computer program incorporating that method. It is another variation on INDO. SINDO1 is designed for the prediction of the binding energies and geometries of the 1st and 2nd row elements as well as the 3rd row transition metals. Some of the parameters were taken directly from experimental or Ab initio results, whereas the rest were parameterized to reproduce geometry and heats of formation. The method was originally designed for modeling ground states of organic molecules. More recently, it has been extended to predict photochemistry and transition metal results.

3.6 AM1

The Austin Model 1 (AM1) method is still popular for modeling organic compounds. AM1 generally predicts the heat of formation (Hf) more accurately than MNDO, although a few exceptions involving Br atoms have been documented. Depending on the nature of the system and information desired, either AM1 or PM3 will often give the most accurate results obtainable for organic molecules with semi empirical methods.

There are some known strengths and limitations in the results obtained from these methods. Activation energies are improved over MNDO. AM1 tends to predict results for aluminum better than PM3. It tends to poorly predict nitrogen pyramidalization. AM1 tends to give O-Si-O bonds that are not bent enough. There are some known limitations to AM1 energies, such as predicting rotational barriers to be one-third the actual barrier and predicting five – membered rings to be too stable. The predicted heat of formation tends to be inaccurate for molecules with a large amount of charge localization. Geometries involving phosphorous are predicted poorly. There are systematic errors in alkyl group energies predicting them to be too stable. Nitro groups are too positive in energy. The peroxide bond is too short by about 0.17 Å. Hydrogen bonds are predicted to have the correct strength, but often the wrong orientation. AM1 predicts energies and geometrics better than MNDO, but not as well as PM3. Computed bond enthalpies are consistently low.

3.7 PM3

Parameterization method 3 (PM3) uses nearly the same equations as the AM1 method along with an improved set of parameters. The PM3 method is also currently extremely popular for organic systems. It is more accurate than AM1 for hydrogen bond angles, but AM1 is more accurate for hydrogen bond energies. The PM3 and AM1 methods are also more popular than other semi empirical methods due to availability of algorithms for including salvation effects in these calculations.

There are also some known strengths and limitations of PM3. Overall heat of formation is more accurate than with MNDO or AM1. Hypervalent molecules are also predicted more accurately. PM3 tends to predict that the barrier to rotation around the C-N bond in peptides is too low. Bonds between Si and the halide atoms are too short. PM3 also tends to predict incorrect electronic states for germanium compounds. It tends to predict Sp³ nitrogen as always being pyramidal. Some spurious minima are predicted. Proton affinities are not accurate. Some polycyclic rings are not flat. The predicted charge on nitrogen is incorrect. Non bonded distances are too short. Hydrogen bonds are too short by 0.1 Å, but the orientation is usually correct. On average, PM3 predicts energies and bond lengths more accurately than AM1 or MNDO.

4. MOLECULAR MECHANICS

The most severe limitation of Ab-initio methods is the limited size of the molecule that can be modelled on even the largest computers. Semi empirical calculations can be used for large organic molecules, but are also too computation-intensive for most bimolecular systems. If a molecule is so big that a semi empirical method cannot be used effectively. It is still possible to model its behaviour avoiding quantum mechanics totally by using molecular mechanics.

Molecular mechanics uses Newtonian mechanics to model molecular systems. The potential energy of all systems in molecular mechanics is calculated using force fields. Molecular mechanics can be used to study small molecules as well as large biological systems or material assemblies with many thousands to millions of atoms.

Molecular mechanics methods have the following properties:

- Each atom is simulated as a single particle.
- Each particle is assigned a radius, polarizability, and a constant net charge.
- Bonded interactions are treated as “springs” with an equilibrium distance equal to the experimental or calculated bond length.

The prototypical application of molecular mechanics is energy minimization. That is, the force field is used as an optimization criterion and the local minimum searched by an appropriate algorithm. The main aim of optimization methods is finding the lowest energy conformation of a molecule or identifying a set of low energy conformers that are in equilibrium with each other. This means that the energy computed is meant to be an energy that will reliably predict the difference in energy from one conformation to the next. The effect of strained bond lengths or angles is also included in this energy. This is not the same as the total energies obtained from Ab initio programs or heat of formation from semi empirical programs. Molecular mechanics methods can be modified to compute heat of formation by including a database or computational scheme to yield bond energies that might be added to the conformational energy and account for the zero of energy. Molecular mechanics are not generally applicable to structures very far from equilibrium, such as transition structures.

❖ FORCE FIELD

A force field refers to the form and parameters of mathematical functions used to describe the potential energy of a system of particles. Force field functions and parameter sets are derived from both experimental work and high-level quantum mechanical calculations. Force field is essentially a relationship between the geometry of a molecule and force on each atom. The force is a vector quantity, the derivative of the energy with respect to co-ordinates. To simplify the expressions, force field are generally presented in the form of energy as a function of co-ordinates. The true zero of the energy is unknown, different for each force field and molecule. Thus, the total energy calculated for any molecule

cannot be interpreted in a physically meaningful way, and no special meaning should be attached to a calculated energy of zero.

The following are some commonly used molecular mechanics force fields.

4.1 AMBER

Assisted model building with energy refinement (AMBER) is the name of both a force field and a molecular mechanics program. It was parameterized specifically for proteins and nucleic acids. AMBER uses only five bonding and non-bonding terms along with a sophisticated electrostatic treatment. No terms are included. Results are very good for proteins and nucleic acids, but can be somewhat erratic for other systems.

4.2 CHARMM

Chemistry at Harvard macromolecular mechanics (CHARMM) is the name of both a force field and a program incorporating that force field. The academic version of this program is designated CHARMM and the commercial version is called CHARMM. It has now been applied to a range of biomolecules, molecular dynamics, salvation, crystal packing, vibrational analysis and QM/MM studies. CHARMM uses five valence terms, one of which is an electrostatic term.

4.3 CFF

The consistent force field (CFF) was developed to yield consistent accuracy of results for conformations, vibrational spectra, strain energy, vibrational enthalpy of proteins. There are several variations on this.

4.4 CHEAT

Carbohydrate hydroxyls represented by external atoms (CHEAT) is a force field designed specifically for modeling carbohydrates.

4.5 MMI, MM2, MM3, MM4

MM1, MM2, MM3, MM4 are general-purpose organic force fields. There have been many variants of the original methods particularly MM2. MM1 is seldom used since the newer versions show measurable improvements. The MM3 method is probably one of the most accurate ways of modeling hydrocarbons. MMX and MM + are variations on MM2. These force fields use five to six valence terms, one of which is an electrostatic term and one to nine cross terms.

Several other force fields like DREIDING, ECEPP, EFF, GROMOS, MMF, MOMEK, OPLS, Tripos, UFF, YETI, are also used in appropriate places.

❖ GEOMETRY OPTIMIZATION

In computational chemistry, geometry optimization methods are used to compute the equilibrium configuration of molecules and solids.

Stable states of molecular systems correspond to global and local minima on their potential energy surface. Starting from a non-equilibrium molecular geometry, energy minimization employs the mathematical procedure of optimization to move atoms so as to reduce the net forces on the atoms until they become negligible.

Molecular energy minimization does not include the effect of temperature, and hence the trajectories of atoms during the calculation do not really make any physical sense, i.e., we can only obtain a final state of system that corresponds to a local minimum of potential energy.

Optimization is also used to locate transition structures, which are represented by saddle points on the potential energy surface. During minimization, the energy of molecules is reduced by adjusting atomic co-ordinates. It is applied to model – built structures as well as to those derived from co-ordinate data banks. Energy minimization is done when using either molecular mechanics or quantum mechanics methods, and it must precede any computational analyze in which these methods are applied.

Geometry optimization can be used to –

- Characterize a potential energy surface.
- Obtain a structure for a single-point quantum mechanical calculation, which provides a large set of structural and electronic properties.
- Prepare a structure for molecular dynamics simulations.

The energy obtained from the potential energy function at the optimized geometry is sometimes called a steric or conformational energy. These energies can be used to calculate differences between stereoisomers and between isologous molecules. These energies apply to molecules in a hypothetical motionless state at 0 K.

IV. COMPOUNDS SELECTED FOR STUDIES

We selected certain Schiff bases for the studies. Schiff bases are compounds with a functional group that contains a carbon – nitrogen double bond with the nitrogen atom connected to an aryl or alkyl group, not hydrogen. Schiff bases have the general formula $R^1R^2C = NR^3$, where R is an organic side chain.

Schiff bases derived from aromatic amines and aromatic aldehydes have a wide variety of applications in many fields; E.g.: - Biological, inorganic and analytical chemistry. Schiff bases are used in optical and electrochemical sensors, as well as in various chromatographic methods, to enable detection of enhance selectively and sensitivity.

Among the organic reagents actually used, Schiff bases possess excellent characteristics, structural similarities with natural biological substances, relatively simple preparation procedures and the synthetic flexibility that enables design of suitable structural properties.

Schiff bases are widely applicable in analytical determination, using reactions of condensation of primary amines and carbonyl compounds in which azomethine bond is formed: using complex forming reactions; or utilizing the variation in their spectroscopic characteristics following changes in pH and solvent.

But most Schiff bases are chemically unstable and show a tendency to be involved in various equilibria, like tautomeric interconversions, hydrolysis, or formation of ionized species. Therefore, successful application of Schiff bases requires a careful study of their characteristics.

