ALGORITHM TO GENERATE GUESS STRUCTURES FOR TRANSITION STATE OPTIMIZATION AND COMPUTATIONAL STUDY OF N-HETEROCYCLIC CARBENE CATALYZED AEROBIC OXIDATION OF ALDEHYDES WITH PHENYL BORONIC ACID

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"Protons give an atom its identity, electrons its personality."

- Bill Bryson, A Short History of Nearly Everything

Certificate of Examination

This is to certify that the dissertation titled **Algorithm to generate guess structures for transition state optimization and computational study of N-Heterocyclic Carbene catalyzed aerobic oxidation of aromatic aldehydes with phenyl boronic acid** submitted by **Ms. Rupali Chawla (Reg. No. MS10074)** for the partial fulfilment of BS-MS dual degree programme of the Institute, has been examined by the thesis committee duly appointed by the Institute. The committee finds the work done by the candidate satisfactory and recommends that the report be accepted.

Professor K. S. Viswanathan	Dr. R. Vijaya Anand (Supervisor)	Dr. P. Balanarayan (Supervisor)

Dated: April 24, 2015

Declaration

The work presented in this dissertation has been carried out by me with Dr. P. Balanarayan and Dr. R. Vijaya Anand at the Indian Institute of Science Education and Research Mohali. This work has not been submitted in part or in full for a degree, a diploma, or a fellowship to any other university or institute. Whenever contributions of others are involved, every effort is made to indicate this clearly, with due acknowledgement of collaborative research and discussions. This thesis is a bonafide record of original work done by me and all sources listed within have been detailed in the bibliography.

Rupali Chawla
(Candidate)
Dated: April 24, 2015

In my capacity as the supervisor of the candidates project work, I certify that the above statements by the candidate are true to the best of my knowledge.

Dr. R. Vijaya Anand	Dr. P. Balanarayan
(Supervisor)	(Supervisor)

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Abbreviations

TS	**T**ransition **S**tate
PES	**P**otential **E**nergy **S**urface
MEP	**M**inimum **E**nergy **P**athway
IRC	**I**ntrinsic **R**eaction **C**oordinate
NHC	**N**ucleophilic **H**eterocyclic **C**arbenes
HF	**H**artree **F**ock
B3LYP	**B**ecke, three-parameter, **L**ee-**Y**ang-**P**arr)
amu	**a**tomic **m**ass **u**nits
au	**a**tomic **u**nits

Dedicated to my parents.
For their endless love, support and encouragement

Abstract

An accurate understanding of any reaction mechanism is obtained by vividly understanding its minima, intermediates, transition states along with the complete reaction pathway. Experimental studies often need computational collaboration to provide an affirmation for any chemical reaction. Where one part of the thesis focuses on developing an algorithm for finding guess structures of transition states, the second part is about computational study of an organic reaction.

Using the vibrational description of pre reaction complex and product, an harmonic oscillator approximation is created at each minimum. The region where these potentials intersect provide an approximation for the transition state structure of the corresponding reaction.

The second problem is concerned with the computational study of Nucleophilic Heterocyclic Carbene catalysis. In the presence of these NHCs,under aerobic conditions, aromatic aldehydes have been experimentally known to undergo esterfication with boronic acids. Using first principles, we analyse the mechanism for this reaction.

Chapter 1

Algorithm To Generate Guess Structures For Transition State Optimization

1.1 Introduction

Exploration of potential energy surfaces for reaction mechanisms has been a rather pronounced area in the field of chemical dynamics. A familiar picture of the reactants going up the hill to reach a transition state and then going downhill from there to form products simplifies the dynamics of a chemical reaction to a great extent.(see figure1.1)

The reaction is said to follow a minimum energy path on the potential energy surface, along the 'intrinsic reaction coordinate', the term first introduced by Fukui[1]. He defined the intrinsic reaction coordinate as "a curve passing through the initial and the transition points and orthogonal to energy equipotential contour surface". Minimum Energy Path, by name, suggests a path on the PES which goes through the minimum energy barrier. The highest point on this path is termed as a transition state. Contrary to a minimum, a TS is a first order saddle point which is maximum in one direction and minimum in all the other.

A potential energy surface can be constructed by a quadratic approximation of the

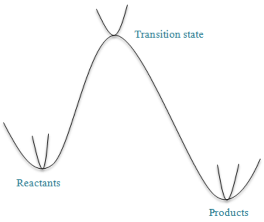

FIGURE 1.1: Minimum Energy Pathway followed by the reaction

energy function.

$$E(x) = E(x_o) + g_o^T \Delta x + \frac{1}{2}\Delta x^T H_o \Delta x \tag{1.1}$$

where g_o is the gradient at x_o, H_o is the Hessian at x_o and $\Delta x = x - x_o$. The Hessian and the gradient provide a great deal of information about the stationary points on the PES. The resultant vector of forces on all the atoms in a molecule is given by the negative of gradient. As the minima and TS are stationary points, the forces (or gradient) are zero at these points. Hessian, also known as the force constant matrix, is the second derivative of energy with respect to x. The eigen vectors of mass weighted Hessian in Cartesian coordinates correspond to the normal modes of vibration. For a minimum, alongside the condition that gradient must be zero, the eigen values of the Hessian must all be positive. This implies that all vibrational frequencies are real.
TS is characterized by a negative eigen value corresponding to an eigenvector of Hessian matrix. Minimum energy path alternatively can be defined as the path followed by this particular eigenvector of the Hessian matrix.[2]

