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SCHEMATIC REACTIONS AND CHARACTERIZATION OF INTERHALOGEN COMPOUNDS, PSEUDOHALOGENS, ALKENES, ALLENE, PHOSPHORUS PENTACHLORIDE, PHOSPHORUS OXYCHLORIDE AND THIONYL CHLORIDE WITH OXATHRENE-S-OXIDE DERIVATIVE FOR SO_2 FIXATION AND STORAGE USING DFT

Anirban Bhar[1]*, Arijit Bag[2] and Ankhi Das[3]
[1]*Department of Chemistry, Brainware University, Kolkata, West Bengal*
[2]*Department of Applied Chemistry, MAKAUT, West Bengal*
[3]*Department of Basic science and Humanities, Rajendranath College of Polytechnic, West Bengal*
**Corresponding Author. Email id: anirbanbhar92@gmail.com*

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Abstract

Carbene compounds are very much reactive to SO_2 to produce Oxathrene-S-Oxide derivative. This Oxathrene-S-oxide derivative are allowed to react with various alkenes, interhalogen compounds, allenes,PCl5, pseudo halogens, Phosphorus oxychloride to seize this greenhouse gas. The present investigation involves the reaction of Oxtharene –S-oxide derivative with various compounds. The HOMO, LUMO and total energy diagram of each reaction are studied in brief here using DFT (Density functional) Methods . Most of the reactions involve decomposition to carbonyl compounds and SO. Most of the reactions are endothermic and Energy is found to be negative. This finding should necessitate the recommencement of the use of cabene for SO_2 fixation technology.

Keywords: *Fixation, greenhouse effect, Gaussian 16, Oxathrene-S-oxide, DFT and endothermic.*

1. Introduction

SO_2 is one of the important components of greenhouse gases. Due to emission of greenhouse gases, global warming occurs and the ice of mountains are going to melt and also causes change in climate. SO_2 also causes bronchitis, asthma and acid rain. Damage of chlorophyll of leaf is also an important effect of SO_2. There are several strategies all over the world which are developed and still developing by the frontier research groups to activate or sequester SO_2. Ionic liquids [1-8], metal organic framework [9-11], electron rich amines [12], metal alkyl or aryl complexes [13-24] are used for this purpose. Carbenes are highly reactive in presence of SO_2 to produce oxathrene-S-oxide derivate. In order to undergo fixation of SO_2 [25-29] the reaction is carried out between oxathrene-S-oxide derivative and Interhalogen compounds, alkenes, pseudo halogens, allenes, PCl_5, $POCl_3$ and $SOCl_2$ separately

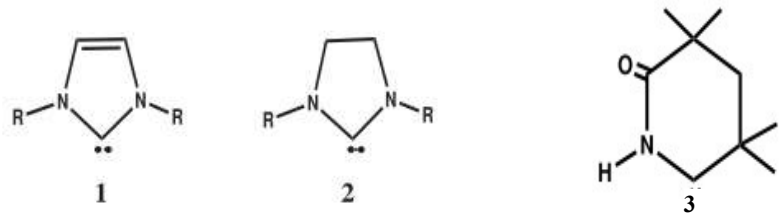
Oxathrene-S-oxide is a little studied compound [26,27,30]. In 1976, Carsel et.al. reported [31] that diaryloxathrene acts as an intermediate in the conversion reaction of diaryl thioketone S-oxide derivative at very low temperature in presence of light which is also confirmed by Electronic spectroscopy. Diaryl Oxathrene are extremely unstable in presence of light and heat and they undergo dissociation to produce ketone with high

yield. Oxathrene -S-oxide, first reported in 1974 by Hiroaka [32] undergo similar dissociation in presence of light and heat to produce carbonyl derivatives and SO[26]. This dissociation reaction gives us an idea about the implementation of carbene for SO_2 fixation. When Carbene reacts with SO_2, then initially S-S dioxide derivatives are produced which are highly unstable and converted into ketone through Oxathrene -S-oxide derivative. SO_2 is converted to SO. The reformation of carbene from this ketone derivate is not trivial. Thus these carbenes could not be used as a catalyst for this purpose

Still now, a very little quantum chemical studies [25,33-35] have been reported about the binding nature and chemical kinetics of S-S-dioxide and their Oxathrene -S-oxide derivatives. There is no report available in literature on energetics and mechanism of oxathrene-S-oxide derivatives to ketone formation. The studies are highly important to find out effective carbenes which will produce stable Oxathrene-S-oxide derivative. The discovery of N-hetero cyclic carbene by Bertrand et.al. [36,37] in 1988 and Arudengo et.al. [38]in 1991 opens up huge possibilities of chemical engineering to model different NHC'S to get our desired carbene. Now a days NHC's [39-42] are used as a catalyst for activation of CO_2 [43-58]and CS_2[46] activation in different organic synthesis [59-66]. These compounds are also used to stabilize assorted Ni carbonyl complexes [67-74]. The Oxathrene -S-oxide was first reported by Hiroaka [32] in 1974. The above-mentioned derivative appears as vibrationally excited intermediate when carbene (CH_2) reacts with SO_2[89-91]. This derivative also acts as a stable intermediate when diphenyl carbene reacts with SO_2. The intermediate undergoes dissociation reaction when it is exposed to sunlight greater than 295 nm to form ketone derivative and SO [89-91]. From the two studies (Hiraoka in 1974[32] and Sander Et.al. in 1997[26]), we are highly determined that large group substitution at the carbene enhances the stability of Oxathrene -S-oxide derivative. Thus, we are prone to study various reactions of oxathrene-S-oxide derivatives.

Till now, S-S dioxide derivatives are considered as donor stabilized compounds [25]. Carbenes can act both as σ donor and π acceptor. If we arrange the substituents at the heteroatom of the carbene, the σ donor and π acceptor ability can be enhanced. We have selected 3 NHC'S [75-80, 89-91]and their Oxathrene-S-oxide derivatives. Finally, the reaction of the selected Oxathrene -S-oxide derivative is carried out using interhalogen compounds, pseudohalogens, alkenes, allenes, PCl_5, $POCl_3$, $SOCl_2$ and oxychloride.

Finally using Gaussian16[84], the reactions of Oxathrene -S-oxide derivative with various compounds are done and optimized to get the most stable products. The HOMO and LUMO interaction are carried out in case of the most stable product [89-91]. The Energy profile diagram has been done in all the cases. The carbenes which are studied and the formation of Oxathrene -S-oxide derivative is given below in the diagram (Figure 1 and 2) respectively



(R=H in all the studies)

Figure 1 Selected carbenes used for the study

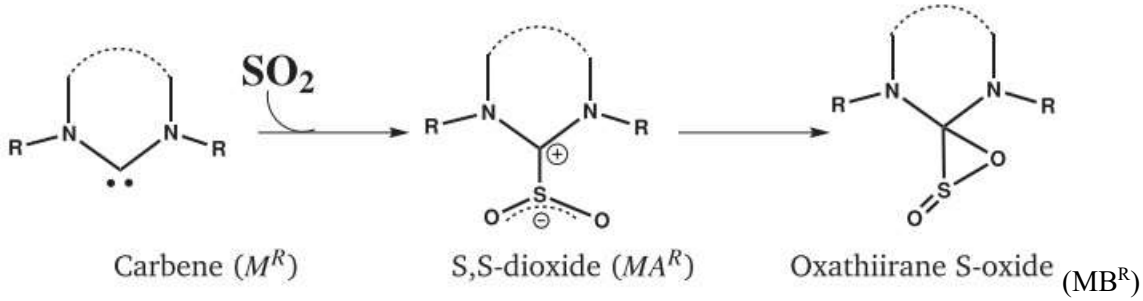


Figure 2 Formation of Oxathrene S-oxide derivative

2. Computational details

The Oxathrene -S-oxide derivatives are optimized using DFT. The optimized structures are allowed to react with Interhalogen compounds, PCl_5, pseudo halogens, alkenes, $POCl_3$, allenes and $SOCl_2$ using Gaussian 16 optimization+frequency methods. Most stable products are obtained using optimization. For optimization, Ground state and B3LYP functional are used. The spin is always taken as singlet. The optimization is carried out in absence of any solvents. The energy calculation is done using TDSCF. During optimization no symmetry constraints are taken into account. The hindered rotational treatment is also excluded in the study. Single point calculations are carried out using MO6-2X [81] functional with 6-311++G* basis set for all atoms. Natural Bond order (NBO) has furnished at the MO6-2X/6-311++G*//MO6-2X/6-311++G* level [85] of theory using NBO6.1 [85] version that is incorporated in Gaussian16-package

3. Reactions and characterization

a) Reactions of Oxathrene -S-Oxide of Carbene-1 with CIS 1,3-Butadiene

Oxathrene-S-Oxide of Carbene-1 reacts with cis-buta-1-3-diene to yield a carbonyl compound and SO. Cis Buta1,3-diene remains unaltered. Here H of N-H interacts with O of SO. This O of SO again interacts with H of cis-Buta-1,3, diene (Figure 3)

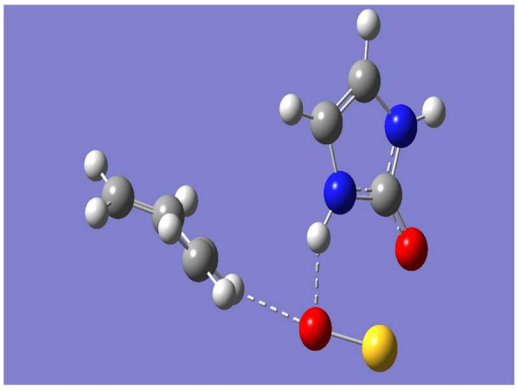


Figure 3 Reactions of Oxathrene -S-Oxide of Carbene-1 with CIS 1,3-Butadiene

a(i) Characterization

HOMO

HOMO proves the interaction between H of cis-Buta-1,3, diene and SO. The interaction between H of N-H and O of SO is also present in HOMO. Due to these interactions, fixation of SO_2 occurs (Figure 4).

LUMO

LUMO also proves the interaction between H of cis-Buta-1,3, diene and SO. The interaction between H of N-H and O of SO is also present in LUMO. Due to these interactions, fixation of SO_2 occurs. (Figure 5).