The following Schiff bases were used for the studies:

- 2-Bromo-N'-[(E)-4-hydroxybenzylidene]-5-methoxybenzohydrazide [C₁₅H₁₃BrN₂O₃]
- 2-Bromo-N'-[(E)-4-chlorobenzylidene]-5-methoxybenzohydrazide [C₁₅H₁₂BrClN₂O₂]
- 2-Bromo-N'-[(E)-(4-fluorophenyl) methylene]-5-methoxybenzohydrazide monohydrate [C₁₅H₁₂BrFN₂O₂.H₂O]
- 2-Bromo-5-methoxy-N'-[(E)-(2-nitrophenyl) methylene] benzohydrazide [C₁₅H₁₂BrN₃O₄]
- 2-Bromo-N'-isopropylidene-5-methoxybenzohydrazide [C₁₁H₁₃BrN₂O₂]
- N'-[(1E)-(4-Fluorophenyl) methylene]-6-methoxy-2-naphthohydrazide [C₁₉H₁₅FN₂O₂]
- N'-Isopropylidene-6-methoxy-2-naphthohydrazide [C₁₅H₁₆N₂O₂]
- 1-[3-[(2-hydroxybenzylidene) amino] phenyl] ethanone [C₁₅H₁₃NO₂]

V. EXPERIMENTAL DETERMINATION

AIM:

To study the geometric parameters of certain Schiff bases using MM+ and PM3 method and compare the values with x-ray crystallographic studies.

PROCEDURE:

We construct the compounds using the HYPERCHEM software and model build using menu options. Then geometry optimization is done by using computational chemistry methods (molecular mechanic & semi empirical). Bond lengths and Bond angles are calculated and are compared with those obtained from x-ray crystallographic studies of corresponding compound.

WAY OF RESULTS:

- BY PM3:

The structure of the compounds are model build by menu bar options and are optimized by semi empirical PM3 method. From the geometry optimized structure of compounds, bond lengths and bond angles are found out by selection option.

- BY MM+:

The structure of the compounds are model build by the menu bar options and are optimized by molecular mechanics MM+ method. From the geometry optimized structure of compounds, bond lengths and bond angles are found out by selection option.

VI. MATERIALS AND METHODS

SOFTWARE USED: HYPERCHEM

HYPERCHEM is an interface graphic, computational and visualization package. It is a sophisticated molecular modeling environment that is known for its quality, flexibility and ease of use. Uniting 3D visualization and animation with quantum chemical calculations, molecular mechanics and dynamics. HYPERCHEM puts more molecular modeling tools at our fingertips than any other windows program. It includes all the components of structure, thermodynamics, spectra and Kinetics.

Building molecules with HYPERCHEM is simple: just choose an element from the periodic table and click and drag with the mouse, prior to applying the model builder to convert 2D sketch to a 3D structure. Hydrogen atoms are added automatically. The sketcher does not set the bond lengths and bond angles, so the use of molecular mechanics optimization before doing more time-consuming calculation is highly advised. The graphic interface incorporates a variety of rendering modes. Building biomolecules is made easier with a sugar builder and amino acid sequence editor.

The calculation results are displayed on screen, but they are not saved to disk. The user can specify that all results for a given session be written to a log file. While a calculation is running, no action can be taken other than changing the molecular orientation on screen.

In molecular mechanics, four force fields (MM+, AMBER, CFF and CHARMM) provide computationally convenient methods for exploring the stability and dynamics of molecular systems. Parameters missing from the force field will be automatically estimated. The user has some control over cut off distances for various terms in the energy expression. Solvent molecules can be included along with the periodic boundary conditions. The molecular mechanics calculations ran without difficulties.

HYPERCHEM offers eleven semi empirical molecular orbital methods, with options for organic and main – group compounds, for transition metal complexes and for spectral simulation. This includes Extended Huckel, CNDO, INDO, MINDO/3, MNDO, AM1, RM1, PM3, ZINDO/1, ZINDO/S and TNDO.

The semi empirical techniques seem to be rather robust in that it did well on some technically difficult test calculations.

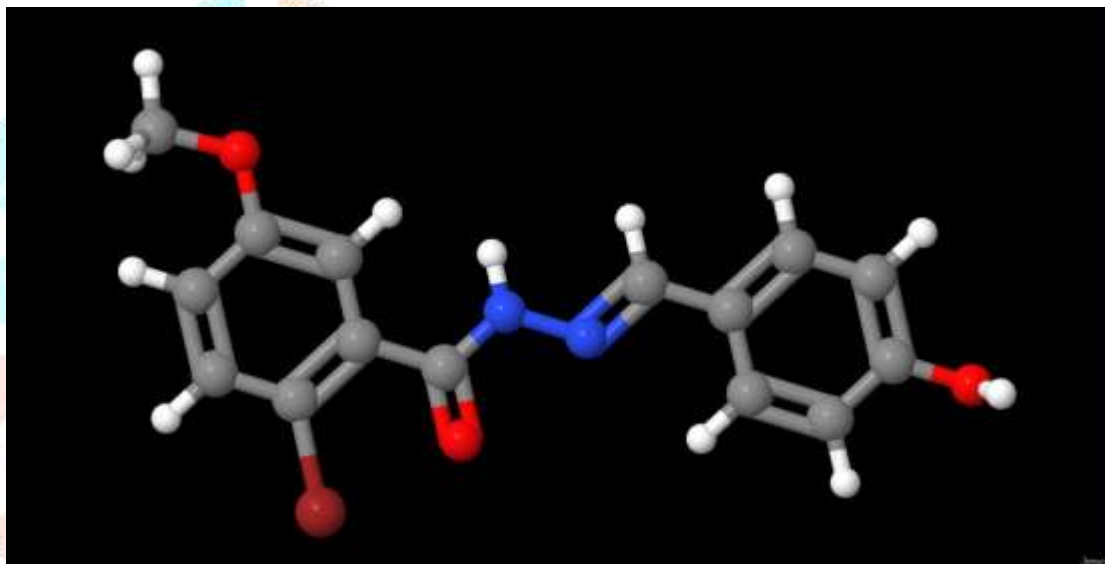
version: HYPERCHEM 8.0.10 student evaluation.

VII. RESULTS AND DISCUSSION

Bond lengths and Bond angles are compared and the results are tabulated.

MOLECULE 1

2 -Bromo- N' -[(E) -4- hydroxybenzylidene]- 5 -methoxybenzohydrazide.



Bond Angles	Molecular Mechanics (MM+) results (deg)	Semi empirical (PM3) results (deg)	Crystallographic Results (deg)
C3-C1-C2	118.127	117.501	119.7(2)
C1-C3-C5	123.756	120.121	119.7(2)
C3-C5-C6	116.499	121.057	120.2(2)
C5-C6-C4	121.223	118.694	120.2(2)
C2-C4-C6	121.194	119.52	119.9(2)
C1-C2-C4	119.201	123.108	120.2(2)
H27-C3-C5	114.533	119.021	120.1
H27-C3-C1	121.71	120.858	120.1
C5-C6-H29	121.175	121.581	119.9
H29-C6-C4	117.602	119.725	119.9

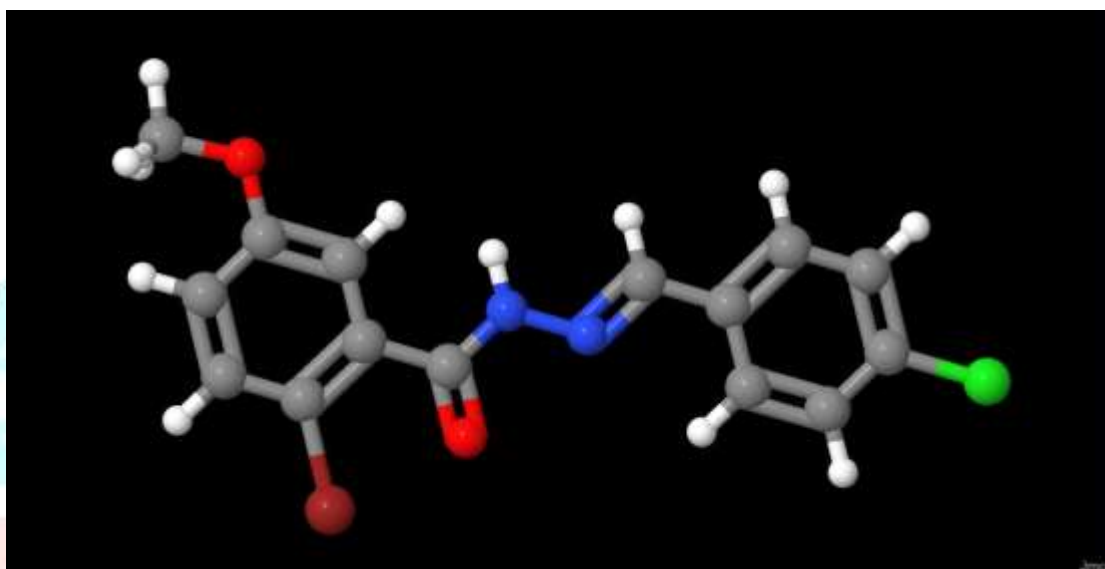
Bond Length	Molecular Mechanics (MM+) results (Å ⁰)	Semi empirical (PM3) results (Å ⁰)	Crystallographic Results (Å ⁰)
C1-C2	1.40411	1.38903	1.393(3)
C2-C4	1.39835	1.38389	1.397(3)
C4-C6	1.39432	1.38911	1.391(4)
C5-C6	1.3994	1.40094	1.390(4)
C3-C5	1.40051	1.40303	1.395(3)
C1-C3	1.4029	1.39818	1.406(3)
C2-Br19	1.90075	1.86721	1.905(2)
C4-H28	1.10403	1.09593	0.9500
C6-H29	1.10145	1.0958	0.9500
C3-H27	1.1005	1.10092	0.9500
C5-O20	1.36916	1.38037	1.373(3)
O20-C21	1.40583	1.40634	1.434(4)
C21-H22	1.11287	1.09371	0.9800
C21-H23	1.11451	1.0959	0.9800
C21-H24	1.11451	1.0959	0.9800
C1-C7	1.36566	1.49836	1.515(3)
C7-O25	1.21016	1.2153	1.234(3)
C7-N8	1.3874	1.43233	1.338(3)
N8-H26	1.01964	1.00415	0.86
N8-N9	1.35767	1.37628	1.398(3)
N9-C10	1.34655	1.30235	1.282(3)
C10-H30	1.1037	1.10444	0.9500
C10-C11	1.34247	1.4631	1.466(3)
C11-C12	1.3998	1.39801	1.396(4)
C12-C16	1.39643	1.38883	1.393(3)
C16-C15	1.39759	1.40038	1.392(4)
C14-C15	1.39725	1.40278	1.394(3)
C13-C14	1.39609	1.38558	1.390(3)
C11-C13	1.3998	1.40154	1.409(3)
C12-H31	1.0318	1.09765	0.9500
C16-H34	1.10295	1.09624	0.9500
C15-O17	1.35921	1.36705	1.375(3)
O17-H18	0.941839	0.94309	0.84
C14-H33	1.10279	1.09567	0.9500
C13H32	1.10375	1.09647	0.9500

