AN ABSTRACT OF THE THESIS OF

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A Quantum Mechanical Study of the Nitration of Simple Aromatic Systems.

Abstract approved: Charles Greenlief

Semi-empirical molecular orbital methods have been employed to predict the effect of nitration of benzene, aniline, chlorobenzene, iodobenzene, and toluene as simple aromatic systems. The effect of substitution at ortho, meta, or para positions on enthalpies of formation, ionization energies, and dipole moments have been calculated employing AM1 and PM3 methods in HyperChem.™ Bond lengths, bond angles and frequencies of infrared absorption were calculated using the PM3 method. The calculated values have been compared with their experimental counterparts.

Both the AM1 and PM3 methods provide useful accuracy. However, the AM1 method gives better results than PM3 for the study of aromatic compounds containing carbon, hydrogen, nitrogen, and oxygen. The PM3 calculations of infrared frequencies give random errors, in contrast to *ab initio* calculations, which give results that are systematically too high.

A QUANTUM MECHANICAL STUDY OF THE NITRATION OF SIMPLE AROMATIC SYSTEMS

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بِسْمِ اللَّهِ الرَّحْمَٰنِ الرَّحِيمِ

In the Name of Allah, the Most Compassionate, the Most Merciful

قُلْ هَلْ يَسْتَوِي الَّذِينَ يَعْلَمُونَ وَالَّذِينَ لَا يَعْلَمُونَ إِنَّمَا يَتَذَكَّرُ أُولُوا الْأَلْبَابِ

"Say: Are those who possess knowledge equal to those who do not know?
Verily only those who are enlightened will make distinction."
(The Holy Qur'an, Chapter 39, Verse 9)

Dedication

إلى روح والدي وروح زوجتي رحمهما الله

I wish to dedicate this humble work to my beloved departed father, and to my deceased wife who left this world in a tragic car accident, may the Most Compassionate grant them peace and elevate their souls.

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INTRODUCTION

1.1 Development of Quantum Chemistry

Early in the twentieth century, physicists came to the conclusion that while classical mechanics had been able to successfully describe the motion of macroscopic objects, classical mechanics could not correctly describe the behavior of very small particles such as the electrons and nuclei of atoms and molecules. Quantum mechanics was developed as a set of laws to describe the behavior of such submicroscopic particles. Quantum mechanics is usually introduced as a set of postulates that are justified only by their ability to predict and correlate experimental facts and by their general applicability. Quantum chemistry applies those postulates to problems in the field of chemistry.

1.2 The Schrödinger Equation for a One-Atom System

The status of a quantum mechanical system is described by a state function or wave function Ψ, which is as a function of the coordinates of the particles of the system and the time [$\Psi = \Psi(x, y, z, t)$]. The concepts of the wave function and the equation governing its change with time were developed in 1926 by the Austrian physicist Erwin Schrödinger.[1] For a one-particle, one-dimensional system, the time-dependent Schrödinger equation is:

$$-\frac{\hbar}{i}\frac{\partial\Psi(x,t)}{\partial t} = -\frac{\hbar^2}{2m}\frac{\partial^2\Psi(x,t)}{\partial x^2} + V(x,t)\Psi(x,t) \qquad \text{Eq. (1.1)}$$

Eq. (1.1) is formulated to be the first derivative of the wave function with respect to time and allows the calculation of the future behavior of the wave function for any known value of *t*. The constant ħ has the value of h/2π; where m is the mass of the particle, $i = (-1)^{1/2}$, and *V(x, t)* is the potential-energy function of the system.

The wave function, Ψ, is not expected to define specifically the position of a particle relating to one of the coordinates (*x*, for example). Max Born[2] postulated that the probability density for finding the particle at various values of the *x* coordinate is given by the following relationship

$$|\Psi(x,t)|^2 dx \qquad (1.2)$$

This equation predicts the probability of finding the particle at time *t* in the region lying between *(x)* and *(x + dx)*.

Frequently, it is not necessary to employ the time-dependent Schrödinger equation. A simpler time-independent form of the equation, Eq. (1.3) is used instead:

$$\frac{-\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} + V(x)\psi(x) = E\psi(x) \qquad (1.3)$$

where *E* is the energy of the particle of mass m moving in one dimension.

1.3 Operators in Quantum Chemistry

An operator is a rule that transforms a given function into another one. This definition can be drawn from Eq. (1.3) when it is redisplayed in the form of Eq. (1.4). When the wavefunction is an eigenfunction of the energy operator, it gives the wave function back again multiplied by the allowed values of the energy. The term within the square brackets is called the Hamiltonian operator for the system.

$$[\frac{-\hbar^2}{2m}\frac{d^2}{dx^2} + V(x)]\psi(x) = E\psi(x) \qquad (1.4)$$

An important vector operator in quantum mechanics is the *Laplacian operator*, ∇^2, which acts as a differential operator on the wavefunction, ψ, as follows:

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \qquad (1.5)$$

1.4 The Schrödinger Equation for Many-Electron Systems

The molecular properties of a chemical system can be calculated once the solutions to the Schrödinger equation have been obtained. The molecular Schrödinger equation ($H_{op}\ \psi = E\psi$) is very complicated and almost impossible to solve exactly except for a few special cases. Exact solutions to the Schrödinger equation can only be obtained for a few systems known collectively as idealized systems; such systems include the particle in a box, the harmonic oscillator, the rigid rotor, and the hydrogen atom.

It is sufficient for the purposes of this research to consider the spin-free, non-relativistic Hamiltonian operator for many-electron systems. This operator provides the major portion of the energy of a stationary state; it includes the kinetic energy terms for the electrons and the potential energy terms for the electron-electron and nucleus-electron interactions. Eq. (1.6) gives the non-relativistic Hamiltonian. The first term, the *Laplacian* operator for the electrons, refers to the kinetic energy of the electrons.

$$H_j = \frac{-\hbar^2}{2m}\sum_j \nabla_j^2 - \sum_j \frac{Ze^2}{r_j} + \sum_{i<j} \frac{e^2}{r_{ij}} \qquad (1.6)$$

The other two terms account for the potential energy due to Coulombic interactions. The second term relates to the nucleus-electron attractions, where Ze is the nuclear charge and r_j is the distance of the electron j from the nucleus. The third term refers to the electron-electron repulsions where r_{ij} is the distance between the two electrons i and j. The notation $i < j$ on the summation sign means that the summation is to be made for all values of i, and that for each value of j there is a further summation over all values of i that are less than j, thus ensuring that each repulsion is taken into account only once.[3]

1.5 Approximation Methods in Quantum Chemistry

For a variety of chemical systems of interest, such as many-electron atoms or molecules, the electrostatic interaction of the electrons with one another, as well as with the nucleus, make accurate calculations of the wave functions and energy levels much more difficult than in the case of any of the idealized systems. For such situations, an approximate solution to the equation frequently can give quite satisfactory results that closely approach the exact solution.

1.5.1 The Variation Method

The variation method is based on the variation principle that states that for any normalized acceptable function ϕ, the Hamiltonian is as shown:

$$H_{av} = \int \phi^* H_{op} \phi d\tau \geq E_o. \tag{1.7}$$

Here E_o is the lowest eigenvalue of the energy. This method, in words, states that if an arbitrary wavefunction is chosen to describe a chemical system, the energy calculated from this function will be greater than or equal to the energy calculated using the true ground state wavefunction. Thus, from among several approximate functions, the one that gives the lowest energy should be the one of choice.

When employing the variation theorem for chemical problems, the first step is to guess a starting function. To assist in the minimization process, the initial function usually includes one or more variable parameters that can be adjusted to obtain the final appropriate function. A mathematical description of the theory can be reviewed in the references cited in the reference section.

1.5.2 Perturbation Theory

Perturbation theory is used to determine the wavefunction of a system if the solution for a similar system is known exactly. One example of this situation is the use of the known eigenfunctions for a hydrogen atom to approximate the wavefunctions of the same atom when it is being affected by external electrostatic fields.

1.6 The Independent-Electron Approximation

This type of approximation begins by neglecting the electron-electron repulsion term, the third term on the right-hand side of Eq. (1.6) that couples the motion of the two electrons. Dropping this term, the Hamiltonian becomes Eq. (1.8):

$$H_j = -\frac{\hbar^2}{2m}\sum_j \nabla_j^2 - \sum_j \frac{Ze^2}{r_j} \tag{1.8}$$

In studying the helium atom as an example of a nucleus with charge +2e and two electrons, the potential energy of the system of the three constituents is related to their interparticle distances, r_1, r_2, and r_{12}. According to classical mechanics, the potential energy is:

$$V(r_1,r_2,r_{12}) = -\frac{2e^2}{r_1} - \frac{2e^2}{r_2} + \frac{e^2}{r_{12}} \tag{1.9}$$

The first two terms of Eq (1.9) relate the attractions between the electrons and the nucleus while the third term deals with the repulsion between the two electrons. Assuming a stationary nucleus, Eq. (1.10) is the Schrödinger equation for this system. The coordinates x, y, and *z* are the Cartesian coordinates of the electrons relative to the nucleus as the origin and m is the mass of the electron.

$$\frac{-\hbar^2}{2m}[(\frac{\partial^2\Psi}{\partial x_1}+\frac{\partial^2\Psi}{\partial y_1}+\frac{\partial^2\Psi}{\partial z_1}) - (\frac{\partial^2\Psi}{\partial x_2}+\frac{\partial^2\Psi}{\partial y_2}+\frac{\partial^2\Psi}{\partial z_1})]+V(r_1,r_2,r_{12})\psi=E\psi \tag{1.10}$$

Substitution of Eq. (1.5) into Eq. (1.10) gives the condensed Eq. (1.11).

$$-\frac{\hbar^2}{2m}\nabla_1^2\psi - \frac{\hbar^2}{2m}\nabla_2^2\psi + V(r_1,r_2,r_{12})\psi = E\psi \tag{1.11}$$

When one employs the independent-electron approximation to obtain a solution for this equation, one begins by neglecting the electron-electron repulsion in the potential-energy term. The resulting equation, Eq. (1.12), shows that neither electron is affected by the presence of the other and the two of them behave completely independently.

$$(-\frac{\hbar^2}{2m}\nabla_1^2 - \frac{2e^2}{r_1})\ \psi + (-\frac{\hbar^2}{2m}\nabla_2^2 - \frac{2e^2}{r_2})\ \psi = E\psi \qquad (1.12)$$

This equation can be written in an even simpler form as in Eq. (1.13):

$$\psi(1,2) = \psi_1(1)\psi_2(2) \qquad (1.13)$$

where $\psi_1(1)$ and $\psi_2(2)$ satisfy Eqs. (1.14) and (1.15) for a hydrogen-like atom with nuclear charge +2e:

$$(-\frac{\hbar^2}{2m}\nabla_1^2 - \frac{2e^2}{r_2})\psi_1 = E_1\psi_1 \qquad (1.14)$$

$$(-\frac{\hbar^2}{2m}\nabla_2^2 - \frac{2e^2}{r_2})\psi_2 = E_2\psi_2 \qquad (1.15)$$

Substitution of Eq. (1.13) into Eq. (1.12) gives:

$$\psi_2(2)[(-\frac{\hbar^2}{2m}\nabla_1^2 - \frac{2e^2}{r_1})\ \psi_1(1)] + \psi_1(1)[(-\frac{\hbar^2}{2m}\nabla_2^2 - \frac{2e^2}{r_2})\ \psi_2(2)] = E\psi_1(1)\psi_2(2) \qquad (1.16)$$

Replacing the term in the square brackets by E_1 and E_2 in Eqs. (1.14) and (1.15) gives:

$$(E_1 + E_2)\psi_1(1)\psi_2(2) = E\psi_1(1)\psi_2(2) \qquad (1.17)$$

In this approximation the total energy of the two electron system is given by the sum of the two individual energies, $E = E_1 + E_2$. Also, according to Eq. (1.13), the probability density function for two electrons is the product of the probability densities for each electron in the field of the bare nucleus:

$$|\psi(1,2)|^2 = |\psi(1)|^2 \, |\psi(2)|^2 \qquad (1.18)$$

The fact that the one-electron probability densities combine in this manner shows clearly that the two electrons move independently of one another in the absence of the electron-electron repulsion term.[4]

1.7 The Born-Oppenheimer Approximation

In 1927 Max Born and J. Robert Oppenheimer showed that an excellent approximation is to treat the electronic and nuclear motions separately.[5] The approximation considers the movement of the nucleus to be very slow relative to that of the electrons. This huge difference in velocities is a result of the nuclear mass being thousands of times greater than the electronic mass. Consequently, one assumes a fixed configuration of the nucleus, and solves an electronic Schrödinger equation for this configuration to find the molecular electronic energy and wavefunction. The process is carried out repeatedly for many different fixed nuclear configurations to give the electronic energy as a function of the positions of the nucleus. The nuclear configuration that corresponds to the minimum value of the electronic energy determines the equilibrium geometry of the molecule. Finally, the different calculated values of the electronic energy represent the potential-energy for the nuclear motion that allows one to obtain the molecular vibrational and rotational energy levels for the given electronic state.

The Hamiltonian in the Born-Oppenheimer approximation, for a molecule with nuclei labeled by *a* and *b*, and two electrons labeled by *i* and *j* is:

$$\hat{H} = -\frac{\hbar^2}{2}\sum_a \frac{\nabla_a^2}{M_a} - \frac{\hbar^2}{2}\sum_i \frac{\nabla_i^2}{m_i} - \sum_i \sum_a \frac{Z_a e^2}{r_{ia}} + \sum_{a<b} \frac{Z_a Z_b e^2}{R_{ab}} + \sum_{i<j} \frac{e^2}{r_{ij}} \qquad (1.19)$$

The first term refers to the kinetic energy of all of the nuclei, where M_a is the mass of the a'th nucleus. The second term refers to the kinetic energy of the electrons and the third term accounts for the nucleus-electron attractive potential energies. The distance between the i'th electron and the a'th nucleus is r_{ia}. The fourth term is due to the nucleus-nucleus repulsion energy where R_{ab} is the distance between the a'th and b'th nuclei. Finally, the last term takes into account electron-electron repulsion energies where the distance between the i'th and j'th electrons is r_{ij}. The Hamiltonian of Eq.(1.19) satisfies the Schrödinger equation:

$$H_{op}\psi(r,R) = E\psi(r,R) \qquad (1.20)$$

where E is the total energy of the system and ψ is a function of the electronic coordinates r and the nuclear coordinates R.

The Born-Oppenheimer approximation introduces ψ as a product function of two components $\psi_R(r)$ and $\chi(R)$:

$$\psi(r,R) = \psi_R(r)\chi(R) \qquad (1.21)$$

$\Psi_R(r)$ is the electronic wavefunction that relates the electronic coordinates r and that depends only upon quantum states. Although it varies for different fixed nuclear positions (R), $\chi(R)$ is called the nuclear wavefunction. It is a function of the nuclear coordinates but depends as well on the electronic energy. The electronic energy can be taken as the potential in which the nuclei move, so that the equation for $\chi(R)$ is:

$$[E_n(R) + E_e(R)]\chi(R) = E\chi(R) \qquad (1.22)$$

where E_n is the nuclear kinetic energy Hamiltonian and E_e is the electronic kinetic energy Hamiltonian. The wavefunction $\psi_R(r)$ in Eq. (1.21) satisfies the following equation:

$$E_e(r, R)\psi_R(r) = E_e(R)\psi_R(r) \qquad (1.23)$$

where $E_e(r, R)$ is the electronic Hamiltonian and $E_e(R)$ is the energy.

Eqs. (1.21), (1.22), and (1.23) are the description of the Born-Oppenheimer approximation. There is clear spectroscopic evidence that this approximation is valid for the ground state of molecules, but the approximation is not as good for the excited states of large polyatomic molecules. The Born-Oppenheimer approximation also breaks down in the case of degeneracy or near degeneracy of electronic states.[6]

1.8 Hartree-Fock Self-Consistent Field Method

The self-consistent field (SCF) method of electronic structure calculations was first developed in the early 1930's by Hartee and by Fock for closed shell atoms or those containing a single electron.[7] Later, the method was extended to the study of open-shell systems. The method is the most commonly employed method in the *ab initio* study of atoms and molecules. The essential physical idea of the SCF calculation is to replace the exact dynamics or energetics of a particle by its evolution in a field averaged over all the other particles. To achieve consistency an initial set of orbital functions is guessed, and then improved by use of the variation theorem. For example, a N-electron atom in its ground state will have a wavefunction ψ,

$$\psi = |\psi_1(1)\psi_2(2)\ldots\psi_N(N)| \tag{1.24}$$

When a complete variation of the spin-orbitals in Eq.(1.24) is employed, the many-electron problem leads to a set of coupled one-electron equations to yield the Hartree-Fock equations:[8]

$$\hat{H}_{eff}(N)\psi_N(N) = E_N\psi_N(N) \tag{1.25}$$

$\hat{H}_{eff}$ is the effective one-electron Hamiltonian, and it is the same for each of the N electrons; E_N are the orbital energies. Usually, $\hat{H}_{eff}$ has two parts: a kinetic energy term and a potential energy term. To determine the potential energy part, one assumes the electron is subject to the potential of the nucleus plus the average potential field created by all the other electrons. In this situation one can write $\hat{H}_{eff}$ as a function of $\hat{h}$, a hydrogen-like Hamiltonian for the electron *i* and the average field of the other electrons, U_{av}:

$$\hat{H}_{eff}(i) = \hat{h}(i) + U_{av}(i) \tag{1.26}$$

To solve the Hartree-Fock equations, one uses an iterative method that starts by making an initial guess for the form of the ψ_i's. Then one uses this set of functions to determine the potential acting on one electron. This allows one to solve for its orbital. Then the procedure is repeated for another electron's orbital, yielding an improved orbital. The process is repeated until all the original orbitals have been replaced by improved orbitals. One then takes the improved set of orbitals and begins the whole procedure over again in order to obtain a second improved set of orbitals. Eventually a set of orbitals that does not change after an iteration is obtained. At this point one says a self-consistent field has been obtained, since the final set of orbitals is able to reproduce the potential field that determined them.

Energies calculated by this method are usually within about one percent of the experimental values. This is quite good in absolute terms, but for most chemical purposes these results are not usually satisfactory.[9]

1.9 Linear Combination of Atomic Orbitals

The most commonly used method for constructing molecular orbitals is the linear combination of atomic orbitals *(LCAO)* method. A glossary of definitions is included in Appendix A. Employing the variation theorem as a source for obtaining an approximate solution for molecular problems, one can generate a trial function by taking a linear combination of the atomic orbitals of the atoms that form the molecule. One can expect the effect of any of the nuclei on the closest electron will be much larger than the effect due to any of the other nuclei on that electron. It is usual to assume the molecular orbital is similar to the isolated atomic orbitals. This assumed picture can be used as a starting point in the *LCAO*, and then the variation theorem permits the determination of the best molecular orbitals that can be constructed.