1.1.1 Algorithm for Geometry Optimizations

Optimization algorithms for finding stationary points have been studied and reviewed numerous times.[3, 4] The algorithms found focus on mainly three things : effective computation of gradients and Hessian, choice of a coordinate system and step size control. Depending on the available cost of computation, analytical or numerical derivatives can be calculated. Choice of a good coordinate system can significantly improve geometry optimizations. The elements of Hessian matrix usually give an idea about the ease of geometry optimization.Comparable magnitude of diagonal and off diagonal terms refer to strong coupling between atoms thus making Cartesian coordinates a poor choice of coordinate system. Similarly a mixture of some very large and some very small eigenvalues refer to a combination of very flexible and stiff coordinates making optimization difficult. In such circumstances, internal coordinates are considered best for the purpose of geometry optimization. The computation of a TS is more rigorous than computation for a minimum. Quadratic approximation of the PES works well around the region of stationary points, however away from the region the approximation does not hold good. Thus step size at every optimization step must be constrained in order to make sure that the structure converges to a stationary point.

1.1.1.1 Newton methods

Differentiating 1.1 wrt the coordinates yields

$$g(x) = g_o + H_o \Delta x \tag{1.2}$$

with g(x)=0 at a stationary point this equation is used to calculate Hessian at the given point. This method is defined as the Newton method. For quasi-Newton method the Hessian is approximated at each step which is cheaper than exact Hessian computation. Potential energy surfaces are almost never quadratic thus only with an efficient step size control, can one achieve the desired stationary point in multiple steps.

1.1.1.2 Conjugate gradient methods

Conjugate gradient method searches for the next step in the direction conjugate to the old one with respect to the Hessian.

$$\Delta x^{new} H \Delta x^{old} = 0 \tag{1.3}$$

The new direction is searched for with the aim of lowering the energy while keeping the whereabouts of minimum point similar to the previous direction. The method searches for the next direction , rather than the next step. Thus, unlike newton methods, it requires a line search. Linear search proves to be useful in case of anharmonicity in

PES. Quadratic approximation may not prove to be a very useful method near the anharmonic regions.

1.1.1.3 GDIIS

Geometry optimization by direct inversion of iterative subspace (GDIIS) constructs a new geometry as a linear combination of previous geometries, which leads to minimization of Δx.

$$x^* = \sum_i c_i x_i \qquad g^* = \sum_i c_i g(x_i) \qquad \sum_i c_i = 1 \tag{1.4}$$

here we minimize $|x^{new} - x^*|^2$ with respect to c_i. The method works with quadratic approximation and thus a combination of GDIIS and quasi-newton method proves to be most efficient for geometry optimizations.

1.1.2 Transition State Optimization

Following a path on PES to obtain one negative eigen value of Hessian is usually a more tiring process than looking for a minimum. The optimization should necessarily proceed uphill in one direction and downhill in all the other direction. Therefore, the initial guess of Hessian becomes very important in quadratic search. Synchronous Transit methods are usually combined with quasi newton methods to generate appropriate guess for TS structures.[5] Linear synchronous transit methods (LST) does a line search from reactants to products and the point with maximum energy along the line is taken as an initial guess for TS structure. In Quadratic Synchronous transit (QST), a parabolic path is made between the reactant and product and a maximum energy structure along this parabola is taken to be an initial guess of TS. Apart from this, the eigen vector following method has also proven efficient for generating an initial guess.The Hessian here is divided into two parts, where one set of coordinates searches for maximum in one direction and the other set search for minima in all the other directions. There can be two types of approach in order to look for TS. They are described below.

1.1.2.1 Single ended methods

These methods take an initial structure and move uphill from there to look for TS. These include Newton and Quasi-Newton methods, GDIIS and conjugate gradient method. They are combined with either synchronous transit methods or eigen vector following for the purpose of generating a guess.

1.1.2.2 Double ended methods

Methods included here generally optimize the entire reaction path in order to look for the saddle point. A series of points are generated , also known as chain of states, and the differences in these methods lie in how the points are generated.
The elastic band method takes a set of points and minimize their total energy.

$$V^{path} = \sum E(x_i) \tag{1.5}$$

An improvement over this method has been made by introducing additional potential between the x_is. The Nudged Elastic Band (NEB) method uses a spring potential between two consecutive points to prevent the path from collapsing to a minimum.

$$V^{spring} = \frac{1}{2} k^{spring} \sum (x_i - x_{i-1})^2 \tag{1.6}$$

Similarly there are doubly NEB method, string method , growing string methods among others.

Some of the above optimization algorithms are used in *Gaussian* in order to simplify the procedure of mechanistic studies of various organic/inorganic reactions. An accurate understanding of any reaction mechanism is obtained by completely understanding its minima structures, intermediates, transition states along with the complete reaction pathway. Experimental studies often need computational collaboration to provide a vivid explanation of the reaction. Where one part of the thesis has work on an algorithm for finding guess structure of transition state, the second part is about mechanistic study of an organic reaction.