H28-C4-C6	117.849	120.993	120.0
H28-C4-C2	120.957	119.487	120.0
Br19-C2-C4	114.688	115.325	118.36(19)
Br19-C2-C1	126.111	121.568	121.37(17)
O20-C5-C3	118.256	113.534	124.1(3)
O20-C5-C6	125.245	125.41	115.7(2)
C7-C1-C3	119.133	121.675	116.9(2)
C7-C1-C2	122.74	120.824	123.5(2)
C5-O20-C21	117.81	117.637	117.1(2)
O20-C21-H22	106.612	102.113	109.5
O20-C21-H24	109.705	112.291	109.5
O20-C21-H23	109.705	112.291	109.5
H22-C21-H23	108.886	110.082	109.5
H22-C21-H24	108.886	110.082	109.5
H24-C21-H23	112.847	109.755	109.5
O25-C7-C1	121.989	124.156	121.5(2)
O25-C7-N8	118.011	119.515	124.5(2)
N8-C7-C1	119.999	116.329	114.0(2)
H26-N8-C7	120.486	119.228	117.8(18)
N9-N8-H26	118.754	119.666	122.7(18)
N9-N8-C7	120.76	121.105	119.3(2)
C10-N9-N8	122.907	121.166	114.07(19)
H30-C10-N9	113.213	123.351	118.6
C11-C10- H30	123.799	116.563	118.6
C11-C10-N9	122.988	120.086	122.8(2)
C13-C11-C10	119.768	118.169	118.8(2)
C10-C11-C12	122.309	122.278	122.1(2)
H32-C13-C11	120.548	119.929	119.5
H32-C13-C14	118.55	119.273	119.5
H33-C14-C15	119.155	120.369	120.4
H33-C14-C13	119.433	120.591	120.4
O17-C15-C14	121.136	116.203	116.9(2)
O17-C15-C16	121.391	123.009	122.3(2)
H34-C16-C15	119.02	120.904	120.1
H34-C16-C12	119.463	119.673	120.1
H31-C12-C16	118.202	119.28	120.0
H31-C12-C11	121.025	120.321	120.0
H18-O17-C15	120.078	107.851	110(3)

C13-C11-C12	117.923	119.553	119.1(2)
C11-C12-C16	120.774	120.399	119.7(2)
C15-C16-C12	121.516	119.423	119.7(2)
C14-C15-C16	117.473	120.787	120.9(2)
C15-C14-C13	121.412	119.04	119.2(2)
C14-C13-C11	120.902	120.799	121.0(2)

MOLECULE-2

2 - Bromo - N'-[(E) - 4 - Chlorobenzylidene]- 5- methoxybenzohydrazide



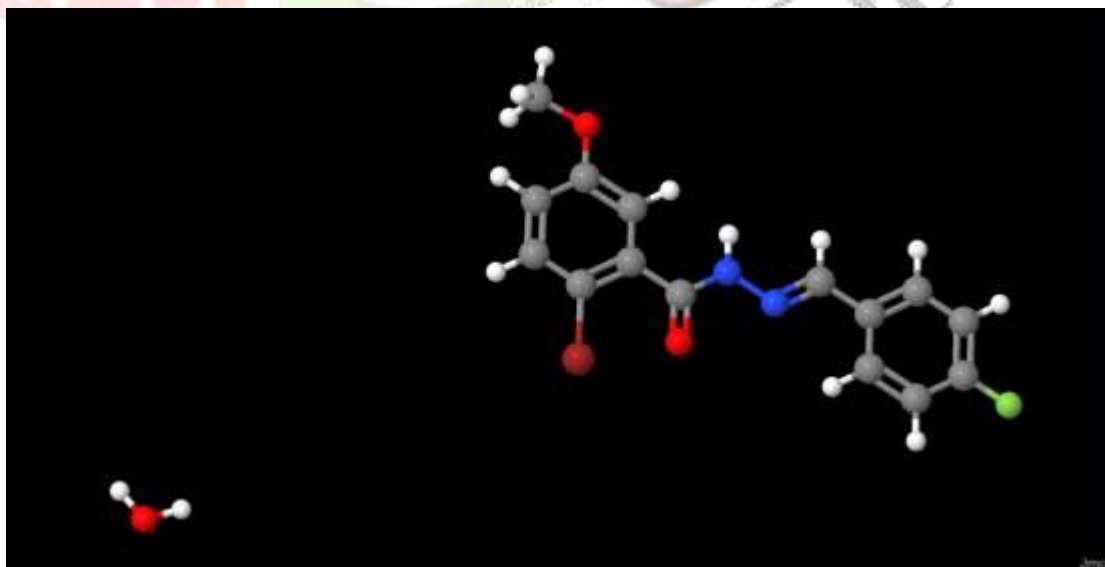
Bond Length	Molecular Mechanics (MM+) (A ⁰)	Semi empirical (PM3) results (A ⁰)	Crystallographic Results (A ⁰)
C1-C2	1.40422	1.38881	1.396(3)
C2-C5	1.39851	1.38396	1.383(3)
C5-C6	1.39446	1.38909	1.369(3)
C4-C6	1.39442	1.401	1.392(3)
C3-C4	1.40038	1.40287	1.380(3)
C1-C3	1.40312	1.39849	1.392(3)
Br21-C2	1.9015	1.86705	1.899(2)
H23-C5	1.0406	1.096	0.9400
H24-C6	1.10175	1.09583	0.9400
C4-O18	1.36951	1.38024	1.365(3)
C3-H22	1.10042	1.10079	0.9400
C1-C7	1.36574	1.49792	1.502(3)
O18-C20	1.40593	1.40638	1.419(3)
C20-H31	1.11298	1.09356	0.9700
C20-H32	1.11439	1.096	0.9700
C20-H33	1.11439	1.096	0.9700
C7-O19	1.21004	1.21486	1.220(2)
C7-N8	1.38718	1.43419	1.353(3)
H25-N8	1.01953	1.00444	0.8700
N8-N9	1.3576	1.37401	1.390(2)
N9-C10	1.34687	1.30232	1.279(3)
H26-C10	1.10383	1.0464	0.9400
C10-C11	1.34252	1.46414	1.461(3)
C11-C13	1.40044	1.39847	1.392(3)
C13-C14	1.39697	1.39031	1.379(3)
C14-C15	1.39581	1.39156	1.388(3)
C15-C16	1.39558	1.39361	1.370(3)
C16-C12	1.3964	1.3873	1.381(3)
C12-C11	1.40075	1.40146	1.394(3)
H28-C13	1.10318	1.09745	0.9400
H29-C14	1.10342	1.09564	0.9400
Cl17-C15	1.72487	1.6851	1.746(2)
C16-H30	1.10324	1.09537	0.9400
C12-H27	1.10347	1.09629	0.9400

Bond Angles	Molecular Mechanics Results (MM+) (deg)	Semi empirical (PM3) results (deg)	Crystallographic Results (deg)
C2-C1-C3	118.198	117.462	119.1(2)
C1-C2-C5	119.094	123.12	119.8(2)
C2-C5-C6	121.223	119.541	120.8(2)
C5-C6-C4	121.293	118.67	119.9(2)
C3-C4-C6	116.41	121.053	119.7(2)
C1-C3-C4	123.782	120.154	120.6(2)
Br21-C2-C5	114.766	115.36	118.72(19)
Br21-C2-C1	126.14	121.521	121.37(17)
H23-C5-C6	117.835	120.973	119.6
H23-C5-C2	120.943	119.485	119.6
H24-C6-C5	117.535	119.751	120.0
H24-C6-C4	121.172	121.579	120.0
O18-C4-C6	125.249	125.404	115.5(2)
O18-C4-C3	118.341	113.543	124.8(2)
H22-C3-C4	114.392	118.974	119.7
C1-C3-H22	121.826	120.872	119.7
C7-C1-C3	118.972	121.682	118.9(2)
C7-C1-C2	122.83	120.856	121.92(19)
C4-O18-C20	119.029	117.656	117.70(19)
O18-C20-H33	109.741	112.304	109.5
O18-C20-H31	106.664	102.08	109.5
O18-C20-H32	109.741	112.304	109.5
H33-C20-H32	112.889	109.73	109.5
H32-C20-H31	108.802	110.098	109.5
O19-C7-C1	121.935	124.308	122.7(2)
H33-C20-H31	108.802	110.098	109.5
O19-C7-N8	118.07	119.48	124.1(2)
N8-C7-C1	119.995	116.213	113.18(19)
H25-N8-C7	120.248	119.091	120.1
H25-N8-N9	118.59	119.505	120.1
N9-N8-C7	121.162	121.404	119.81(19)
C10-N9-N8	122.598	120.99	114.2(2)
H26-C10-N9	113.113	123.362	119.5
H26-C10-C11	123.688	116.352	119.5
C11-C10-N9	123.199	120.286	121.1(2)
C13-C11-C12	118.437	119.582	118.5(2)

