

Experiment [COM]: Computational Methods - Exploring the inversion of Pyramidal Centres and Analysing Carbene Complexes

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Abstract

This experiment was based on computational methods including "Molecular Mechanics" and "Semi-Empirical" since the energy of a molecule was hard to determine through wet-lab experiments. The inversion activation energy of 16 different trigonal pyramidal molecules with N or P as the central atom was obtained. The difference among the activation energies was discussed based on the nature of the central atom, the substituent effect, the steric effect, the conjugation effect, and the ring strain effect. The properties of two types of carbene ligand, Fischer and Schrock, were studied. The ground electronic state, the electron orbitals, the partial double bond properties of C-Y bond in Fischer carbene, and the reactivity of both types of carbene were discussed based on the computational calculation. Further relative wet-lab experiment could be process to support the computational calculated results.

1 Introduction

The inversion of the pyramidal centres of a molecule like amine was very fast, which would results in racemic mixture. The energy barrier of the inversion of a pyramidal centre is called the activation energy of inversion (E_a) as shown in Figure 1. During the transition state of the inversion, the sp^3 orbital changed to sp^2 orbital. The activation energy of inversion is related to the nature of the central atom, the substituent effect, the steric effect, the conjugation effect, and the ring strain effect, which would be discussed in this experiment through a computational method.

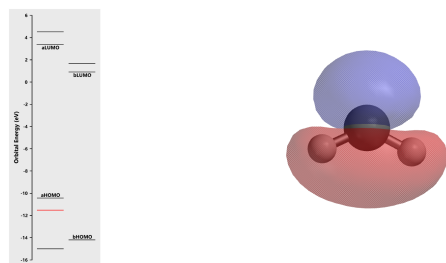


Figure 1: Same

A carbene ligand was a $-CR_2$ group with two non-bonding electrons. There were two types of carbene: Fischer and Schrock as shown in Figure 2. The molecular orbitals, bond properties, and reactivity of these two types of carbene would be discussed based on computa-

tional method.

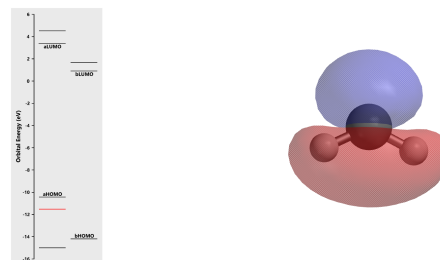


Figure 2: Same

The Computational method was used in this experiment as the energy of a molecule could not be detected directly through a wet-lab experiment. The first method used was "Molecular Mechanics" method, which was based on empirical potential energy functions.¹ It calculated the molecular energy and predicted the most stable structure of the molecule.² This method was relatively simple and fast, which would save time for the next method. The second method used was "Semi-Empirical" method, which was more accurate but would take a much longer time. This method was based on the quantum mechanics, and it would calculate the energy of the molecule, electron density, and molecular orbitals.

2 Methodology

Since the energy value was impossible to be measured experimentally, the computational method was used in the experiment to obtain the molecular energy.

Trimethylamine was built via Spartan Student version8. It was optimised using "Equilibrium Geometry" and "Molecular Mechanics" (MMFF). This calculation was repeated using "Semi-Empirical" (PM3) instead of MMFF to obtain more accurate properties about the molecule. The energy and dihedrals of the molecule were recorded. Trimethylamine was constrained to a planar by constraining the dihedral angle to 180 degrees. The planar NH_3 was optimised with the same method. The energy of the planar NH_3 was recorded. These steps were repeated with different molecules: PMe_3 , N^iPr_3 , P^iPr_3 , PBr_3 , PCl_3 , PF_3 , $PPhMe_2$, $PPhMe^tBu$, $P(C_6H_{11})Me^nPr$, $PPhMe^nPr$, $PPhMe(4 - MePh)$, $PPhMe(SiH_3)$, PPh^iPr^tBu , PPh^iPr^tBu , $(H_2CCH_2)NMe$.