1.2 Methodology

The method studied here has a very simple idea. The aim was to be able to construct a guess structure geometry which when optimized would lead to the actual TS. A good starting guess point has always been of importance while starting TS search. Before starting, the complete information regarding minima points on reaction pathway was obtained. The computation of energies, gradient and full Hessian matrix with all positive eigen values was done. As explained above in chapter 1, along the reaction pathway one and only one eigen vector leads to a TS. The vibration (or eigen value) corresponding to this eigen vector indicates the major bond breaking/making for the reaction. Therefore all the 3N-6 modes of vibration (3N-5 for linear molecule) were visualized to look for the mode which seems to be leading to the other respective minimum. With the vibrational data of this particular mode in reactant and product, an harmonic oscillator potential was plotted. The following equations were formulated :

$$U - U_R = \frac{1}{2}k_R(X - (R + \Delta R))^2 \tag{1.7}$$

$$U - U_P = \frac{1}{2}k_P(X - (P + \Delta P))^2 \tag{1.8}$$

where U_R and U_P are minimized energies of reactant and product respectively. Similarly k_R and k_P are force constants of the vibrational mode in consideration. Looking into the equations, the terms $R+\Delta R$ and $P+\Delta P$ refer to the position of the molecule along with their displacement vectors (denoted by the Δ term). The displacement vector would point towards the direction in which the reaction would proceed. X here refers to the coordinate system used to represent the minima. In case of Cartesian coordinates there would be three set of equations for X, Y and Z coordinates.similarly, for internal coordinates a set of 3N-5 equations would be solved. Solving 1.7 and 1.8 simultaneously, the following equation is obtained :

$$X^2(k_R - k_P) - 2X[k_R(R+\Delta R) - k_P(P+\Delta P)] + [k_R(R+\Delta R)^2 - k_P(P+\Delta P)^2] + 2(U_R - U_P) = 0 \tag{1.9}$$

Upon solving this simple quadratic equation, we obtained a set of coordinates which gave us an approximate geometry of the TS. Figure 1.2 shows the basic schematic of the the idea described above. If the equations were to be solved in Cartesian coordinates, we would obtain 3N set of equations, with two solutions for each equation. For

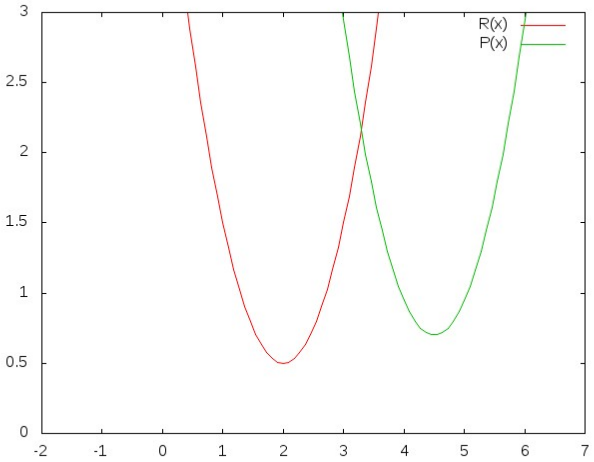

FIGURE 1.2: Basic schematic of the algorithm

internal coordinates, 3N-6 (or 3N-5) set of equations.

1.2.1 The Beginning

The work was started with taking two simple model reactions and back calculating their TS from *Gaussian09* calculations of the reaction. The two reactions were ammonia inversion and diels alder reaction.

1. AMMONIA INVERSION The reaction of dipole reversal of ammonia is a very familiar example. It is known to pass through a planar TS (Figure 1.3). The irc for the reaction was calculated on *Gaussian09*. The symmetric bending mode of the Hydrogens in the ammonia molecule was taken as the vibrational mode which led us to the inversion of the molecule.

   Simplified version of equations 1.7 and 1.8 was used :

$$U - U_R = \frac{1}{2}k_R(X - R)^2 \tag{1.10}$$

$$U - U_P = \frac{1}{2}k_P(X - P)^2 \tag{1.11}$$

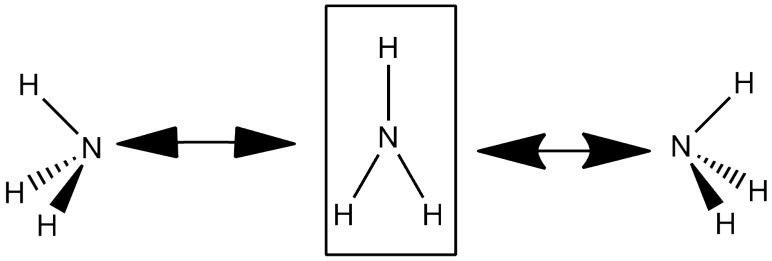

FIGURE 1.3: Ammonia Inversion

The harmonic oscillators were constructed on the minima points with 1.10 and 1.11 (Figure 1.4). The X in the concerned equations is the reaction coordinate calculated in G09. (Refer appendix A for the derivation)

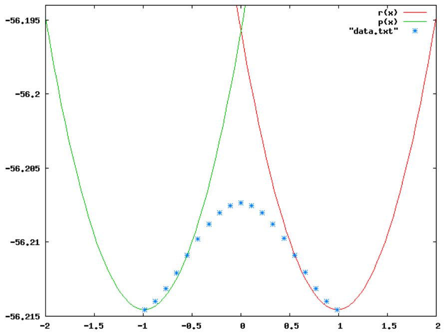

FIGURE 1.4: The dotted line shows the irc of ammonia calculated in G09 at 6-311+g(d,p). the green and the red curve refers to harmonic oscillator constructed on the IRC to get an intersection point.