C16-C12-C11	121.034	120.419	121.3(2)
C15-C16-C12	119.876	119.378	118.9(2)
C14-C15-C16	119.771	120.849	121.5(2)
C15-C14-C13	120.024	119.666	119.1(2)
C14-C13-C11	120.86	120.106	120.8(2)
C10-C11-C13	122.024	122.506	121.8(2)
C10-C11-C12	119.54	117.912	119.7(2)
H27-C12-C11	120.57	120.106	119.4
H27-C12-C16	118.397	119.476	119.4
H30-C16-C12	119.448	120.668	120.6
H30-C16-C15	120.676	119.954	120.6
Cl17-C15-C16	120.113	119.469	119.54
Cl17-C15-C14	120.116	119.682	119.0(2)
H29-C14-C15	120.559	119.911	120.4
H29-C14-C13	119.417	120.422	120.4
H28-C13-C14	118.144	119.47	119.6
H28-C13-C11	120.996	120.424	119.6

MOLECULE- 3

2-Bromo-N'-[(E)-(4-Fluorophenyl) methylene]-5- Methoxybenzohydrazide monohydrate

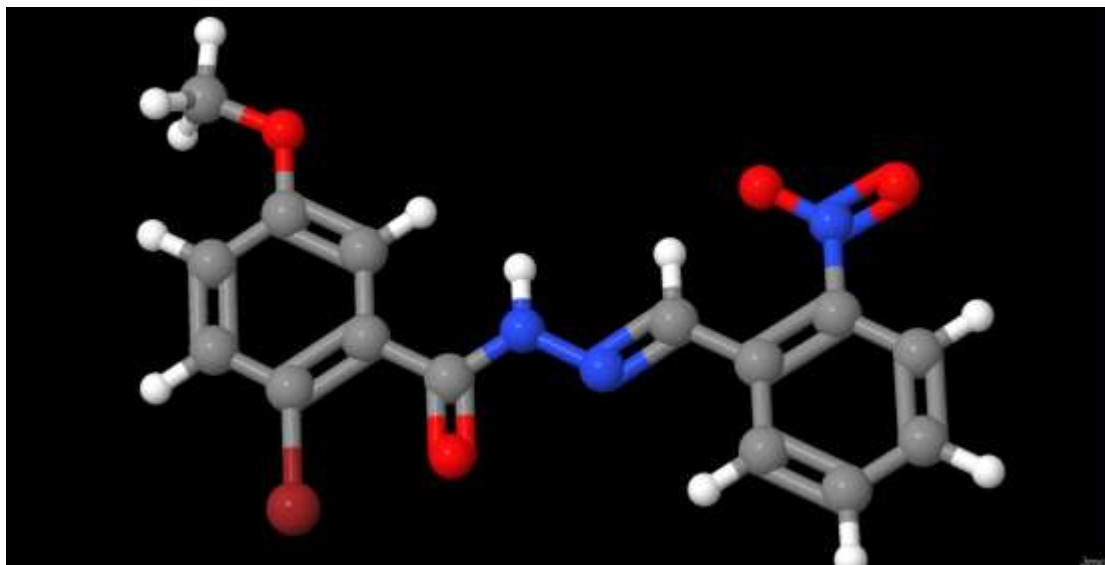


Bond Length	Molecular Mechanics Results (MM+) (A ⁰)	Semi empirical (PM3) results (A ⁰)	Crystallographic Results (A ⁰)
C1-C2	1.40431	1.3874	1.381(11)
C2-C5	1.39865	1.38174	1.408(12)
C5-C6	1.3945	1.39056	1.379(13)
C4-C6	1.39946	1.40101	1.386(12)
C3-C4	1.40035	1.40396	1.380(11)
C1-C3	1.40208	1.3957	1.405(11)
C1-C13	1.36558	1.49646	1.510(10)
C2-Br12	1.90143	1.8647	1.908(7)
H27-C5	1.10383	1.09547	0.9500
H28-C6	1.10161	1.09589	0.9500
C4-O7	1.36905	1.38134	1.352(11)
H26-C3	1.09927	1.10164	0.9500
O7-C8	1.40556	1.40691	1.444(11)
C8-H9	1.11297	1.09343	0.9800
C8-H11	1.11421	1.09629	0.9800
C8-H10	1.11421	1.09613	0.9800
C13-O24	1.21005	1.21411	1.216(9)
C13-N14	1.38829	1.44851	1.358(10)
H25-N14	1.01989	1.00683	0.8800
N14-N15	1.35745	1.3853	1.396(10)
N15-C16	1.34628	1.30046	1.254(11)
C16-H29	1.10267	1.10555	0.9500
C16-C17	1.34272	1.46573	1.480(12)
C17-C18	1.40058	1.39857	1.401(12)
C18-C22	1.39638	1.38972	1.370(12)
C21-C22	1.39557	1.39935	1.389(13)
C20-C21	1.39552	1.40126	1.368(13)
C19-C20	1.39639	1.387	1.396(13)
C17-C19	1.40056	1.40052	1.423(12)
C18-H30	1.10329	1.09778	0.9500
C22-H33	1.10303	1.09554	0.9500
C21-F123	1.32243	1.34332	1.363(10)
C20-H32	1.10295	1.09522	0.9500
C19-H31	1.10368	1.09639	0.9500
O1W-H3W	0.942048	0.950924	0.8401

O1W-H2W	0.942322	0.951689	0.8401
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Bond Angles	Molecular Mechanics Results (MM+) (deg)	Semi empirical (PM3) results (deg)	Crystallographic Results (deg)
C2-C1-C3	118.05	118.122	119.2(7)
C1-C2-C5	119.168	123.04	121.0(7)
C2-C5-C6	121.275	119.193	118.2(7)
C5-C6-C4	121.151	118.951	121.9(7)
C3-C4-C6	116.454	121.108	119.2(7)
C1-C3-C4	123.901	119.581	120.4(7)
C13-C1-C2	122.787	120.453	122.1(7)
C13-C1-C3	119.163	121.42	118.6(6)
Br12-C2-C1	126.108	120.034	122.9(6)
Br12-C2-C5	114.724	116.926	116.0(6)
H27-C5-C2	120.929	119.627	120.9
H27-C5-C6	117.797	121.18	120.9
H28-C6-C5	117.601	119.483	119.0
H28-C6-C4	121.248	121.566	119.0
O7-C4-C6	125.344	125.204	116.2(7)
O7-C4-C3	118.202	113.688	124.6(7)
H26-C3-C4	114.479	120.312	119.8
H26-C3-C1	121.62	120.104	119.8
C4-O7-C8	119.074	117.434	116.9(6)
O7-C8-H9	106.538	102.236	109.5

O7-C8-H11	109.731	112.435	109.5
O7-C8-H10	109.735	112.119	109.5
H11-C8-H10	112.922	109.722	109.5
H10-C8-H9	108.849	110.066	109.5
H11-C8-H9	108.856	110.044	109.5
O24-C13-C1	121.863	123.401	122.1(7)
O24-C13-N14	118.132	121.358	124.3(7)
C1-C3-N14	120.004	115.141	113.6(6)
H25-N14-C13	121.077	113.221	121.6
H25-N14-N15	118.843	115.954	121.6
N15-N14-C13	120.08	117.768	116.9(6)
C16-N15-N14	123.49	121.316	115.4(7)
H29-C16-N15	113.608	123.388	119.7
N15-C16-C17	122.623	119.864	120.6(8)
C18-C17-C19	118.356	119.644	118.6(7)
H29-C16-C17	123.769	116.746	119.7
C17-C19-C20	120.894	120.716	120.4(8)
C21-C20-C19	120.359	118.923	117.5(8)
C22-C21-C20	119.139	121.115	124.3(8)
C21-C22-C18	120.457	119.169	117.7(8)
C22-C18-C17	120.795	120.43	121.5(7)
C16-C17-C18	121.827	122.239	122.6(7)
C16-C17-C19	119.816	118.113	118.7(8)
H30-C18-C17	121.096	120.266	119.3
H30-C18-C22	118.109	119.304	119.3
H33-C22-C18	119.822	120.404	121.1
H33-C22-C21	119.721	120.427	121.1
Fl23C21-C22	120.364	119.519	117.9(8)
Fl23-C21-C20	120.496	119.366	117.9(8)
H32-C20-C21	119.721	120.386	121.3
H32-C20-C19	119.921	120.691	121.3
H31-C19-C20	118.488	119.31	119.8
H31-C19-C17	120.618	119.973	119.8
H3W-O1W-H2W	104.193	108.03	85.1