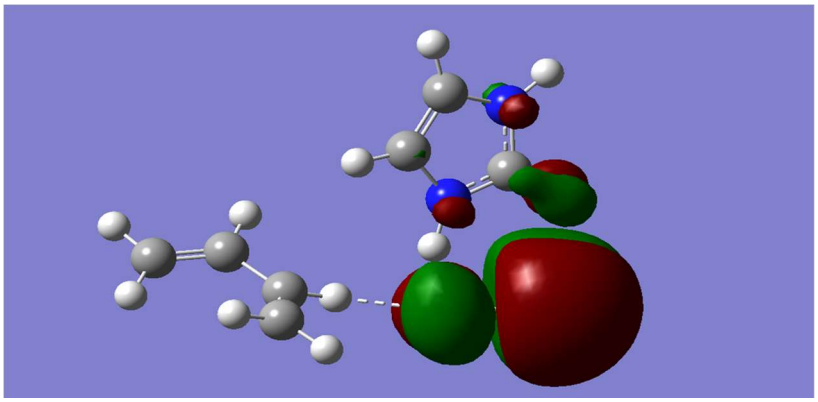


Figure 4 HOMO

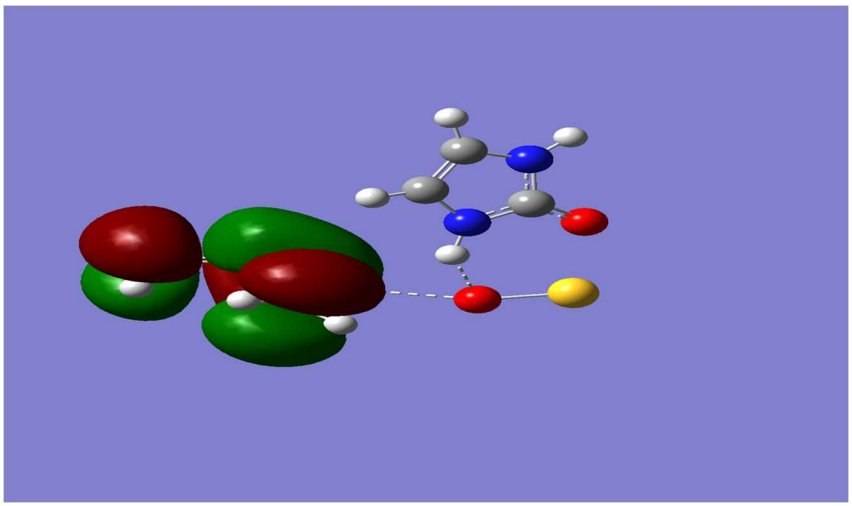
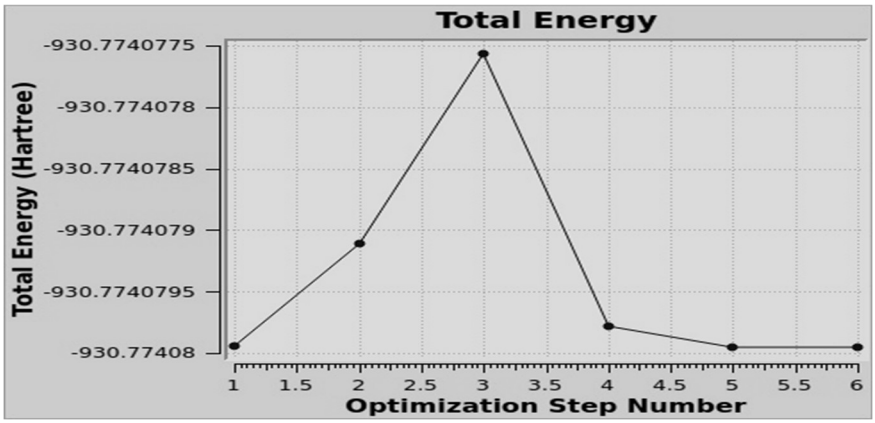


Figure 5 LUMO

a(ii) Energy Profile Diagram



Graph 1 Energy profile diagram

In case of final product (Figure 4), the energy is – ve. The energy at first rises to a maximum, then drops to a minimum and the overall reaction is endothermic

b) Reactions of Oxathrene-S-Oxide of Carbene-1 with Trans But-2-Ene

In this reaction, breakage of Oxathrene -S-oxide derivative occurs. Carbonyl compounds and SO are formed. Trans-But-2-ene remains unaltered. There is an interaction between O of CO and S of SO. This S of SO again interacts with H of CH_3 of trans But-2-ene. The O of SO interacts with H of NH of broken fragments of Oxathrene -S-oxide derivative (Figure 6)

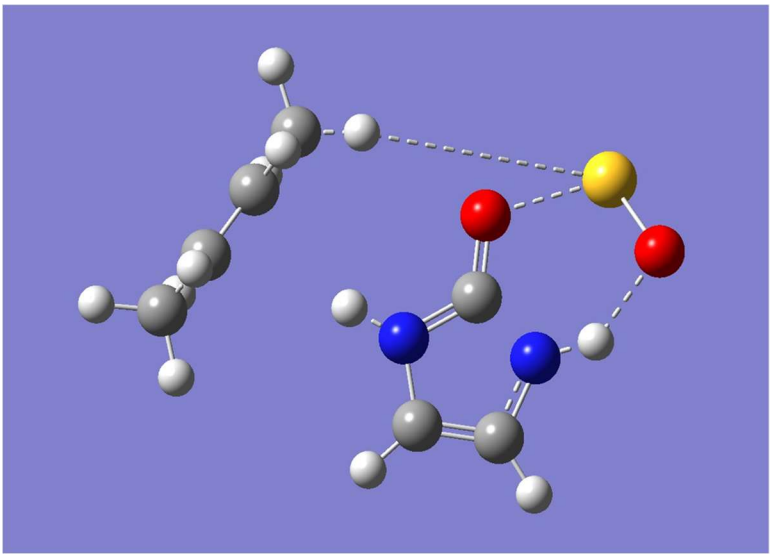


Figure 6 Reactions of Oxathrene-S-Oxide of Carbene-1 with Trans But-2-Ene

b(i)Characterization

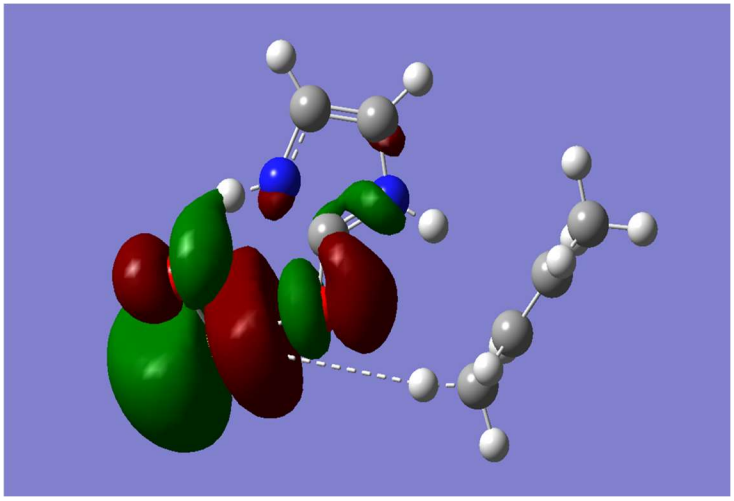


Figure 7 HOMO

HOMO

HOMO proves the breakage of Oxathrene -S-oxide. There is an interaction between O of CO and S of SO. This S of SO again interacts with H of CH_3 of trans But-2-ene. The O of SO interacts with H of NH of broken fragments of Oxathrene -S-oxide derivative. Due to these interactions, fixation of SO_2occurs. (Figure 7)

LUMO

LUMO also proves the breakage of Oxathrene -S-oxide. There is an interaction between O of CO and S of SO. This S of SO again interacts with H of CH_3 of trans But-2-ene. The O of SO interacts with H of NH of broken fragments of Oxathrene -S-oxide derivative. Due to these interactions, fixation of SO_2 occurs. (Figure 8)

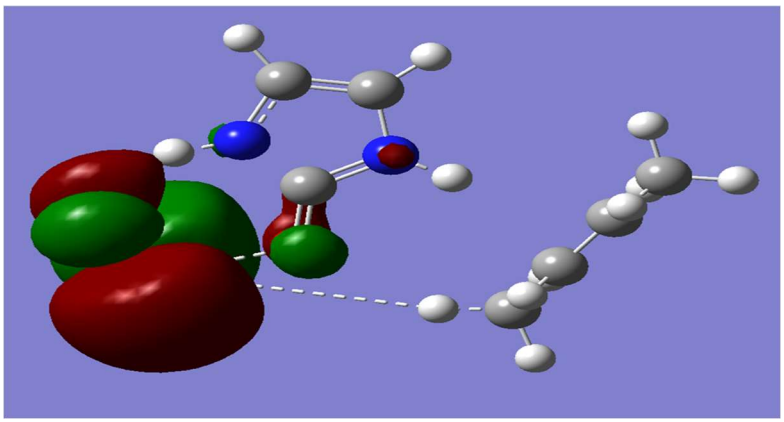
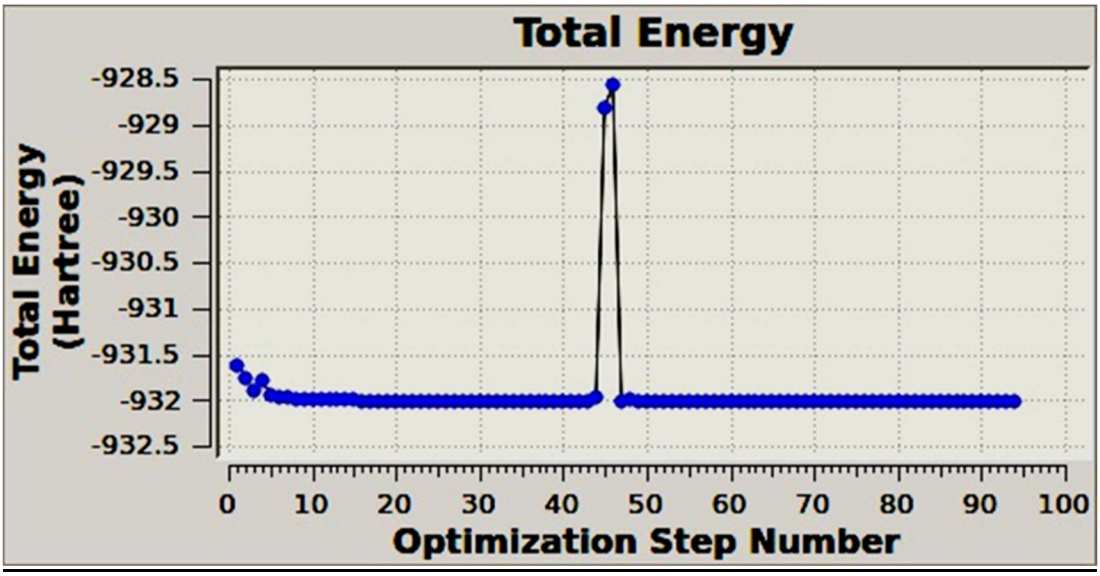


Figure 8 LUMO



Graph-2 Energy Profile Diagram

b(ii) Energy Profile Diagram

After the entire optimization, the energy obtained in case of final product is-ve. The energy at first rises to a maximum, then drops to a minimum and the overall reaction is endothermic. (Graph-2)

c) Reactions of Oxathrene-S-Oxide of Carbene-2 with Allene

In this reaction carbonyl and S=O are produced. Allene remains unaltered. Here H of NH interacts with O of SO which in turn interacts with H of allene.