1.2.2 HCN Isomerization

The HCN isomerization reaction was worked out in detail for generating a guess structure for its TS.

$$\mathrm{HCN} \rightleftharpoons \mathrm{HNC}$$

The chemical species Hydrogen Cyanide and Hydrogen Isocyanide were optimized in G09 at Hartree Fock(HF) level with STO-3G basis set. The four vibrational modes in HCN and HNC were visualized(Figure 1.5). The mode in a) , b) part of figure 1.5 were believed to be leading to the isomerization. The equations 1.7 and 1.8 were solved

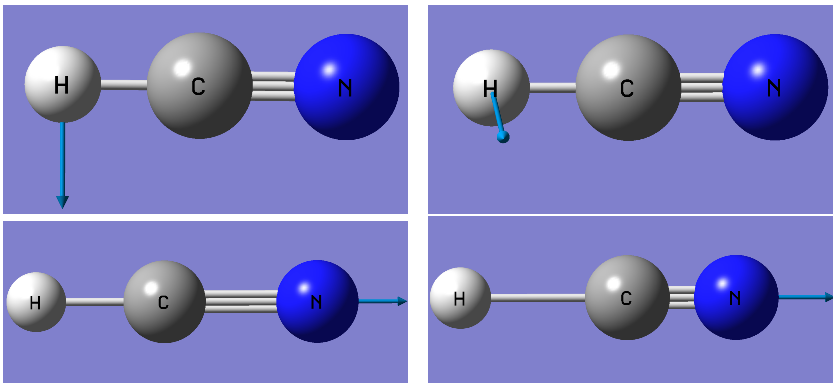

FIGURE 1.5: Four vibrational modes of HCN and HNC : a),b) wagging mode in x and y direction c) symmetric stretch d)asymmetric stretch.

in Cartesian coordinates for the system. Thus for three atom system, 9 simultaneous equations like 1.9 were formed. The Cartesian coordinates were in Å. However the vibrational modes displacement vectors (defined by Δ terms in the equations) were defined as normal coordinates. Normal coordinates by definition are mass weighted Cartesian coordinates with units Å$*amu^{-1}$. These were converted to Å. For the detailed solution refer to appendix B.

1.3 Results and discussions

Referring to the calculations done in Appendix A for ammonia inversion reaction, the back calculation for finding the location of TS was successful. The error was almost negligible giving us the affirmation to proceed with a fully detailed solution of a model reaction.

1.3.1 HCN Isomerization

Referring to B, different combinations of the coordinates were plotted in GaussView to look for a meaningful guess structure. One of the combination gave a very close approximation to the TS structure. (Figure 1.6) The internal coordinates of the calculated guess structure were compared to that of the optimized structure. The results are summarized in Table 1.1

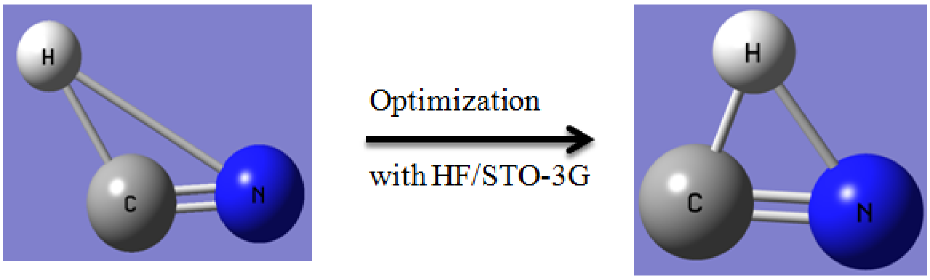

FIGURE 1.6: The left side shows the guess structure generated with the set of coordinates found. It was then submitted for optimization in G09 at HF/STO-3G level. The structure optimized within 6 convergence cycle giving an optimized TS.

Internal coordinates of HCN		
Interatomic Distance	Guess Structure	Optimized TS
R(C,H)	1.47	1.20
R(N,H)	2.28	1.44
R(C,N)	1.19	1.22

TABLE 1.1: The comparison of interatomic distances for the found guess structure and the optimized TS structure. Units : R (in Å)

1.4 Conclusion

The back calculation of ammonia inversion reaction from Gaussian computation gave the confirmation for the idea proposed for the algorithm. The successful generation of a guess structure for the model reaction of HCN isomerization gave affirmation for the validity of the method.

However, in case of higher number of atoms there could be more than one vibrational mode of the minima structure which together leads to a TS. In such cases, finding an appropriate combination of the involved degrees of freedom would be extremely important.