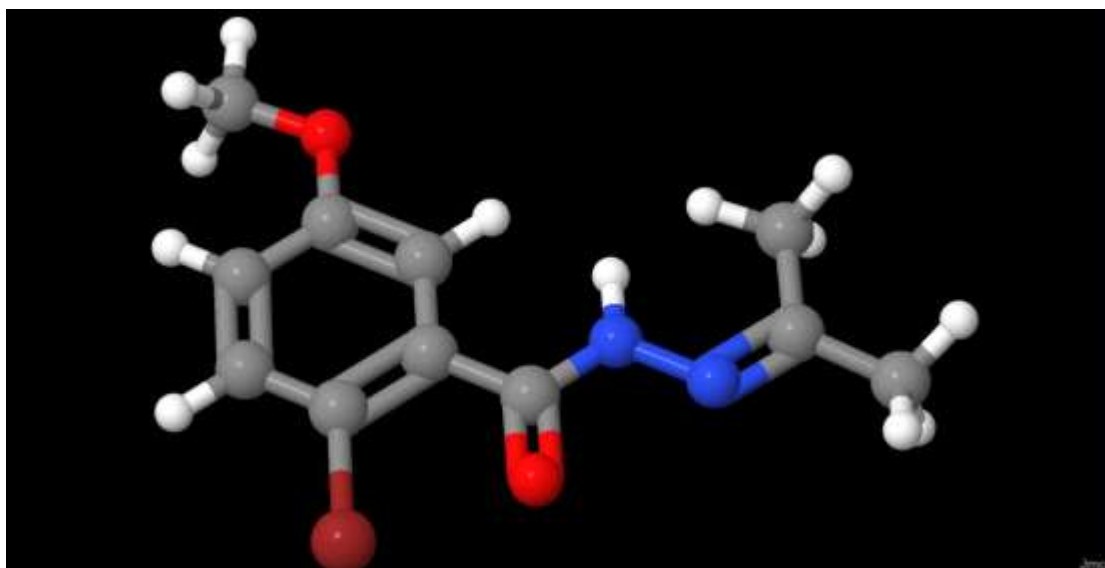
MOLECULE-4**2-Bromo-5-methoxy-N'-[(E)-(2-nitrophenyl)-methylene] benzohydrazide**

Bond Length	Molecular Mechanics Results (MM+) (Å ⁰)	Semi empirical (PM3) results (Å ⁰)	Crystallographic Results (Å ⁰)
C1-C2	1.40454	1.38848	1.395(3)
C2-C5	1.39867	1.38236	1.389(3)
C5-C6	1.39444	1.3901	1.381(4)
C4-C6	1.39934	1.40102	1.398(3)
C3-C4	1.40075	1.40406	1.405(3)
C1-C3	1.40296	1.39673	1.387(3)
C1-C7	1.36605	1.49522	1.519(3)
Br22-C2	1.90126	1.86574	1.905(2)
H26-C5	1.10422	1.09551	0.9500
H27-C6	1.10162	1.09603	0.9500
O17-C4	1.36946	1.37956	1.365(3)
H25-C3	1.1005	1.10139	0.9500
O17-C18	1.40636	1.40666	1.440(3)
C18-H19	1.11307	1.09347	0.9800
H20-C18	1.11451	1.09601	0.9800
C18-H21	1.11451	1.09617	0.9800
O23-C7	1.21007	1.21356	1.225(3)
C7-N8	1.38802	1.45144	1.345(3)
H24-N8	1.01972	1.00644	0.86(3)
N8-N9	1.35814	1.37738	1.387(2)
N9-C10	1.34824	1.30164	1.276(3)
H28-C10	1.09845	1.11883	0.9500

C10-C11	1.34657	1.46842	1.482(3)
C11-C12	1.40638	1.40029	1.402(3)
C16-C12	1.3949	1.38792	1.396(3)
C16-C15	1.39147	1.3909	1.386(4)
C14-C15	1.39388	1.38644	1.388(3)
C13-C14	1.4026	1.4035	1.394(3)
C11-C13	1.41062	1.41279	1.402(3)
H29-C12	1.10303	1.0992	0.9500
C16-H32	1.10328	1.09593	0.9500
H31-C15	1.1036	1.09564	0.9500
H30-C14	1.10239	1.1	0.9500
N33-C13	1.48563	1.49484	1.478(3)
N33-O35	1.21782	1.22209	1.230(3)
N33-O34	1.22244	1.21413	1.228(3)

Bond Angle	Molecular Mechanics Results (MM+) (deg)	Semi empirical (PM3) results (deg)	Crystallographic Results (deg)
C2-C1-C3	118.125	117.891	119.29(19)
C1-C2-C5	119.176	123.052	120.6(2)
C2-C5-C6	121.203	119.319	120.3(2)
C5-C6-C4	121.239	118.892	119.9(2)
C6-C4-C3	116.481	121.045	119.5(2)
C1-C3-C4	123.776	119.797	120.4(2)
C7-C1-C2	122.701	120.626	121.6(2)
C7-C1-C3	119.174	121.481	119.10(19)
Br22-C2-C1	126.189	120.684	119.51(16)
Br22-C2-C5	114.635	116.264	119.77(7)
C2-C5-H26	121.044	119.603	119.8
H26-C5-C6	117.753	121.078	119.8
H27-C6-C5	117.529	119.583	120.0
H27-C6-C4	121.232	121.525	120.0
O17-C4-C6	125.139	125.328	124.8(2)
O17-C4-C3	118.381	113.626	115.7(2)
H25-C3-C4	114.579	119.629	119.8
H25-C3-C1	121.645	120.573	119.8
C4-O17-C18	119.048	117.58	117.21(19)

O17-C18-H20	109.765	112.14	109.5
O17-C18-H21	109.765	112.427	109.5
O17-C18-H19	106.662	102.13	109.5
H20-C18-H21	112.824	109.735	109.5
H20-C18-H19	108.814	110.108	109.5
H21-C18-H19	108.814	110.077	109.5
O23-C7-C1	121.996	124.069	122.3(2)
O23-C7-C8	118.001	120.336	125.8(2)
N8-C7-C1	120.002	115.529	111.86(18)
H24-N8-C7	120.638	113.897	119.3(18)
H24-N8-N9	118.882	116.275	119.8(18)
N9-N8-C7	120.48	118.409	120.90(18)
C10-N9-N8	123.952	120.984	112.79(18)
H28-C10-N9	109.801	124.541	120.2
H28-C10-C11	127.236	115.77	120.2
N9-C10-C11	122.963	119.686	119.58(19)
C12-C11-C13	116.915	118.863	116.39(19)
C16-C12-C11	122.628	121.057	121.2(2)
C15-C16-C12	119.632	120.011	120.6(2)
C15-C14-C13	121.254	120.788	118.8(2)
C14-C13-C11	120.474	119.352	123.1(2)
C10-C11-C12	116.796	120.256	119.9(2)
C10-C11-C13	126.289	120.876	123.7(2)
H29-C12-C16	115.792	119.11	119.4
H32-C16-C12	120.398	119.893	119.7
H32-C16-C15	119.97	120.096	119.7
H31-C15-C16	120.282	120.209	120.1
H30-C14-C15	116.609	118.562	120.6
H30-C14-C13	122.137	120.649	120.6
H31-C15-C14	120.623	119.866	120.6
N33-C13-C11	124.081	123.159	121.25(18)
N33-C13-C14	115.445	117.488	115.7(2)
O35-N33-C13	118.581	120.598	118.63(19)
O34-N33-C13	117.167	119.698	123.3(2)
O34-N33-O35	124.251	119.705	118.03
C14-C15-C16	119.095	119.924	119.9(2)
H29-C12-C11	121.58	119.833	119.4

MOLECULE-5**2-Bromo-N'-isopropylidene-5-methoxybenzohydrazide**

Bond Length	Molecular Mechanics Results (MM+) (A ⁰)	Semi empirical (PM3) results (A ⁰)	Crystallographic Results (A ⁰)
C1-C2	1.40466	1.38915	1.393(3)
C2-C5	1.39835	1.38371	1.391(3)
C5-C6	1.39423	1.38916	1.394(3)
C4-C6	1.39942	1.40079	1.386(3)
C3-C4	1.40051	1.40292	1.405(3)
C1-C3	1.40283	1.39832	1.390(3)
C1-C13	1.36557	1.49965	1.512(3)
C2-Br12	1.9017	1.86741	1.902(2)
H28-C5	1.0405	1.09569	0.9500
H29-C6	1.10145	1.09609	0.9500
C4-O7	1.36914	1.38083	1.364(3)
H27-C3	1.10059	1.10102	0.9500
O7-C8	1.406	1.40643	1.436(3)
C8-H10	1.11465	1.09612	0.9800
C8-H11	1.11465	1.09612	0.9800
C8-H9	1.11303	1.09346	0.9800
O19-C13	1.21011	1.21564	1.235(2)
C13-N14	1.38743	1.43064	1.346(3)
H20-N14	1.01946	1.00388	0.85(3)
N14-N15	1.35632	1.3765	1.398(2)
C16-N15	1.34885	1.30601	1.280(3)

