Ab Initio Molecular Orbital and Density Functional Studies on the Ring-Opening Reaction of
1, 2-Dihydroazete

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Abstract - **Electrocyclic ring opening (ERO) reaction of 1, 2-dihydroazete has been carried out computationally in the gas phase and ring opening barrier has been computed. When comparing the ERO reaction of 1, 2-dihydroazete with the parent hydrocarbon (cyclobutene), the ring opening of 1, 2-dihydroazete is found to exhibit pericyclic nature. Bond order analysis and extent of reaction calculation at the transition state indicate that the ring opening reaction is exothermic in nature. Computation of the nucleus-independent chemical shift (NICS) adds evidence for pericyclic behavior. By locking of lone pair of electrons by hydrogen bonding to conform whether the lone pair electron present in nitrogen atom involve in ERO are not. It is seen that the lone pair electron not involve in ERO and hence ERO of 1, 2-dihydroazete is pericyclic in nature.**

KeyWord **-** *ERO; Pseudopericyclic; MP2; DFT; Exothermic reaction; NICS; LLPE.*

I. INTRODUCTION

There are many reactions in organic chemistry that give no evidence of involving intermediates. Absence of evidence of intermediates leads to the conclusion that the reactions are single-step processes in which bond making and bond breaking both contributes to the structure at the transition state. Such processes are called concerted reactions. An important group of concerted reactions are the concerted pericyclic reaction[1]. Pericyclic reactions must occur through cyclic transition states. The key to understanding the mechanism of the concerted pericyclic reactions was the recognition by Woodward and Hoffmann[2] that the pathways of such reactions were determined by the symmetry properties of the orbital that were directly involved. There are three types of pericyclic reactions cycloaddition, sigmatropic migration reactions and electrocyclic reactions. In some pericyclic reaction non-bonding electron also take part in the cyclic transition state such reaction called pseudopericyclic reactions are

attracting attention in recent years though they were first identified by Lemal *et al*., in 1976[3]. After that there was a long gap until Birney and coworkers[4-8] later studied them in detail. These reactions are concerted transformations where primary changes in bonding encompass a cyclic array of atoms, at one (or more) of which nonbonding and bonding atomic orbital interchange roles. Pseudopericyclic reactions fell into oblivion until Birney first and several other authors[9-18] later revived interest in them by showing that a number of organic syntheses involve this type of process. However, until now, no universally accepted clear-cut, absolute criterion exists for distinguishing a pseudopericyclic reaction from a normal pericyclic reaction. This has raised some controversy in classifying some reactions[19-23]. Evaluation of magnetic properties can be very useful to assess aromatization along the reaction. This fact can be interesting to study the pericyclic character of a reaction since the cyclic loop of a pericyclic reaction yields an aromatic transition state[24], as quantitatively confirmed for various reactions.[25-28] Herges *et al* showed that, in the vicinity of the transition state (TS) in the Diels–Alder reaction, the magnetic susceptibility χ and its anisotropy χ_{anis} exhibit well defined minima with respect to the reactant and product[25]. On the other hand, the typical disconnection of pseudopericyclic reactions would have prevented this enhanced aromatization, Pseudopericyclic reactions typically have nearly-planar transition states, low activation energies, disconnections in orbital overlap and are symmetry allowed. The most widely employed method to analyze the aromaticity is the NICS index[29-35]. This magnetic-based descriptor of aromaticity was introduced by Schleyer and co-workers[36]. It is defined as the negative value of the absolute shielding computed at a ring center or at some other point, usually at 1 Å above and below the ring center. Rings with large negative NICS values are considered aromatic, non-aromatic species have NICS values close to zero and positive NICS values indicates antiaromaticity. We have studied the thermolysis of 1, 2-

dihydroazeteand on comparison with cyclobutene it is evident that the Nitrogen atom substantially alters the potential energy surface for ERO. This has motivated us to look at the pericyclic/ pseudoopericyclic character of ERO of 1,2-Dihydroazete . Therefore ERO reactions of 1, 2-dihydroazetehave been investigated with a view to bring out the role of nitrogen in altering their pericyclic / pseudopericyclic behaviors. Locking of lone pair electron (LLPE) method is used to investigate pseudopericyclic nature in addition to NICS.

II.   COMPUTATIONAL METHOD

Electrocyclic ring-opening reaction of 1, 2-dihydroazetewas studied using *ab initio* molecular orbital and density functional theory at different level of calculations. The levels used are MP2/6-31+G**,B3LYP/6-31+G**, MP2/6-311+G** and B3LYP/6-311+G**.The geometries of the reactants, transition states and the products were examined by complete structural optimization using the software PC GAMESS/Firefly QC package[37], which is partially based on the GAMESS (US)[38] source code. Transition state of this reaction was located and intrinsic reaction coordinates (IRC) calculations were performed at MP2/6-31+G**, B3LYP/6-31+G**. MP2/6-