The linear combination of n atomic orbitals, ϕ_i, is expressed by a trial function, Eq. (1.27), that was first used by Finkelstine and Horowitz in 1928:[10]

$$\psi = a_1\phi_1 + a_2\phi_2 + \ldots + a_n\phi_n = \sum a_j\phi_j \qquad (1.27)$$

The variation theorem will give the best values for the coefficients, a_i, that correspond to the lowest value of the energy. Using the theorem to deal with the function in Eq. (1.27), we obtain E_o, the lowest eigenvalue of the Hamiltonian in Eq. (1.28):

$$\frac{\int \psi^* H_{op} \psi d\tau}{\int \psi^* \psi d\tau} \geq E_o \tag{1.28}$$

The substitution of Eq. (1.27) into Eq. (1.28) will give Eq. (1.29), such that one can write it in the form of Eq. (1.30):

$$\frac{\int \sum_i (a_i \phi_i) \hat{H} \sum_j (a_j \phi_j) d\tau}{\int \sum_i a_i \phi_i \sum_j a_j \phi_j d\tau} \geq E_o \tag{1.29}$$

$$\frac{\sum_{ij} a_i a_j H_{ij}}{\sum_{ij} a_i a_j S_i} \geq E_o \tag{1.30}$$

The integrals, H_{ij}, are matrix elements of the operator in an imaginary matrix of the integrals in which the *i*'s and *j*'s take on all possible values.

$$H_{ij} = \int \phi_i^* \hat{H} \phi_j d\tau \tag{1.31}$$

The overlap integrals S_{ij} play an important role in bonding. They are:

$$S_{ij} = \int \phi_i^* \phi_j d\tau \tag{1.32}$$

If one defines the left side of Eq. (1.30) as E, the energy associated with ψ, then one obtains Eq. (1.33) or equivalently Eq. (1.34):

$$E = \frac{\sum_{ij} a_i a_j H_{ij}}{\sum_{ij} a_i a_j S_{ij}} \tag{1.33}$$

$$\sum_{ij} a_i a_j (H_{ij} - ES_{ij}) = 0 \tag{1.34}$$

Differentiating Eq. (1.34) with respect to one of the coefficients, a_m for example, while keeping the others constant gives:

$$\sum_i a_i H_{mi} + \sum_i a_i H_{mi} - E(\sum_i a_i S_{mi} + \sum_i a_i S_{mi}) - \frac{\partial E}{\partial a_m} \sum_{ij} a_i a_j S_{ij} = 0 \tag{1.35}$$

The energy is a minimum when $\partial E/\partial a_m = 0$. Also, $S_{mi} = S_{im}$, and $H_{mi} = H_{im}$ for the assumed real function. Thus, this establishes Eq. (1.36):

$$\sum_i a_i (H_{mi} - ES_{mi}) = 0 \tag{1.36}$$

There will be *n* equations of this type, one for each coefficient that can be varied. A set of *n* linear equations in *n* unknowns is obtained. This equation has a non-trivial solution only if the determinant of the factors that multiply the unknowns a_i is zero, i.e.,

$$\begin{bmatrix} H_{11}-ES_{11} & H_{12}-ES_{12} & \cdots\cdots & H_{1n}-ES_{1n} \\ H_{21}-ES_{21} & H_{22}-ES_{22} & \cdots\cdots & H_{2n}-ES_{2n} \\ \cdots & \cdots & \cdots & \cdots \\ H_{n1}-ES_{n1} & H_{n2}-ES_{n2} & \cdots\cdots & H_{nn}-ES_{nn} \end{bmatrix} = 0 \tag{1.37}$$

In abbreviated form, this may be writen as:

$$|H_{mi} - ES_{mi}| = 0 \tag{1.38}$$

When the secular determinants in Eqs. (1.37) and (1.38) are expanded, one obtains a *n*'th degree polynomial in E. The lowest of the *n* values for E is the best value for the ground state energy obtainable from a function of type Eq. (1.27). To determine the function corresponding to this energy, one substitutes the value for E into Eq. (1.36) and solves for the coefficients to be put into Eq. (1.28). This procedure gives the ratios of the coefficients to be placed in Eq. (1.27). Normalization of the resulting function completes the determination of its form. The other (n-1) values for E are approximations to the energies of excited states.

1.10 The Pauli Principle

In classical mechanics the identities of a set of particles convey no important consequences. However, this is not the case in quantum mechanics. The Uncertainty Principle states that one cannot follow the expected path of a submicroscopic particle. Some properties such as mass, charge, or spin might be used to describe the particle when it is in a system of different particles. Thus, the wavefunction of a system of interacting identical particles cannot distinguish among the particles.[11] The wavefunction of a system of identical particles may behave in two possible ways, symmetric and anti-symmetric. Symmetric describes the situation when a function of the system of two particles has the property of being unchanged when the two particles are interchanged. The function is said to be anti-symmetric if its sign is changed when particles are interchanged. Experimental evidence shows that for electrons the symmetric case does not occur. The Pauli Principle states that the wavefunction of a system of electrons must be antisymmetric with respect to interchange of any two electrons.

The Pauli Principle has an interesting consequence for a system of *n* identical fermions (particles having antisymmetric wavefunctions). This consequence is:

$$\psi(q_{1,}\ q_2,\ \ldots,\ q_n) = \psi(q_2,\ q_1,\ \ldots,\ q_n) \qquad (1.39)$$

where q stands for the variables that describe each of the particles, the Cartesian coordinates (x, y, and z) and their spins (m_s). If electrons 1 and 2 have the same values for these variables, Eq. (1.39) becomes:

$$\psi(q_{1,}\ q_2,\ \ldots,\ q_n) = 0 \qquad (1.40)$$

Thus, two electrons with the same spin have zero probability of being found at the same point in three-dimensional space. Eq. (1.40) means that the probability of finding two electrons with the same spin close to each other in space is quite small.

Chapter 2

COMPUTATIONAL METHODS IN CHEMISTRY

2.1 Background and Historical Approach

Chemistry, as one of the applied sciences, has frequently been regarded as a pure experimental science. This non-precise identification has made it apparent, to the nonspecialist, that for any chemical system to be investigated or studied, it must first be synthesized. Nevertheless, in recent years through the combined employment of ever faster computer systems and better software a new scientific era is dawning. One individual from this era has noted that computational chemistry requires none of the steps usually needed in the other branches of the "classical science" such as preparation, separation or purification.[12] To this extent computational chemistry does not even require a chemistry laboratory! Computational quantum chemistry has proven useful as a tool for the elucidation of molecular structures, molecular properties and chemical reaction mechanisms. As a consequence it has been possible to study the chemical reactivities, transition states, kinetics, electronic structures, spectra, and other distinctive properties of chemical systems.

Over the past two decades, computational chemistry has undergone considerable change. During the seventies tens of untested methods, particularly in the field of semi-empirical theory and of questionable accuracy and limited applicability, were appearing frequently. However, in the last few years, different methods of computational applications have become more accepted and gained considerable popularity. Molecular mechanics, semi-empirical, and *ab initio* (Gaussian methods) are the main three most widely accepted computational methods at this time. Each of these methods has carved out a niche where it tends to reign supreme, and from which it can recognize the eminence of the other two. Along this line, while the conformations of macro molecules are most successfully studied using the techniques of molecular mechanics, the electronic properties of small molecules are most accurately calculated using *ab initio* methods. The semi-empirical methods are superior in the realm between the other two methods.

2.1.1 Molecular Mechanics Methods

The molecular mechanics methods (MM), also known as the empirical force field method, does not deal with an electronic Hamiltonian or wavefunction. This feature excludes the method from being classified as a quantum mechanical method. Instead, MM deals with any multi-atomic systems from the view of the mutual interactions between atoms expressed by an analytical function. The methods can handle very large organic and organometallic ground-state molecules with as many as a thousand atoms. They deal with the contributions to a molecule's electronic energy due to bond stretching, bond bending, van der Waals attractions and repulsions between nonbonded atoms, electrostatic interactions due to polar bonds, and energy changes accompanying internal rotation about single bonds. To apply the molecular-mechanics methods, one needs sufficient data to choose values for the parameters. The calculations are very fast and generally give accurate molecular structures. Unfortunately, MM methods are parametrerized only for ground state systems, and as a result they are unable to adequately represent the geometries involved in bond-making and bond-breaking processes. However, bond lengths and angles are usually determined by this method within 0.01 Å and 3° of the experimental values.[13]

2.1.2 Semi-Empirical Methods

Semi-empirical methods are a series of molecular orbital computational techniques that were developed specifically for applications to organic chemistry. They use a simpler Hamiltonian than the correct molecular Hamiltonian, and parameters whose values are adjusted to fit experimental data or the results of *ab initio* calculations. The development of semi-empirical methods has been aimed at evaluating molecular properties of chemical system at a reasonable costof computer time. The first generation of the methods was intended to reproduce some electronic properties, such as the dipole moment, but could not simultaneously produce the molecular geometries and heats of formation. Like molecular mechanics methods, semi-empirical methods use experimentally determined parameters, and like *ab initio* methods, they are basically quantum-mechanical in nature but make extensive use of approximations.

2.1.3 *Ab Initio* Methods

Ab initio is Latin for “from the beginning” and indicates a calculation based on fundamental principles.[14] Such calculations use the correct Hamiltonian and do not use experimental data other than the values of the fundamental constants. This basic feature causes the methods to be classified as a non-parametrized molecular orbital treatment of a chemical system. Generally, the accuracy of *ab initio* calculations is comparable with experiments for heats of formation and is at least as accurate as experiments for the determination of molecular geometries. The methods are also versatile enough to calculate transition states and excited states. However, wider applications of *ab initio* calculations are limited by the costly requirement of computational facilities, their long calculation periods and their non-applicability to large molecular systems.

2.2 Basis Sets

Most molecular quantum-mechanical methods begin the calculations with the selection of a basis set. The use of an appropriate set is an essential condition for the success of the calculations. Two of the basis sets, Slater-type orbitals (STO) and Gaussian-type orbitals (GTO), have come to dominate the area of molecular calculations.

2.2.1 Slater-Type Orbitals

Atomic orbitals at large distances from the nucleus have the exponential decay characteristics of hydrogen atomic orbitals. Nearer to the nucleus, the atomic orbitals oscillate as *r* changes. Slater proposed a simple algebraic form for atomic orbitals that is capable of representing the atomic wavefunction at large *r*.[15] The essence of the STO basis set is to place on each nucleus a chosen number of STO.

Generally, the larger the number of STO and the greater the care taken in choosing orbital exponents, the more accurate the final wavefunction and energy will be. If one chooses a minimal basis set of STO, then one must also decide how to evaluate the orbital exponents in the STO. Slater's rules, minimization of the molecular energy by variation of the orbital exponents, or choosing the values that were found best for each type of atom in smaller molecules, are considered when making a choice of the basis set. It is common to approximate the rather unwieldily orbital functions in Hartree-Fock calculations with STO that have the general form:

$$R_{n,l}(r)Y_{l,m}(\theta,\Phi) \qquad (2.1)$$

where the radial part of the wavefunction is given by Eq. (2.2):

$$R(r) = Nr^{(n^{*}-1)}\, e^{-\zeta r} \qquad (2.2)$$

N is a normalizing constant, n^{*} is the effective quantum number, ζ, the orbital exponent, is a parameter that allows for the screening of the nucleus by the electrons. The set of all such functions with n, l, and m as integers, but with ζ having all possible positive values, forms a complete basis set.

Accurate representation of a many-electron atomic orbital (AO) requires a linear combination of several STO. Slater suggested his approximation for an AO by taking ζ as:

$$\zeta = (Z - s)/n \qquad (2.3)$$

where Z is the atomic number and s is a screening constant calculated by a set of rules. A single Slater orbital does not have the proper number of radial nodes and does not represent the inner part of an orbital well.

In order for molecules to have a complete set of AO basis functions, an infinite number of orbitals are needed. A minimal basis set for a molecular SCF calculation consists of a single basis function for each inner-shell AO and each valence-shell AO of each atom. However, an extended basis set calculation is considerably more accurate.

2.2.2 Gaussian-Type Orbitals

The use of STO as basis functions in polyatomic-molecule calculations produce integrals that are very time-consuming and often impossible to evaluate either numerically or analytically. Beginning in 1950 Boys proposed the use of Gaussian orbitals.[16] A Gaussian function contains the factor $\exp(-\zeta r^2)$ instead of the factor $\exp(-\zeta r)$ in an STO, and thus enables molecular integrals with Gaussian basis functions to be evaluated more rapidly using a computer.

GTO are widely used in molecular structure calculations. However, the solutions “fall off” too rapidly with *r*. Gaussian orbitals have the wrong behavior at r = 0, and this incorrect behavior can have serious consequences for properties that depend on electron density at nuclear positions. Almost all modern *ab initio* calculations employ GTO basis sets. This basis set in which each atomic orbital is made up of a number of Gaussian probability functions has considerable advantages over other types of basis sets for the evaluation of one- and two-electron integrals. They are therefore much faster computationally than equivalent Slater orbitals.

A STO can be represented by a linear combination of Gaussian orbitals. In order to obtain a STO/3G fit to a hydrogen 1s STO, one needs three primitive Gaussians. STO/3G means that three Gaussians have been used to fit a Slater-type atomic orbital. The fit is shown in Figure 1.

2.3 Semi-Empirical Molecular Orbital Methods

A series of semi-empirical methods has been developed to treat medium and large polyatomic molecules that commonly present difficulties when studied by *ab initio* methods. The series has the methods CNDO, INDO, and NDDO, MINDO/1, MINDO/2, MINDO/3, MINDO, AM1, as well as PM3. These are known as Dewar semi-empirical molecular orbital methods.[15] These methods have played a major role in the theoretical and computational study of organic chemistry, and are now being used increasingly in areas that were previously reserved for force-field methods. The most recent additions to this series, namely AM1 and PM3, have shrunk the debate that has long been circulated regarding the efficiency of these methods. Hence, these semi-empirical methods have become accepted and their ability to treat "large" systems at low cost in computer facilities and time are now appreciated by many experimentally and theoretically oriented chemists.

2.3.1 The CNDO, INDO, and NDDO Methods

The early semi-empirical molecular orbital methods, CNDO, INDO, and NDDO, were developed at a time when computers could deal with *ab initio* calculations for only very small systems. These methods were not intended to reproduce molecular geometries and heats of formation, but rather other electronic properties, such as the dipole moment. The ***complete neglect of differential overlap*** (CNDO) method was proposed by Pople, Santry, and Segal in 1965.[15] In this method, differential terms such as the $\phi_\mu(1)\ \phi_\nu(1)$ product are set to zero whenever μ and ν refer to different atomic orbitals. This approximation eliminates a large number of electron-electron repulsion integrals. When evaluating electron repulsion integrals this approximation assumes that the atomic orbitals are spherically symmetrical. The directionality of p-orbitals is included only via the one-electron resonance integrals; the size of the orbital depends on the orientations and distances of the orbitals and on a constant assigned to each type of bond.

The ***intermediate neglect of differential overlap*** (INDO) method was proposed by Pople, Beveridge, and Dobosh in 1967.[15] Both the CNDO and INDO methods treat only the valence electrons explicitly. In INDO, which is an improvement on the CNDO method, differential overlap between atomic orbitals on the same atom is not neglected in the calculation of one-center electron-repulsion integrals, but differential overlap is neglected in two-center electron-repulsion integrals. Thus, fewer two-electron integrals are neglected, as compared with CNDO; otherwise, the two methods are the same.

The ***neglect of diatomic differential overlap*** (NDDO) method was suggested by Pople, Santry, and Segal[15] as an improvement on INDO. The method was the first to include the directionality of the atomic orbitals in calculating the repulsion integrals. In this case the three- and four-center integrals where the overlap occurs between atomic orbitals on the same atom were included. The degree of neglect of differential overlap in NDDO is more justifiable than in CNDO or INDO. The method was little used until 1977 when Dewar and Thiel modified it to produce the MNDO method, after attempts of parametrizing the earlier methods were unsuccessful.

2.3.2 The MINDO and MNDO Methods

Because of the use of approximations in the SCF calculation, one can expect that the results of CNDO and INDO methods are similar but less accurate than minimal-basis *ab initio* SCF results. Thus, these methods do reasonablely well on molecular geometry but poorly on binding energies. The parameters in PNDO ***(partial neglect of differential overlap)*** and MINDO/1 ***(modified intermediate neglect of differential overlap)*** theories were chosen so as to have the predicted molecular heats of formation fit experimental data as accurately as possible. MINDO does not neglect differential overlap between orbitals on the same atom in one-center electron-electron integrals, but differential overlap is neglected in two-center electron-electron repulsion integrals. The MINDO/1 method uses parameters that give the best fit to heats of formation for molecules in their ground state. Both PNDO and MNDO theories produced acceptable values for heats of formation but they produce poor values for molecular geometries. Therefore, in the early beginnings of the 1970s Dewar and others proposed MNDO/2 and then MNDO/3. In the former a careful choice of parameters allowed molecular geometries and heats of formation to be calculated rather accurately in most cases. The theory was updated in the form of MINDO/2 to improve calculations of dipole moments and bond lengths in hydrogen-bonded species.[17]

The MINDO/3 method, the last in the series of MINDO and a substantially improved version, has been parametrized for hydrocarbons, C-H-O-N compounds, C-H-F-Cl compounds, and for some types of molecules containing Si, P, and S.[18] The method has been widely applied to calculate properties of ground-state organic molecules and to calculate potential-energy surfaces of chemical reactions. It uses a set of readily approximated parameters that, along with the constants used to evaluate the resonance integrals, allow the results to be fitted to experimental data. For a sample of a large number of compounds, the average absolute errors in MINDO/3-calculated properties are 11 kcal/mol in heats of formation, 0.02 Å in bond lengths, 5° in bond angles, 0.4 D in dipole moments, and 0.8 eV in ionization potentials.[19] Among the wide variety of applications of MINDO/3 to problems other than structure and energy calculations are the calculations of NMR coupling constants and chemical shifts, ^{14}N nuclear quadrupole resonance coupling constants, polarizabilities, nonlinear optical coefficients, and vibrational frequencies.[20] The discussion of the success or failure of the method to these applications is beyond our current interest.

Dewar and co-workers developed the MNDO ***(modified neglect of diatomic overlap)*** method in 1977 to avoid some of the systematic MINDO/3 errors for molecules and to extend MINDO/3 to include metallic elements. The method has been parametrized for compounds containing H, Li, Be, B, C, N, O, F, Al, Si, P, S, Cl, Ge, Br, Sn, I, Hg and Pb. MNDO gives substantially improved results in the same calculation time as compared to MINDO/3. Its major improvements were with unsaturated molecules, compounds with adjacent lone-pairs, the calculation of bond angles, and the ordering of molecular orbitals. It is often the method of choice for systems that are too large for good *ab initio* calculations and it is usually preferable to minimal-basis-set Hartree-Fock calculations. MNDO's average absolute errors are 9 kcal/mol, 3°, 0.025 Å, 0.35 D, and 0.5 eV in heats of formation, bond angles, bond lengths, dipole moments, and ionization potentials respectively.[21]

The advantage of MINDO/3 and MNDO over *ab initio* calculations is not only that they are several orders of magnitude faster, but also that calculations for some very large molecules are possible only with the semi-empirical methods. The neglect of large numbers of integrals not only saves computer time, but also reduces the core and disk space requirements in comparison with those for an equivalent *ab initio* calculation.

2.3.3 AM1 and PM3 Methods

AM1 ***(Austin model 1)*** and PM3 **(parametric method number 3)** are the most recent parametric quantum mechanical molecular models based on the NDDO approximation. AM1 is a well-balanced and reliable method for the standard organic chemistry of molecules composed of the elements C, H, N and O. However, the method suffers from the traditional problems that NDDO methods have in dealing with lone pairs of electrons on adjacent atoms and does not perform well for phosphorous- and sulfur-containing molecules. AM1 was proposed to improve the hydrogen-bond and π-rotation-barrier problems with MNDO. However, there is a very small difference in the values of energies for the correct geometries of hydrogen-bonded systems and the AM1-predicted structures. These differences have been considered a minor problem for most chemical systems. The essential development in the AM1-methodology compared to MNDO is the addition of a series of Gaussian core-repulsion-functions (CRF) as adjustable parameters that enable tuning the methods more finely and then modifies the core-core repulsions.