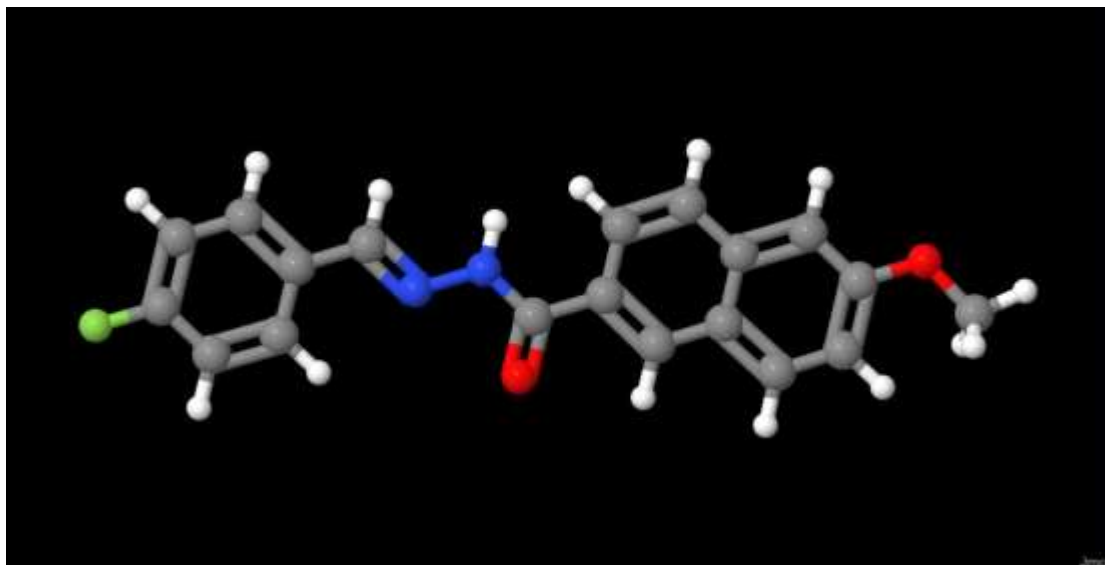
C16-C17	1.50447	1.49591	1.503(3)
C16-C18	1.50572	1.4942	1.505(3)
C17-H21	1.11306	1.0989	0.9800
C17-H22	1.11377	1.09872	0.9800
C17-H23	1.11378	1.09872	0.9800
C18-H25	1.11342	1.09987	0.9800
C18-H26	1.11342	1.09987	0.9800
C18-H24	1.1129	1.09935	0.9800

Bond Angle	Molecular Mechanics Results (MM+) (deg)	Semi empirical (PM3) results (deg)	Crystallographic Results (deg)
C2-C1-C3	118.21	117.431	118.91(17)
C1-C2-C5	119.189	123.132	120.8(2)
C2-C5-C6	121.131	119.549	120.2(2)
C5-C6-C4	121.284	118.657	119.57(18)
C3-C4-C6	116.528	121.059	120.0(2)
C1-C3-C4	123.659	120.174	120.54(19)
C13-C1-C2	122.623	120.861	122.28(18)
C13-C1-C3	119.167	121.708	118.64(18)
Br12-C2-C1	126.163	121.579	120.29(15)
Br12-C2-C5	114.648	115.289	118.92(17)
H28-C5-C2	121.037	119.513	119.9
H28-C5-C6	117.832	120.938	119.9
H29-C6-C5	117.483	119.735	120.2
H29-C6-C4	121.234	121.608	120.2
O7-C4-C6	125.143	125.362	125.03(18)
O7-C4-C3	118.329	113.579	114.97(19)
H27-C3-C4	114.564	118.948	119.7
H27-C3-C1	121.777	120.88	119.7
C4-O7-C8	119.013	117.552	117.17(19)
O7-C8-H10	109.723	112.286	109.5
O7-C8-H11	109.723	112.286	109.5
O7-C8-H9	106.532	102.168	109.5
H10-C8-H11	112.87	109.738	109.5
H10-C8-H9	108.893	110.069	109.5
H9-C8-H11	108.893	110.069	109.5
O19-C13-C1	121.919	124.039	120.00(18)
O19-C13-N14	118.079	119.806	121.77(18)

CI-C13-N14	120.002	116.155	118.21(17)
H20-N14-C13	120.639	118.994	116.7(19)
H20-N14-N15	118.951	119.492	123.7 (19)
C13-N14-N15	120.409	121.513	119.46(16)
C16-N15-N14	123.901	122.634	117.28(17)
N15-C16-C18	121.467	125.842	116.3(2)
N15-C16-C17	118.552	116.844	126.8(2)
C17-C16-C18	119.981	117.314	116.8(2)
C16-C18-H25	110.278	112.023	109.5
C16-C18-H26	110.278	112.023	109.5
C16-C18-H24	112.386	111.07	109.5
H25-C18-H26	108.652	107.727	109.5
H26-C18-H24	107.558	106.852	109.5
H25-C18-H24	107.558	106.852	109.5
H23-C17-C16	109.888	111.606	109.5
H22-C17-C16	109.888	111.606	109.5
H21-C17-C16	112.623	111.265	109.5
H23-C17-H22	108.351	107.302	109.5
H22-C17-H21	107.986	107.414	109.5
H23-C17-H21	107.986	107.413	109.5

MOLECULE-6

N' – [(1E) -(4-Fluorophenyl) methylene]-6 - methoxy - 2- naphthohydrazide.



Bond Length	Molecular Mechanics Results (MM+) (A ⁰)	Semi empirical (PM3) results (A ⁰)	Crystallographic Results (A ⁰)
C1-C2	1.39927	1.42468	1.427(7)
C2-C3	1.40232	1.38797	1.379(7)
C3-C4	1.39954	1.41745	1.417(7)
C4-C6	1.39861	1.41757	1.439(6)
C5-C6	1.39724	1.42156	1.436(6)
C1-C5	1.39508	1.37489	1.346(7)
O23-C2	1.36894	1.37751	1.377(6)
O23-C24	1.40614	1.40638	1.442(7)
C24-H25	1.11291	1.09334	0.9800
H26-C24	1.11438	1.09621	0.9800
C24-H27	1.11438	1.09618	0.9800
C4-C8	1.39811	1.41979	1.428(6)
C6-C7	1.39977	1.41672	1.408(7)
C8-C9	1.39585	1.37699	1.353(7)
C9-C10	1.39988	1.41663	1.424(7)
C7-C10	1.39979	1.38636	1.384(6)
H30-C3	1.10111	1.0966	0.9500
H29-C1	1.10307	1.09645	0.9500
H31-C5	1.1031	1.0963	0.9500
H33-C8	1.10329	1.09594	0.9500
H34-C9	1.1033	1.09929	0.9500
H32-C7	1.10154	1.09867	0.9500

C10-C11	1.36288	1.4932	1.492(7)
C11-O12	1.21147	1.21668	1.238(5)
C11-N13	1.38563	1.45029	1.359(6)
H28-N13	1.0201	1.00554	0.8800
N13-N14	1.35673	1.38312	1.381(5)
N14-C15	1.34662	1.3048	1.281(6)
H35-C15	1.10385	1.10447	0.9500
C16-C15	1.34269	1.46144	1.460(7)
C16-C18	1.40069	1.40414	1.399(6)
C18-C20	1.39628	1.3883	1.381(8)
C20-C21	1.39544	1.40386	1.389(7)
C19-C21	1.39546	1.40214	1.378(7)
C17-C19	1.39644	1.39083	1.399(8)
C16-C17	1.40063	1.40174	1.407(7)
C18-H37	1.10318	1.09634	0.9500
C20-H39	1.10314	1.09519	0.9500
C21-Fl22	1.32231	1.34254	1.360(6)
C19-H38	1.10288	1.09557	0.9500
C17-H36	1.10366	1.0978	0.9500

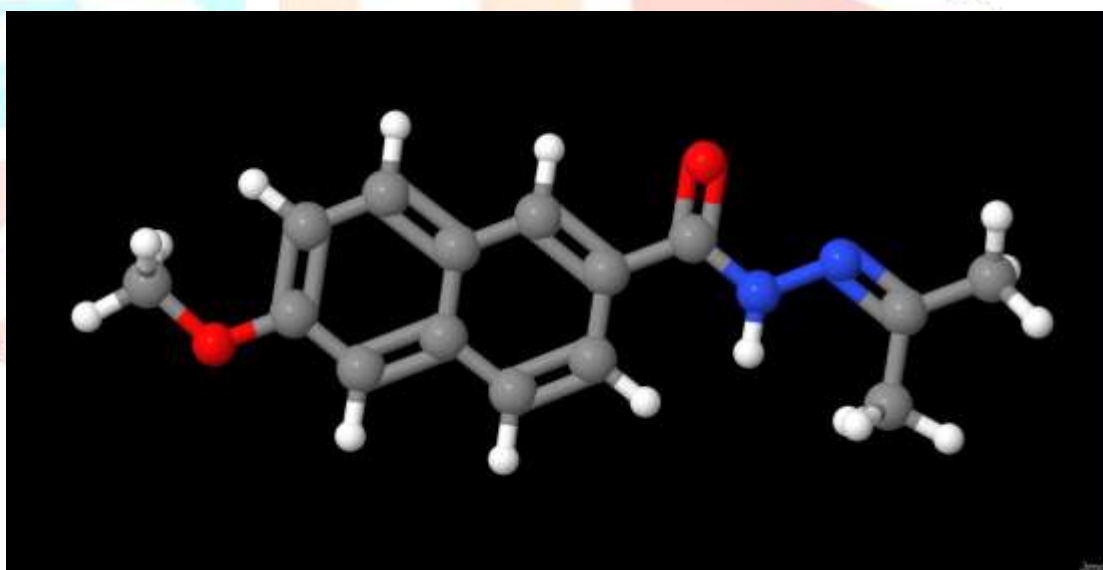
Bond Angle	Molecular Mechanics Results (MM+) (deg)	Semi empirical (PM3) results (deg)	Crystallographic Results (deg)
C1-C2-C3	116.368	121.138	120.5(4)
C2-C3-C4	122.284	119.309	120.1(5)
C3-C4-C6	120.093	119.892	119.6(4)
C4-C6-C5	118.557	119.402	117.7(4)
C1-C5-C6	120.415	120.636	121.8(5)
C2-C1-C5	122.284	119.619	120.2(4)
O23-C2-C3	125.419	125.704	125.1(5)
O23-C2-C1	118.213	113.158	114.3(4)
H30-C3-C2	119.924	121.974	119.9
H30-C3-C4	117.792	118.717	119.9
H31-C5-C6	120.675	118.971	119.1
H31-C5-C1	118.91	120.393	119.1
H29-C1-C5	118.937	120.656	119.9
H29-C1-C2	118.779	119.725	119.9
C2-O23-C24	119.18	117.54	115.8(4)