Triplet carbene ligand ($-C(OMe)Me$) was built and optimised using MMFF first followed by PM3 method with "Equilibrium Geometry". This step was repeated with Singlet ($-C(OMe)Me$), Triplet ($-CH_2$), Singlet($-CH_2$). The energy of triplet states and Singlet states for each carbene ligand were compared to determine the ground electronic state of Fischer ($-C(OMe)Me$) and Schrock ($-CH_2$) structure. The molecular orbitals of $-C(OMe)Me$ and $-CH_2$ were obtained, and the energy of the σ -donating and π -accepting orbitals were recorded.

Four different structures of $Ph(OMe)CCr(CO)_5$ - (syn, eclipsed), (syn, staggered), (anti, eclipsed), and (anti, staggered) - were built and optimised. Their energy were compared to determine the stablest structure. The C-O bond distance and the electrostatic of the central carbon were recorded.

$Ph(NH_2)CCr(CO)_5$, $TaCp_2Me(CH_2)$, and $TaCp_2Me(CH_2)AlMe_3$ were built and optimised using the same method. The electrostatic of the central carbon for each molecule was recorded.

3 Results

The ground state energy, the energy after constrained to a planar, and the dihedral angles of NMe_3 , PMe_3 , N^iPr_3 , P^iPr_3 , PBr_3 , PCl_3 , PF_3 , $PPhMe_2$, $PPhMe^tBu$, $P(C_6H_{11})Me^nPr$, $PPhMe^nPr$, $PPhMe(4 - MePh)$, $PPhMe(SiH_3)$, PPh^iPr^tBu , PPh^iPr^tBu , $(H_2CCH_2)NMe$ were recorded in Table 1. The activation energy of inversion for a molecule was calculated by subtracting the ground state energy from the energy of planar, and the result was recorded in Table 1.

The energy of Fischer ($-C(OMe)Me$) and Schrock ($-CH_2$) in both Triplet states and Singlet states were recorded in

Table 1: Energy of each molecule in the ground state (E), and the energy of the molecule when it constrained to a planar (E') were recorded. The activation energy of inversion (E_a).

Name of the Molecules	E (kJ/mol)	E' (kJ/mol)	E_a (kJ/mol)
Line 1	68.28	45.30	56.79
Line 1	68.28	45.30	56.79
Line 1	68.28	45.30	56.79
Line 1	68.28	45.30	56.79
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Line 1	68.28	45.30	56.79
Line 1	68.28	45.30	56.79
Line 1	68.28	45.30	56.79
Line 1	68.28	45.30	56.79
Line 1	68.28	45.30	56.79
Line 2	54.06	38.63	46.35
Line 3	61.17	41.97	

Table 2.

Table 2: The energy of Fischer and Schrock carbene ligand in triplet and singlet state.

Name of the molecules	E (Triplet) (kJ/mol)	E (Singlet) (kJ/mol)
$-C(OMe)Me$	51.41	14.56
$-CH_2$	299.72	473.74

The σ -donating and π -accepting orbital of Fischer ($-C(OMe)Me$) and Schrock ($-CH_2$) carbene ligand were shown in **Figure x**. The energy of the HOMO for $-C(OMe)Me$ was -9.1 eV and LUMO was 0.5 eV. The energy of HOMO for $-CH_2$ was -10.4eV and HOMO-1 was 11.5 eV.

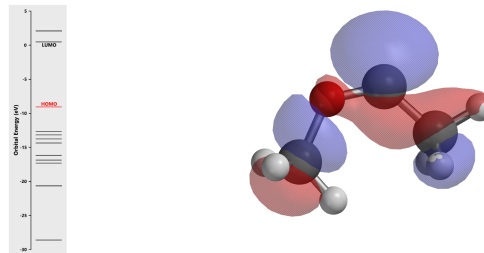


Figure 3: Same

The energy and C-O bond length of $Ph(OMe)CCr(CO)_5$ in four different structures were recorded in Table 3. The syn-conformation had lower