PM3 is Stewart's reparametrization of AM1. It was conceived to perform better than AM1 for nitro-compounds and hypervalent molecules. Its reparametrization depends mainly on statistical methods while it embraces chemical sense and experience gained prior to the development of AM1 . While the former excludes any bias that the chemist may build into the parametrization, the latter has the advantage that differences in stabilities, but not heats of formation, play a major role in chemical processes. Surprisingly, Stewart's PM3-parametrization showed that hypervalent compounds could be treated satisfactorily and reproduce their geometries and energies. PM3 produces good results for hypervalent compounds because it makes them very polar. This apparent overemphasis of ionic character leads to good geometries and energetics for these hypervalent structures, but leads to very high atomic charges compared to those calculated by other methods. Even though these atomic charges have no physical meaning, the associated incorrect atomic charges are seen as a deficiency of PM3.[22]

PM3 is usually better than AM1 for describing lone-pairs on adjacent atoms and for reproducing the geometries of hydrogen-bonded structures. However, AM1 gives slightly better results for compounds containing C, H, N and O.[22]

Chapter 3

SEMI-EMPIRICAL METHODS APPLICATIONS TO AROMATIC SYSTEMS

3.1 Introduction

Hückel molecular orbital theory (HMO) was the first semi-empirical method that enabled the studying of conjugated organic systems through the utilization of the so-called π-electron approximation. The theory is known for its simplicity and limited computational effort. The first consistent improvement of the method utilized the *LCAO* approximation within the Hartee-Fock method to introduce electron interactions into the π-electron Hamiltonian. This improvement helps yield a deeper understanding of the effective energy operator in the Hückel scheme. The PPP method introduced by Pople, Parr, and Pariser[21] has been of great value in the interpretation of conjugated and aromatic systems. The method improves the Hückel scheme by considering electron-electron interactions. However, some researchers are of the opinion that the use of Hückel theory is no longer warranted given the availability of high-speed computers and more sophisticated MO methods.[23]

Semi-empirical molecular orbital theory is becoming an increasingly effective tool for the study of large organic molecules. In recent years a substantial amount of work has gone toward explaining and estimating the effect of substituents on various chemical properties such as equilibria and reactivities of aromatics. Usually, this substitutional effect can be explained by electronic or stearic effects. To explain the electronic part, one should be aware of the electronic structure of the molecule of interest where semi-empirical methods play a useful role. The following pages describe the methodology, or the essence in some cases, of the semi-empirical methods in the calculation of representative molecular properties. Since the semi-empirical methods in the HyperChem™ program were used for the current calculations, most of the descriptions will relate to the software program itself.

3.2 Semi-Empirical MO Theory of Conjugated Molecules

A planar unsaturated organic molecule, benzene for example, is divided into σ and π molecular orbitals. Semi-empirical approximations deal with electrons in σ and π orbitals separately. This is mainly due to the difference in the symmetries of the orbitals in addition to the greater polarizability of the π electrons compared with that of σ electrons.

In the π-electron approximation, π-electrons are treated separately by combining the effects of the σ-electrons and the nuclei into some kind of effective π-electron Hamiltonian as in Eq. (3.1). The first summation refers to the Hamiltonian of the core electrons, where V_i is the potential energy of the i'th π-electron produced by the nuclei and the σ-electrons. The variation principle is then applied to determine a π-electron wavefunction ψ_π that minimizes the variational integral and gives a π-electron energy E_π. The Hamiltonian for this effective Hamiltonian is given by Eq. (3.1):

$$\hat{H}_{\pi} = \sum_{i=1}^{n_{\pi}} \left(-\frac{\hbar}{2\mu}\nabla_i^2 + V_i\right) + \sum_{i=1}^{n_{\pi}} \sum_{j>i} \frac{Ze^2}{r_{ij}} \tag{3.1}$$

This approximation is not possible when studying non-planar unsaturated organic systems. Consequently, all the σ and *π*-valence electrons must be considered together.[24]

3.3 Single Point Calculations

A single point calculation performs the calculations of the static properties of the system at only a single point. The point that is reached at the last step of geometry optimization of the molecule is preferably a minimum or a transition state on the potential surface. The calculations allow the determination of the potential energy, derivatives of the potential energy, electrostatic potential, molecular potential, molecular orbital energies, the coefficients of molecular orbitals for ground or exited states, and the vibrational frequencies.[25]

3.4 Geometry Optimization (Minimization)

Application of molecular orbital theory demands a specification of the molecular geometry. A complete theoretical treatment of a molecule's equilibrium structure would involve minimization of the energy with respect to each independent geometrical parameter to yield an optimized structure. One may need to consider the system, the calculated values and the available computational resources in order to choose an appropriate geometrical model for a particular study. It is sometimes necessary to use simple models of partial optimized geometry when complete optimization requires great computational effort.

The optimized geometry is one in which no unexpected distortion of the geometry would lead to a change in the calculation of heat of formation. For the current purposes, the calculations of geometry optimization are performed with two goals in mind. First, characterize the potential energy minimum where the geometry optimization results in a new structure with new atomic coordinates and energy. Second, obtain a new stable structure as a starting point for a single point calculation that contributes a large collection of structural and electronic properties. The geometry is considered minimized if the predicted change in geometry and/or in heat of formation, or the current gradient norm, is sufficiently small.

Frequently, semi-empirical methods employ one of three techniques to optimize the geometry of the molecule, a steepest descent method or one of two conjugate gradient methods. A mathematical description of methods used to determine the parametrization of the semi-empirical methods is discussed in detail in the literature.[26]

3.4.1 Steepest Descent

Steepest descent is the simplest method of optimization. It is a first order minimizer that uses the first derivative of the potential energy with respect to the Cartesian coordinates. The method moves down the steepest slope of the interatomic forces on the potential energy surface. The descent is attained by adding an increment to the coordinates in the direction of the negative gradient of the potential energy, or the force.

3.4.2 Conjugate Gradient Methods

The conjugate gradient methods use both current gradient and the previous search direction to drive the minimization. This provides an advantage since it uses the minimization history to calculate the search direction, and converges faster than the steepest descent technique. The method also contains a scaling factor for determining an optimal step size.

3.5 Computing Molecular Properties

In quantum mechanical calculations most of the electronic molecular properties of a system, such as the dipole moment, are evaluated at a fixed molecular geometry by techniques such as calculating the value of an operator or using perturbation theory. However, some properties, such as bond angles, bond lengths, and vibrational frequencies of the system are calculated as a function of their molecular geometry, and they depend on the shape of the potential energy surface.

3.5.1 Koopmans' Theorem

In 1933 T. C. Koopmans showed that the energy required to remove an electron from a closed-shell atom or molecule is reasonably well approximated by the negative of the orbital energy of the molecular orbital from which the electron is removed. This result is the basis of Koopmans' theorem, which states that for closed-shell systems the ionization potential is the negative of the corresponding molecular orbital eigenvalue.[27] The method neglects the change in the newlyformed molecular orbitals of the ionized molecule. Thus, the difference between the Hartee-Fock energies of the ion molecule and the neutral closed-shell one equals the orbital energy of the molecular orbital from which the electron was removed.

3.5.2 First Ionization Energy

The first ionization energy is defined as the minimum energy required to remove a single electron from a gas phase system, M, as represented in Eq. (3.2).

$$M(g) \rightarrow M^{+}(g) + e^{-}(g) \tag{3.2}$$

The potentials within the orbital approximation require a model for the process involving the loss of an electron from the *i*'th orbital of system M. The electron released by this process has zero energy, and thus the orbital model leads to the definition:

$$I_j = -\epsilon_j \tag{3.3}$$

The ionization potential of an electron from the i'th orbital, or more precisely, the orbital ionization potential, and Eq. (3.3) can be regarded as consequences of Koopmans' theorem. The first ionization potential corresponds to removal of the most loosely bound electron in a given molecule. Within the orbital model it corresponds to the energy necessary to remove an electron from the highest occupied molecular orbitals. Higher ionization potentials (for *i* > 1) refer to the removal of an electron from inner shells of the neutral molecule. Thus, within the orbital model a molecule will have as many ionization potentials as it has electrons occupying orbitals. The method assumes that despite the removal of an electron, the molecular orbitals of M^+ are identical with those of M, and that there are no geometrical changes during the transition $M \rightarrow M^+$.[28]

3.5.3 Heats of Formation

The heat of formation (ΔH_f) represents one of the most important characteristic properties of a molecule. Mathematically it is defined in Eq. (3.4) where the first term represents the sum of the heats of formation of all atoms in the molecule and D is the dissociation energy.

$$\Delta H_f = \sum_A \Delta H_{f,A} - D \qquad (3.4)$$

The dissociation energy characterizes the energy of the i'th molecule with respect to that of the constituent atoms. Consequently, the heat of formation reflects the stability of the molecule with respect to the simple substrates from which it is formed. The larger the absolute value of the heat of formation the more stable the molecule.[29]

3.5.4 Molecular Geometries and Force Constants

The equilibrium molecular geometry is defined as the set of nuclear coordinates corresponding to the global energy minimum. Thus, the equilibrium geometry should be calculated by systematic minimization of the total energy with respect to all independent internal coordinates, that is bond lengths, bond angles and torsional angles.

A molecular configuration is described by parameters q_1, q_2,..., q_M, that may be identified with appropriate internal coordinates. In the neighborhood of the equilibrium configuration, for which all net forces acting upon the nuclei are zero, the total energy has the form:

$$E = E_o + \frac{1}{2}\sum_{i,j}\left(\frac{\partial^2 E}{\partial q_i \partial q_j}\right)_o dq_i\, dq_j + \dots \tag{3.5}$$

where E_o is the total energy at the equilibrium configuration. The term in parentheses is an equilibrium property that defines the force constant for a given pair of internal coordinates q_i and q_j, and is defined by Eq. (3.6):

$$\left(\frac{\partial^2 E}{\partial q_i \partial q_j}\right)_o = k_{ij} \tag{3.6}$$

The first-order energy derivative with respect to q_i can be interpreted as the negative of the force F_i acting along the coordinate q_i:

$$F_i = -\frac{\partial E}{\partial q_i} \tag{3.7}$$

At equilibrium this force must vanish because, by definition, for a stable configuration all internal forces must vanish and the situation is described by Eq. (3.8):

$$-F_i(q_o) = \left(\frac{\partial E}{\partial q_i}\right)_o = 0 \tag{3.8}$$

The dimensional vector q_o defines the set of internal coordinates at the equilibrium molecular configuration. To determine the molecular geometry the total energy E(q) is minimized with respect to all variables q_i.

Although the calculation of the first-order energy derivatives (3.7) is formidable, the most efficient minimization procedures involve at least some approximation to the second-order energy derivatives. Thus, most of the geometry optimization schemes are based on algorithms that either completely or at least partly eliminate the calculation of second-order derivatives. A detailed description of the most frequently employed geometry optimization schemes is described in the literature.[30]

3.5.5 Dipole Moment

A molecule that consists of an assembly of charged particles may at any moment in time have an instantaneous dipole moment μ. The classical definition of this quantity for a collection of N particles of charge q_i and position vectors r_i is given by Eq. (3.9). However, in neutral species μ does not depend on the choice of the origin:

$$\mu = \sum_i q_i r_i \tag{3.9}$$

The quantum mechanical description of the dipole moment depicts the charge as a distribution that is a function of r, and the dipole moment is an average over the wavefunction of the dipole moment operator μ:

$$\mu = \sum_i (-er_i) + \sum_A Z_A e R_A \tag{3.10}$$

where Z_a is the charge of the nuclear core and R_A is the distance between the origin and electron i.[31]

3.6 Application of Semi-Empirical Methods to Infrared Spectroscopy

Spectroscopic methods are a practical approach to provide accurate information about molecular structure and different properties of chemical systems.

However, theoretical approaches can describe, to a large extent, both the physical origin of spectra and the relation between microscopic molecular structure and spectral parameters. The role of theory in molecular spectroscopy is mainly to provide a simple model, permitting a concise description of the spectrum by some set of empirical parameters. These parameters depend on the nature of the constituents of the molecule and on their mutual interactions, and may be calculated using theoretical methods.

3.6.1 Vibrational Spectral Parameters

Infrared spectra result from radiative transitions between vibrational levels of the same molecular electronic state. The spectra are characterized by their absorption frequencies and the corresponding band intensities. The determination of intermolecular vibration frequencies is achieved by the normal coordinate analysis. This analysis requires an assumption that the oscillation of atoms are so small that the harmonic approximation is valid.

If the equilibrium molecular geometry is completely determined by some set of internal coordinates (bond lengths, bond angles, torsion angles) q_0^1, ..., $q^0{}_{3N-6}$, where N is the number of atoms, then the energy change resulting from a small distortion dq_1, dq_2 ..., dq_{3N-6} of the equilibrium nuclear configuration is given by Eq. (3.11). The second-order energy derivatives are vibrational force constants:

$$\Delta E = \frac{1}{2}\sum_{i=1}^{3N-6}\sum_{j=1}^{3N-6}\left(\frac{\partial^2 E}{\partial q_i \partial q_j}\right)_0 dq_i\, dq_j, \qquad (3.11)$$

Within the harmonic approximation the energy change defines the potential energy for nuclear motion. For the potential energy given by Eq. (3.11), the separate vibrations along the coordinates q_i are not independent.

The solution of the corresponding classical equation is obtained by transforming the q_i into a new set of normal vibrational coordinates Q_1, Q_2 ,..., Q_N according to:

$$q_i = \sum_{j=1}^{3N-6} L_{ij} Q_j \tag{3.12}$$

Thus, the original coupled-classical equations of motion are separated into 3N-6 equations for independent harmonic motion.

The determination of the vibration frequencies and the form of the transformation matrix *L* varies the masses of all atoms, the molecular geometry and the force constants. The shape of the infrared spectrum is determined by the band intensity. Band intensities are more non-local in character than band frequencies. For a number of vibrational frequencies, they can be ascribed to the vibration of some well-localized molecular fragments, whereas dipole moment derivatives with respect to normal coordinates depend critically on the vibration of all atomic groups. In this study the determination of vibrational modes and frequencies was considered to be the result of semi-empirical calculations of infrared band intensities. The simplest approximation to a molecular diatomic oscillator is a model of two masses connected by a spring of a given force constant. Using this approximation the frequency ν of a molecular oscillator is given by Eq. (3.13), where k is the force constant and μ is the reduced mass of the oscillator.

$$\nu = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}} \qquad (3.13)$$

In a polyatomic molecule, each pair of atoms can be considered as a diatomic oscillator. However, these oscillators are not independent as they exert forces on each other when they oscillate; they are coupled. It can be shown that for a nonlinear molecule of N atoms, there are *3N-6* independent vibrations. In each normal mode of vibration, all the atoms in the molecule vibrate with the same frequency and all the atoms pass through their equilibrium positions simultaneously. Once the mass, the molecular geometry, and the force constants are known, the complete mathematical procedures are known for calculating both the form and the frequency of the normal modes of vibration of the molecule.[32]

3.7 HyperChem™ Visualization of Vibrational Analysis and IR Spectroscopy

HyperChem™ models the vibrations of a molecule as a set of N point masses where the points refer to the nuclei and atoms. Each of the points vibrates about its equilibrium position. The mass-weighted Cartesian displacement coordinates q_i are defined in Eq. (3.14):

$$q_i = m_i^{0.5}(x_i - x_i^{eq}) \qquad (3.14)$$

The classical kinetic energy T of vibration about the equilibrium position is

$$T = \frac{1}{2}\sum_{i=1}^{3N}(\partial q/\partial t)^2 \qquad (3.15)$$

The potential energy U may be expanded in a Taylor series about the equilibrium positions of the atoms, thus giving:

$$U = U_e + \sum_{i=1}^{3N} (\partial U/\partial q_i)_e \, q_i + \frac{1}{2}\sum_{i=1}^{3N}\sum_{j=1}^{3N} (\partial^2 U/\partial q_i \, \partial q_j)_e \, q_i \, q_j + \dots \tag{3.16}$$

The subscript indicates these terms are to be evaluated at the equilibrium position. For the equilibrium configuration of the molecule, *U* is a minimum and the gradient is given by:

$$\left(\frac{\partial U}{\partial q_i}\right)_e = 0 \text{ vanishes, where } i = 1, 2, \dots 3N \tag{3.17}$$

If the vibrations are small, we may safely neglect terms higher than second-order. Thus, the potential energy simplifies to Eq. (3.18):

$$U = U_e + \frac{1}{2}\sum_{i=1}^{3N}\sum_{j=1}^{3N} u_{ij} \, q_i \, q_j + \dots \tag{3.18}$$

where u_{ij} is given by (Eq. (3.19)):

$$U_{ij} = \left(\frac{d^2U}{dq_i \, dq_j}\right)_e \tag{3.19}$$

The classical-mechanical problem for the vibrational motion may now be solved using Newton's second law. The force on the x component of the *I*'th atom is

$$F_{ix} = m_i a_{ix} = m_i \frac{d^2x}{dt^2} = -\frac{\partial U}{\partial x_i} \tag{3.20}$$

Transforming to mass-weighted coordinates, one obtains a set of 3*N* simultaneous linear differential equations:

$$\frac{d^2q}{dt^2} + \frac{\partial U}{\partial q_i} = 0 \qquad \text{for } i = 1, \ldots, 3N \tag{3.21}$$

Each differential equation contains all the coordinates q_j, since $\partial U/\partial q_i$ is expressed as a single summation over the q_j's:

$$\partial U/\partial q_i = \sum_{j=1}^{3N} u_{ij} q_j \tag{3.22}$$

To obtain a simpler set of differential equations of one coordinate, one performs an orthogonal similarity transformation on the matrix U having elements u_{ij}. The problem is stated in matrix form as:

$$UL = L\Lambda \tag{3.23}$$

and then:

$$L^{-1}\,UL = \Lambda \tag{3.24}$$

where L is an orthogonal matrix that diagonalizes the force constant matrix U into Λ, L is the matrix of eigenvectors and Λ is the diagonal matrix of eigenvalues λ_n. Each column of L represents an eigenvector that is a series of coefficients that provide the transformation from the Cartesian coordinates to separable coordinates.

One can define the normal coordinates Q_i in Eq. (3.25) as a linear combination of mass-weighted Cartesian displacement coordinates q_i, where l_{ki} are the matrix elements of L, according to:

$$Q_i = \sum_{k=1}^{3N} l_{ki} q_k \tag{3.25}$$

In matrix notation Eq. (3.25) becomes:

$$Q = L^{-1} q \tag{3.26}$$

Using normal coordinates Newton's second law may be solved to yield Eq. (3.27):

$$Q_j = B_j [\sin (\lambda_j^{½} t + b_k] \tag{3.27}$$

Motion along each normal coordinate is described by each atom vibrating in phase with the same frequency U_j. The vibrational frequency is related to the eigenvalues by:

$$U_j = \lambda_j^{½}/(2\pi) \tag{3.28}$$

Although the energies and forces are evaluated quantum mechanically in HyperChem,™ the vibrational analysis is performed in a purely classical manner.[33]

3.7.1 Infrared Absorption

During the absorption of infrared light the oscillating electric dipole of the light beam induces a mirror image oscillating electric dipole in the molecule. Energy in the form of photons may be exchanged between the molecule and the light beam if the frequency of the light closely corresponds to an energy difference between allowed levels of the molecule. Einstein's formula, Eq. (3.29), correlates energy, E and frequency, v. The relation indicates that each line in an IR spectrum represents a transition from one vibrational state to another:

$$E = hv \tag{3.29}$$

When infrared light passes through a molecule, the electrons see an essentially constant electric field rather than an oscillating dipole. The nuclei move so as to create a molecular dipole that is synchronized with that of the light. To a first approximation each normal mode of vibration interacts independently with IR light. A normal mode can absorb IR light if the molecular dipole moment changes during the course of a normal vibration. A molecule absorbs IR light at frequencies corresponding to the asymmetric stretch, and bend because the IR light is "shaking" the atoms of the molecule along the asymmetric stretch and bending coordinates. The induced dipole is a quantitative measure of how "shakeable" a given normal mode will be under the influence of IR light. Eq. (3.30) gives the mathematical form of the relation:

$$\mu = \mu_o + \left(\frac{d\mu}{dq}\right)_0 dq + \left(\frac{d^2\mu}{dq^2}\right)_o dq^2 + \ldots \qquad (3.30)$$

Keeping only the linear term, the transition dipole moment is given by (Eq. (3.31)):

$$\langle \mu_{fi} \rangle = \int \psi_f^{vib} \left(\frac{d\mu}{dq}\right) q \psi_i^{vib}\, dq \qquad (3.31)$$

Assuming that all higher derivatives are essentially zero, then *dμ/dq* is a constant. Therefore, it may be taken out of the integral as in Eq. (3.32)

$$\langle \mu_{fi} \rangle = \left(\frac{d\mu}{dq}\right) \int \psi_f^{vib} q \psi_i^{vib} dq \qquad (3.32)$$

Qualitatively, the selection rule for IR absorption for a given mode is that the symmetry of $q\psi_i^{vib}$ must be the same as $q\psi_f^{vib}$. Quantitatively, the transition dipole moment is proportional to the dipole derivative with respect to a given normal mode $d\mu/dq$. In HyperChem,™ all infrared lines correspond to transitions from the ground vibrational state to an excited vibrational state due to the addition of one quantum of energy to a given vibrational mode.[34]

3.8 Studying Reactions and the Reaction Path

An increasing collection of information is being gathered on using computational methods for the study of reaction pathways. Studying a reaction begins with a full optimization of the geometries of the reactants and products, normally when no constraints are applied. The minimum is then characterized by a calculation of the force constant matrix to ensure the system is ,indeed, at an energy minimum with all eigenvalues of the force constant matrix positive. At this point the transition states can be located as points on the potential energy surface that are characterized by one negative eigenvalue of the second derivative Hessian matrix. [35]

If an internal or Cartesian coordinate can be identified with the reaction coordinate, then the energy profile of the reaction path can be mapped by monotonically increasing or decreasing that coordinate. The transition state is the highest point along the reaction path between reactants and products.[36]

Chapter 4

ELECTROPHILIC AROMATIC SUBSTITUTION REACTIONS

4.1 Definitions and Basics

This study focuses on the theoretical calculation of equilibrium properties of the simple aromatic hydrocarbons and their nitrated products. The kinetics of the nitration process and the transition state are vital parts of physical organic chemistry.