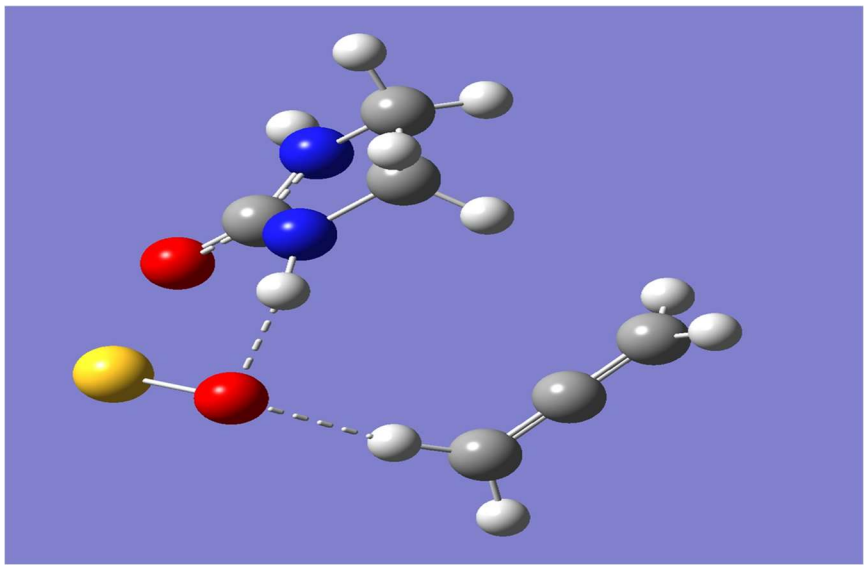


Figure 9 Reactions of Oxathrene-S-Oxide of Carbene-2 with Allene

c(i) Characterization

HOMO

HOMO also proves the interaction between H of N-H with O of SO which in turn interacts with H of allene. Thus SO_2 fixation occurs here.

LUMO

LUMO also proves the interaction between H of N-H with O of SO which in turn interacts with H of allene. Thus SO_2 fixation occurs here.

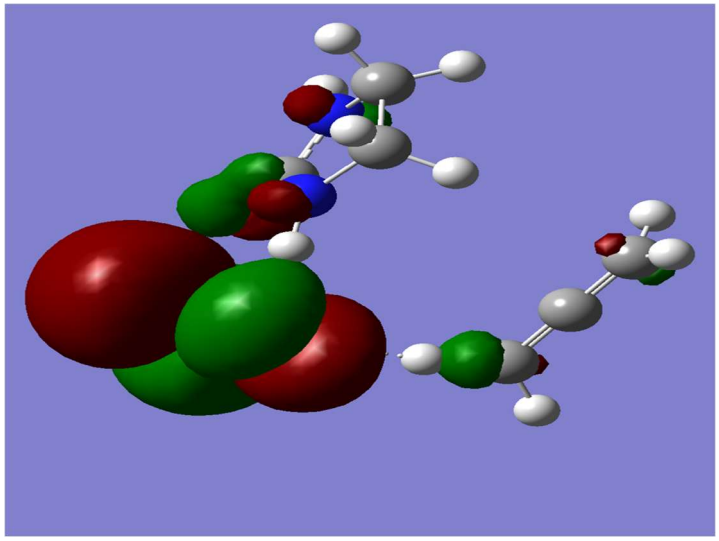


Figure 10 HOMO

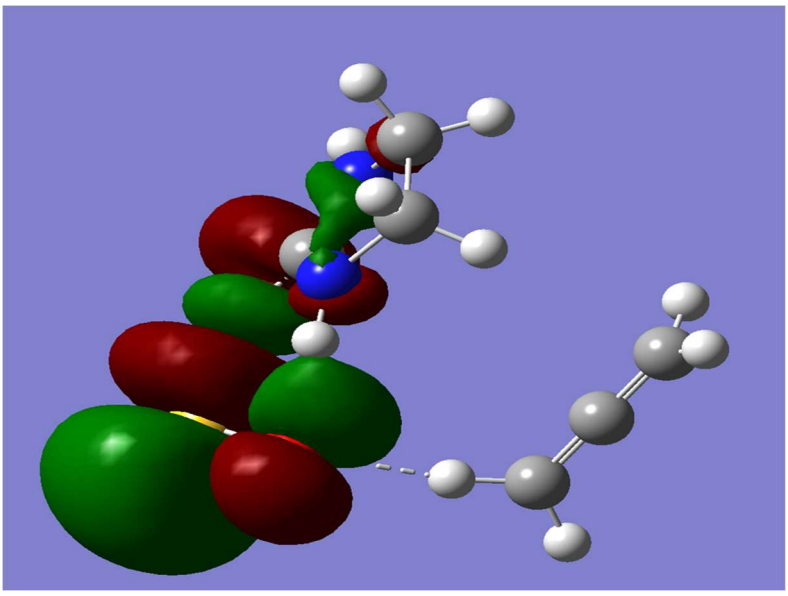


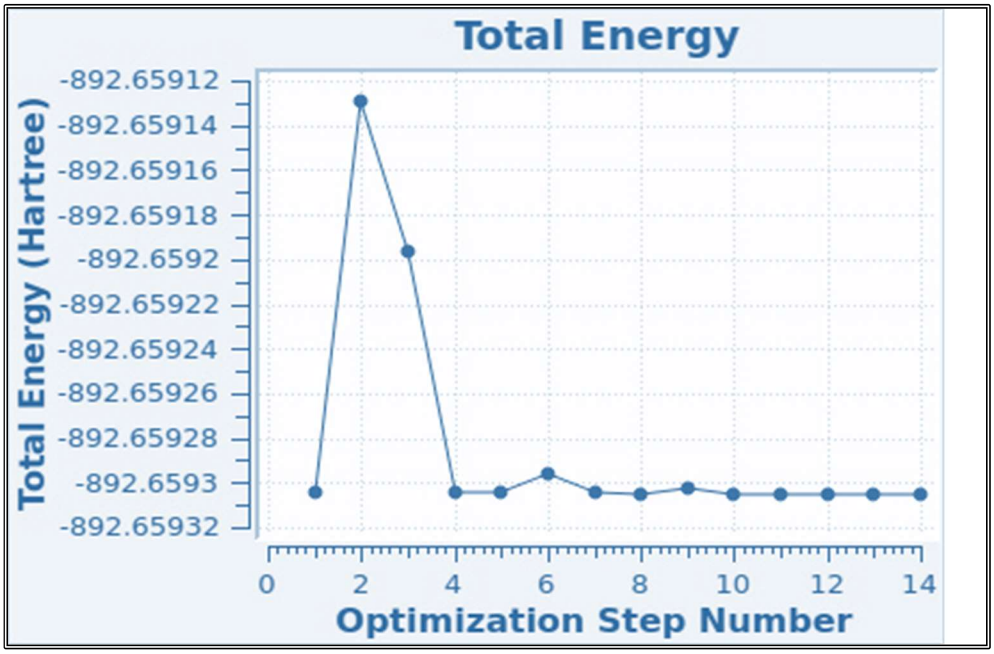
Figure 11 LUMO

c(ii) Energy Profile Diagram

After the entire optimization, the energy obtained in case of final product is -ve. The energy at first rises to a maximum, then drops to a minimum and the overall reaction is endothermic. (Graph 3)

d) Reactions of Oxathrene-S-Oxide of Carbene-1 with Styrene

The oxygen of CO interacts with S of SO which in turn interacts with C of CO. The Oxygen of SO interacts with H of benzene of styrene. (Figure12)



Graph 3 Energy Profile Diagram

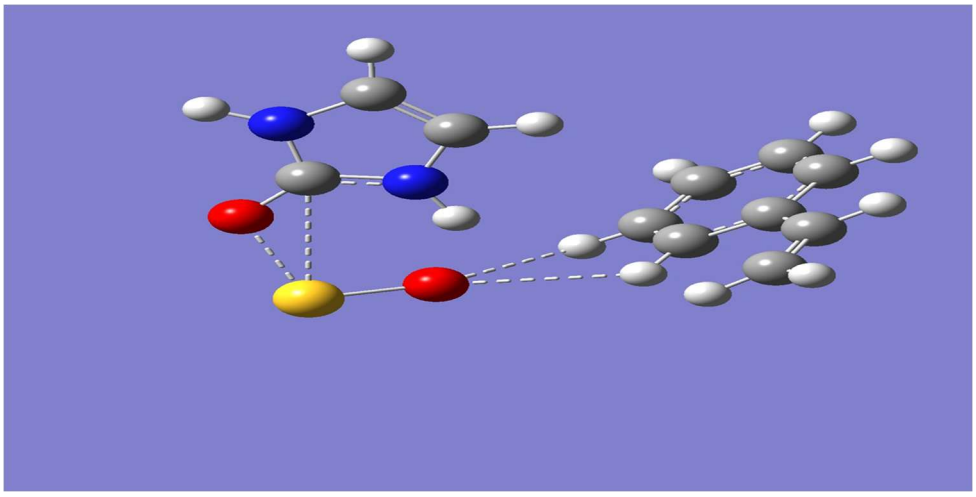


Figure 12 Reactions of Oxathrene -S-Oxide of Carbene-1 with Styrene

d(i) Characterization

HOMO

HOMO also shows the interaction between O of CO and S of SO. This S again interacts with C of CO. The Oxygen of SO interacts with H of benzene of styrene. Thus SO_2 fixation occurs here. (Figure 13)