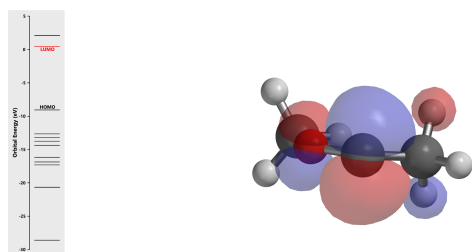


Figure 4: Same

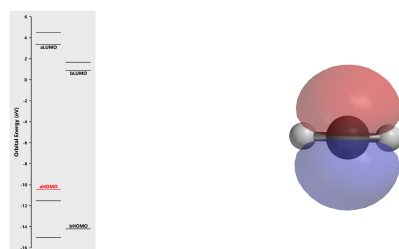
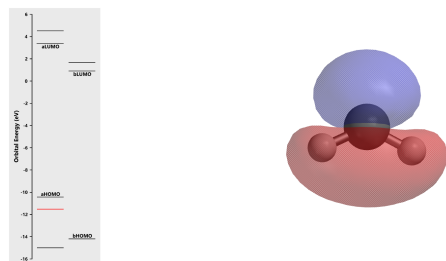


Figure 5: Same

energy than the anti-conformation, and the eclipsed form had lower energy than the staggered form. The syn-eclipsed structure had the lowest energy, meaning that the molecule was most stable under this structure. **data needed**

The charge of the central carbon of $Ph(OMe)CCr(CO)_5$, $Ph(NH_2)CCr(CO)_5$, $TaCp_2Me(CH_2)$, and $TaCp_2Me(CH_2)AlMe_3$ were recorded in Table 4. For Fischer carbene ($-C(OMe)Me$) molecule, the charge of the central carbon was less positive as the $-OMe$ group was replaced by $-NH_2$ group. For Schrock ($-CH_2$) carbene, the charge of the central carbon become less negative when $AlMe_3$ was added to the central carbon.

4 Discussion

Part 1

The activation energy needed for inversion varies among different molecules.

1. Nature of the central atom

$NiPr_3$ vs. $PiPr_3$

Table 3: The energy of $Ph(OMe)CCr(CO)_5$ in four different structures

Conformation	Syn	Anti
Eclipsed	-774.75 kJ/mol	-751.85 kJ/mol
Staggered	-772.83 kJ/mol	-755.68 kJ/mol

Table 4: The charge of the central carbon of Fischer and Schrock carbenes

Name of the molecules	electrostatic (eV)
$Ph(OMe)CCr(CO)_5$	
$Ph(NH_2)CCr(CO)_5$	
$TaCp_2Me(CH_2)$	
$TaCp_2Me(CH_2)AlMe_3$	

2. Substituent Effect

PBr_3 vs. PF_3 vs. PCl_3

3. Steric effect

$PPhMe_2$ vs. $PPhMe^tBu$

4. Conjugation effects

$P(C_6H_11)Me^nPr$ vs. $PPhMe^nPr$

5. Ring strain effects

Part 2

The energy of a triplet Fischer ligand ($C(OMe)Me$) was higher than the energy of its singlet form as shown in Table x, meaning that it was more stable for a Fischer molecule to stay in a singlet form. Thus, the ground electronic state of Fischer ligands were singlet states instead of triplet states. However, for a Schrock ligand (CH_2), the energy of its triplet state was lower than its singlet states, meaning that triplet states was more stable for Schrock ligands. Therefore, the ground electronic state of Schrock ligands was triplet states.

The molecular orbital diagram of both CH_2 and $C(OMe)Me$ were shown in the Figure x. The Fischer carbene ligand $C(OMe)Me$ contained an enelctron donating group (EDG), which increase the energy of π -orbital. Thus, the difference between the energy of σ -donating orbital and π -accepting orbital was large (**data needed**), and the two electrons would both stay in the σ -donating orbital, which makes the Fischer ligand a singlet state. The σ -donating orbital for $C(OMe)Me$ ligand was HOMO as shwon in Figure x, (a), and the π -accepting orbital was LUMO as shown in Figure x, (b). However, the Schrock carbene ligand CH_2 does not contained an EDG. Thus, the difference between the energy of σ -donating orbital and π -accepting orbital was small enough to allow the two electrons stay in both orbitals as the electron repulsion force might be larger than the energy gap between the two or-

bitals. Therefore, the Schrock ligand was a triplet state. The σ -donating orbital was HOMO-1 as shown in **Figure x**, (c), and the π -accepting orbital was HOMO as shown in **Figure x**, (d).