4.1.1 Aromaticity

Aromaticity is a useful concept for correlating the properties of conjugated unsaturated ring systems. It is necessary, but not sufficient, that an aromatic system has cyclic conjugation; that is, overlapping *p* orbitals are present in a ring without beginning or end. The cyclic conjugation must be continuous; that is, every member atom of the aromatic ring contributes a properly aligned *p* orbital to the π system. If the conjugation is interrupted at any point, then the special characteristic of aromatic systems will not occur. The cyclic π-orbitals contain all the electrons in the conjugated double bonds that are part of the aromatic ring. π-orbitals may also include nonbonding-electron pairs that occupy one of the overlapping *p* orbitals in the ring. It is believed that not all of the nonbonding (unshared) electron pairs of the ring atoms are necessarily part of the aromatic π-electron system.

4.1.2 Electrophilic Aromatic Substitution Reactions

Electrophilic aromatic substitution is a class of reactions in which a strong electrophilic reagent affects a substitution on the aromatic ring. One of the driving forces for the reaction is the fact that a neutral aromatic system such as benzene has the characteristic that if it is disturbed, by substitution for example, it tends to regain its aromaticity. The addition of a nitronium ion to the benzene ring is expected to initially disturb the aromatic system. The tetrahedrally bonded carbon atom in the carbonium ion intermediate is sp^3 hybridized, and thus this cation is no longer aromatic. However, as means of regaining aromaticity, a proton is expelled.[37]

4.1.3 Mechanism of Electrophilic Aromatic Substitution

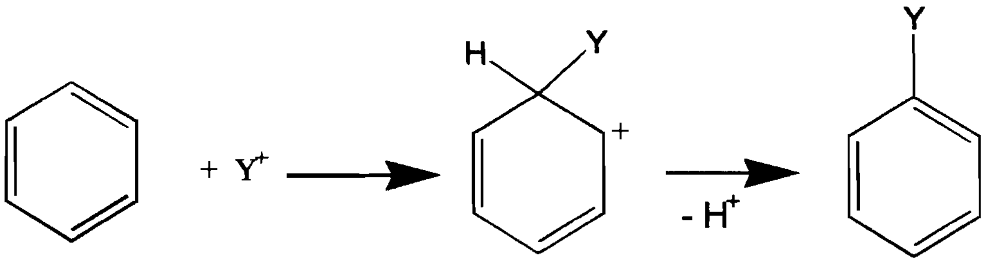
The two successive processes of disturbance and regaining an aromatic system are most likely taking place through the following mechanism that is summarized in Eq. (4.1), where Y represents an electrophile.

1- *Generation of an electrophile.*

The electrophile is NO_2^+, the nitronium ion. As shown in Eqs. (4.2A) and (4.2B), the ion is fomed by the acid-catalyzed removal of water from HNO_3.

2- *Attack of the π-electrons of the aromatic ring on the electrophile and formation of a resonance-stabilized carbocation.*

3- *Loss of a proton from the carbocation intermediate at the site of substitution to generate the substituted aromatic compound.*[38]


(4.1)

4.1.4 Orientation in Electrophilic Aromatic Substitution

When a monosubstituted benzene molecule undergoes an electrophilic substitution reaction, a problem arises as to where the electrophile will attack. A benzene derivative, (Z-ϕ), where some group Z has replaced one of the aromatic hydrogens, gives rise to *ortho, meta*, and *para* products. Since five positions (two *ortho-*, two *meta-*, and one *para-*) are available, the expected isomer distribution is 40% *ortho*, 40% *meta*, and 20% *para*. However, this purely statistical result is never obtained and the attainable isomer distribution varies due to several different factors. The influencing factors include the group *Z*, solvent, temperature, substituting agent, and others. In other words, it is found experimentally that a second substitution is not random, but is regioselective.

The most well-known effect of group *Z* is its electronic influence upon the rate of substitution and upon the isomer distribution. An electron-deficient reagent attacks the aromatic ring, and the system develops a positive charge. If *Z* is an electron donor, it has the ability to stabilize the transition states and thereby increase the rate of attack at all positions. However, when *Z* stabilizes the transition states, a consequence is that it makes an attack at the ortho and para positions most effectively, and then these positions are attacked preferentially. It occasionally happens that *Z* is an electron donor by resonance, and an electron-withdrawing group due to its inductive effect. In such a case it may increase the attack at the ortho and para positions, where the resonance effect comes into play and deactivates the meta position. This alters the relative rates of attack at the various positions, but still leads to ortho-para substitution.

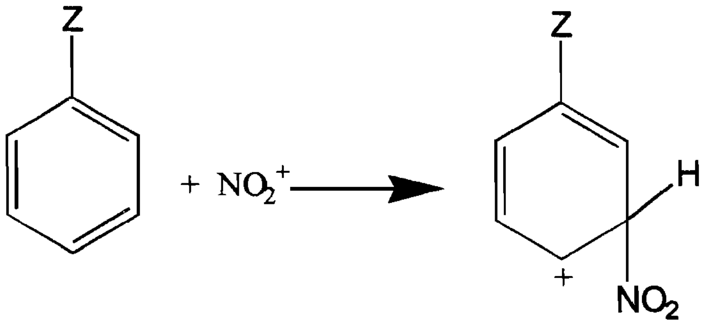
On the other hand, if *Z* is an electron-withdrawing group, it deactivates the system at all positions. The rate of attack by an electrophile Y^+ at any position in the system is decreased as compared to the rate of attack of non-substituted benzene under the same conditions and positions. However, attack at a meta position is least affected by the presence of an electron-withdrawing group. The rate decreases at all positions, but least at the meta position.[39]

4.1.5 Aromatic Nitration

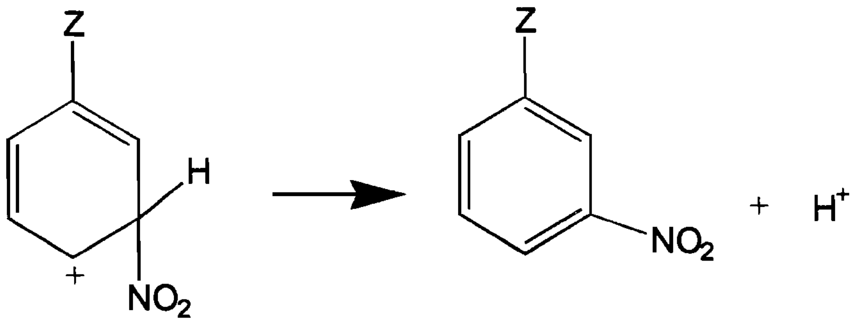
Aromatic hydrocarbons are efficiently nitrated by treatment with a mixture of concentrated nitric and sulfuric acids. The active electrophilic species in these mixed acids has been identified as the nitronium ion NO_2^+:

$$HONO_2 + HNO_3 \underset{K_1}{\rightleftharpoons} H\text{-}^{+}OH\text{-}NO_2 + NO_3^- \qquad (4.2A)$$

$$H\text{-}^{+}OH\text{-}NO_2 \underset{K_2}{\rightleftharpoons} NO_2^+ + H_2O \qquad (4.2B)$$



(4.3A)



(4.3B)

The electron deficient nitronium ion then attacks an aromatic compound to form the substituted products, and the mechanism for product formation is shown in Eqs. (4.3 A) and (4.3 B).

The rate-limiting step in the reaction varies with the choice of the group Z. When Z is an electron-withdrawing group, the rate-limiting step is attack of the aromatic compound by NO_2^+. However, when Z is an electron donor, the rate-limiting step depends upon the reaction conditions, and it can be the formation of nitronium ion from $H_2ONO_2^+$. The concentration of NO_2^+ is given by the expression in Eq. (4.4):

$$[NO_2^+] = K_1 K_2 \frac{[HNO_3]^2}{[H_2O][NO_3^-]} \tag{4.4}$$

Kinetic evidence suggests that in certain circumstances the rate-limiting step is the formation of NO_2^+. When compounds such as benzene and toluene are nitrated, the rate of reaction is independent of the concentration of the aromatic compound. The rate of the nitration reaction does not depend upon the concentration of the material being nitrated. A mechanism with the formation of NO_2^+ as the rate-limiting step leads to kinetics that are zeroth order in the aromatic compound, and will be observed whenever the term $k\,[Z\text{-}\phi][NO_2^+]$ is much greater than the term $k'\,[H_2O][NO_2^+]$. Thus, increasing the concentration of $(Z\text{-}\phi)$ favors a rate-limiting step dealing with the formation of NO_2^+. Increasing the concentration of H_2O favors this step and limits attack by NO_2^+ on the aromatic compound.

When NO_2^+ reacts with water much more frequently than with the aromatic compound, the rate limiting step is reaction with $(Z\text{-}\phi)$. On the other hand, under certain conditions the nitronium ion reacts with the aromatic compound much more frequently than it reacts with water, and under those conditions formation of NO_2^+ becomes rate limiting.

When Z is an electron withdrawing group, the general rate expression for the nitration of $(Z\text{-}\phi)$ in concentrated sulfuric acid follows moderately well the general rate law given by Eq. (4.5), or alternately by Eq. (4.6):

$$k[Z\text{-}\Phi][HNO_3]\frac{f_{Z\text{-}\Phi}\,f_{NO_2^+}}{f'''_{TS}} \qquad (4.5)$$

$$k[Z\text{-}\Phi][NO_2^+]\frac{f_{Z\text{-}\Phi}\,f_{NO_2^+}}{f'''_{TS}} \qquad (4.6)$$

Since sulfuric acid is the solvent, this rate expression is in agreement with a rate-limiting attack of the aromatic compound by the nitronium ion.

The species NO_2^+ is known to be present in solution when the nitrations are conducted in concentrated sulfuric acid; it satisfies the kinetic requirements. The evidence suggests NO_2^+ is the active species, and in most nitrations it is this agent that attacks the aromatic compound to form the substituted products. It remains to be demonstrated that the other species, nitric acid and its conjugate acid $H_2ONO_2^+$, actually can affect nitration, although it certainly seems reasonable to assume that these materials, especially the latter, could affect nitration. These reactions are much slower than nitration by the nitronium ion and have not been observed.[40]

Other methods for introducing the NO_2 group into an aromatic compound do exist. However, a discussion of these methods is not of a concern in this thesis. In future work one should consider the details of the transition state intermediate formed during the nitration of these aromatic systems.

Chapter 5

SEMI-EMPIRICAL STUDY OF THE NITRATION OF SIMPLE AROMATIC SYSTEMS

5.1 Introduction

AM1 and PM3 are known to yield acceptable results when employed in the field of organic chemistry. The two methods are employed in this research to study the nitration reactions of 22 simple aromatic systems.

The values of different physical and chemical properties of the systems before and after nitration were calculated. Calculated results are then compared with their experimental counterparts and explained in terms of physical organic chemistry.

A long-term goal is the understanding of the kinetics of the nitration process within the concept of computational chemistry. This is expected to include the study of the transition state and the potential surface energy of each reaction.

The aromatic molecules studied were benzene, phenol, aniline, toluene, iodobenzene, chlorobenzene and their *ortho, meta*, and *para* monosubstituted nitro-compounds. Most of the values of enthalpy of formations and ionization energies considered many different experimental methods, and thus the best values and error limits have been established through a critical data analysis by the National

Institute of Standards and Technology, NIST. Estimated values do not include error limits.

5.2 Computational Calculations, Results, and Interpretation

The following sections, as well as the accompanying tables, summarize the calculations. The tables include both the experimental and the calculated results. The differences between the experimental and calculated values are discussed in each section.

5.2.1 Heats of Formation

Tables I-A and I-B compare the calculated heats of formation by AM1 and PM3, respectively, with the experimental values for 22 aromatic molecules. The calculated results are for isolated atoms, and thus the results are compared to the gas phase experimental values.[41, 42] The fourth column of the data tables show the differences between the experimental (observed) and the calculated values. However, the absolute differences between the two values are used to calculate the average error in each calculated property. This step was considered to minimize the cancellation of errors that occurs in the use of the signed differences. The calculated enthalpies of formation are higher than the observed values for most of the molecules. The average error is determined to be 5.92 and 2.90 kcal/mol in AM1 and PM3, respectively.

5.3 Ionization Potentials

Tables II-A and II-B include the observed[43] and calculated values of the first ionization potentials (in eV) for the same set of aromatics. The differences between the observed and the calculated values are listed in column four in both of the two tables. The average absolute error of the calculations is 0.74 and 0.66 eV for AM1 and PM3, respectively. Those averages are consistent with Stewart's computations for aromatic compounds in which he calculated average absolute errors of 0.49 and 0.65 eV for the two methods respectively.[44]

5.4 Dipole Moments

Tables III-A and III-B compare the experimental[45] and the calculated dipole moments of the compounds. The fourth column in each of the tables shows the differences between the observed and the calculated values by AM1 and PM3 respectively. The average absolute error for the AM1 calculation is 0.92 D, and it is 1.02 D in the case of PM3. These values are substantially higher than Stewart's values of 0.11 and 0.10 for AM1 and PM3 calculations of seven compounds.[46]

5.5 Molecular Geometries

Bond lengths and bond angles were calculated for PM3 optimized geometries. Normally, all methods reproduce ground-state geometries without significant differences. In Stewart's calculations the average errors in bond lengths and bond angles for PM3 calculations are 0.036 Å and 3.9 deg respectively.[47]

Tables IV-A and IV-B show the bond lengths and bond angles for benzene and nitrobenzene. In benzene the calculated lengths of C-C and C-H bonds are 1.400 Å and 1.100 Å. The averages of errors for both calculations are 0.001 Å and -0.016 Å with a negligible difference from the observed values of 1.399 Å and 1.084 Å for the two bonds, respectively. The average errors in Stewart's application of the

PM3 method is 0.01 and 0.00 Å for the two bonds. Each of the angles in the benzene ring has an established value of 120.0 deg with an average error of less than 0.1 deg.

In nitrobenzene the C-C bonds range between 1.393 and 1.405 Å with an average of 1.397 Å. C-N and O-N bonds have values of 1.487 and 1.202 Å respectively. The C-C-C angles of the ring range between 119.8 and 120.3 deg with an average of 120.0 deg. The O-N-O angle of the nitro group is 121.1 deg. Figures 2 and 3 display the molecular geometries of benzene and nitrobenzene, respectively.

Bond lengths of phenol and its nitrated derivatives are listed in Table V-A, where the subscript *I* refers to *ortho, meta*, or *para* compounds. The average C-C bond lengths are 1.394, 1.399, 1.396, and 1.397 Å, while the average C-H bond lengths are 1.095, 1.102, 1.101, 1.098 Å for these compounds. The average N-O bond length is 1.215 Å for all the isomers. The reported experimental values of the C-C bond, and the average of C-H bonds of phenol are 1.397 and 1.081 Å. This yields average errors of 0.003 and 0.014 Å. The carbon angles in the ring range between 118.5 and 121.7 deg with an average of 120.0 deg. The geometrical structures (including bond lengths and bond angles) of phenol and its nitro-derivatives are shown in Figure 4 through Figure 7.

For chlorobenzene the averages of calculated C-C bond lengths are 1.391, 1.3945, 1.394 and 1.394 Å for the compound itself and its *ortho, meta*, and *para* nitro-derivatives. The calculated bond lengths range between 1.386 and 1.403 Å.

The C-H bond lengths range between 1.094 and 1.100 Å with averages of 1.095, 1.097, 1.098, and 1.097 Å for chlorobenzene and its *ortho, meta*, and *para* nitro-components. The observed C-C bond length in the chlorobenzene ring is 1.400 Å, and it is 1.083 Å for the C-H bond lengths. The average errors in the calculation of both lengths are 0.009 and 0.012 Å. Calculations of C-Cl bond lengths in the four molecules showed slightly different errors in the case of chlorobenzene, where it is 0.051 Å. The N-O bond length has an average of 1.215 Å. The calculated average for the carbon angles in the ring is 120.0 deg. However, the average error for individual angles is 0.48 deg.

In iodobenzene the average calculated C-C bond length is 1.389 Å, but it is 1.393, 1.393, and 1.392 Å for its *ortho, meta*, and *para* nitro-derivatives. Calculations of C-H bond lengths show an average length of 1.093 Å in the case of iodobenzene, and 1.097 Å for the bond in any of its mono-nitrated products. The N-O bond lengths show average values of 1.214, 1.214, and 1.215 Å for each of *ortho, meta*, and *para*-iodobenzene derivatives. While the values of C-C-C angles in the aromatic ring vary widely, from 118.0 to 123.5 deg, the O-N-O angles show similar trends with values of 120.7, 121.3, and 121.2 deg in *ortho, meta*, and *para* nitro-molecules.

The average length of C-C bonds in the aniline ring is 1.395 Å, while such lengths are 1.399, 1.396, and 1.398 Å in *ortho-, meta-*, and *para*-nitroaniline. An observed C-C bond length in aniline of 1.392 Å results in a calculated average error of 0.007 Å. Calculated values of C-H bond lengths show averages of 1.095, 1.097, 1.098, and 1.098 Å for aniline, and its *ortho, meta*, and *para* nitro-derivatives. The observed C-N bond length of aniline has a value of 1.431 Å and thus the calculated value is in error by 0.031 Å. While the reported value for the N-H bond length is 0.998 Å, its averages in the four compounds are 0.988, 0.994, 0.995 and 0.988 Å. This means that the average error in aniline is 0.010 Å. Figure 8 shows the geometrical structure of aniline with its bond angles and lengths.

The average calculated values of C-C-C angles in the aniline ring and its derivatives are 120.0 deg. However, the calculations yield values between 118.8 and 120.8 deg. This range was most noticeable between the observed and calculated H-N-H angle with a difference of 0.6 deg.

In the calculations for toluene and its *ortho, meta,* and *para* nitro-derivatives the average of C-C bond lengths are found to be 1.392, 1.420, 1.395, and 1.394 Å. An average error of 0.007 Å results from the difference with the observed value of 1.399 Å in toluene. The reported value of C-H bond length is 1.110 Å which yields an average error of 0.015 Å. For the methyl group, the observed values of C-CH_3 and C-H bond lengths are 1.524 and 1.100 Å, respectively. Therefore, the average errors are 0.038 and 0.002 Å. The average C-H bond length is 1.095 Å.

The average of the calculated values of the internal C-C-C angles is 120.0 deg for toluene and its derivatives. However, the carbon angle in the methyl group, H-C-H, has a slightly different value in some cases, and an average of 107.5 deg in toluene.