LUMO

LUMO also shows the interaction between O of CO and S of SO. This S again interacts with C of CO. The Oxygen of SO interacts with H of benzene of styrene. Thus SO_2 fixation occurs here. (Figure 14)

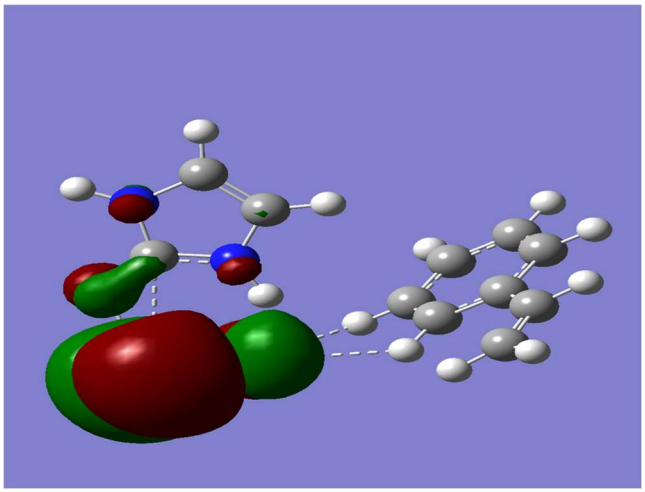


Figure 13 HOMO

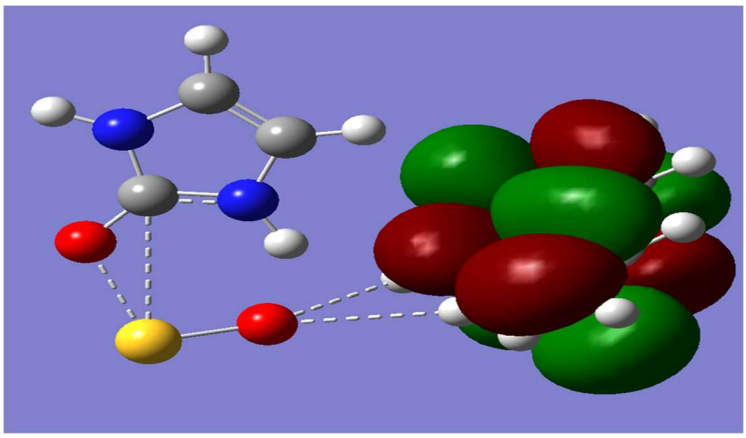
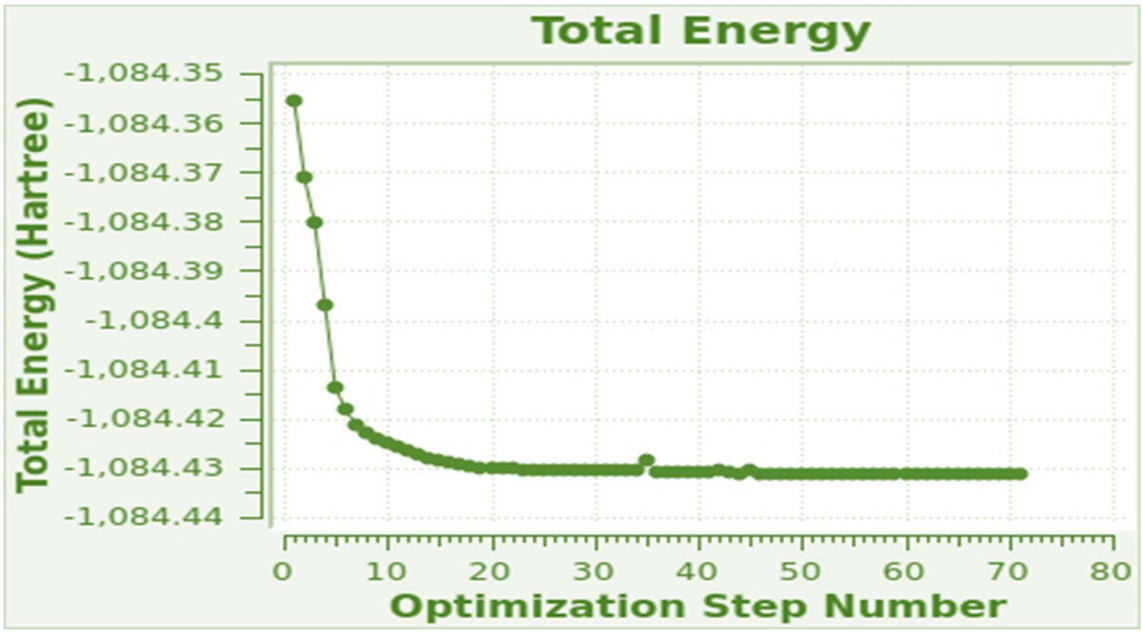


Figure 14 LUMO



Graph-4 Energy Profile Diagram

d(ii) Energy Profile Diagram

After the entire optimization, the energy obtained in case of final product is -ve. The energy drops from maximum to minimum after the end of optimization and at the end it becomes endothermic. (Graph-4)

e) Reactions of Oxathrene-S-Oxide of Carbene-1 with $POCl_3$

$POCl_3$ gets converted into PO and all the Cl gets eliminated. In this case unusual C-O bond is produced. This O of C-O interacts with S which in turn interacts with Cl. There is an added interaction between N of C=N with H which in turn interacts with O of PO. The P of PO interacts with Cl also. (Figure 15)

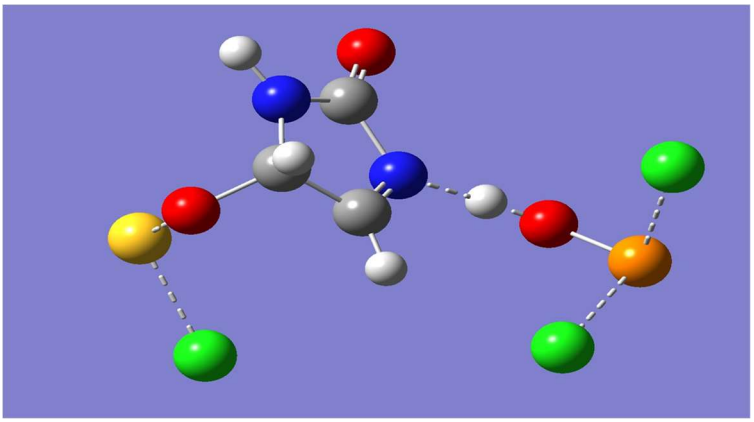


Figure 15 Reactions of Oxathrene-S-Oxide of Carbene-1 with $POCl_3$

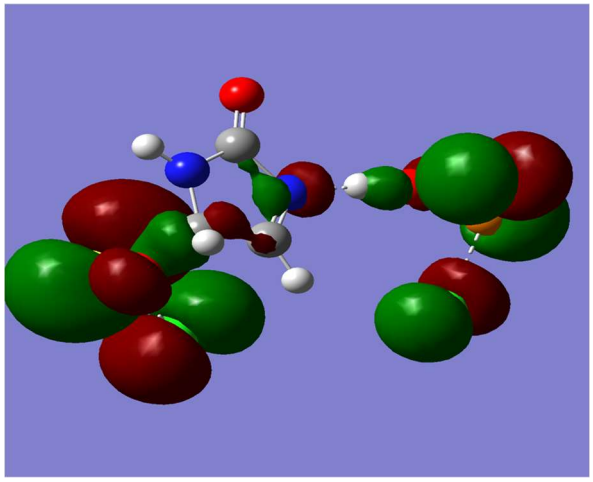


Figure 16 HOMO

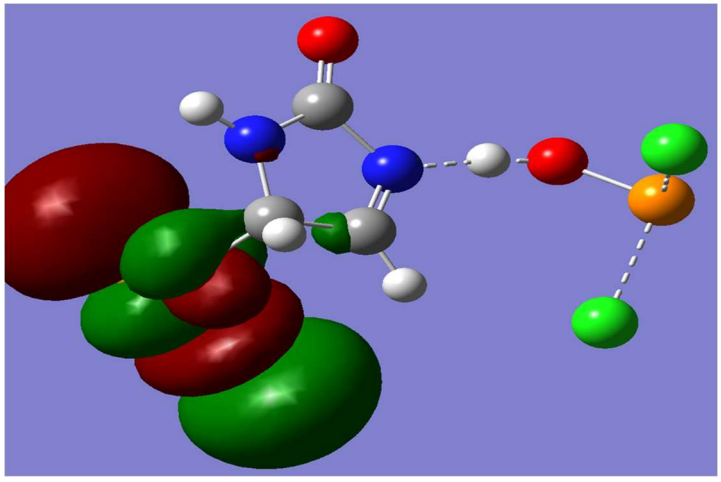


Figure 17 LUMO

e(i) Characterization

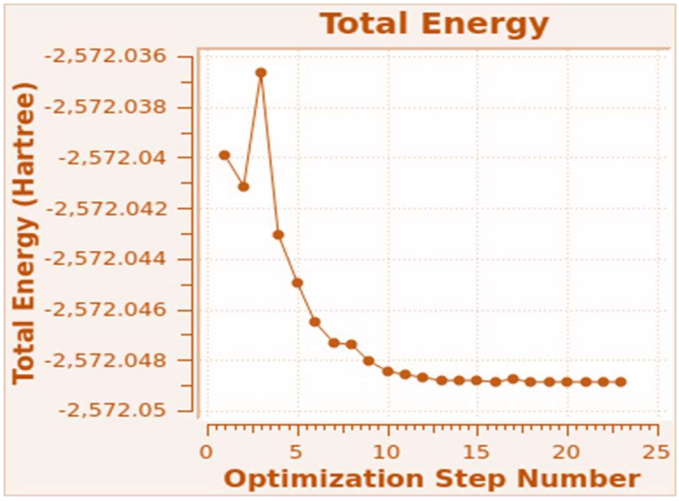
HOMO

HOMO also proves the interaction between O of CO and S which in turn interacts with Cl. There is an added interaction between N of C=N with H which in turn interacts with O of PO. The P of PO interacts with Cl also. (Figure 16)

LUMO

LUMO also proves the interaction between O of CO and S which in turn interacts with Cl. There is an added interaction between N of C=N with H which in turn interacts with O of PO. The P of PO interacts with Cl also. (Figure 17)

e(ii) Energy Profile Diagram



Graph 5 Energy Profile Diagram

After the entire optimization, the energy obtained in case of final product is -ve. The energy rises to a maximum and drops to a minimum at the end of optimization and the overall reaction is endothermic (Graph-5)

f) Reactions of Oxathrene-S-Oxide of Carbene-3 with $POCl_3$

In this case first oxathrene-S-oxide of Carbene3 is optimized. In this case C=O and S-O is formed. It should be allowed to react with $POCl_3$. The O of C=O gets an interaction with S of SO.