As the Fischer carbene ligand was in a singlet state, the lone pair electrons were both in the HOMO orbital, which was σ donating, while the empty LUMO was acting as π -accepting orbital. A pair of electrons from the π -orbital of the metal donated to the empty LUMO orbital of the carbene ligand, forming the π back-bonding as shown in the **Figure x**. The Schrock carbene ligand was in a triplet state, and one of the electron in the σ -orbital of the carbene ligand was paired with another electron from the metal, forming a σ bond. The other electron in the π orbital of the carbene ligand paired with another electrons from the π orbital of the metal, forming a π bonding as shown in the **Figure x**.

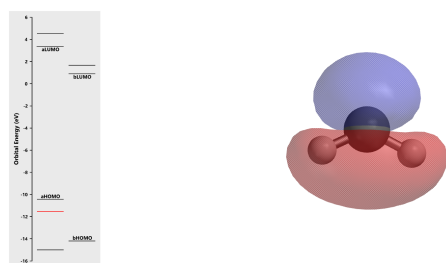


Figure 6: Same

The four different structures of $Ph(OMe)CCr(CO)_5$ were shown in **Figure x**, and their energy was recorded in Table 3. The syn-eclipsed form had the lowest structure, which means that it was the most stable structure. This was further proven by the experimental crystal structure of $[Cr(CO)_5(C(OMe)Ph)]$. The difference of energy between the syn-conformation and anti-conformation was large as comparing to the difference between the eclipsed structure and the staggered structure. This indicated that it was more difficult to transform from the syn-conformation to the anti-conformation, which proved the restricted rotation of C-Y (C-O) bond. The bond length of the C-O bond was **data needed**, which was between the length of a single bond (1.43 Å) and a double bond (1.23 Å) **reference needed**. This indicated that the C-O bond was a partial double bond, and the bond length of C-O was closer to a double bond rather than a single bond, indicating that the C-O bond had more double bond properties. Thus, $[Cr(CO)_5(C(OMe)Ph)]$ would prefer the left resonance structure as shown in **Figure x**.

The reaction from $Ph(OMe)CCr(CO)_5$ to $Ph(NH_2)CCr(CO)_5$ was shown in **Figure x**. The charge of the central carbon of Fischer carbene ligand was positive as shown in Table 4, meaning that it was electrophilic. When -OMe group was replaced by -NH₂ group, the electron density of the central carbon was

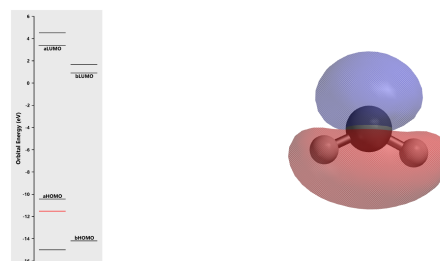


Figure 7: Same

increased as -NH₂ group was more electron donating than -OMe. For this reason, the charge of the central carbon became less positive, meaning it was less electrophilic and less reactive.

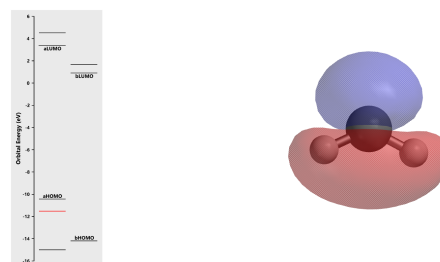


Figure 8: Same

The reaction from $TaCp_2Me(CH_2)$ to $TaCp_2Me(CH_2)AlMe_3$ was shown in **Figure x**. For Schrock carbene, the charge of the central carbon become less negative, which indicates that the carbon become less nucleophilic when $AlMe_3$ was added to the central carbon. Therefore, the Schrock molecule was less reactive.