Continuing in the area of chemical dynamics, the next section describes the second project of the thesis. The work involved finding of the reaction pathway of esterification of aromatic aldehydes with phenyl boronic acid using N-Heterocyclic Carbene as organocatalyst.

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Chapter 2

Computational Study of Aerobic Oxidation of Aromatic Aldehydes with Phenyl Boronic Acids

2.1 Introduction

The scope of nucleophilic heterocyclic carbenes (NHCs) has been extensively studied in organocatalysis as well as organometallic chemistry.[1–4]The reaction of NHC with electrophilic aldehydes results in the polarity reversal of the carbonyl carbon leading to the formation of **Breslow intermediate** with a nucleophilic character. The reactions with such polarity reversal are referred to as umpolung reactions. One of the earliest evidence of nucleophilic carbenes used in polarity reversal of aldehydes was in Benzoin condensation reaction.[5]Formation of Breslow intermediate leads to a variety of unconventional reactions.[6] Recent advances include the oxidative reaction of aryl aldehydes to acids or esters under aerobic conditions.[7–10]Some of the examples include conversion of halogenated aldehydes in the presence of NHCs to halo-esters, reaction of alkyl/aryl alcohols with aldehydes to produce esters, reduction of carbon-dioxide to carbon monoxide with aromatic aldehydes acting as oxygen acceptor.

In 2012, Arde et. al. reported NHC catalyzed oxidative esterification of aldehydes with boronic acids under aerobic conditions.[11]The reaction provided an excellent way of ester generation without the use of metal catalysts. The reaction scheme is

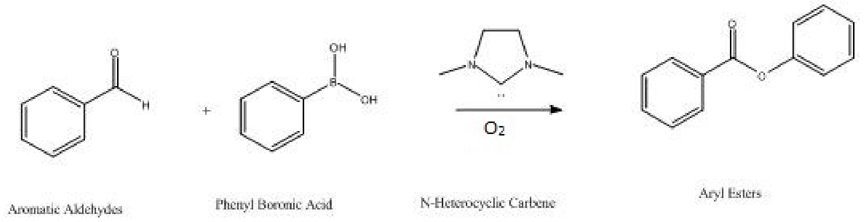

Figure 2.1: The reaction scheme for aerobic oxidation mechanism

given in figure 2.1. Following this, a detailed mass spectrometric study was conducted to look for a concrete mechanism for generation of acids or esters from aromatic aldehydes.[12]Two commonly proposed reaction pathway named as oxygenation (forming acids) and oxidation (forming esters) were studied with mass spectrometry techniques. The charge tagged NHC was used to detect intermediates formed within the mechanism. Following this, Bortolini et. al. proposed a mechanism indicating formation of zwitterionic radical species.(See figure2.2)It was the first time, that a radical species formation was proposed in such reactions. However, a mechanistic study for the aerobic oxidation pathway with NHC which could infact answer the fate of the reaction, is not yet known. This project attempts to provide a computational study of figure 2.1 in *Gaussian09* software using first principles.

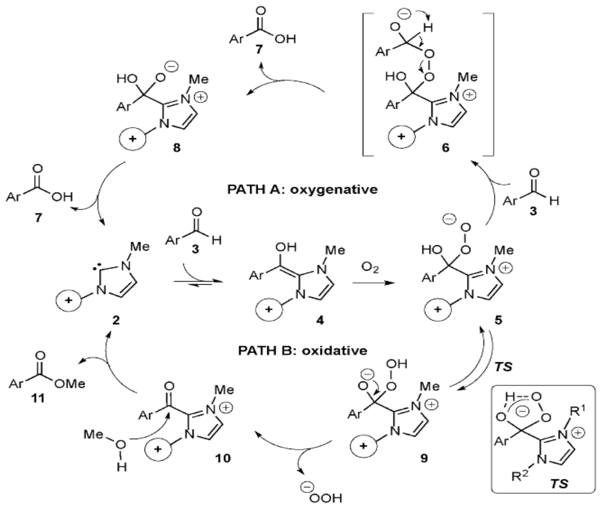

Figure 2.2: On the basis of detection of intermediates with mass spectrometry technique, a mechanism was proposed for the oxidation of aldehydes to acids/esters

2.2 Methodology

A model reaction with the simplest possible reactants was taken for the calculation purposes (see 2.1). *Gaussian09* software was used for the computational study. The aim of the project was to look for a MEP on the PES of the reaction. The calculations were started with Hartree Fock (HF) method with Slater Type Orbital (STO-3G) basis set. STO-3G is of the category of a minimal basis sets, that is, it uses a minimum number of required basis sets for each atom in the molecule. These basis functions are of Slater Type orbital (hence the part ”STO”) each of which are made from 3 contracted primitive Gaussian function (hence the part ”3G”). Because of the small number of functions used, the results are usually inaccurate. However, the depiction of chemical structures and bonding in a qualitative manner can still be obtained. Therefore, the calculations were started with STO-3G in order to obtain a rough estimate of the reaction pathway. Following input file serves as the prototype for the calculations performed:

```
%mem=5GB
%nprocshared=20
%chk=checkpoint_file.chk
#opt=(ts,calcall,noeigentest) hf/sto-3g

Title Line

0 1
Full Cartesian coordinates of all the atoms
```