The O of SO interacts with H. The H also interacts with C here. Lastly the H of CH_3 interacts with Cl. The Cl also interacts with P of PO. (Figure 18)

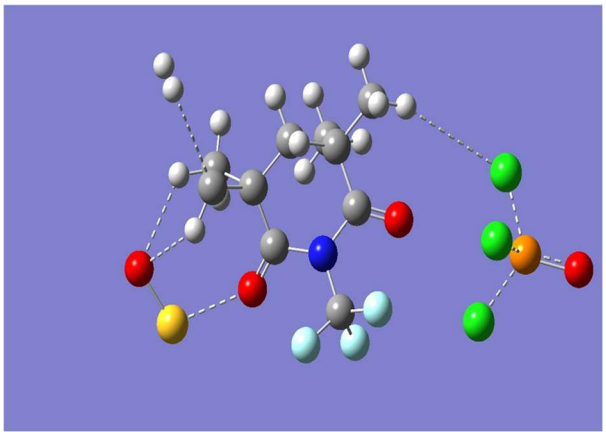


Figure 18 Reactions of Oxathrene-S-Oxide of Carbene-3 with $POCl_3$

f(i) Characterization

HOMO

HOMO also proves the interaction between O of CO and S of SO. There is also an interaction between O of CO and H. The H also interacts with C here. Lastly the H of CH_3 interacts with Cl. The Cl also interacts with P of PO. Thus, SO_2 fixation occurs here (Figure 19)

LUMO

LUMO also proves the interaction between O of CO and S of SO. There is also an interaction between O of CO and H. The H also interacts with C here. Lastly the H of CH_3 interacts with Cl. The Cl also interacts with P of PO. Thus SO_2 fixation occurs here
(Figure 20)

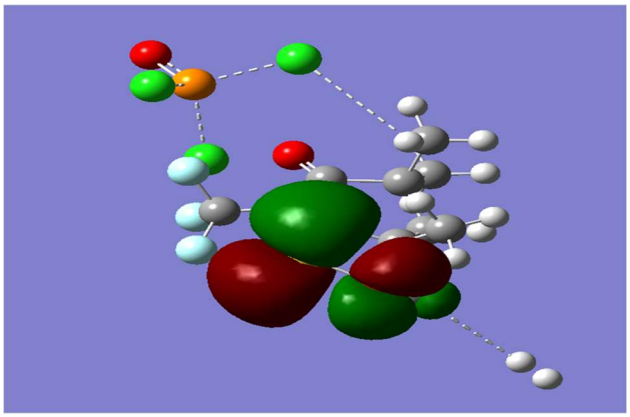


Figure 19 HOMO

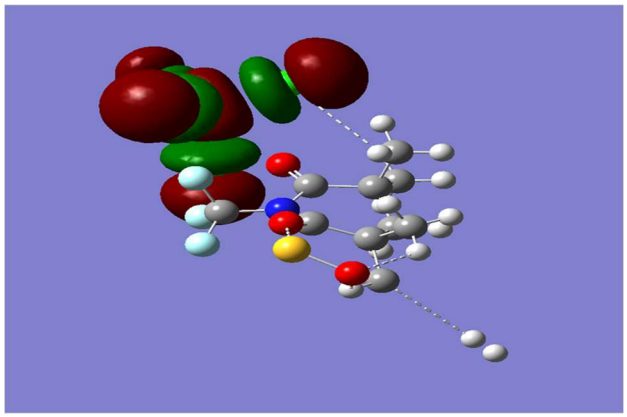
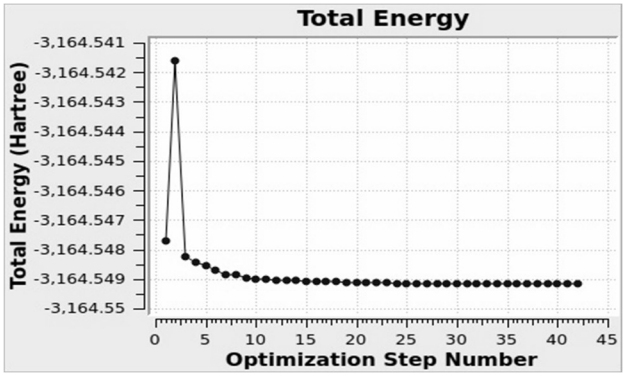


Figure 20 LUMO



Graph 6 Energy Profile Diagram

f(ii)Energy Profile Diagram

After the entire optimization, the energy obtained in case of final product is-ve. The energy rises to a maximum and drops to a minimum at the end of optimization and the overall reaction is endothermic (Graph-6)

g) Reactions of Oxathrene-S-Oxide of Carbene-1 with Pseudo Halogens (ICN)

In this case Carbonyl compound and SO are produced. The ICN remains unaltered. The N of NH interacts with S of SO. The H of NH interacts with I of ICN. (Figure 21)

g(i) Characterization

HOMO

HOMO also shows the interaction of N of NH with S of SO. Besides this the H of NH interacts with I of ICN. Thus, SO_2 fixation occurs here. (Figure 22)

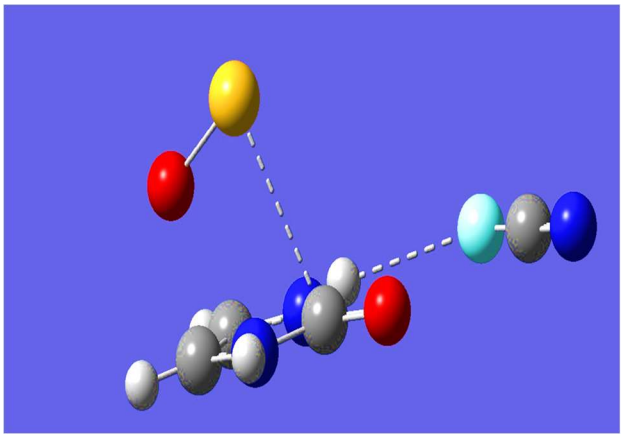


Figure 21 Reactions of Oxathrene-S-Oxide of Carbene-1 with Pseudo Halogens (ICN)

LUMO

LUMO also shows the interaction of N of NH with S of SO. Besides this the H of NH interacts with I of ICN. Thus SO_2 fixation occurs here. (Figure 23)

g(ii)Energy Profile Diagram

After the entire optimization, the energy obtained in case of final product is-ve. The energy drops from maximum to minimum after the end of optimization and at the end it becomes endothermic. (Graph-7)

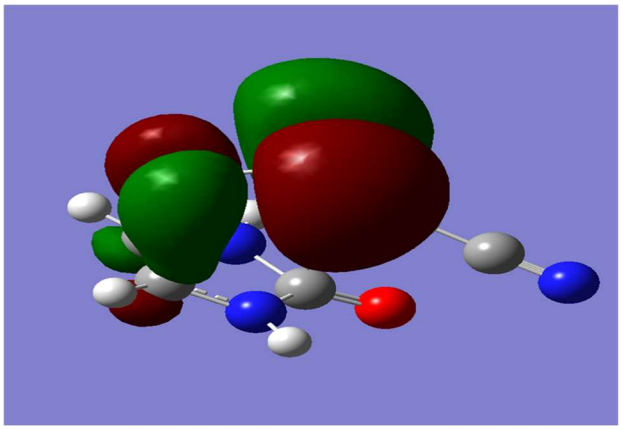


Figure 22 HOMO

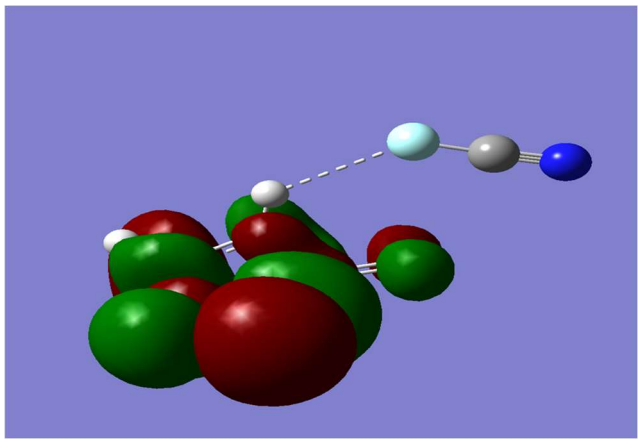
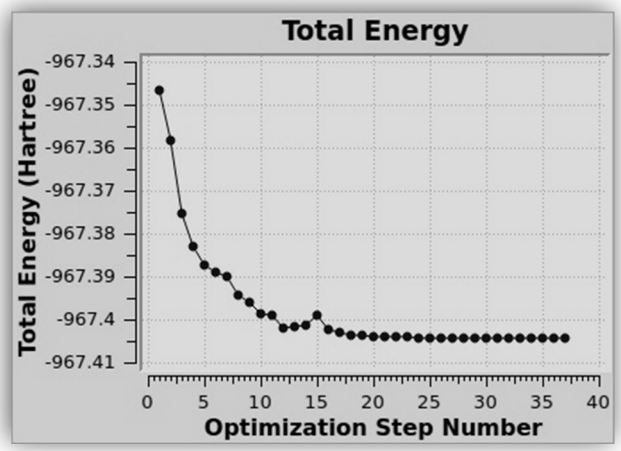


Figure 23 LUMO



Graph 7 Energy Profile Diagram

h) Reactions of Oxathrene-S-Oxide of Carbene-1 with Thionyl Chloride ($SOCl_2$)

In this case C=O and SO are formed. The C of C=O interacts with S of S=O. The H of CH also interacts with Cl . There is also an interaction between S and Cl. (Figure 24)

h(i) Characterization

HOMO

HOMO also proves the interaction between the C of C=O and S of SO. The H of CH also interacts with Cl. There is also an interaction between S and Cl. So, this is a case of SO_2 fixation. (Figure 25)