5.6 Infrared Frequencies

The infrared absorption frequencies of the aromatic systems were calculated for optimized geometries by PM3 followed by single-point configuration interaction calculations on these geometries. These calculations aim at reproducing the frequencies of the infrared absorptions but not their intensities. This means that in the process of comparing the observed and calculated frequencies, emphasis was placed on the frequency at which the absorption takes place and not on the intensity of the absorption. The first calculated value at about 600 cm^{-1} was compared with the first experimental value in the same range and so on. The main disadvantage of this method is the opportunity of including or excluding overtone and combination bands, such as those that frequently appear as weak absorptions in the range 1660-2000 cm^{-1}. Though signed differences between the observed and calculated frequencies are listed, the absolute value of the differences was used to calculate the average absolute error.

5.6.1 Benzene and Nitrobenzene

Tables X-A and X-B list the calculated frequencies of both benzene and nitrobenzene, respectively. The differences between the observed values[44, 48-50] and the calculated values show an irregular pattern, especially in the case of nitrobenzene. A calculated value of 1547 cm^{-1} in benzene and 1546 cm^{-1} in nitrobenzene are believed to represent the ring's carbon-carbon stretching absorptions in both of the molecules. The vibrations of Ar-H bond are well represented by the absorptions 3073 cm^{-1} in benzene and both 3068 and 3086 cm^{-1}

in nitrobenzene. Frequently, aromatic rings show a strong absorption around 1600 and 1500 cm^{-1}, while the Ar-H bond shows the absorption between 3030 and 3000 cm^{-1}. In nitrobenzene the calculated frequencies at 1560, 1546, and 1325 cm^{-1} refer to the nitro-group absorption that is experimentally reported to be 1560-1490 and 1360-1320 cm^{-1}. Different absorptions took place below 900 cm^{-1} as a characteristic of C-H bending and ring puckering. The absolute averages of error in the calculations of IR frequencies for benzene and nitrobenzene are 34.5 and 15.3 cm^{-1} respectively.

5.6.2 Phenol, *ortho*-, *meta*-, and *para*-Nitrophenol

Calculated and experimental values for the infrared frequencies of phenol and its nitrated derivatives are given in Table XI-A through Table XI-D.[44, 48-50] They give common absorptions at 1609 and 1569 cm^{-1} that are likely to refer to the aromatic ring. Similarly, each of the nitrophenol isomers shows absorptions around 1600 and 1500 cm^{-1}. Absorptions above 3700 cm^{-1} in each of the molecules probably represent the stretch due to the hydroxyl group that is usually observed in the 3200-3600 cm^{-1} region. Meanwhile, C-O stretching causes absorptions at 1200-1250 cm^{-1} in each compound. Absolute averages of error of the calculations are 18.9, 20.6, 17.1, and 21.2 cm^{-1}, respectively.

5.6.3 Chlorobenzene, *ortho-*, *meta-*, and *para*-Nitrochlorobenzene

In Tables XII-A through XII-D, the calculations of infrared frequencies of chlorobenzene and its *ortho, meta,* and *para* nitro-derivatives were compared with their experimental values.[44, 48-50] The differences between the two groups give averages of error of 26.5, 17.0, 14.2, and 15.9 cm^{-1}, respectively. Beside the common absorptions with the other compounds, such as those related to the ring, Ar-H, and the nitro group, the compounds in this group show absorptions around the region of 600-800 cm^{-1} that relate to C-Cl stretching.

5.6.4 Iodobenzene, *ortho-*, *meta-*, and *para*-Nitroiodobenzene

The observed absorption due to C-I bond stretching takes place around 500 cm^{-1}, although it is expected to go beyond this range due to the nature of the aromatic ring in the case of Ar-I.[44, 48-51] Although the calculations in Tables XIII-A through XIII-D show values around 600 cm^{-1}, one cannot claim with certainty that these refer to Ar-I. The average error for the calculations of IR frequencies of iodobenzene, *o-*, *m-*, and *p*-nitroiodobenzene are 33.3, 12.5, 18.7, 18.2 cm^{-1}, respectively.

5.6.5 Aniline, *ortho-*, *meta-*, and *para*-Nitroaniline

Tables XIV-A through XIV-B compare the calculated frequencies of aniline, *ortho-*, *meta-*, and *para*-nitroaniline with their observed frequencies.[44, 48-50] The differences between the two values give the averages of errors 23.77, 14.61, 13.56, and 33.61 cm^{-1}. Beside the absorptions due to the previously mentioned functional groups such as the aromatic ring and nitro group, each of the four molecules shows absorptions around the regions 3500-3300 cm^{-1} and 1180-1360 cm^{-1} for both N-H and C-N, respectively. Consider aniline for example: the calculated values of 3411, 3532 and 1169, 1328, and 1369 cm^{-1} are within the two regions, and thus reasonably refer to the stretching of N-H and C-H bonds, respectively.

5.6.6 Toluene, *ortho-*, *meta-*, and *para*-Nitrotoluene

The calculated frequencies of toluene, *o*-, *m*-, and *p*-nitrotoluene are listed in Tables XV-A through XV-D along with the experimental values[44, 48-50] and the differences between both. The calculations yield average errors of 16.2, 11.5, 26.9, and 18.9 cm^{-1} for the compounds, respectively. The calculations give regions of C-H bending, ring puckering, and rings' C-C and Ar-H stretching.

Table I-A. Enthalpy of Formation of Simple Aromatics, kcal/mol - AM1

Compound	Enthalpy of Formation		
	Obs	Calc	Obs-Calc
Benzene	19.8 ± 0.1	21.87	- 2.07
Nitrobenzene	16.1	25.12	- 9.02
Phenol	-23.0 ± 0.2	-22.41	- 0.59
o-Nitrophenol	-23.0	-20.35	- 2.65
m-Nitrophenol	-27.0	-18.14	- 8.86
p-Nitrophenol	-28.0	-19.73	- 8.27
Chlorobenzene	13.0	14.63	- 1.63
o-Nitrochlorobenzene	-	24.56	-
m-Nitrochlorobenzene	9.1 ± 2.0	19.61	- 10.51
p-Nitrochlorobenzene	9.1 ± 2.0	19.04	- 9.94
Iodobenzene	39.4 ± 1.4	37.97	1.43
o-Nitroiodobenzene	-	51.08	-
m Nitroiodobenzene	-	42.75	-
p-Nitroiodobenzene	-	42.84	-
Toluene	12.0 ± 0.1	14.22	- 2.22
o-Nitrotoluene	13.0	18.71	- 5.71
m-Nitrotoluene	7.0	17.39	- 10.39
p-Nitrotoluene	7.0 ± 1.0	17.04	- 10.04
Aniline	20.8 ± 0.2	20.32	0.48
o-Nitroaniline	15.0 ± 1.0	20.54	- 5.54
m-Nitroaniline	15.0 ± 0.5	23.82	- 8.82
p-Nitroaniline	13.0 ± 0.5	21.36	- 8.36

Table I-B. Enthalpy of Formation of Simple Aromatics kcal/mol - PM3

Compound	Enthalpy of Formation		
	Obs	Calc	Obs-Calc
Benzene	19.8 ± 0.1	23.29	- 3.49
Nitrobenzene	16.1	14.33	1.77
Phenol	-23.0 ± 0.2	-21.85	- 1.15
o-Nitrophenol	-23.0	-33.47	10.47
m-Nitrophenol	-27.0	-30.14	3.14
p-Nitrophenol	-28.0	-31.91	3.91
Chlorobenzene	13.0	16.51	- 3.51
o-Nitrochlorobenzene	-	11.35	-
m-Nitrochlorobenzene	9.1 ± 2.0	8.70	0.40
p-Nitrochlorobenzene	9.1 ± 2.0	8.24	0.86
Iodobenzene	39.4 ± 1.4	44.59	- 5.19
o-Nitroiodobenzene	-	45.80	-
m-Nitroiodobenzene	-	36.64	-
p-Nitroiodobenzene	-	36.52	-
Toluene	12.0 ± 0.1	13.89	- 1.89
o-Nitrotoluene	13.0	9.30	3.7
m-Nitrotoluene	7.0	4.83	2.17
p-Nitrotoluene	7.0 ± 1.0	4.44	2.56
Aniline	20.8 ± 0.2	21.12	- 0.32
o-Nitroaniline	15.0 ± 1.0	12.60	2.40
m-Nitroaniline	15.0 ± 0.5	12.31	2.69
p-Nitroaniline	13.0 ± 0.5	10.46	2.54

Table II-A. First Ionization Energy of Simple Aromatics, eV- AM1

Compound	First Ionization Energy		
	Obs	Calc	Obs-Calc
Benzene	9.25 ± 0.00	9.25	0.00
Nitrobenzene	9.86 ± 0.02	10.56	- 0.70
Phenol	8.51 ± 0.00	9.11	- 0.60
o-Nitrophenol	9.1	9.91	- 0.81
m-Nitrophenol	9.0	9.97	- 0.97
p-Nitrophenol	9.1	10.07	- 0.97
Chlorobenzene	9.07 ± 0.02	9.56	- 0.49
o-Nitrochlorobenzene	-	10.32	-
m-Nitrochlorobenzene	9.92 ± 0.1	10.37	- 0.45
p-Nitrochlorobenzene	9.96 ± 0.1	10.47	- 0.51
Iodobenzene	8.69	9.65	- 0.96
o-Nitroiodobenzene	-	10.33	-
m-Nitroiodobenzene	-	10.40	-
p-Nitroiodobenzene	9.24	10.49	- 1.25
Toluene	8.82 ± 0.01	9.33	- 0.51
o-Nitrotoluene	9.24	10.17	- 0.93
m-Nitrotoluene	9.49 ± 0.02	10.20	- 0.71
p-Nitrotoluene	9.1 ± 0.1	10.30	- 1.20
Aniline	7.72 ± 0.00	8.21	- 0.49
o-Nitroaniline	8.27 ± 0.01	9.07	- 0.80
m-Nitroaniline	8.31 ± 0.02	9.25	- 0.94
p-Nitroaniline	8.34 ± 0.01	9.16	- 0.82

Table II-B. First Ionization Energy of Simple Aromatics, eV- PM3

Compound	First Ionization Energy		
	Obs	Calc	Obs-Calc
Benzene	9.25 ± 0.00	9.75	- 0.50
Nitrobenzene	9.86 ± 0.02	10.60	- 0.74
Phenol	8.51 ± 0.00	9.18	- 0.67
o-Nitrophenol	9.1	9.90	- 0.80
m-Nitrophenol	9.0	9.99	- 0.99
p-Nitrophenol	9.1	10.17	- 1.07
Chlorobenzene	9.07 ± 0.02	9.39	- 0.32
o-Nitrochlorobenzene	-	9.94	-
m-Nitrochlorobenzene	9.92 ± 0.1	10.06	- 0.14
p-Nitrochlorobenzene	9.96 ± 0.1	10.22	- 0.26
Iodobenzene	8.69	9.04	- 0.35
o-Nitroiodobenzene	-	9.29	-
m-Nitroiodobenzene	-	9.51	-
p-Nitroiodobenzene	9.24	9.63	- 0.39
Toluene	8.82 ± 0.01	9.44	- 0.62
o-Nitrotoluene	9.24	10.24	- 1.00
m-Nitrotoluene	9.49 ± 0.02	10.28	- 0.79
p-Nitrotoluene	9.1 ± 0.1	10.47	- 1.37
Aniline	7.72 ± 0.00	8.07	- 0.35
o-Nitroaniline	8.27 ± 0.01	8.84	- 0.57
m-Nitroaniline	8.31 ± 0.02	9.29	- 0.98
p-Nitroaniline	8.34 ± 0.01	9.00	- 0.66

Table III-A. Dipole Moment of Simple Aromatics, D- AM1

Compound	Dipole Moment		
	Obs	Calc	Obs-Calc
Benzene	0.00	0.00	0.00
Nitrobenzene	3.93	5.24	- 1.31
Phenol	1.55	1.23	0.32
o-Nitrophenol	3.14	4.33	- 1.19
m-Nitrophenol	3.90	4.01	- 0.11
p-Nitrophenol	5.07	5.26	- 0.19
Chlorobenzene	1.75	1.31	0.44
o-Nitrochlorobenzene	4.63	5.55	- 0.92
m-Nitrochlorobenzene	3.40	4.67	- 1.27
p-Nitrochlorobenzene	2.60	4.18	- 1.58
Iodobenzene	1.70	1.43	0.27
o-Nitroiodobenzene	3.69	5.49	- 1.80
m-Nitroiodobenzene	3.54	4.67	- 1.13
p-Nitroiodobenzene	2.18	4.02	- 1.84
Toluene	0.43	0.26	0.17
o-Nitrotoluene	3.63	5.15	-1.52
m-Nitrotoluene	4.23	5.46	- 1.23
p-Nitrotoluene	4.39	5.73	- 1.34
Aniline	1.56	1.58	- 0.02
o-Nitroaniline	4.06	5.29	- 1.23
m-Nitroaniline	4.90	5.94	- 1.04
p-Nitroaniline	6.29	7.64	- 1.35

Table III-B. Dipole Moments of Simple Aromatics, D- PM3

Compound	Dipole Moment		
	Obs	Calc	Obs-Calc
Benzene	0.00	0.00	0.00
Nitrobenzene	3.93	5.25	- 1.32
Phenol	1.55	1.14	0.41
o-Nitrophenol	3.14	4.18	- 1.04
m-Nitrophenol	3.90	4.19	- 0.29
p-Nitrophenol	5.07	5.57	- 0.50
Chlorobenzene	1.75	0.95	0.80
o-Nitrochlorobenzene	4.63	5.38	- 0.75
m-Nitrochlorobenzene	3.40	4.83	- 1.43
p-Nitrochlorobenzene	2.60	4.59	- 1.99
Iodobenzene	1.70	0.79	0.91
o-Nitroiodobenzene	3.69	5.17	- 1.48
m-Nitrochlorobenzene	3.54	5.03	- 1.49
p-Nitrochlorobenzene	2.18	4.87	- 2.69
Toluene	0.43	0.26	0.17
o-Nitrotoluene	3.63	5.00	- 1.37
m-Nitrotoluene	4.23	5.44	- 1.21
p-Nitrotoluene	4.39	5.73	- 1.34
Aniline	1.56	1.57	- 0.01
o-Nitroaniline	4.06	5.05	- 0.99
m-Nitroaniline	4.90	5.70	- 0.8
p-Nitroaniline	6.29	7.84	- 1.55

Table IV-A. Bond Lengths, Å, of Benzene and Nitrobenzene-PM3

Bond	Bond Length	
	Benzene	Nitrobenzene
C_1-C_2	1.400	1.405
C_2-C_3	1.400	1.393
C_3-C_4	1.400	1.395
C_4-C_5	1.400	1.395
C_5-C_6	1.400	1.393
C_6-C_1	1.400	1.400
C_1-H_1	1.100	-
C_2-H_2	1.100	1.080
C_3-H_3	1.100	1.080
C_4-H_4	1.100	1.080
C_5-H_5	1.100	1.080
C_6-H_6	1.100	1.080
C_1-N	-	1.487
O_1-N	-	1.202
O_2-N	-	1.202

Table IV-B. Bond Angles, deg, of Benzene and Nitrobenzene- PM3

Angle	Bond Angles	
	Benzene	Nitrobenzene
C_1	120.0	119.8
C_2	120.0	119.8
C_3	120.0	120.3
C_4	120.0	120.1
C_5	120.0	120.3
C_6	120.0	119.8
N	-	121.1

Table V-A. Bond Lengths, Å, of Phenol and Nitrophenol - PM3

Bond	Phenol	Nitrophenol		
		Ortho	Meta	Para
C_1-C_2	1.402	1.414	1.398	1.404
C_2-C_3	1.388	1.410	1.399	1.384
C_3-C_4	1.392	1.379	1.397	1.403
C_4-C_5	1.390	1.401	1.393	1.401
C_5-C_6	1.390	1.379	1.386	1.386
C_6-C_1	1.401	1.412	1.404	1.404
C_2-H_2	1.096	-	1.102	1.097
C_3-H_3	1.095	1.101	-	1.100
C_4-H_4	1.095	1.102	1.103	-
C_5-H_5	1.095	1.100	1.101	1.100
C_6-H_6	1.095	1.105	1.100	1.097
C_1-O_1	1.369	1.361	1.374	1.359
H_7-O_1	0.949	0.963	0.949	0.950
C_i-N^*	-	1.477	1.499	1.492
O_2-N	-	1.210	1.215	1.216
O_3-N	-	1.230	1.216	1.216

Table V-B. Bond Angles, deg, of Phenol and Nitrophenol - PM3

Angle	Phenol	Nitrophenol		
		Ortho	*Meta*	*Para*
C_1	120.9	120.0	121.1	120.7
C_2	118.9	118.8	119.0	119.3
C_3	120.6	120.5	120.3	120.4
C_4	120.1	120.4	119.9	119.8
C_5	120.4	120.6	120.9	120.3
C_6	119.0	119.7	118.9	119.4
O_1	107.8	109.9	108.3	108.5
N	-	120.8	121.1	121.0

Table VI-A. Bond Lengths, Å, of Chlorobenzene and Nitrochlorobenzene - PM3

Bond	Chlorobenzene	Nitrochlorobenzene		
		Ortho	*Meta*	*Para*
C_1-C_2	1.393	1.403	1.391	1.393
C_2-C_3	1.390	1.404	1.399	1.388
C_3-C_4	1.392	1.386	1.400	1.401
C_4-C_5	1.391	1.393	1.391	1.401
C_5-C_6	1.390	1.387	1.390	1.388
C_6-C_1	1.392	1.398	1.394	1.394
C_2-H_2	1.095	-	1.100	1.096
C_3-H_3	1.095	1.100	-	1.099
C_4-H_4	1.094	1.096	1.099	-
C_5-H_5	1.094	1.096	1.096	1.099
C_6-H_6	1.095	1.097	1.096	1.096
C_1-Cl	1.686	1.675	1.684	1.677
C_i-N^*	-	1.499	1.499	1.500
O_1-N	-	1.213	1.215	1.215
O_2-N	-	1.216	1.215	1.215

Table VI-B. Bond Angles, deg, of Chlorobenzene and Nitrochlorobenzene - PM3

Angle	Chlorobenzene	Nitrochlorobenzene		
		Ortho	*Meta*	*Para*
C_1	121.0	120.0	121.1	120.7
C_2	119.3	118.8	119.2	119.7
C_3	120.1	120.7	120.0	120.0
C_4	120.2	120.2	119.9	119.9
C_5	120.2	119.8	120.5	120.0
C_6	119.3	120.5	119.4	119.7
N	-	120.8	121.3	121.2

Table VII-A. Bond Lengths, Å, of Iodobenzene and Nitroiodobenzene - PM3

Bond	Iodobenzene	Nitroiodobenzene		
		Ortho	*Meta*	*Para*
C_1-C_2	1.381	1.392	1.380	1.382
C_2-C_3	1.394	1.407	1.402	1.392
C_3-C_4	1.392	1.387	1.402	1.402
C_4-C_5	1.393	1.393	1.391	1.402
C_5-C_6	1.393	1.389	1.393	1.392
C_6-C_1	1.380	1.389	1.393	1.382
C_2-H_2	1.094	-	1.099	1.096
C_3-H_3	1.094	1.100	-	1.099
C_4-H_4	1.095	1.096	1.100	-
C_5-H_5	1.094	1.096	1.096	1.099
C_6-H_6	1.090	1.096	1.095	1.096
C_1- I	1.970	1.968	1.966	1.966
C_i-N^*	-	1.502	1.498	1.498
O_1-N	-	1.211	1.214	1.215
O_2-N	-	1.218	1.215	1.215

Table VII-B. Bond Angles, deg, of Iodobenzene and Nitroiodobenzene - PM3

Angle	Iodobenzene	Nitroiodobenzene		
		Ortho	*Meta*	*Para*
C_1	123.5	121.7	123.3	123.0
C_2	118.0	117.8	118.1	118.5
C_3	120.0	120.7	119.8	119.8
C_4	120.6	120.4	120.3	120.3
C_5	120.0	119.6	120.3	119.8
C_6	118.0	119.8	118.2	118.5
N	-	120.7	121.3	121.2