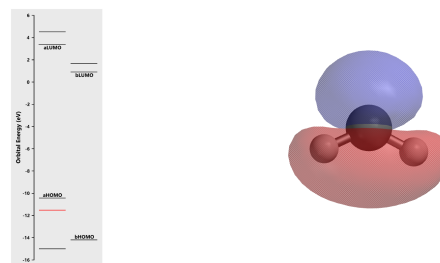


Figure 9: Same

This experiment was fully based on computational methods including "Molecular Mechanics" and "Semi-Empirical" methods using Spartan Student version8. The first part of this experiment calculate the inversion activation energy of 16 different trigonal pyramidal molecules with N or P as the central atoms. The energy difference were explained by the nature of the central atom, the substituent effect, the steric effect, the conjugation effect, and

the ring strain effect. The second part of the experiment was focused on carbene. The two types of carbene, Fischer ($-\text{C}(\text{OMe})\text{Me}$) and Schrock ($-\text{CH}_2$), were analysed. The ground electronic state of a Fischer carbene was a singlet state due to the electron donating group $-\text{OMe}$, while the ground electronic state for Schrock carbene was triplet. The HOMO orbital containing the lone pair electrons of Fischer carbene acting as σ -donating orbital, while the empty LUMO orbital acting as a π -accepting orbital. For a Schrock carbene, the HOMO-1 orbital containing one electron was the σ -donating orbital, while the other HOMO containing one electron acted as π orbital. The C-O bond for the Fischer carbene had partial double bond properties and its rotation was restricted. The charge of the central carbon of the Fischer carbene was positive, indicating that it was electrophilic, while the Schrock carbene was nucleophilic as the charge of its central carbon was negative. As this experiment was based on a computational calculation, further wet-lab experiment could be done to confirm the information obtained by calculation.

brief conclusion and further work

5 Investigation Question

The efficiency of solar materials was largely depended on the band gap of the molecule. The band gap was the energy between valence band and conduction band³, representing the minimum energy required for the excitation of an electron to a higher energy level⁴. The ideal band gap for a photovoltaic material was around 1.4 eV with an limiting efficiency around 33.7% (Shockley–Queisser limit).⁵

A computational method could be used to select the potential photovoltaic material. The advantages of using the computational method include:

1. It was much faster than the wet-lab experiment. Therefore, it could be used to screen a large number of molecules in a short time.

2. The cost of computational methods was much lower than the wet-lab experiment as no chemicals were needed.

There were several methods could be used to calculate the band gap of a molecule. DFT could provide information about the structures and stabilities of photovoltaic materials in a relatively short time. However, it would greatly underestimate the band gap. While GW could provide accurate information about molecules but facing some challenges including spin-orbital coupling effects and a high computational cost. Thus, the most suitable method was DFT-1/2, which could model the band gap with an accuracy close to the GM method and had a lower cost similar to DFT method. DFT-1/2 had been proved that it could calculate the band energy of metal halide perovskites AMX_3 , while $A = \text{Cs}, \text{CH}_3\text{NH}_3, \text{CH}_2\text{NHCH}_2$, $M = \text{Sn}, \text{Pb}$; $X = \text{I}, \text{Br}, \text{Cl}$, with high accuracy.

To select the new potential solar materials, the band energy of possible candidates could be calculated using DFT-1/2 method. For example, each component of metal halide perovskites, A/M/X , could be changed, and the band gap would be calculated for each molecule. The molecule with the band gap close to 1.4 eV would be selected, and further analysis would be required for these molecules to determine if it was a suitable solar materials.

The solar materials selected by using the computational method might not be suitable for industrial for several reasons:

1. The experimental data might be different from computational calculation.

2. The material selected might be rare in nature.

3. The cost of producing the material might be high.

4. The process of producing this material might be harmful to the environment.

Therefore, once the solar materials were selected based on the computational calculation, further wet-lab experiments were necessary to ensure that it was suitable for industrial.

References

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