H25-C24-O23	106.587	102.228	109.5
O23-C24-H26	109.75	112.292	109.5
O23-C24-H27	109.75	112.261	109.5
H25-C24-H27	108.844	110.113	109.5
H25-C24-H26	108.844	110.086	109.5
H26-C24-H27	112.861	109.65	109.5
C3-C4-C8	120.789	121.126	122.6(5)
C5-C6-C7	121.159	120.978	123.3(5)
H33-C8-C4	120.475	121.974	119.3
H33-C8-C9	118.764	120.4	119.3
H34-C9-C8	117.72	119.528	119.3
H34-C9-C10	122.12	119.71	119.3
C11-C10-C9	119.425	118.769	118.8(4)
C11-C10-C7	121.34	121.634	122.8(5)
H32-C7-C10	121.536	120.484	119.0
H32-C7-C6	118.024	118.977	119.0
O12-C11-C10	119.812	123.68	121.2(4)
C10-C11-N13	120.005	116.241	115.7(4)
H28-N13-C11	120.553	113.546	120.0
H28-N13-N14	119.212	115.769	120.0
C11-N13-N14	120.235	121.242	120.1(3)
H35-C15-N14	113.423	123.373	119.1
H35-C15-C16	124.131	116.649	119.1
N14-C15-C16	122.446	119.978	121.7(4)
C15-C16-C18	121.724	122.307	121.9(4)
C15-C16-C17	119.986	118.066	119.2(4)
H37-C18-C16	121.079	120.253	119.5
H37-C18-C20	118.06	119.316	119.5
H39-C20-C18	119.822	120.441	120.4
H39-C20-C21	119.744	120.381	120.4
Fl22-C21-C20	120.335	119.51	119.4(4)
Fl22-C21-C19	120.54	119.357	118.9(5)
H38-C19-C21	119.646	120.39	120.4
H38-C19-C17	119.972	120.686	120.4
H36-C17-C19	118.463	119.296	120.0
H36-C17-C16	120.63	119.994	120.0
C4-C8-C9	120.761	120.494	121.4(5)
C6-C4-C8	119.119	118.981	117.7(4)

C4-C6-C7	120.284	119.62	119.0(4)
C6-C7-C10	120.44	120.538	122.0(5)
C7-C10-C9	119.236	119.597	118.2(4)
C8-C9-C10	120.16	120.762	121.5(4)
C15-N14-N13	123.65	118.067	114.8(4)
C18-C16-C17	118.29	119.621	118.9(4)
C16-C18-C20	120.861	120.709	120.9(5)
C18-C20-C21	120.435	118.924	119.2(4)
C20-C21-C19	119.125	121.133	121.6(5)
C17-C19-C21	120.382	119.178	119.2(5)
C16-C17-C19	120.907	120.431	120.1(4)
O12-C11-N13	120.183	119.974	123.0(4)

MOLECULE – 7

N' - Isopropylidene -6-methoxy- 2 - naphthohydrazide



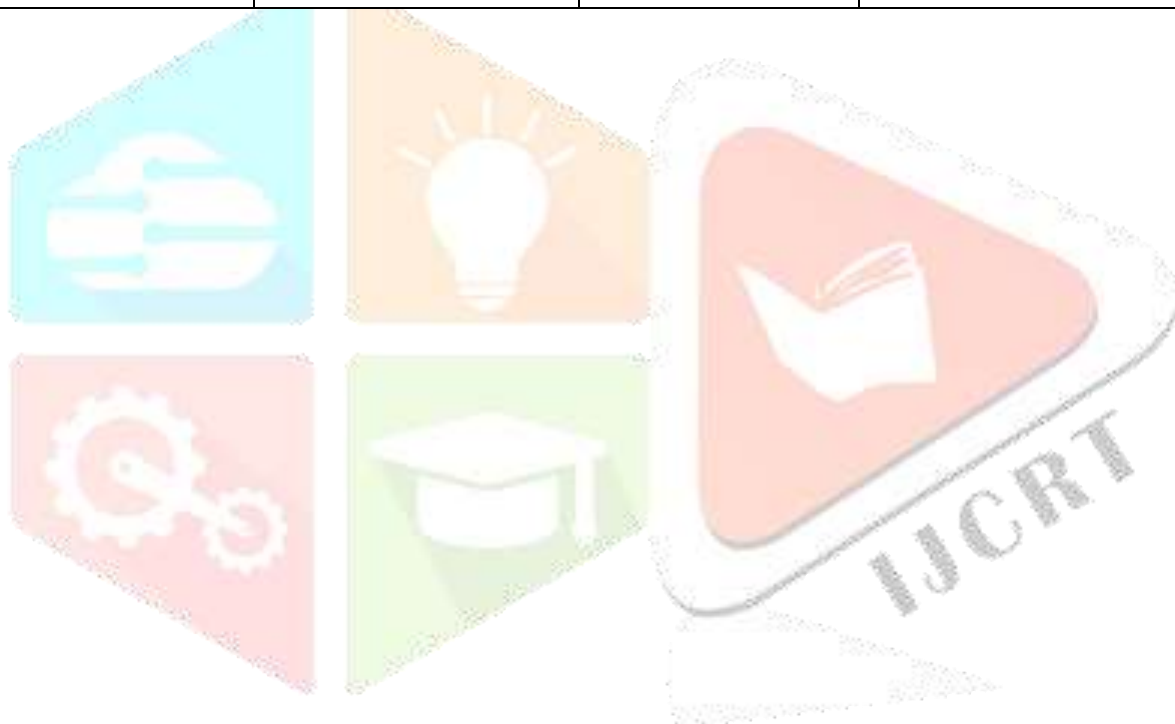
Bond Length	Molecular Mechanics Results (MM+) (A ⁰)	Semi empirical (PM3) results (A ⁰)	Crystallographic Results (A ⁰)
C1-C2	1.39512	1.36482	1.364(2)
C2-C5	1.39932	1.42874	1.424(2)
C5-C6	1.4023	1.37732	1.380(2)
C4-C6	1.39966	1.41986	1.431(2)
C3-C4	1.39832	1.40951	1.4245(18)
C1-C3	1.39709	1.42385	1.432(2)
H30-C1	1.10348	1.09608	0.9500
H31-C2	1.1034	1.09645	0.9500

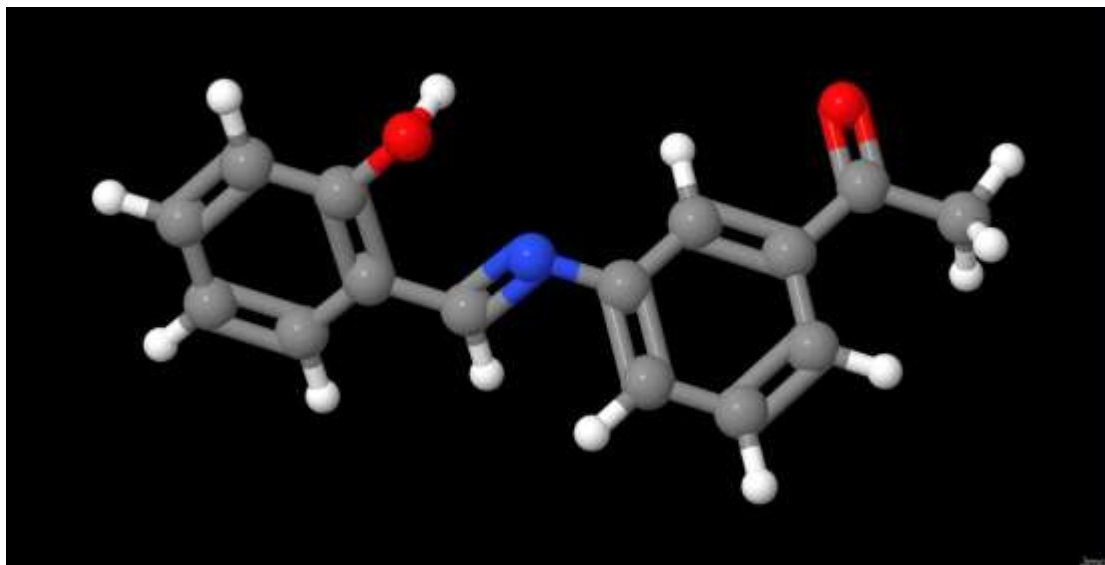
O25-C5	1.36894	1.3781	1.3733(19)
H32-C6	1.1011	1.09667	0.9500
O25-C26	1.40606	1.40677	1.434(2)
H28-C26	1.11443	1.09627	0.9800
H29-C26	1.11443	1.09627	0.9800
H27-C26	1.11284	1.09323	0.9800
C4-C9	1.39831	1.41987	1.431(2)
C24-C3	1.39982	1.41687	1.419(2)
C8-C9	1.39637	1.36841	1.376(2)
C7-C8	1.39996	1.41999	1.426(2)
C24-C7	1.40007	1.37691	1.385(2)
C24-H35	1.10202	1.10088	0.9500
H33-C8	1.10327	1.09778	0.9500
H34-C9	1.10344	1.09593	0.9500
C7-C10	1.36301	1.49655	1.502
O23-C10	1.21127	1.21805	1.2352(19)
C10-N11	1.3851	1.43006	1.355(2)
H16-N11	1.01997	1.00387	0.88(2)
N11-N12	1.35613	1.37624	1.4017(18)
N12-C13	1.34915	1.30548	1.286(2)
C13-C14	1.50449	1.49614	1.496(2)
C13-C15	1.50622	1.49376	1.496(3)
H17-C14	1.11317	1.09899	0.9800
H19-C14	1.11373	1.0988	0.9800
H18-C14	1.11373	1.09879	0.9800
H20-C15	1.11293	1.0928	0.9800
H21-C15	1.11361	1.09971	0.9800
H22-C15	1.11361	1.09972	0.9800