Table VIII-A. Bond Lengths, Å, of Aniline and Nitroaniline - PM3

Bond	Aniline	Nitroaniline		
		Ortho	*Meta*	*Para*
C_1-C_2	1.406	1.419	1.401	1.410
C_2-C_3	1.387	1.402	1.397	1.381
C_3-C_4	1.391	1.376	1.398	1.404
C_4-C_5	1.391	1.404	1.390	1.404
C_5-C_6	1.387	1.374	1.387	1.381
C_6-C_1	1.406	1.421	1.403	1.410
C_2-H_2	1.096	-	1.101	1.097
C_3-H_3	1.095	1.099	-	1.099
C_4-H_4	1.094	1.095	1.098	-
C_5-H_5	1.095	1.096	1.096	1.099
C_6-H_6	1.096	1.097	1.097	1.096
C_1-N_1	1.400	1.378	1.427	1.387
H_7-N_1	0.988	1.001	0.995	0.988
H_8-N_1	0.988	0.987	0.995	0.988
C_i-N_2*	-	1.472	1.498	1.484
O_1-N_2	-	1.214	1.215	1.217
O_2-N_2	-	1.229	1.216	1.217

Table VIII-B. Bond Angles, deg, of Aniline and Nitroaniline - PM3

Angle	Aniline	Nitroaniline		
		Ortho	*Meta*	*Para*
C_1	119.9	119.1	119.9	119.5
C_2	119.6	118.8	119.6	120.0
C_3	120.6	121.0	120.3	120.5
C_4	119.8	120.1	119.6	119.4
C_5	120.6	120.5	120.8	120.5
C_6	119.6	120.4	119.8	120.0
N_1	119.9	121.1	111.6	119.6
N_2	-	119.8	121.0	120.5

Table IX-A. Bond Lengths, Å, of Toluene and Nitrotoluene - PM3

Bond	Toluene	Nitrotoluene		
		Ortho	*Meta*	*Para*
C_1-C_2	1.396	1.467	1.396	1.397
C_2-C_3	1.389	1.460	1.390	1.388
C_3-C_4	1.391	1.345	1.389	1.401
C_4-C_5	1.390	1.443	1.400	1.400
C_5-C_6	1.390	1.345	1.399	1.389
C_6-C_1	1.396	1.461	1.394	1.396
C_2-H_2	1.096	-	1.097	1.096
C_3-H_3	1.095	1.098	-	1.099
C_4-H_4	1.095	1.096	1.099	-
C_5-H_5	1.095	1.095	1.096	1.099
C_6-H_6	1.096	1.096	1.096	1.097
C_1-C_7	1.486	1.344	1.486	1.484
C_7-H_7	1.098	1.106	1.098	1.098
C_7-H_8	1.098	1.098	1.098	1.098
C_7-H_9	1.098	1.098	1.098	1.098
C_i-N^*	-	1.496	1.496	1.495
O_1-N	-	1.215	1.216	1.216
O_2-N	-	1.219	1.215	1.216

Table IX-B. Bond Angles, deg, of Toluene and Nitrotoluene-PM3

Angle	Toluene	Nitrotoluene		
		Ortho	*Meta*	*Para*
C_1	119.5	119.1	119.9	119.5
C_2	120.2	118.8	119.6	120.0
C_3	120.1	121.0	120.3	120.5
C_4	119.9	120.1	119.6	119.4
C_5	120.2	120.5	120.8	120.5
C_6	120.2	120.4	119.8	120.0
H_7 -C_7-H_8	107.5	107.9	107.5	107.5
H_8 -C_7-H_9	107.5	107.5	107.5	107.6
H_7 -C_7-H_9	107.6	107.9	107.6	107.7
N	-	120.1	121.0	121.0