Further, the calculations were carried out with a hybrid functional B3LYP along with 6-31G(d) basis set. The hybrid functional combines exchange correlational energy from density functional theory along with exact exchange energy from HF theory. The method is of a significant advancement from just HF theory, thus usually gives a more accurate picture of the chemical interactions. Increasing the complexity of basis set to 6-31G(d) (or 6-31G*) incorporates polarization effects on the orbitals involved thus improving the calculated chemical properties of the atoms. The inner shell orbitals here are a combination of 6 contracted *d* type functionals for atoms with unoccupied d orbitals. For incorporating the valence orbital effect, the outer shell orbitals are made of 3 contracted Gaussians with 1 uncontracted Gaussian function. Hence the name, 6-31G(d).

Following is the prototype input file nsubmitted to G09 software:

```
%mem=5GB
%nprocshared=10
%chk=checkpoint_file.chk
# opt=(calcall,ts,loose,noeigentest) b3lyp/6-31g(d)

Title Line

0 1
Full Cartesian coordinates of all the atoms
```

The mechanisms proposed in the experimental organic literature([11, 12]) served as the starting point for our guess structures. Using the software *GaussView*, the chemical structure of the first proposed TS was drawn and calculations were started on the same. Upon obtaining a TS, an IRC calculation in G09 was performed which led to the pre reaction complex and the first intermediate. Following that, this first intermediate (with a few changes in geometry) served as the starting point for the second transition state calculation. The similar procedure was followed in both the methods until a meaningful TS with a high enough negative frequency was obtained for each barrier. Chemical species throughout the reaction were either neutral or in the form of zwitter ions thus the charge in input *Gaussian* file was set to zero. Further, in accordance with the popular belief of anionic/cationic intermediates, the spin multiplicity was taken to 1, that is, all the species were assumed to exist in the singlet state. The reaction was found to have multiple steps, leading to more than one transition state. The detailed mechanism is discussed in the following section.

2.3 Results and discussions

HF/STO-3G calculation results were not archived due to their lack of accuracy in chemical depictions. However, the structures optimized were used as the guess structures for starting B3LYP calculations. The structure submitted for the first TS did not optimize with the default convergence criteria of *Gaussian*. The enrgy for the first TS kept on optimizing. The calculations were then performed with the keyword "loose", implying the convergence criteria being set to a very low threshold. The reaction mechanism obtained did not give the desired product as produced in the experimental studies.[11](Figure 2.3) The reaction started with interaction of **I** with **II** forming Breslow intermediate (**III**). Followed, the interaction of **III** with molecualr oxygen forming a peroxy linkage in **IV**. The species existed in the form of Zwitter ion. The first transition state (**V**) indicated the migration of H from the hydroxy group in Breslow intermediate to the peroxy group attached to the activated carbon forming **IV**. Following step was the attachment of **VII** to **VI** to form an intermediate **VIII**. The second transition state (**IX**) was the insertion of B between the peroxy

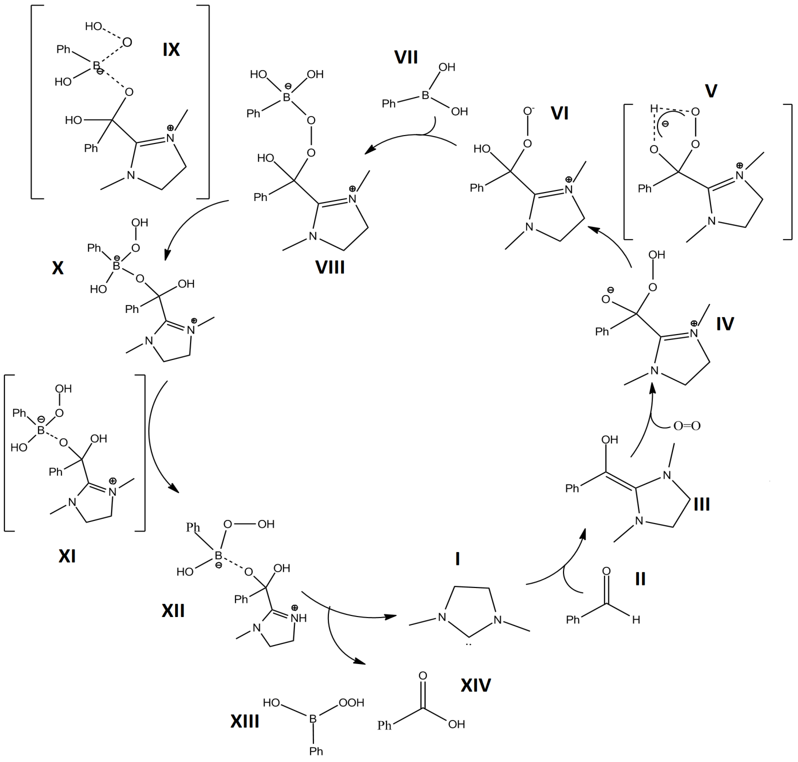

FIGURE 2.3: The mechanism for for the aerobic oxidation of benzaldehyde with methyl substituted N-Heterocyclic Carbenes.