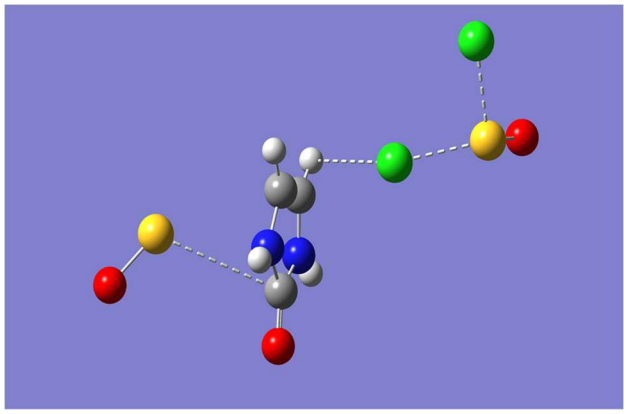


Figure 24 Reactions of Oxathrene-S-Oxide of Carbene-1 with Thionyl Chloride ($SOCl_2$)

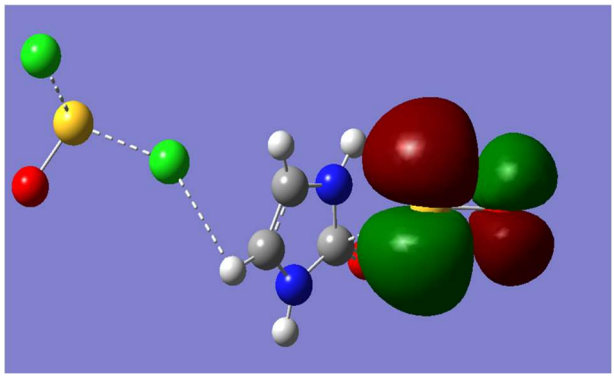


Figure 25 HOMO

LUMO

LUMO also proves the interaction between the C of C=O and S of SO. The H of CH also interacts with Cl. There is also an interaction between S and Cl. So, this is a case of SO_2 fixation. (Figure 26)

h(ii) Energy Profile Diagram

After the entire optimization, the energy obtained in case of final product is -ve The energy rises to a maximum and drops to a minimum at the end of optimization and the overall reaction is endothermic (Graph-8).

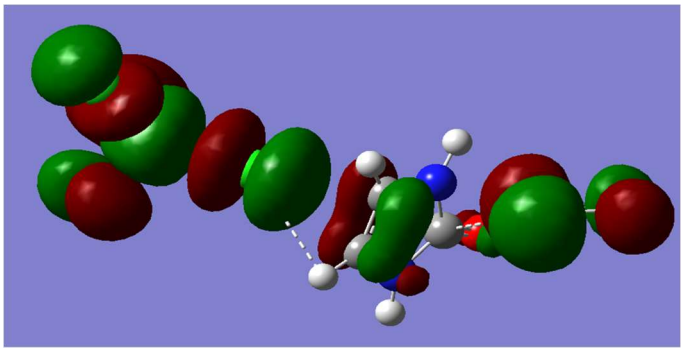
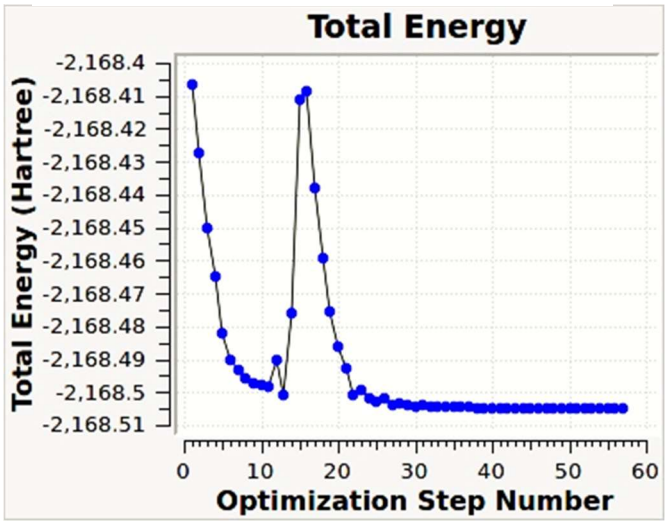


Figure 26 LUMO



Graph 8 Energy Profile Diagram

i) Reactions of Oxathrene-S-Oxide of Carbene-1 with Oxychloride (Cl_2O)

In this case also C=O and SO are formed. There is an interaction between N of NH and S of SO. There is also an interaction between H of CH and O which in turn interacts with Cl (Figure 27)

i(i) Characterization

HOMO

HOMO shows the interaction between N of NH and S of SO. There is also an interaction between H of CH and O which in turn interacts with Cl. Thus there is SO_2 fixation (Figure 28).

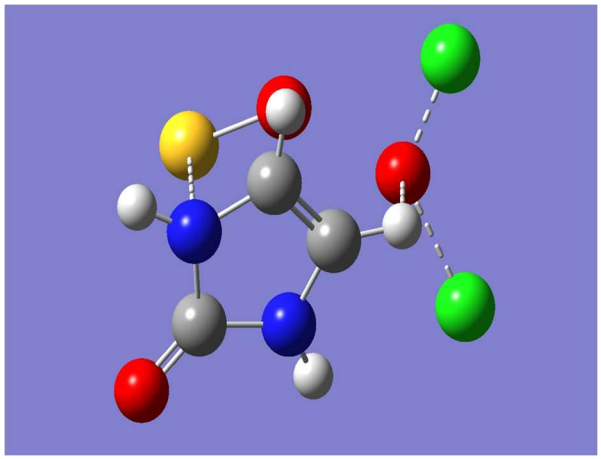


Figure 27 Reactions of Oxathrene-S-Oxide of Carbene-1 with Oxychloride (Cl_2O)

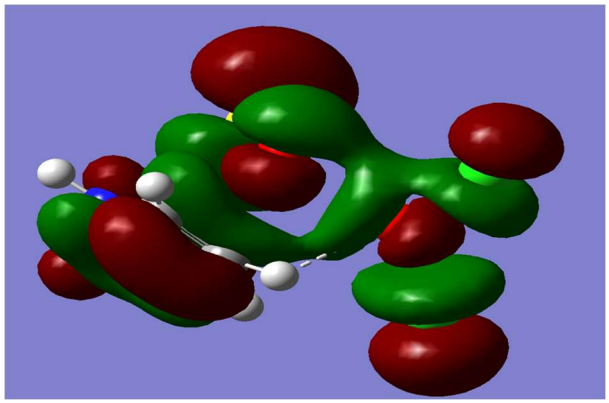


Figure 29 LUMO

LUMO

LUMO shows the interaction between N of NH and S of SO. There is also an interaction between H of CH and O which in turn interacts with Cl. Thus there is SO_2 fixation (Figure 29).

i(ii) Energy Profile Diagram

After the entire optimization, the energy obtained in case of final product is -ve. The energy drops from maximum to minimum after the end of optimization and at the end it becomes endothermic(Graph-9).

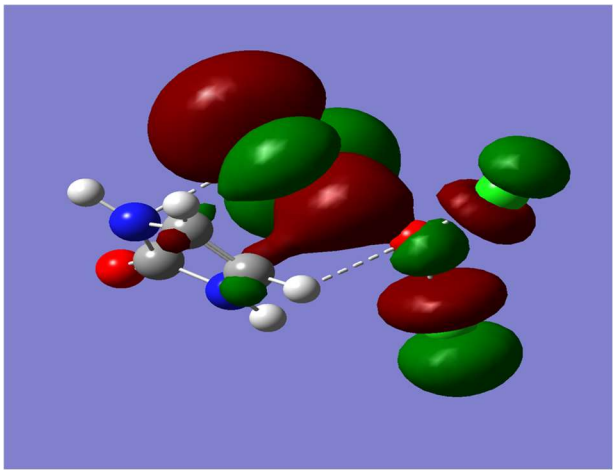
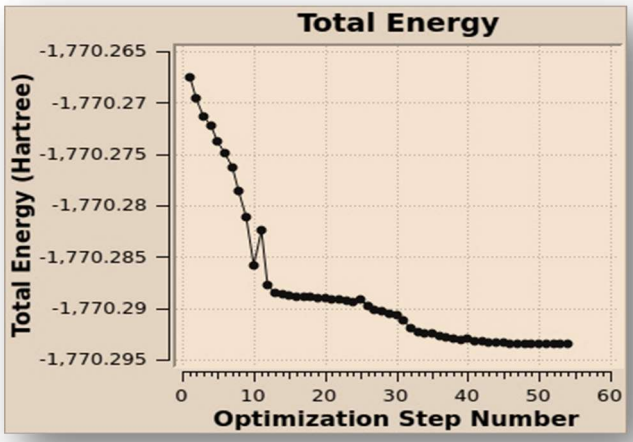


Figure 28 HOMO



Graph 9 Energy Profile Diagram

j) Reactions of Oxathrene-S-Oxide of Carbene-3 with Interhalogens (BrF_3)

In this case SO and C=O are formed. There is an interaction between O of CO and S of SO. There is also an added interaction between O of SO and H of CH_3. Br is bonded to F which in turn interacts with another F. (Figure 30).

j(i) Characterization

HOMO

HOMO shows the interaction between O of CO and S of SO. There is also an added interaction between O of SO and H of CH_3. Br is bonded to F which in turn interacts with another F. Thus SO_2 gets fixed (Figure 31).

LUMO

LUMO shows the interaction between O of CO and S of SO. There is also an added interaction between O of SO and H of CH_3. Br is bonded to F which in turn interacts with another F. Thus SO_2 gets fixed (Figure 32).

j(ii) Energy Profile Diagram

After the entire optimization, the energy obtained in case of final product is-ve. The energy rises to a maximum and drops to a minimum at the end of optimization and the overall reaction is endothermic. (Graph-10).