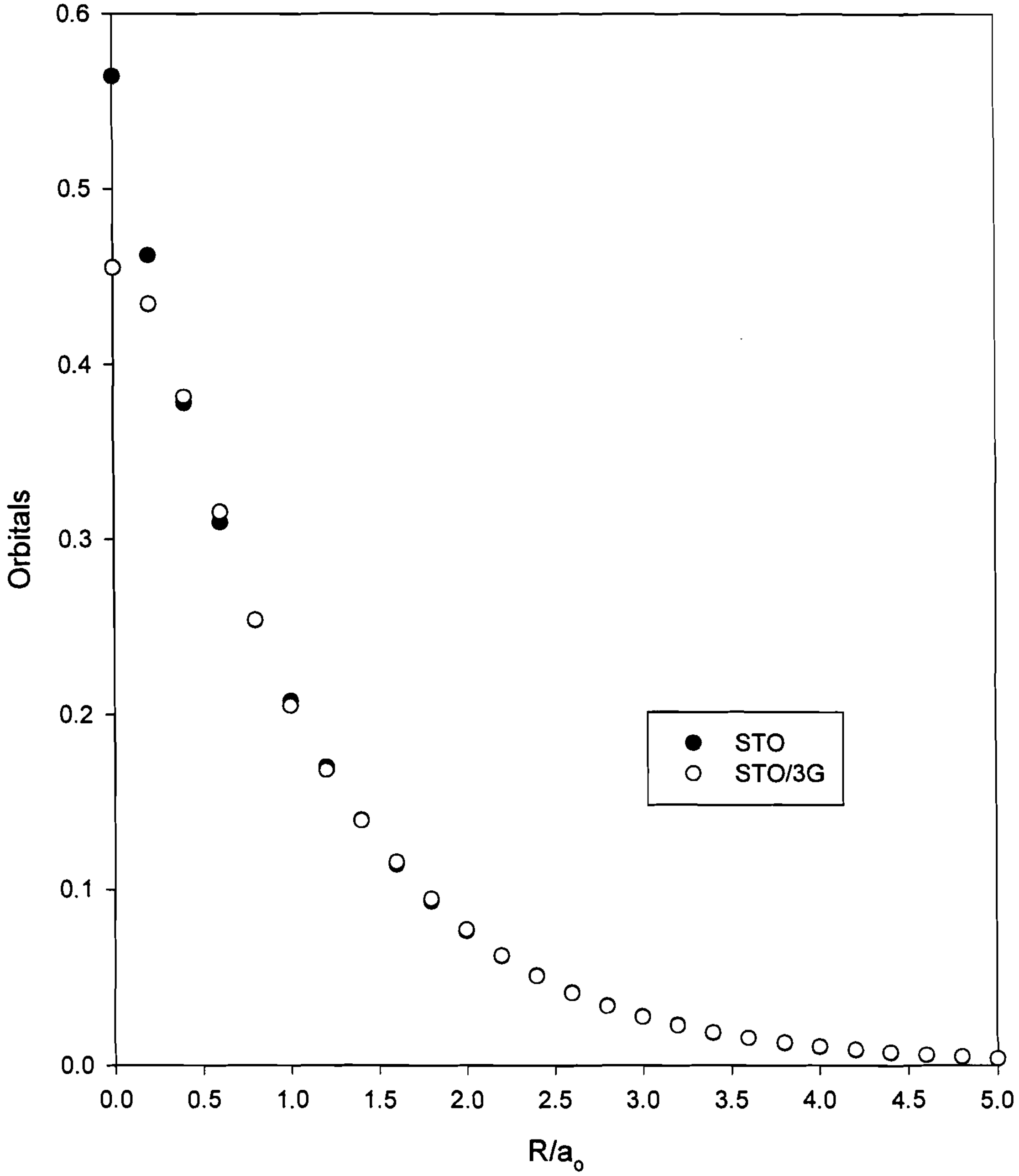


Figure 1. A Fit of Three Gaussians to a Slater Type Orbitals

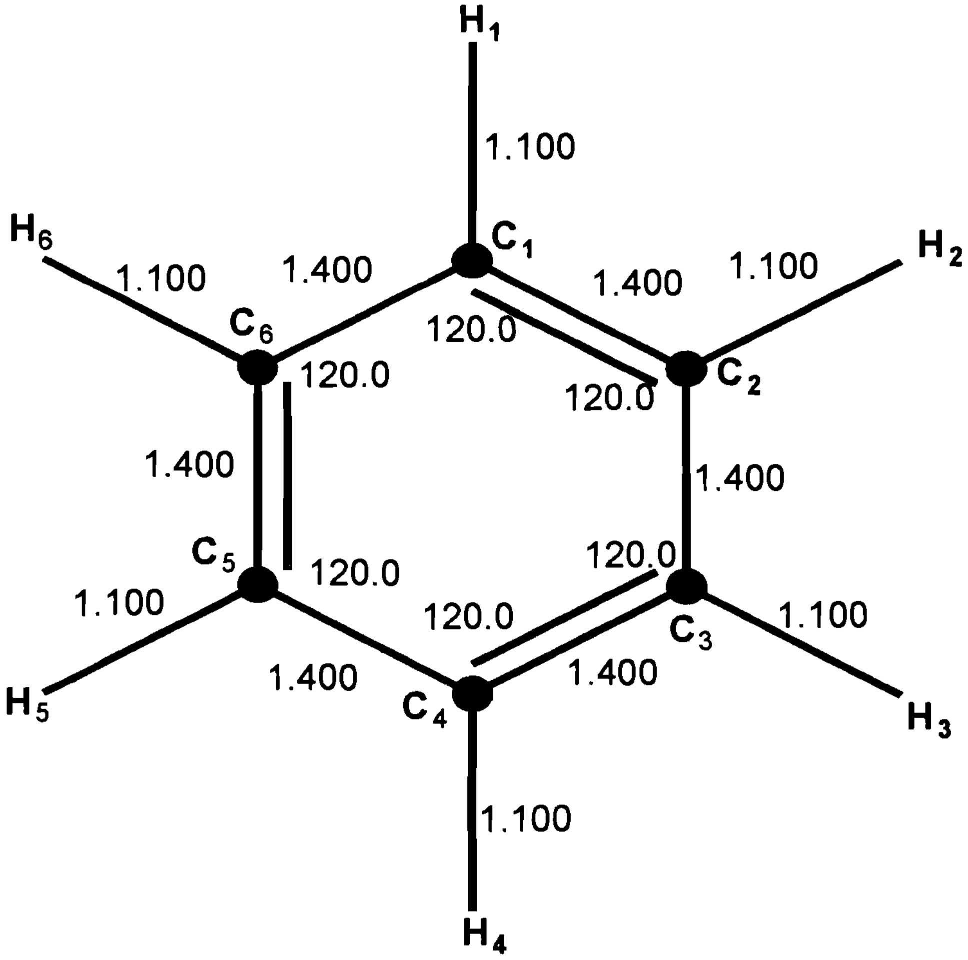


Figure 2. Bond Lengths, Å, and Bond Angles, deg, of Benzene - PM3

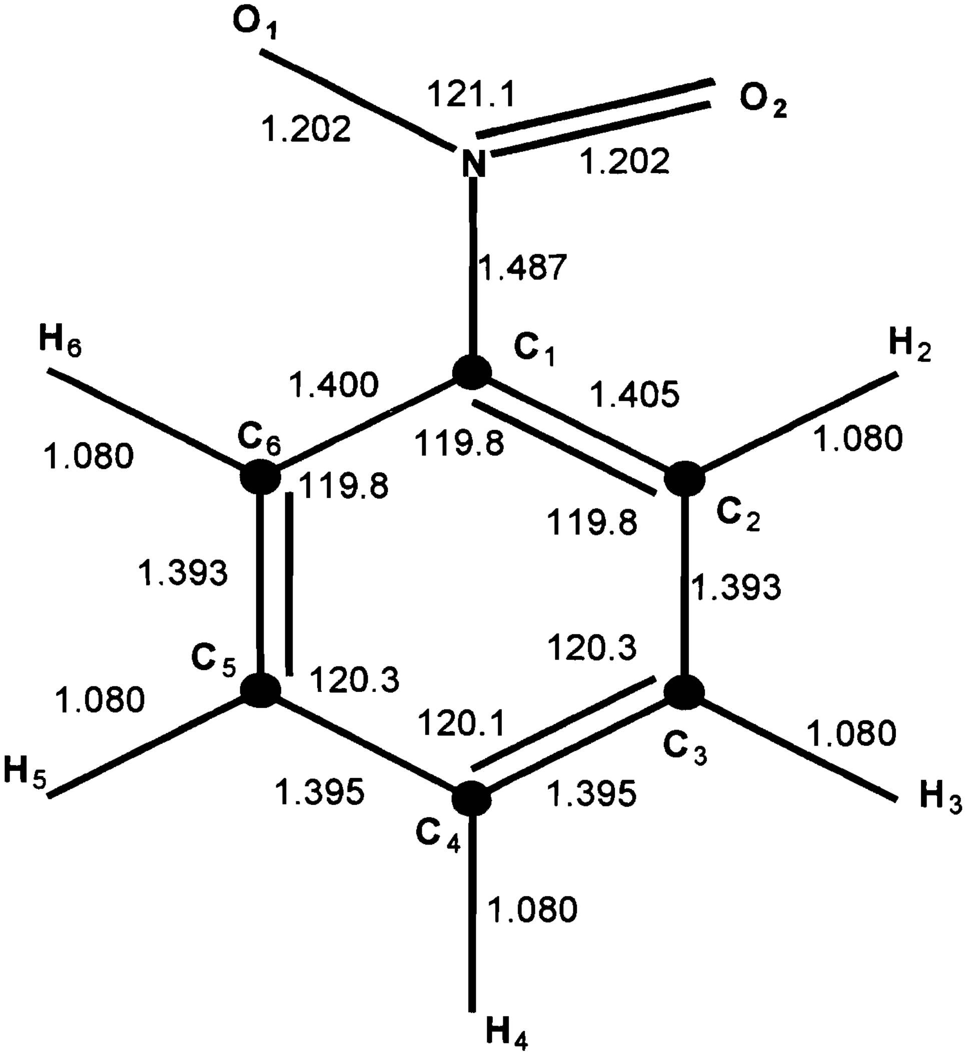


Figure 3. Bond Lengths, Å, and Bond Angles, deg, of Nitrobenzene - PM3

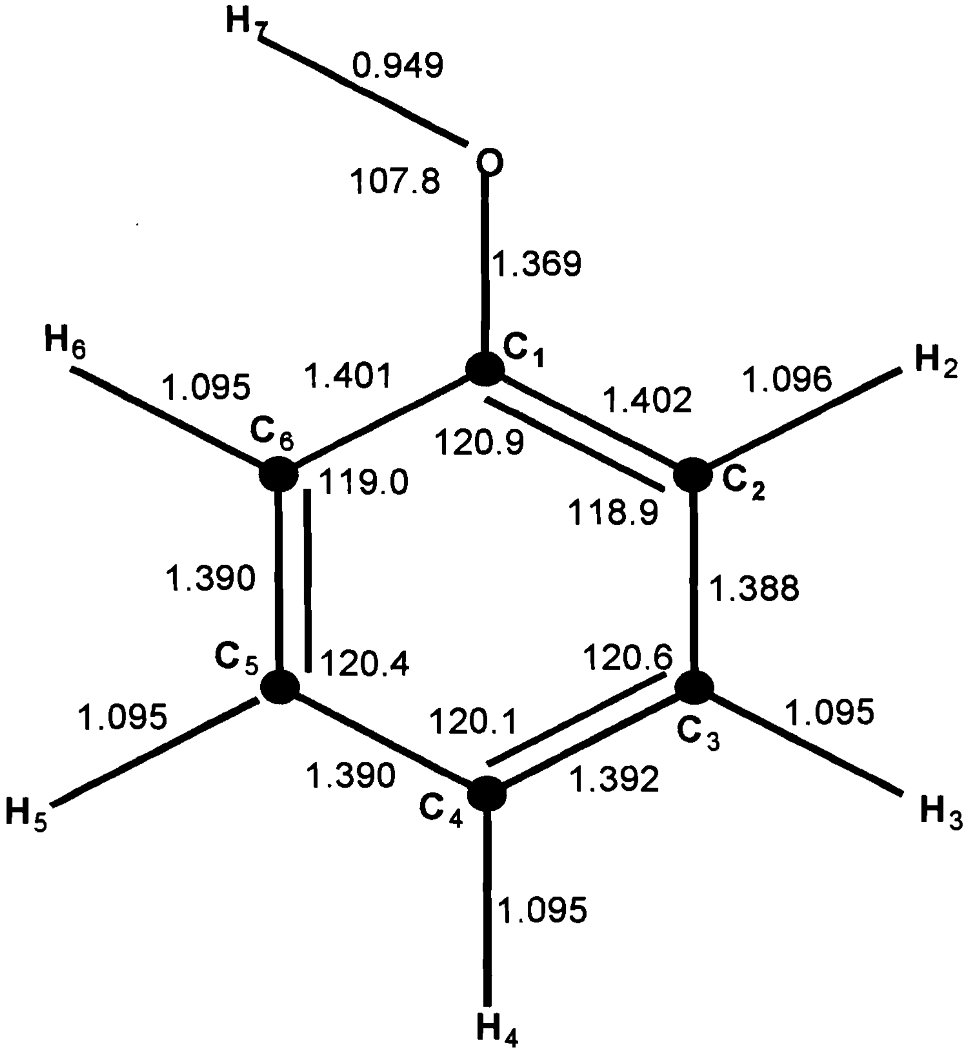


Figure 4. Bond Lengths, Å, and Bond Angles, deg, of Phenol - PM3

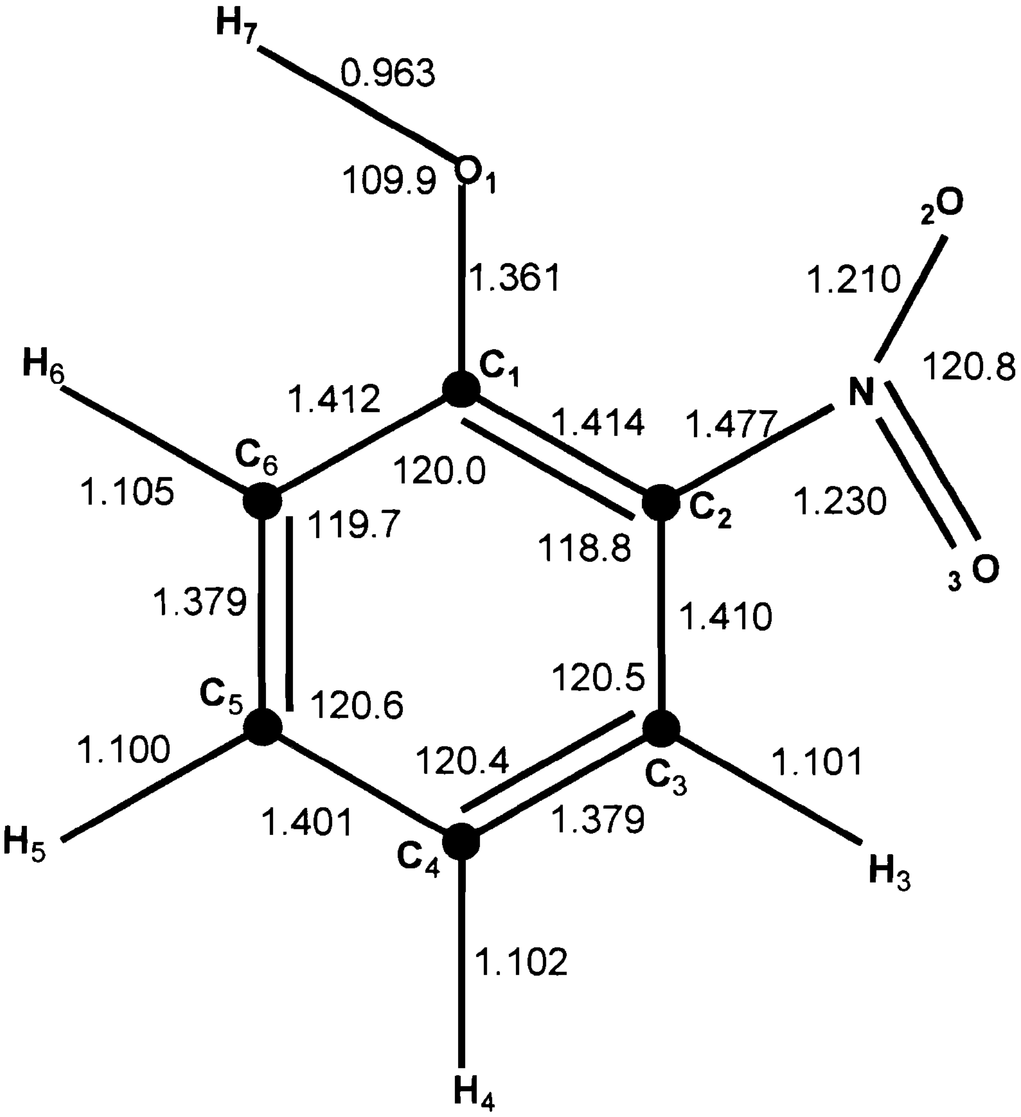


Figure 5. Bond Lengths, Å, and Bond Angles, deg, of *o*-Nitrophenol - PM3

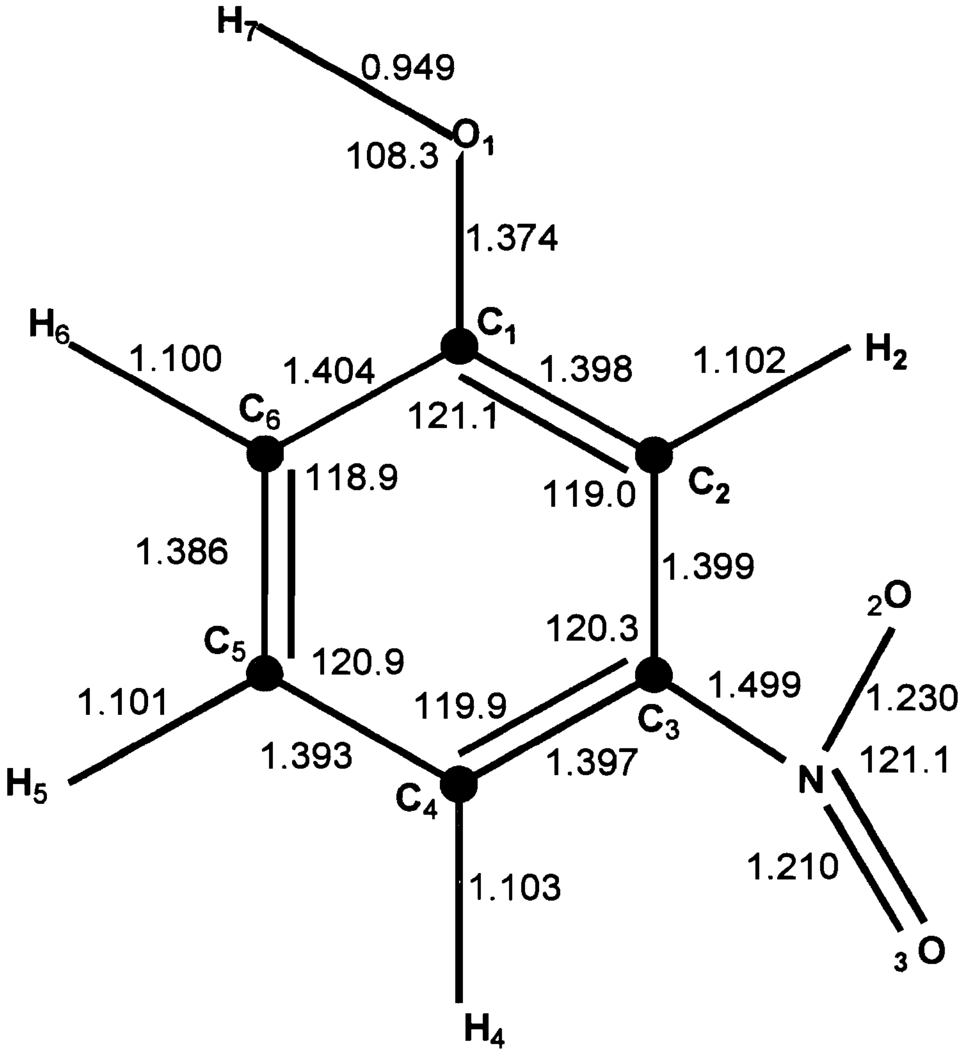


Figure 6. Bond Lengths, Å, and Bond Angles, deg, of *m*-Nitrophenol - PM3

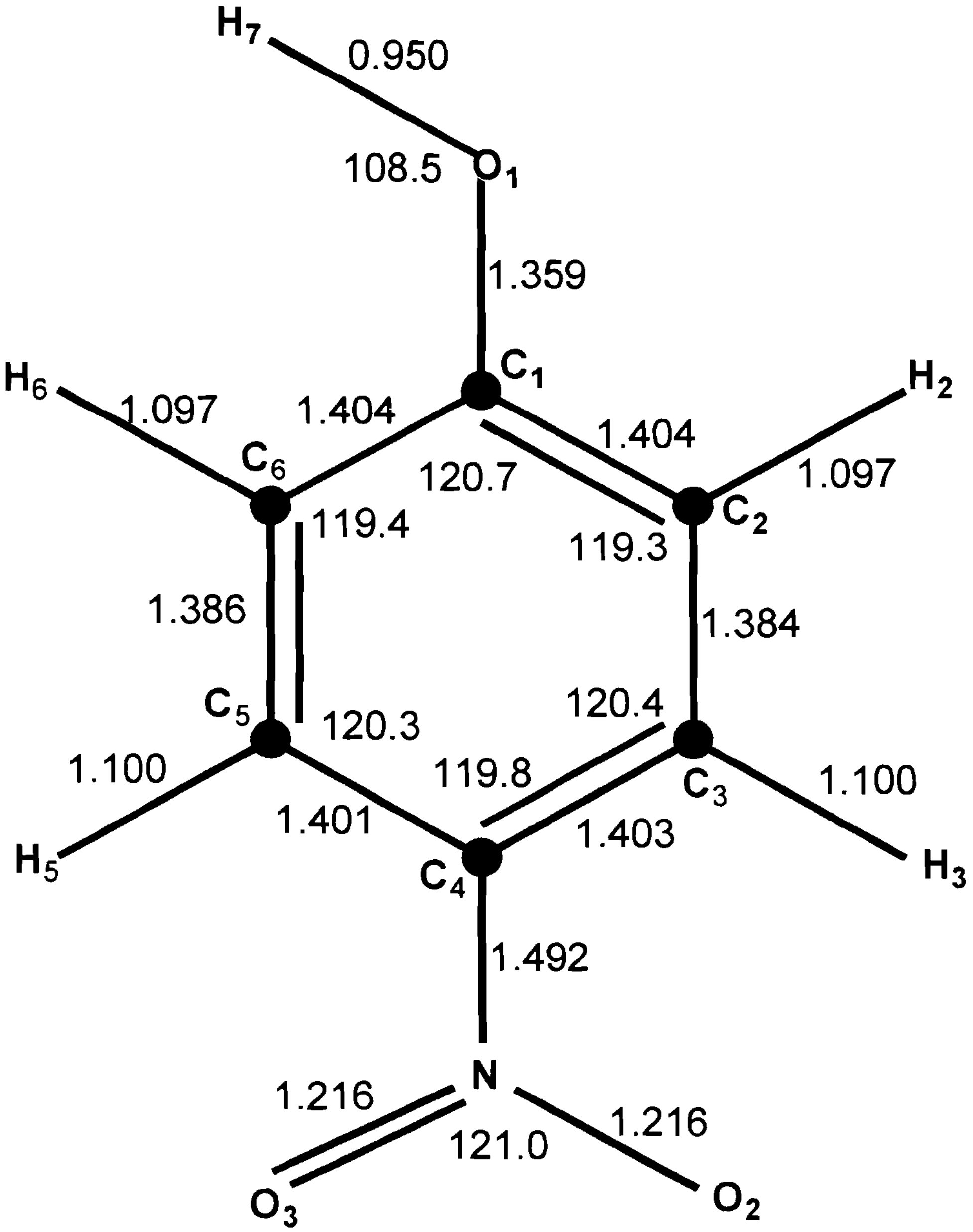


Figure 7. Bond Lengths, Å, and Bond Angles, deg, of *p*-Nitrophenol - PM3

Table X-A. Infrared Frequencies (cm^{-1}) of Benzene - PM3

Frequency			Frequency		
Obs.	**Calc.**	**Obs.- Calc.**	**Obs.**	**Calc.**	**Obs.- Calc.**
554	No	-	1394	No	-
572	No	-	1481	1547	-66
604	No	-	1755	No	-
655	No	-	1803	No	-
672	No	-	1949	No	-
691	712	-21	2320	No	-
779	No	-	2896[1]	No	-
1035	1069	-34	3056	3703	-17
1379	No	-	3066	No	-

Table X-B. Infrared Frequencies (cm^{-1}) of Nitrobenzene - PM 3

Frequency			Frequency		
Obs.	Calc.	Obs. - Calc.	Obs.	Calc.	Obs. - Calc.
680 677	671	9 6	1485	No	-
703	727	-24	1527	1546	-19
790 793	814	-24 -21	1545	1560	-15
853	837	16	1610 1603	1606	4 -3
932	963	-31	1803	1785	18
1022	1031	-9	No	1893	-
1069	1108	-39	2889	No	-
1109	1114	-5	No	3029	-
1176	1182	-6	No	3032	-
1244	1240	4	No	3053	-
1306	1297	9	3068	3062	6
1355 1351	1325	30 26	3086	3073	13

Table XI-A. Infrared Frequencies (cm^{-1}) of Phenol - PM3

Frequency			Frequency		
Obs.	Calc.	Obs. - Calc.	Obs.	Calc.	Obs. - Calc.
588	No	-	1499	No	-
632	634	-2	1515	1569	-54
688	No	-	1595 1620	1609	-14 11
748 753	773	-25 -20	1693	No	-
810 816	No	- -	1768	1786	-18
881	875	6	1838	1792	46
No	921	-	1930	No	-
1000 1013	1009	-9 4	2420	No	-
1061	1047	14	3057	3055	2
No	1103	-	No	3066	-
No	1130	-	No	3072	-
1168	1152	16	No	3082	-
1185 1224	1213	-28 11	3652	No	-
1259	1271	-12	No	3889	-
1336 1350	1377	-41 -27			

Table XI-B. Infrared Frequencies (cm^{-1}) of o-Nitrophenol - PM 3

Frequency			Frequency		
Obs.	Calc.	Obs. - Calc.	Obs.	Calc.	Obs. - Calc.
No	660	-	1593	1590	3
679	688	-9	1620	1628	-8
747	779	-32	1690	No	-
819	813	6	1729	No	-
871	852	19	1746	1765	-19
No	890	-	1807	1793	14
952	907	45	1929	1888	41
1029	1020	9	1953	No	-
1079	1111	-32	No	3028	-
No	1124	-	No	3049	-
1148	1165	-17	No	3062	-
1202	1224	-22	3090	3073	17
1262 1258	1253	9 5	3269	No	-
1335 1331	1331	4 0	3722	No	-
1474 1457	1434	40 23	3787	3725	62
1546 1536	1512	34 24	3881	No	-
1535	1556	-21			

Table XI-C. Infrared Frequencies (cm^{-1}) of m-Nitrophenol - PM 3

Frequency			Frequency		
Obs.	**Calc.**	**Obs. - Calc.**	**Obs.**	**Calc.**	**Obs. - Calc.**
598	570	28	1360	1391	-31
671	671	0	1487	No	-
735 742	759	-24 -17	1548	1579	-31
796	788	8	1616	1606	10
813 818	827	-14 -9	1624	1609	15
871	No	-	1668	No	-
927 933	948	-21 -15	1762	1780	-18
1001	1011	-10	No	1785	-
1075	1023	52	No	1893	-
1080	1080	0	No	3024	-
No	1133	-	3044	3033	11
1163	-1177	14	No	3053	-
1180	1181	-1	3081	3068	13
1256 1214	1237	19 -23	3652	No	-
1304	1278	26	No	3883	-

Table XI-D. Infrared Frequencies (cm^{-1}) of p-Nitrophenol - PM 3

Frequency			Frequency		
Obs.	**Calc.**	**Obs. - Calc.**	**Obs.**	**Calc.**	**Obs. - Calc.**
623	626	-3	1540 1587	1569	-29 18
679	643	36	1601	1603	-2
749	772	-23	No	1622	-
No	794	-	1746	1769	-23
856 850	891	-35 -41	No	1786	-
No	962	-	1896	1891	5
No	1010	-	2455	No	-
1109 1164	1155	-46 9	2878	No	-
1179	1184	-5	No	3025	-
1214	1218	-4	3047	3027	20
1269	1228	41	No	3058	-
1284	1296	-12	3083	3064	19
1350	1399	-49	3646	No	-
1439	1435	4	No	3880	-

Table XII-A. Infrared Frequencies (cm^{-1}) of Chlorobenzene - PM3

	Frequency	
Obs.	**Calc.**	**Obs. - Calc.**
682	633	49
713 701	706	7 -5
739	768	-29
903	No	-
9181	932	-14
No	992	-
1022	1016	6
No	1067	-
1088	1093	-5
1124	1143	-19
1229	1254	-25
1370	No	-
1442	No	-
1482	1536	54
1587 1580	1545	42 35
1628	No	-
1726	1779	-53
1787	No	-
1869	No	-
1946	No	-
No	3056	-
No	3059	-
No	3066	-
No	3072	-
3083	3081	2

Table XII-B. Infrared Frequencies (cm^{-1}) of o-Nitrochlorobenzene - PM3

Frequency			Frequency		
Obs.	Calc.	Obs. - Calc.	Obs.	Calc.	Obs. - Calc.
574	544	30	No	1295	-
595	No	-	1312	1333	-21
654	659	-5	1359	No	-
No	676	-	1473	No	-
732	711	21	1532	1529	3
767 777	771	-4 6	1553	1556	-3
No	808	-	1587	1604	-17
854	832	22	No	1766	-
No	906	-	1805	1778	27
948	974	-26	1923	1890	33
No	1023	-	2901	No	-
1060	1066	-6	No	3030	-
No	1111	-	No	3050	-
1133	1141	-8	No	3059	-
No	1158	-	3085	3072	13
1258	1214	44			

Table XII-C. Infrared Frequencies (cm^{-1}) of m-Nitrochlorobenzene - PM3

Frequency			Frequency		
Obs.	Calc.	Obs. - Calc.	Obs.	Calc.	Obs. - Calc.
No	618	-	1352	1329	23
668	664	4	1469	No	-
No	714	-	1537	1540	-3
750	756	-6	1552	1553	-1
795	829	-34	No	1603	-
881 877	885	-4 -8	No	1769	-
No	946	-	No	1780	-
No	1018	-	No	1897	-
1068	1040	28	2865	No	-
No	1106	-	No	3025	-
1132 1129	1127	5 2	No	3029	-
No	1173	-	No	3053	-
1273	1229	44	3090	3067	23
No	1312	-			

Table XII-D: Infrared Frequencies (cm^{-1}) of p-Nitrochlorobenzene, PM3

Frequency		
Obs.	**Calc.**	**Obs. - Calc.**
675	638	37
No	709	-
741	765	-24
853	852	1
No	889	-
939	No	-
1016	1014	2
1100	1119	-19
No	1138	-
1173	1181	-8
1227	1228	-1
1275 1281	1310	-35 -29
1350 1343	1333	17 10
1481	No	-
1543 1518	1534	9 -16
1585 1577	1557	28 20
1603	1603	0
1656	No	-
1780	1780	0
1914	1896	18
2877	No	-
No	3026	-
No	3029	-
No	3059	-
3091	3062	29

Table XIII-A. Infrared Frequencies (cm^{-1}) of Iodobenzene - PM3

Frequency			Frequency		
Obs.	**Calc.**	**Obs. - Calc.**	**Obs.**	**Calc.**	**Obs. - Calc.**
656	626	30	1438	No	-
685	No	-	1476	No	-
729	747	-18	1577	1539	38
No	764	-	1631	1570	61
882 998	930	-48 58	1727	1773	-46
1016	1012	4	1793	No	-
1061	1015	46	1877	No	-
No	1083	-	1953	No	-
1089	1149	40	2370	No	-
1229	No	-	3028	3064	-36
1260	1294	-34	No	3071	-
1322	1317	5	3076	3078	-2
1377	No	-	No	3084	-

Table XIII-B. Infrared Frequencies (cm^{-1}) of o-Nitroiodobenzene - PM3

Frequency			Frequency		
Obs.	Calc.	Obs. - Calc.	Obs.	Calc.	Obs. - Calc.
640	661	-21	1334	1321	13
697	673	24	1356	1338	18
729	749	-20	1462	No	-
773	766	7	1551 1524	1538	13 -14
No	805	-	1586 1583	1581	5 2
851	833	18	No	1602	-
No	903	-	No	1769	-
952	973	-21	1806	1797	9
1026	1022	4	1925	1897	28
No	1101	-	2898	No	-
1115	1114	1	No	3033	-
1164	1166	-2	No	3054	-
No	1168	-	No	3062	-
1253	No	-	3079	3074	5
1289	No	-			

Table XIII-C. Infrared Frequencies (cm^{-1}) of m-Nitroiodobenzene - PM3

Frequency			Frequency		
Obs.	Calc.	Obs. - Calc.	Obs.	Calc.	Obs. - Calc.
643	612	31	1295	1339	-44
665	666	-1	1344 1381	1346	-2 35
715 725	736	-21 -11	1417	No	-
No	754	-	1458	No	-
800 860	827	-27 33	1516	1549	-33
885	No	-	1564	1573	-9
920	930	-10	1591	1603	-12
No	945	-	No	1770	-
992	965	27	No	1798	-
No	1018	-	No	1896	-
1052	1044	8	3010	3027	-17
1100	1126	-26	No	3034	-
1138	1138	0	3053	3058	-5
No	1177	-	3075	3072	3
1274	1236	38	3092	No	-

Table XIII-D. Infrared Frequencies (cm^{-1}) of p-Nitroiodobenzene - PM3

Frequency			Frequency		
Obs.	Calc.	Obs. - Calc.	Obs.	Calc.	Obs. - Calc.
625	629	-4	1334	1339	-5
670	No	-	1385	1343	42
724	728	-4	1400 1462	No	- -
748	762	-14	1516	1537	-21
832	877	-45	1564	1580	-16
953	No	-	1588	1603	-15
850	885	-35	No	1776	-
1003	1011	-8	No	1789	-
1043	1049	-6	No	1896	-
1096	No	-	3010	3029	-19
No	1148	-	No	3031	-
1170	1150	20	3045	3067	-22
No	1184	-	3070	3070	0
1264	1231	33	3090	No	-
1300	No	-			

Table XIV-A. Infrared Frequencies (cm^{-1}) of Aniline - PM3

Frequency		
Obs.	**Calc.**	**Obs. - Calc.**
664	634	30
745 752	766	-21 -14
874	866	8
No	909	-
985	988	-3
No	1012	-
No	1049	-
1080	1086	-6
No	1125	-
1179 1175	1169	10 6
1273 1277	1328	-55 -51
1314	1369	-55
1502	1553	-51
1564	1580	-16
1620	1679	-59
1691	No	-
1754	No	-
1769	1776	-7
1829	1791	38
1924	No	-
2906	No	-
3047	3052	-5
No	3062	-
3037	3067	-30
3085	3081	4
3229	No	-
3414 3394	3411	3 -17
3498	3532	-34
3855	No	-

Table XIV-B. Infrared Frequencies (cm^{-1}) of o-Nitroaniline - PM3

Frequency			Frequency		
Obs.	**Calc.**	**Obs. - Calc.**	**Obs.**	**Calc.**	**Obs. - Calc.**
568	569	-1	1346	1335	11
No	658	-	1433	1422	11
681	679	2	1523	1548	-25
741 748	758	-17 -10	1579 1575	1552	27 23
No	798	-	1625	1602	23
818	819	-1	1634	1676	-42
868	847	21	No	1752	-
No	890	-	1791	1791	0
No	909	-	1917	1876	41
No	971	-	No	3026	-
1026	1016	10	No	3044	-
1110	1107	3	No	3058	-
No	1119	-	3073	3074	-1
No	1150	-	3300 33484	3336	-36 12
1162	1173	-11	3409	No	-
1243	1238	5	No	3503	-
1263	1260	3	3526	No	-