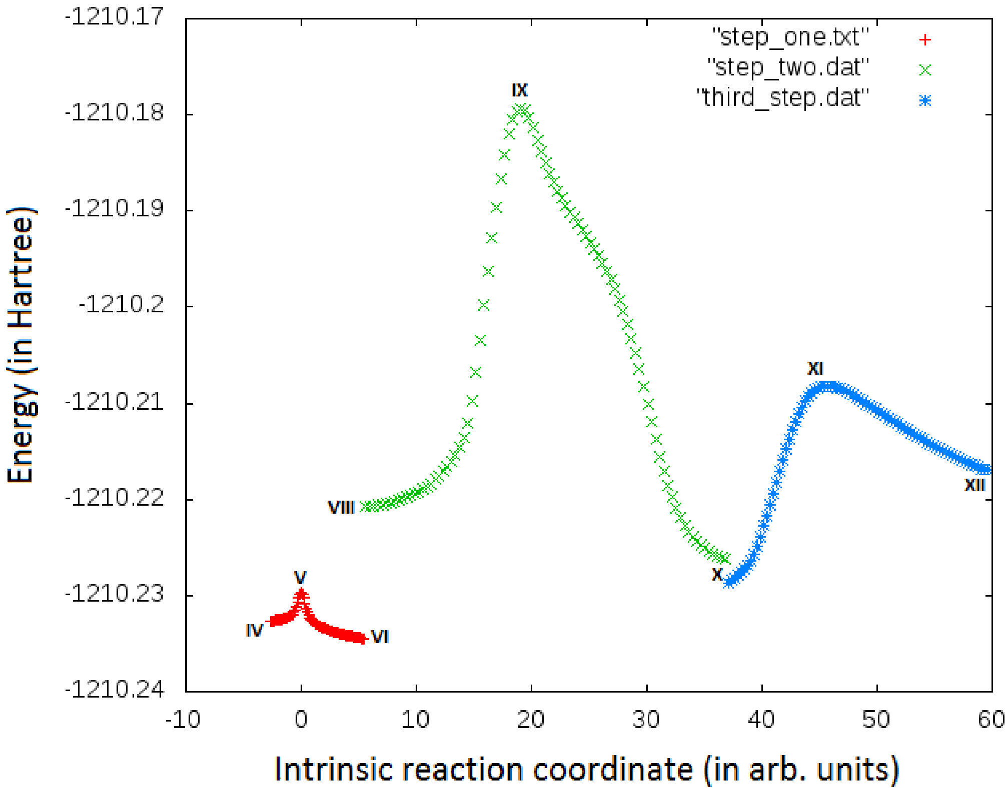

Figure 2.4: The minimum energy pathway for the mechanism. The numbering indicated on the curves for the minima, intermediates and transition states is consistent with figure 2.3.

linkage together with insertion of one the oxygen atom in B–O bond, thus forming another peroxy linkage (**X**). The consecutive transition state **XI** took the reaction in the direction of detachment of one of the B–O bond formed in the previous step giving the intermediate **XII**. XII then further dissociated into **XIII** and **XIV** giving back the NHC **I**. The IRC for the given mechanism is shown in figure 2.4. The reaction coordinates have been scaled in order to create a continous reaction pathway.
The energy differences between the minima and the following transition states were calculated. The energy hierarchy of the steps is shown in figure 2.5.

2.4 Conclusion

The mechanism given in figure 2.3 was not in coherence with the experimental studies.[11] There could have been a number of reasons for the same.