Bond Angle	Molecular Mechanics Results (MM+) (deg)	Semi empirical (PM3) results (deg)	Crystallographic Results (deg)
C3-C1-C2	120.39	120.716	120.66(14)
C1-C2-C5	122.294	119.564	120.35(15)
C5-C6-C2	116.35	121.14	120.15
C4-C6-C5	122.309	119.369	119.52(1)
C3-C4-C6	120.054	119.857	120.68(2)
C4-C3-C1	118.603	119.354	118.87(13)

H30-C1-C3	120.65	118.824	119.7
H30-C1-C2	118.96	120.459	119.7
H31-C2-C1	118.882	120.938	119.8
H31-C2-C5	118.824	119.498	119.8
O25-C5-C6	125.508	125.847	125.58(15)
O25-C5-C2	118.142	113.013	113.48(14)
C5-O25-C26	119.199	117.395	117.03(15)
O25-C26-H28	109.773	112.217	109.5
O25-C26-H29	109.773	112.217	109.5
O25-C26-H27	106.497	102.299	109.5
H28-C26-H29	112.867	109.625	109.5
H28-C26-H27	108.86	110.141	109.5
H29-C26-H27	108.86	110.141	109.5
C24-C3-C1	121.114	121.133	121.29(13)
C9-C4-C6	120.863	121.122	122.13(13)
H35-C24-C3	117.882	118.101	119.5
H35-C24-C7	121.626	121.165	119.5
C10-C7-C24	121.116	122.816	122.73(13)
C10-C7-C8	119.684	117.709	118.26(12)
H33-C8-C7	122.084	119.036	119.4
H33-C8-C9	117.788	120.259	119.4
H34-C9-C8	118.782	120.442	119.7
H34-C9-C4	120.404	119.007	119.7
C24-C3-C4	119.513	120.283	119.83(12)
C7-C24-C3	120.492	120.734	121.09(13)
C8-C7-C24	119.2	119.476	118.95(14)
C7-C8-C9	120.129	120.705	121.18(13)
C8-C9-C4	120.814	120.552	120.66(13)
C9-C4-C3	119.083	119.021	119.61(13)
O23-C10-C7	119.738	123.922	120.72(14)
C7-C10-N11	119.999	116.311	115.98(12)
O23-C10-N11	120.263	119.767	123.28(15)
H16-N11-C10	120.107	118.658	121.1(3)
H16-N11-N12	118.873	119.809	118.2(13)
N12-N11-C10	121.02	121.533	118.32(12)
C13-N12-N11	122.917	122.836	115.58(13)
C14-C13-N12	119.016	116.968	116.84(16)
N12-C13-C15	121.146	125.857	126.69(15)

C13-C14-H18	110.059	111.63	109.5
C13-C14-H19	110.059	111.627	109.5
C13-C14-H17	112.512	111.192	109.5
H18-C14-H19	108.428	107.313	109.5
H18-C14-H17	107.831	107.425	109.5
H19-C14-H17	107.831	107.422	109.5
C13-C15-H20	112.445	110.948	109.5
C13-C15-H21	110.18	112.038	109.5
C13-C15-H22	110.18	112.033	109.5
H20-C15-H22	107.651	106.896	109.5
H20-C15-H21	107.651	106.897	109.5
H21-C15-H22	108.609	107.74	109.5
C14-C13-C15	119.838	117.174	116.47(16)



MOLECULE – 8**1-[3 - {(2- hydroxybenzylidene)amino} phenyl]ethanone**

Bond Length	Molecular Mechanics Results (MM+) (A ⁰)	Semi empirical (PM3) results (A ⁰)	Crystallographic Results (A ⁰)
C1-C2	1.39884	1.39823	1.387(2)
C2-C5	1.40078	1.39684	1.382(5)
C5-C6	1.40035	1.40097	1.385(2)
C4-C6	1.3989	1.39904	1.389(2)
C3-C4	1.39621	1.3887	1.375(2)
C1-C3	1.39604	1.38962	1.375(2)
C2-C7	1.36192	1.49517	1.492(2)
O22-C7	1.21184	1.21865	1.211(2)
C7-C8	1.52282	1.50685	1.492(2)
C8-H9	1.11447	1.09856	0.9500
C8-H10	1.11407	1.09803	0.9500
C8-H11	1.11407	1.09803	0.9500
C6-N12	1.34974	1.43187	1.416(1)
H26-C5	1.10374	1.09954	0.9500
H23-C1	1.10151	1.0968	0.9500
H24-C3	1.10367	1.09517	0.9500
H25-C4	1.10066	1.10122	0.9500
N12-C13	1.34624	1.29745	1.277(1)
H27-C13	1.0992	1.10748	0.9800
C13-C14	1.34521	1.46436	1.443
C16-C14	1.40527	1.4116	1.406(2)
C14-C15	1.40179	1.39906	1.393(2)

C18-C15	1.39561	1.38957	1.373(2)
C18-C19	1.39335	1.3903	1.382(3)
C17-C19	1.39434	1.38816	1.366(2)
C16-C17	1.39917	1.40214	1.388(2)
H28-C15	1.10307	1.09793	0.9500
C18-H30	1.10322	1.09492	0.9800
C19-H31	1.10313	1.09504	0.9800
C17-H29	1.10321	1.0965	0.9800
C16-O20	1.36035	1.36853	1.342(1)
O20-H21	0.941602	0.94929	0.8200

Bond Angle	Molecular Mechanics Results (MM+) (deg)	Semi empirical (PM3) results (deg)	Crystallographic Results (deg)
C2-C1-C3	119.715	120.543	119.8
C1-C2-C5	119.294	119.393	119.7
C2-C5-C6	121.236	119.895	120.7
C5-C6-C4	118.908	120.25	118.7
C6-C4-C3	120.107	119.566	120.9
C1-C3-C4	120.739	120.354	120.3
C7-C2-C1	121.441	121.366	122.2
C7-C2-C5	119.264	119.244	118.1
N12-C6-C5	114.84	116.482	124.9
N12-C6-C4	126.252	123.268	116.5
O22-C7-C2	122.076	121.365	120.6
O22-C7-C8	117.105	120.459	119.9
C8-C7-C2	120.819	118.176	119.6
C7-C8-C9	110.786	112.185	109.5
C7-C8-C10	111.117	110.826	109.5
C11-C8-C7	111.117	110.826	109.5
H9-C8-H11	106.709	107.423	109.5
H9-C8-H10	106.709	107.423	109.5
H10-C8-H11	110.222	107.97	109.5
C6-N12-C13	126.172	121.973	121.72
N12-C13-C14	121.593	120.482	122.2
C15-C14-C13	121.145	121.445	119.8
C13-C14-C16	119.553	120.486	121.6

O20-C16-C17	119.522	121.464	119.1
O20-C16-C14	121.579	117.663	121.4
C15-C14-C16	119.302	118.068	118.7
C14-C16-C17	118.899	120.873	119.5
C16-C17-C19	121.645	119.578	120.3
C17-C19-C18	119.355	120.177	121.3
C19-C18-C15	119.65	120.318	119.1
C18-C15-C14	121.15	120.986	121.4

VIII. RESULT ANALYSIS

BOND LENGTHS AND BOND ANGLES

Comparison of bond lengths and bond angles using x-ray crystallographic data and by using molecular mechanics (MM+) and semi empirical (PM3) methods.

Ideally a “chemically accurate” calculation should give the results below:

Bong lengths: calculated values within $0.01 - 0.02 \text{ \AA}$ of experiment.

Bond angles: calculated values within $1-2^\circ$ of experiment.

Some of bond lengths and bond angles were in agreement with x-ray crystallographic results. They do not always satisfy the criteria we set for chemical accuracy. PM3 calculations generally give bond lengths with in $\pm 0.036 \text{ \AA}$ and bond angles with in $\pm 3.9^\circ$, not always “accurate” but still pretty good.

IX. CONCLUSION

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.

In this study, we have seen that computational results of some Schiff bases are comparable with x-ray crystallographic results. Hence computational chemistry can be used for determination of properties that are inaccessible experimentally. And also, it can be used for interpretation of experimental data.

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