Table XIV-C. Infrared Frequencies (cm^{-1}) of m-Nitroaniline - PM3

Frequency			Frequency		
Obs.	**Calc.**	**Obs. - Calc.**	**Obs.**	**Calc.**	**Obs. - Calc.**
No	619	-	1357 1346	1350	7 -4
676 670	671	5 -1	No	1402	-
731 739	755	-24 -16	1491	No	-
810	789	21	1544 1569	1562	-18 7
818	823	-5	No	1580	-
868 870	No	- -	1630 1624	1607	23 17
No	915	-	No	1674	-
No	947	-	1740	1772	-32
No	971	-	No	1783	-
No	1010	-	No	1891	-
No	1017	-	2892	No	-
1093	1074	19	No	3018	-
1105	1102	3	No	3055	-
No	1145	-	No	3047	-
No	1171	-	3074	3065	9
No	1188	-	3348	No	-
1268	1260	8	3400 3422	No	- -
1337	No	-	3509	3534	-25

Table XIV-D. Infrared Frequencies (cm^{-1}) of p-Nitroaniline - PM3

Frequency			Frequency		
Obs.	**Calc.**	**Obs. - Calc.**	**Obs.**	**Calc.**	**Obs. - Calc.**
633	626	7	1481	No	-
No	641	-	1503	1554	-51
750	766	-16	1587	1587	0
No	794	-	1597	1605	-8
839 842	849	-10 -7	1631 1641	1677	-46 -36
858	908	-50	No	1757	-
998	961	37	No	1783	-
1000	1009	-9	No	1887	-
1050	1069	-19	No	3025	-
1111	1083	28	No	3028	-
1178	1167	11	No	3052	-
1181	1193	-12	No	3055	-
1295	1222	73	3356	3426	-70
1328	1374	-46	No	3536	-
1471	1402	69			

Table XV-A. Infrared Frequencies (cm^{-1}) of Toluene - PM3

Frequency			Frequency		
Obs.	**Calc.**	**Obs. - Calc.**	**Obs.**	**Calc.**	**Obs. - Calc.**
690	634	56	1796	1800	-4
727	758	-31	1861	No	-
892	907	-15	1946	No	-
919	991	-	2749	No	-
No	998	-	2936	No	-
1035	1034	1	No	3054	-
1073 1057	1045	28 12	3040	3055	-15
No	1103	-	No	3063	-
1214	No	-	3076	3070	6
No	1312	-	No	3078	-
1387	1393	-6	No	3081	-
1498	No	-	No	3171	-
1607	1611	-4			

Table XV-B. Infrared Frequencies (cm^{-1}) of o-Nitrotoluene - PM3

Frequency			Frequency		
Obs.	**Calc.**	**Obs. - Calc.**	**Obs.**	**Calc.**	**Obs. - Calc.**
668	688	-20	1484 1522	1517	-33 5
No	713	-	1544 1580	1568	-24 12
729	735	-6	1613	No	-
784	780	4	1676	No	-
859	850	9	No	1796	-
No	879	-	No	1825	-
No	934	-	No	1855	-
No	959	-	No	1857	-
No	967	-	2887	No	-
No	1002	-	2948	No	-
1048	1048	0	2990	No	-
1091	1095	-4	No	3036	-
No	1128	-	3045	3049	-4
1157	1164	-7	No	3066	-
1207	1230	-23	3079	3077	2
1310	1332	-22	No	3127	-
1359 1348	1349	10 -1	No	3147	-
1385	1398	-13	No	3793	-
1429 1460	1453	-24 7			

Table XV-C. Infrared Frequencies (cm^{-1}) of m-Nitrotoluene - PM3

Frequency		
Obs.	**Calc.**	**Obs.-Calc.**
No	617	-
672	670	2
727 730	752	-25 -22
801	788	13
No	827	-
906	962	-56
No	987	-
No	1000	-
No	1021	-
No	1041	-
1097 1081	1072	25 9
No	1130	-
No	1162	-
No	1179	-
1296 1290	1244	52 46
1358 1314	1335	23 -21
1351	1349	2
No	1390	-
1453	1397	56
1490 1481	1436	54 45
1546 1560	1553	-7 7
1585	1606	-21
1667	1608	59
No	1778	-
No	1793	-
No	1892	-
2885	No	-
2938	No	-
No	3021	-
No	3032	-
3040	3049	-9
3079	3067	12
No	3071	-
No	3078	-
No	3171	-

Table XV-D. Infrared Frequencies (cm^{-1}) of p-Nitrotoluene - PM3

Frequency		
Obs.	**Calc.**	**Obs.-Calc.**
615	628	-13
680	637	43
736 741	759	-23 -18
785 787	790	-5 -3
856 859	866	-10 -7
1019	949	70
1051	1038	13
1109	1152	-43
1181 1179	1177	4 2
1209	1205	4
1232	1239	-7
No	1339	-
1353 1325 1345	1345	8 -20 0
1368	1387	-19
No	1395	-
1415	1438	-23
No	1390	-
1471 1513	No	- -
1539	1542	-3
1603 1597	1605	-2 -8
1654	1617	37
1700	1769	-69
1918	1891	27
2883	No	-
2939	No	-
3013	3028	-15
No	3030	-
3052	3054	-2
No	3058	-
No	3058	-
No	3069	-
No	3079	-
No	3170	-

Chapter 6

SUMMARY

6.1 Quality of Semi-Empirical Calculations

Semi-empirical methods are parametrized on the basis of selected properties for a given set of molecules. Reasonable performance can be expected for related compounds, but problems can remain for molecules not covered by the" training set" and sometimes the reliability is limited. In this respect, even a low-level *ab initio* may be more widely applicable.

6.2 Conclusion

Semi-empirical molecular theory is becoming an increasingly important tool for the study of organic molecules. Both the AM1 and the PM3 methods provide useful accuracy when employed to study physical properties of chemical systems. Although the methods are parametrized to reproduce heats of formation, among other properties, the results of energy calculations are not always completely satisfactory. For some particular systems one of the two methods performs markedly better than the other. The AM1 method gives better results than the PM3 method for the heat of formation, ionization energy, and dipole moment of closed-shell simple aromatic compounds containing C, H, N, and O. This conclusion is based on a comparison of average absolute errors.

The PM3 method calculations of molecular geometry, bond lengths and bond angles give good results. Trends in Infrared frequencies of related aromatic systems are usually reproduced by PM3 calculations. However, errors are random and therefore uncorrectable. In *ab initio* calculations, the calculated infrared frequencies are systematically too high and are corrected by multiplying the calculated values by a correction factor of 0.89.[52]

6.2 Thoughts for Future Work

Taking advantage of the recent developments in the computational facilities including both the hardware components and the software packages, important computational studies can be carried out. Experimentally, the field of organic reactions is widely studied but not well understood. The lack of understanding is mostly related to the kinetics, transition states, reaction paths, different substituents interactions and solvent effects on the reaction. High level computational studies of the chemical reaction are expected to provide, to a good extent, important information about these points.

Directly related to the study of nitration of simple aromatic systems, different computational methods and applications can be employed to study the multi-nitration process under different conditions. *Ab initio* calculations, for example, are expected to provide excellent results when employed to study the energy and the geometrical changes accompanying the transition state of the reaction.

REFERENCES

1. Levine, I. N. *Quantum Chemistry*; 4th ed., Prentice Hall, Englewood Cliffs, N.J., 1991; p 10.

2. Levine, I. N. *Quantum Chemistry*; 4th ed., Prentice Hall, Englewood Cliffs, N.J., 1991; p 10.

3. George, D. V. *Principles of Quantum Chemistry*; Pergamon Press, Elmsford, New York, 1972; p 141.

4. Karplus, M; Porter, R. *Atoms and Molecules: An Introduction for Students of Physical Chemistry*; Benjamin, New York, 1970; p 170.

5. Levine, I. N. *Physical Chemistry*; 4th ed., McGraw-Hill, New York, 1995; p 634.

6. George, D. V. *Principles of Quantum Chemistry*; Pergamon Press, Elmsford, New York, 1972; p 172.

7. George, D. V. *Principles of Quantum Chemistry*; Pergamon Press, Elmsford, New York, 1972; p 161.

8. George, D. V. *Principles of Quantum Chemistry*; Pergamon Press, Elmsford, New York, 1972; p 162.

9. George, D. V. *Principles of Quantum Chemistry*; Pergamon Press, Elmsford, New York, 1972; p 164.

10. Levine, I. N. *Quantum Chemistry*; 4th ed., Prentice Hall, Englewood Cliffs, N.J., 1991; p 357.

11. Levine, I. N. *Quantum Chemistry*; 4th ed., Prentice Hall, Englewood Cliffs, N.J., 1991; p 262.

12. Clark, T. *A Handbook of Computational Chemistry*; Wiley, New York, 1985; p V.

13. Levine, I. N. *Quantum Chemistry*; 4th ed., Prentice Hall, Englewood Cliffs, N.J., 1991; p 587.

14. Lowe, J. P. *Quantum Chemistry*; Academic Press, New York, 1978; p 309.

15. George, D. V. *Principles of Quantum Chemistry*; Pergamon Press, Elmsford, New York, 1972; p 165.

16. Levine, I. N. *Quantum Chemistry*; 4th ed., Prentice Hall, Englewood Cliffs, N.J., 1991; p 462.

17. Levine, I. N. *Quantum Chemistry*; 4th ed., Prentice Hall, Englewood Cliffs, N.J., 1991; p 579-582.

18. Clark, T. *A Handbook of Computational Chemistry*; Wiley, New York, 1985; p 144

19. Levine, I. N. *Quantum Chemistry*; 4th ed., Prentice Hall, Englewood Cliffs, N.J., 1991; p 583.

20. Clark, T. *A Handbook of Computational Chemistry*; Wiley, New York, 1985; p 145.

21. Levine, I. N. *Quantum Chemistry*; 4th ed., Prentice Hall, Englewood Cliffs, N.J., 1991; p 582.

22. Clark, T. In *Recent Experimental and Computational Advances in Molecular Spectroscopy*; Fausto, Ed; Kluwer Academic, Netherlands, 1993; p 370.

23. Sadlej, J. *Semi-Empirical Methods of Quantum Chemistry*; Wiley, New York. 1985; p 2.

24. Levine, I. N. *Quantum Chemistry*; 4th ed., Prentice Hall, Englewood Cliffs, N.J., 1991; p 576.

25. HyperChem,^{TM} *Computational Chemistry*; Hypercube, 1994; p 16.

26. HyperChem,^{TM} *Computational Chemistry*; Hypercube, 1994; p 53 - 55.

27. Stewart, J. J. P. In *Reviews in Computational Chemistry*; Lipkowitz, K. B. ; Boyd, D. B., Eds.; Vol. 1, VCH Publishers, New York, 1990; p 70.

28. Sadlej, J. *Semi-Empirical Methods of Quantum Chemistry*; Wiley, New York, 1985; p 132.

29. Sadlej, J. *Semi-Empirical Methods of Quantum Chemistry*; Wiley, New York, 1985; p 134.

30. Sadlej, J. *Semi-Empirical Methods of Quantum Chemistry*; Wiley, New York, 1985; p 137-138.

31. HyperChem,^{TM} *Computational Chemistry*; Hypercube, 1994, p 48.

32. Sadlej, J. *Semi-Empirical Methods of Quantum Chemistry*; Wiley, New York, 1985; p 265-266.

33. HyperChem,^{TM} *Computational Chemistry*; Hypercube, 1994; p 280 - 283.

34. HyperChem,^{TM} *Computational Chemistry*; Hypercube, 1994; p 283 -285.

35. Zerner, M. C. In *Reviews in Computational Chemistry*; Lipkowitz, K. B.; Boyd, D. B., Eds.; Vol. 2, VCH Publishers, New York, 1991; p 325.

36. Stewart, J. J. P. In *Reviews in Computational Chemistry*; Lipkowitz, K. B.; Boyd, D. B., Eds.; Vol. 1, VCH Publishers, New York, 1990; p 75.

37. Liberles, A. *Introduction to Theoretical Organic Chemistry*; Macmillan, New York, 1968; p 423.

38. Loudon, G.M. *Organic Chemistry*; 2nd ed., Benjamin, California, 1988.

39. Liberles, A. *Introduction to Theoretical Organic Chemistry*; Macmillan, New York, 1968; p 439-440.

40. Liberles, A. *Introduction to Theoretical Organic Chemistry*; Macmillan, New York, 1968; p 452-456.

41. Personal communication from Joan Sauerwein, National Institute of Standards and Technology, August 1996. The same spectra are available from the *NIST/EPA Gas Phase Infrared Database*.

42. Daubert, T. E.; Danner, R. P. *Physical and Thermodynamic Properties of Pure Chemicals*, 1989, Hemisphere, New York.

43. *NIST Chemistry WebBook* at http://webook.nist.gov/chemistry/form-ser.html, August 1996. The following three references were cited as the original data sources: Pedley, J.B.; Rylance, J. *Computer Analyzed Thermochemical Data: Organic and Organometallic Compounds*, University of Sussex,

Brighton, England, 1977. Stull, D. R.; Westrum, Jr, E. F.; Sinke, G. C. *The Chemical Thermodynamics of Organic Compounds*, John Wiley, New York, 1969. Lias, S. G.; Bartmess, J. E.; Liebman, J. F.; Holmes, J. L.; Levin, R. D.; Mallard, W. G. *J. Phys. Chem. Ref. Data* **1988** 17, Supplement 1.

44. Stewart, J. J. P. In *Reviews in Computational Chemistry*; Lipkowitz, K. B.; Boyd, D. B., Eds.; Vol. 1, VCH Publishers, New York, 1990; p 71.

45. Nelson, R. D.; Lide, D. R.; Maryott, A. A. *Selected Values of Electric Dipole Moments for Molecules in the Gas Phase*, Washington, D.C., NSRDS-NBS 10, 1967.

46. Stewart, J. J. P. In *Reviews in Computational Chemistry*; Lipkowitz, K. B.; Boyd, D. B., Eds.; Vol. 1, VCH Publishers, New York, 1990; p 72.

47. Stewart, J. J. P. In *Reviews in Computational Chemistry*; Lipkowitz, K. B.; Boyd, D. B., Eds.; Vol. 1, VCH Publishers, New York, 1990; p 69.

48. *Butterworths Working Atlas of Infrared Spectroscopy*, Buttersworth, London, 1972.

49. Szymanski, H. A. *Infrared Band Handbook*, Plenum, New York, 1963.

50. Pochert, C. J. *The Aldrich Library of FTIR Spectra*, Ed. I, Volume 1 and 2, Aldrich, Wisconsin, 1985.

51. Shabbir, A; Mathew, S; Verma, P. K. *Indian Journal of Pure & Applied Physics* **1993** 31, 395.

52. Foresman, J. B; Frisch, E *Exploring Chemistry with Electronic Structure Methods*, 2nd ed; Gaussian, Pittsburgh, 1996.

APPENDIX A

GLOSSARY

Austin Model 1 (AM1)	the most recent generation of semi-empirical methods devised by Dewar at the University of Texas, Austin. Generally it is one of the most accurate semi-empirical methods. It is an improvement over MNDO where it includes some changes in its theoretical framework as the function describing repulsion between atomic cores, and it assigned new parameters to improve the performance. Advantages: it deals with hydrogen bonds properly, produces accurate predictions of activation barriers for many reactions and predicts heats of formation of molecules with a smaller error than MNDO.
Atomic Orbital (AO)	the wavefunction of an electron in an atom. Its square gives the probability of finding the electron at each point.
Basis Set	a collection of atom-centered functions from which delocalized molecular orbitals are constructed.
Complete Neglect of Differential Overlap (CNDO)	assumes that the atomic orbital basis functions do not overlap. The electron repulsion between electrons in different orbitals depends only on the nature of the atoms involved, and not on the particular orbital. This creates a very simple picture. One of its disadvantages is that because it neglects almost all exchange integrals, thus this method cannot calculate differences between states of differing multiplicity arising from the same electronic configuration.
Coulomb Integral (J)	is the contribution of the classical Coulombic interaction between charge distributions to the total energy of an atom or molecule. The total electrostatic interaction between two electrons. It is calculated by summing the interactions between the electron densities in two volume elements.
Degeneracy	different states having the same energy.
Gaussian Type Orbital (GT	a mathematical expression that has the functional form e^{-ar^2}. It is used to simplify the calculations of the electron-electron interaction integrals that must be evaluated. The integrals are on up to 4 centers over atomic orbitals.

Hessian	the matrix of second derivatives of the energy with respect to the 3N - 6 geometrical coordinates.
Highest Occupied Molecular Orbital (HOMO)	highest energy occupied molecular orbital. Its energy equals the negative of the ionization energy of the system.
Intermediate Neglect of Differential Overlap (INDO)	developed after CNDO. Corrects some of It can deal with spin effects.
Linear Combination of Atomic Orbitals (LCAO)	an approximation expresses a molecular orbital as a sum of atomic orbitals centered each nucleus. Thus, the σ and σ^* orbitals of the H_2 molecule are expressed as a superposition of the two H 1s orbitals. In general, superposition of n atomic orbitals will yield n molecular orbitals. If ψ_i represents a molecular orbital and ϕ_μ an atomic orbital, then the LCAO representation of molecular orbital is: $\psi_i = {}_\mu\Sigma \; C_{\mu i} \; \phi_\mu$ where $C_{\mu i}$ is the coefficient of the μ'th AO in the i'th MO.
Lowest Unoccupied Molecular Orbital (LUMO)	lowest energy unfilled molecular orbital. The LUMO energy is equal to the negative of the electron affinity of a molecule.
Modified Intermediate Neglect of Differential Overlap (MINDO)	Less draconian than complete neglect, differential overlap between orbitals on the same atom is not neglected in one-center electron-electron repulsion integrals but it is neglected in two-center electron-electron repulsion integrals. The remaining integrals are estimated.
Molecular Mechanics (MM)	the structure and the molecular energy of a molecule are regarded as the result of classical mechanics operating, through the medium of chemical bonds, on the connected masses of the atoms making up the molecule.
Modified Neglect of Diatomic Overlap (MNDO)	a modification of NDDO where various terms are not evaluated analytically. Rather some terms are determined from semi-empirical expressions that contain parameters that are adjusted to fit experimental data.

Molecular Orbitals (MO)	function that is declocalized over the entire molecule and is formed from the valence orbitals. In general, *n* atomic orbitals overlap to form *n* molecular orbitals.
Neglect of Diatomic Differential Overlap (NDDO)	the basis for MNDO, AM1, and PM3. Neglects differential overlap only when atomic orbitals are on different atoms. It retains all one-center differential overlap terms when Coulomb and exchange integrals are computed.
Orbital	the wavefunction for a single particle.
Overlap Integral	the overlap of two normalized wavefunctions is a measure of the mutual resemblance and coincidence of the two functions, $\int \psi_1^* \psi_2 \, d\tau$.
Parametrized Method 3 (PM3)	differs from AM1 only in the values of the parameters. Its parameters were derived by comparing a much larger number and wider variety of experimental versus computed molecular properties. It was initially used for organic molecules, but has now been parametrized for many main group elements.
Pople, Parr, Pariser (PPP)	quantum mechanical method introduced by Pople, Parr, and Pariser to interpret the conjugated and aromatic systems the method improves the Huckel scheme by considering electron-electron interactions.
radial node	the point where the probability of finding the electron is zero, $\psi=0$. Usually for s orbitals, ns orbital have ns-1 radial nodes.
resonance integral	takes into account that the electron is not restricted to a specific orbital on either atom, but that it can exchange places between two orbitals.
Slater Type Orbital (ST	a mathematical expression involving a function of the form e^{-ar} used to simplify the calculations of the electron-electron interaction integrals that must be evaluated.

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