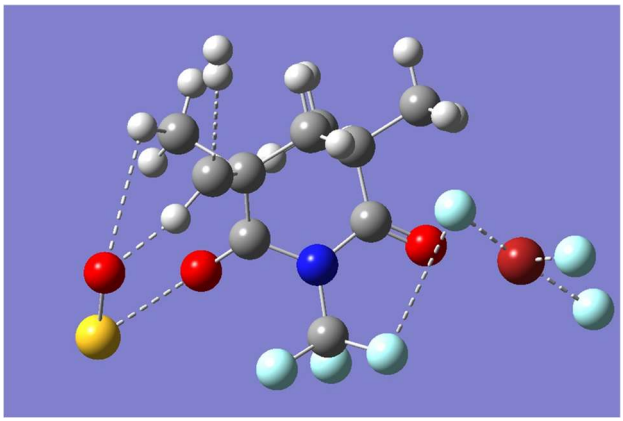


Figure 30 Reactions of Oxathrene-S-Oxide of Carbene-3 with Interhalogens (BrF_3)

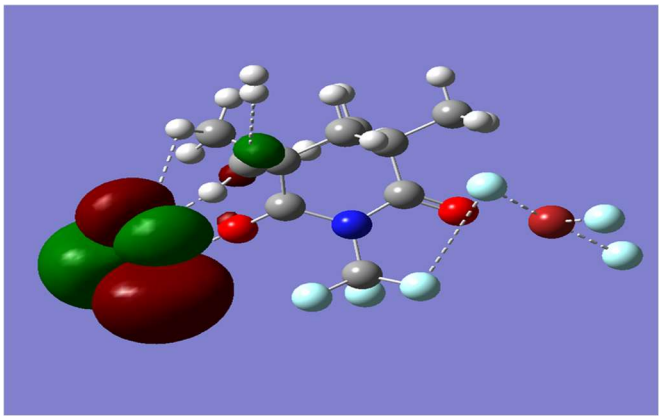


Figure 31 HOMO

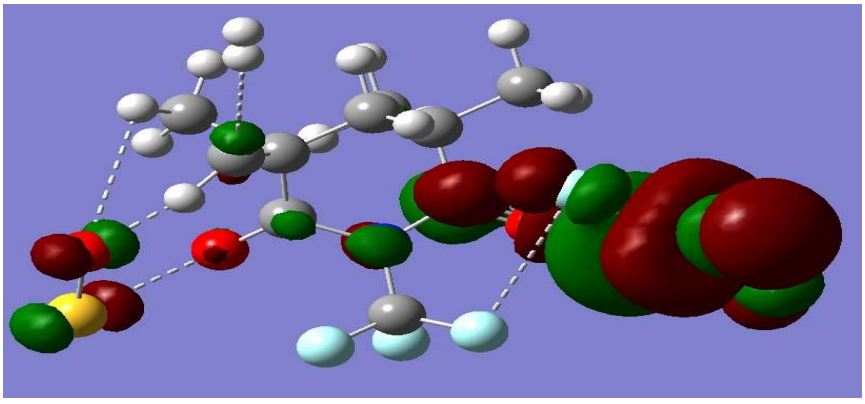
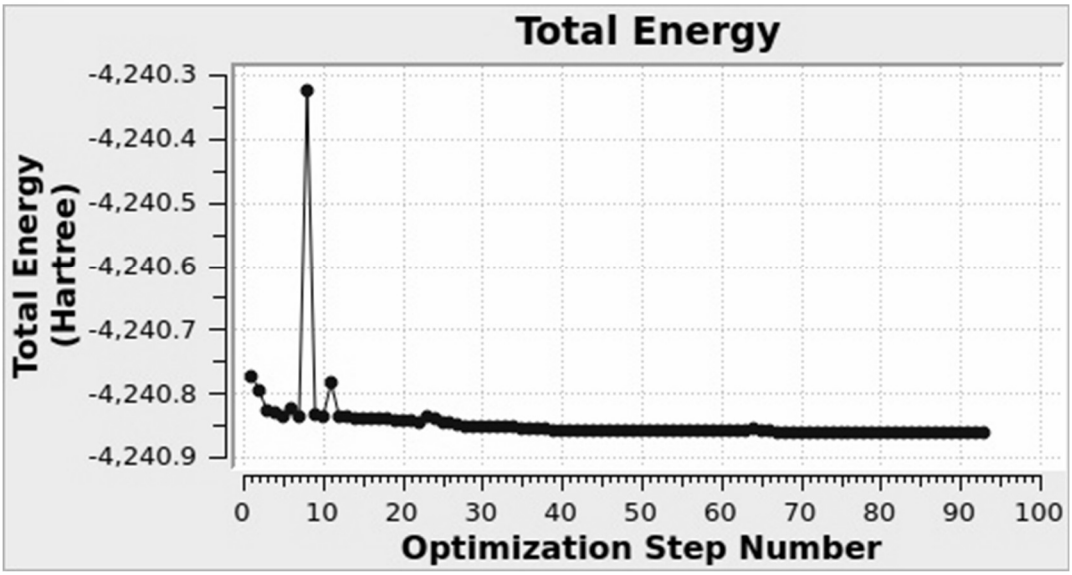


Figure 32 LUMO



Graph 10 Energy Profile Diagram

k) Reactions of Oxathrene-S-Oxide of Carbene-1 with Interhalogens (BrF_3)

There is a weak interaction between H of CH with F. Another weak interaction occurs between H of NH and F. The Br present here also interacts with F. O present in the optimized structure also interacts with S. (Figure 33).

k(i) Characterization

HOMO

HOMO shows the weak interaction between H of CH and F. Another weak interaction occurs between H of NH and F in HOMO. The Br present here also interacts with F. O present in the optimized structure also interacts with S. (Figure 34).

LOMO

LUMO shows the weak interaction between H of CH and F. Another weak interaction occurs between H of NH and F in HOMO. The Br present here also interacts with F. O present in the optimized structure also interacts with S. (Figure 35).

k(ii) Energy Profile Diagram

After the entire optimization, the energy obtained in case of final product is -ve. The energy rises to a maximum and drops to a minimum at the end of optimization and the overall reaction is endothermic. (Graph-11).

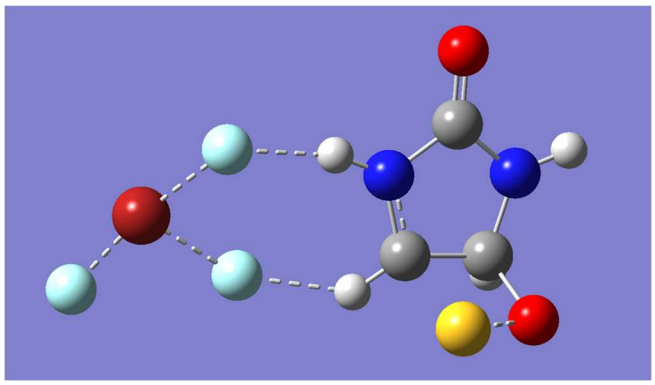


Figure 33 Reactions of Oxathrene-S-Oxide of Carbene-1 with Interhalogens (BrF_3)

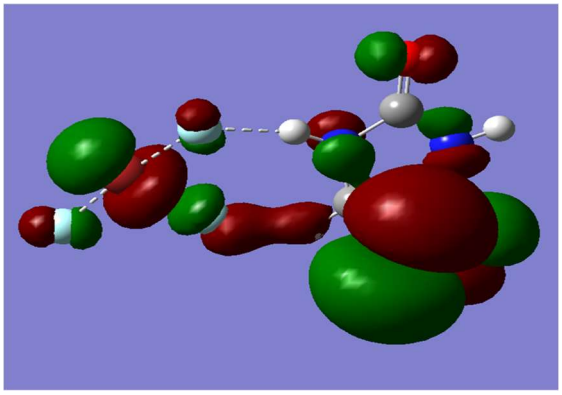


Figure 34 HOMO

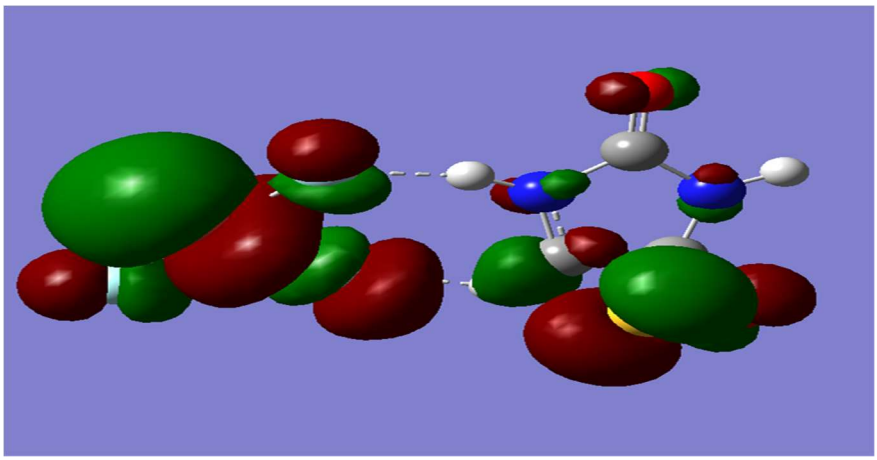
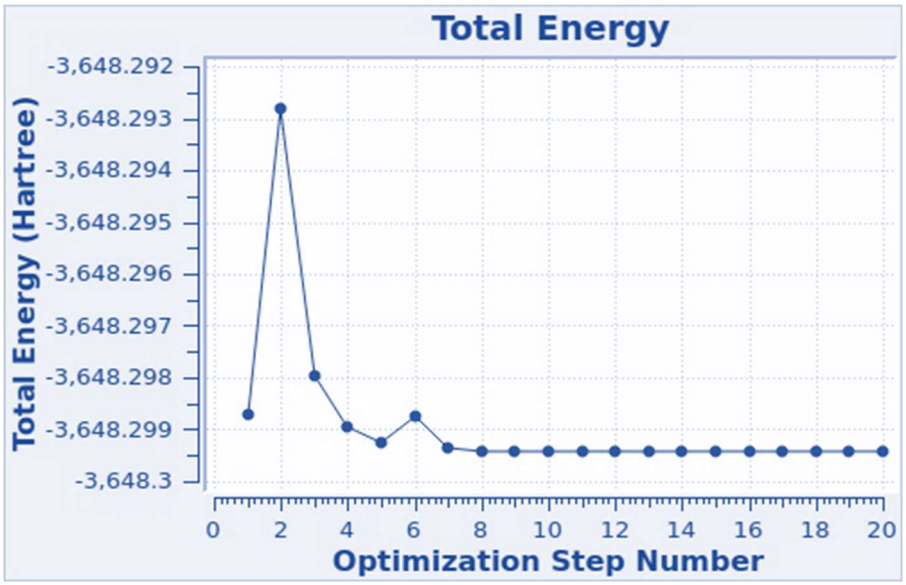


Figure 35 LUMO



Graph 11 Energy Profile Diagram

l) Reactions of Oxathrene-S-Oxide of Carbene-1 with Alkynes (Acetylene)

One beautiful example is that oxathrene-S-oxygen remains noninteractive. Thus, this oxathrene-S-oxide is extremely stable. Acetylene also remains unreacted. There is an interaction between H of N-H and H of Acetylene (Figure 36).

l(i) Characterization

HOMO

HOMO also proves that oxathrene-S-oxygen remains non-interactive. Thus this oxathrene-S-oxide is extremely stable. There is an interaction between H of N-H and H of Acetylene (Figure 37).