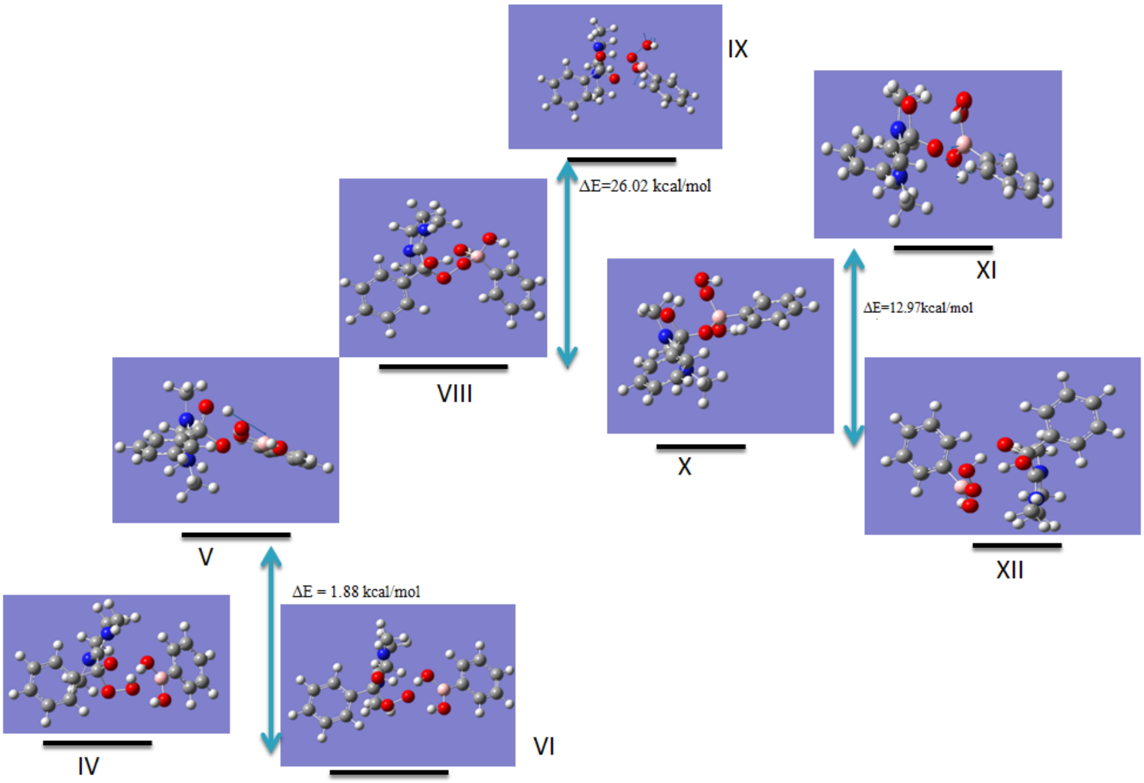

FIGURE 2.5: The energy hierarchy along with the snapshots of the structures at each point.

1. The reactivity of NHCs depend greatly on the substituents attached to the Nitrogen atoms. A bigger and bulkier group could have provided the necessary steric hindrance for the reaction to proceed towards esterification.

2. Benzaldehyde gave a good amount of yield in the experimental studies [11]. However, it is experimentally known that electron deficient aldehydes react at a faster rate. Therefore attaching a electron withdrawing group at -*ortho* or -*para* position of the phenyl ring could have facilitated the mechanistic studies by making the phenyl ring shift easier.

3. Bortolini et. al. proposed a mechanism with radical intermdeiates. Thus the spin multiplicity for these structures, if calculated, would be triplet.[12] Perhaps performing calculations with intermediates in triplet change would change the reaction pathway leading to esterification of the aldehydes.

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Appendix A

The symmetric bend of ammonia molecule was taken as the vibrational mode. Values from G09 optimized files were used in 1.10 and 1.11.
k_R = 0.7137 mDyne $\mathring{A}^{-1}$
k_P = 0.7096 mDyne $\mathring{A}^{-1}$
R = -0.98824 and P = 0.98824 (in atomic units)
Substituting these in the equation,

$$U = \frac{1}{2}(0.7137)(X + 0.98824)^2 \tag{A.1}$$

$$U = \frac{1}{2}(0.7096)(X - 0.98824)^2 \tag{A.2}$$

Being the same molecule, $U_R = U_P$

$$X = -0.00143$$

$$X^{ref} = 0.000$$

Therefore, error in X is

$$\Delta X = 1.43 * 10^{-3}$$

Appendix B

The standard orientations of the HCN and CNH molecules were taken from the *Gaussian* output file. Similarly, the displacement vectors for the wagging mode of the vibration were also taken from the output files.

Standard orientation for HCN			
Atom	X	Y	Z
C	0.00	0.00	-0.50
H	0.00	0.00	-1.57
N	0.00	0.00	0.65

TABLE B.1: Standard orientation of the HCN molecule. The coordinates are in Å.

Standard orientation for CNH			
Atom	X	Y	Z
C	0.00	0.00	-0.74
N	0.00	0.00	0.43
H	0.00	0.00	1.44

TABLE B.2: Standard orientation of the CNH molecule. The coordinates are in Å.

Displacement vectors for HCN vibration			
Atom	X	Y	Z
C	0.00	0.16	0.00
H	0.00	-0.99	0.00
N	0.00	-0.07	0.00

TABLE B.3: The vibrational vector of the wagging mode of HCN defined as normal coordinates ($\text{Å} * amu^{-1/2}$)

The normal coordinates for the vibration were converted to Å. The energy (given in a.u.) was converted to the units of force constant and Cartesian coordinates, in order

Displacement vectors for CNH vibration			
Atom	X	Y	Z
C	0.00	0.07	0.00
N	0.00	-0.13	0.00
H	0.00	0.99	0.00

Table B.4: The vibrational vector of the wagging mode of CNH defined as normal coordinates (Å$*amu^{-1/2}$)

to solve for the variable in Å. Following are the values of the variables used in equation 1.9:

1. $k_R = 0.7183\ mDyne\AA^{-1}$
2. $k_P = 0.3765\ mDyne\AA^{-1}$
3. μ_R = 1.3437 amu
4. μ_P = 1.2930 amu
5. $\Delta U(U_R - U_P)$ = -0.135 Hartree

The conversion factor : 1 Hartree = 4.357 mDyneÅ
Substituting the values in equation 1.9, we get :

Calculated coordinates of the guess structure			
Atom	X	Y	Z
C	0.73	1.14	0.00
N	1.89	0.89	0.00
H	-0.22	0.02	0.00

Table B.5: The solution of the quadratic equation 1.9 for each atom in XYZ space.