LUMO

LUMO also proves that oxathrene-S-oxygen remains non-interactive. Thus, this oxathrene-S-oxide is extremely stable. There is an interaction between H of N-H and H of Acetylene (Figure 38)

l(ii) Energy Profile Diagram

After the entire optimization, the energy obtained in case of final product is -ve. The energy drops from maximum to minimum after the end of optimization and at the end it becomes endothermic. (Graph-12).

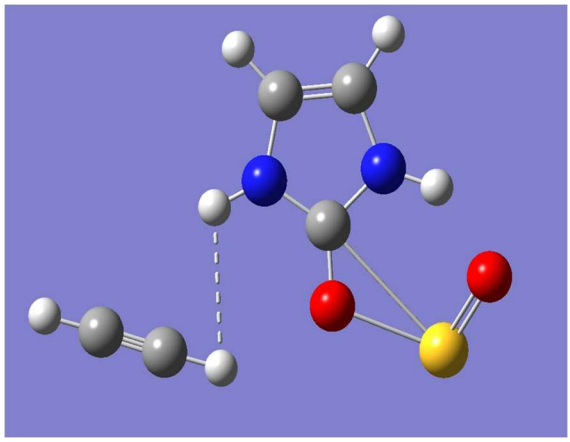


Figure 36 Reactions of Oxathrene-S-Oxide of Carbene-1 with Alkynes (Acetylene)

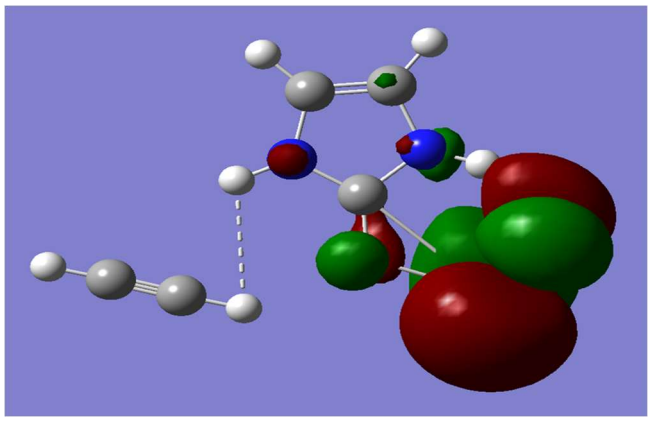


Figure 37 HOMO

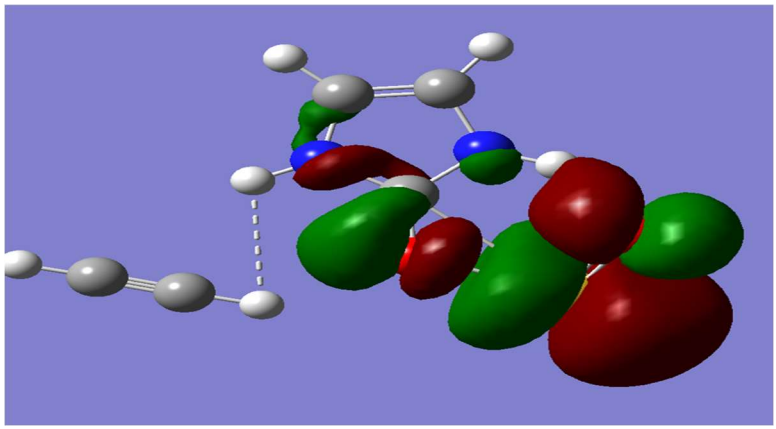
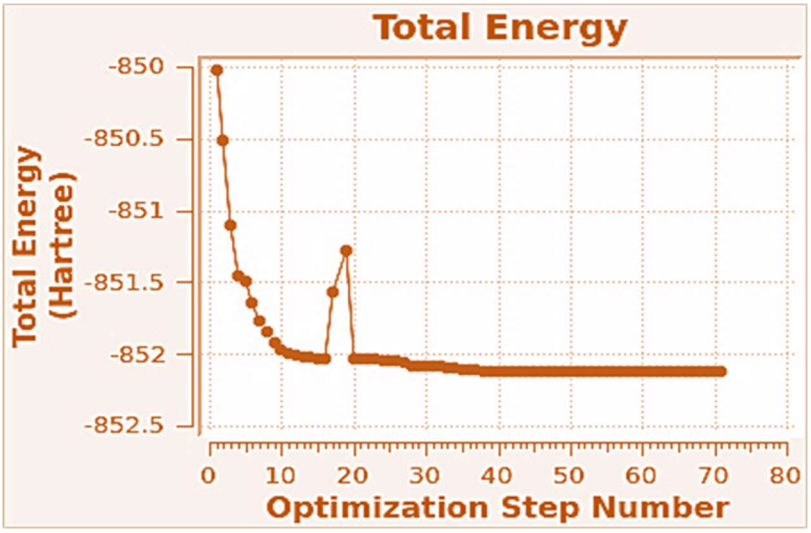


Figure 38 LUMO



Graph 12 Energy Profile Diagram

m) Reactions of Oxathrene -S-Oxide of Carbene-1 with Allenes

In this case a C=O species is seen. Along this a beautiful rare species SOH is seen in which H of SOH interacts with C of CH_2. Another interaction occurs between H of NH with O of SOH. (Figure 39).

m(i) Characterization

HOMO

HOMO/LUMO also shows presence of one of the rarest SOH species. Another interaction occurs between H of NH with O of SOH. (Figure 40).

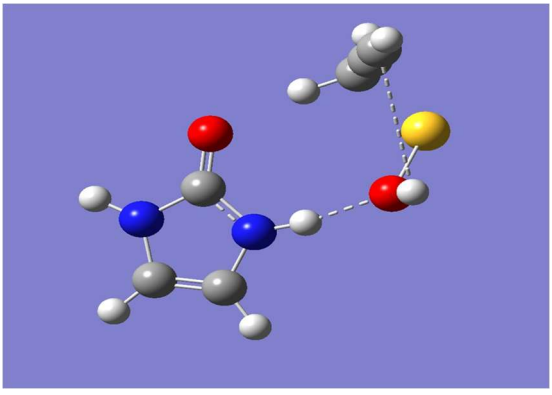


Figure 39 Reactions of Oxathrene -S-Oxide of Carbene-1 with Allenes

LUMO

HOMO/LUMO also shows presence of one of the rarest SOH species. Another interaction occurs between H of NH with O of SOH. (Figure 41).

m(ii) Energy Profile Diagram

After the entire optimization, the energy obtained in case of final product is -ve. The energy drops from maximum to minimum after the end of optimization and at the end it becomes endothermic(Graph-13).

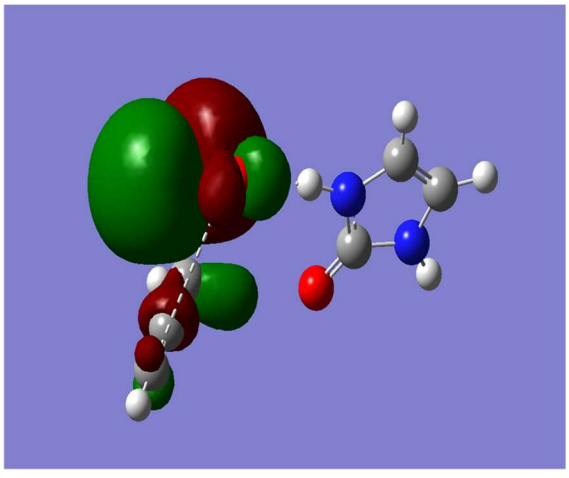


Figure 40 HOMO

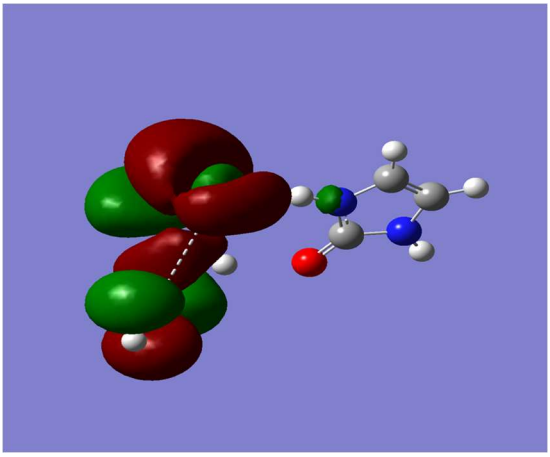
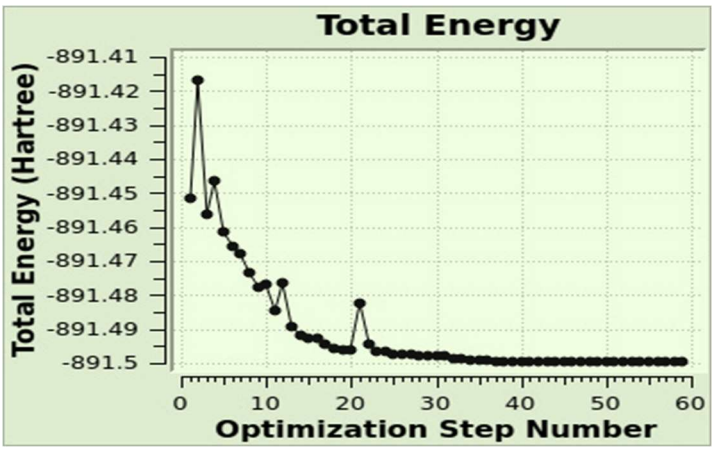


Figure 41 LUMO



Graph 13 Energy Profile Diagram

4. Conclusion

SO_2 fixation occurs in most of the reactions. Rarest SOH species is also shown in the optimized structure. As a result of this, the greenhouse activity of SO_2 might get reduced which is one of the primary aims of green chemistry. Another advantage is in the case of reaction of acetylene with oxathrene-S-oxide derivative is the stability of oxathrene-S-oxide derivative.

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