311+G** and B3LYP/6-311+G** to conform that the transition state (TS) connects particular reactant and product. All the frequencies of reactants and products have real values while the transition states have one imaginary frequency. NICS values were also computed with the B3LYP/6-311+G** basis using the gauge including atomic orbital method (GIAO[39]) implemented in GAUSSION-03[40]. The magnetic shielding tensor was calculated for ghost atoms located at the ring critical points (RCP), the point of lowest density in the ring plane[41], as suggested by Cossı´o *et al*[42]. These values are denoted as NICS (0), according to the practice described by Schleyer *et al*.[43] who calculated the NICS at the geometrical center (GC) of the ring. When highly symmetric molecules are studied, both points RCP and GC, usually coincide. Similarly, NICS values at 1.0 Å above the perpendicular plane of the ring, NICS (1)[44], as well as the NICS (1) zz tensor component have been calculated or at some other interesting point of the system. This quantity gives probably the best measure of aromaticity among the different NICS related definitions[45]. These values of NICS were calculated with the aim to measure the aromaticity due to π-system, sometimes obscured by the σ-current. The graphical outputs are visualized in this work were generated using MacMolplt[46].
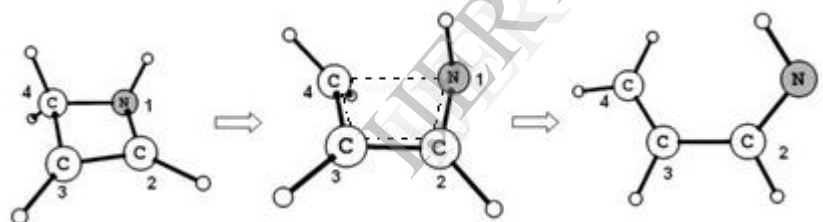
III.   RESULT AND DISCUSSION

FIGURE 1. STRUCTURE OF THE REACTANT, TRANSITION STATE AND

PRODUCT FOR THE ERO REACTION OF 1, 2-DIHYDROAZETE.

Energies of the reactant, transition state, and the product for the ERO reaction of 1, 2-dihydroazete was calculated and is given in Table 1. Energy values are in hartrees and the relative energies are given in kcal mol^{-1}.The transition sate for the ring-opening of 1, 2-dihydroazete has one imaginary frequency and has a value of 801.24 i cm^{-1} at the B3LYP/6-311+G** level of calculation. All other frequencies were found to be positive. This shows the obtained transition state is a first order saddle point. The ring opening of 1, 2-dihydroazete has energy barrier of 35.0 - 73.7 kcal mol^{-1} at varies levels of calculations to give the product. The structure of reactant, transition state and product in the ring opening of 1, 2-dihydroazete is shown in Fig. 1. The extents

to which the bonds have been broken or formed at the transition state have been calculated from the bond order values.

The percentages of bond formation (BF_i) and cleavage (BC_j) at the transition state, have be defined by Manoharan and Venuvanalingam[47, 48] as follows

$$BF_i \text{ or } BC_j = \frac{(BO_{i/j}^{TS} - BO_{i/j}^{R})}{(BO_{i/j}^{P} - BO_{i/j}^{R})} *100\% \qquad (1)$$

TABLE 1. ENERGIES IN (HARTREES) AND RELATIVE ENERGY IN (KCAL MOL^{-1}) GIVEN IN PARENTHESES FOR THE ELECTROCYCLIC RING OPENING OF 1, 2-DIHYDROAZETE.

Levels of calculation	Reactant (1,2-Dihydroazete)	Transition sate	Product (Prop-2-en-1-imine)
MP2/6-31+G**	-171.5377537 (17.6)	-171.4202810 (91.3)	-171.5658470 (0.0)
B3LYP/6-31+G**	-172.0176403 (19.7)	-171.9608109 (55.3)	-172.0489544 (0.0)
MP2/6-311+G**	-171.5377536 (17.6)	-171.4820282 (52.6)	-171.5658472 (0.0)
B3LYP/6-311+G**	-172.0548308 (20.2)	-171.9982899 (55.7)	-172.0870965 (0.0)

Where $BO_{i/j}^{TS}$ is the bond order between atoms i and j at the transition state, while $BO_{i/j}^{R}$ and $BO_{i/j}^{P}$ represent the bond order at the reactant and the product stage respectively. From this calculation it shows that the atoms N_1, C_2, C_3 and C_4 involve in electrocyclic ring opening reaction and the percentage of reaction is below 50% is given in table 2. This shows that transition state is closer to the reactant, thus characterizing an exothermic reaction. Intrinsic reaction coordinates (IRC) calculations have been performed to confirm that the transition state connects the particular reactant and product.

TABLE 2. PERCENTAGE OF REACTION COMPUTED AT B3LYP/6-311+G**

Bond order between	Reactant (1,2-Dihydroazete)	Transition state	Product (Prop-2-en-1-imine)	Percentage of reaction
C_4-C_3	1.017	1.194	1.874	20.7
C_3-C_2	1.915	1.692	0.995	24.2
C_2-N_1	0.978	1.265	1.913	30.7
C_4- N_1	0.885	0.647	0.078	29.5

A. PSEUDOPERICYCLIC REACTION

According to Birney et al[4-8], pseudopericyclic reactions have planar or nearly planar transition states and usually exhibit small reaction barrier. Figure 1 presents the ERO reactions. Energy barrier profile for ERO of 1, 2-dihydroazeteand cyclobutene calculated at varies level of calculation is presented in Table 3. Experimental value for ERO of cyclobutene is also given in Table 3. When comparing theoretical values of 1, 2-dihydroazete with theoretical and experimental values of cyclobutene, the slight higher energy barrier 35.0 - 35.5 kcal mol^{-1} of the

ERO of 1, 2-dihydroazete indicates it is in pericyclic nature. At the TS the dihedral angle of 1, 2-dihydroazete is much less compared to that of cyclobutene. The less dihedral angle (more planar geometry) of 1, 2-dihydroazete in TS indicates pseudopericyclic character. To understand the pericyclic/pseudopericyclic nature better NICS and LLPE methods were applied.

Table 3. Energy barrier in (kcal mol^{-1}) for the ring-opening reaction of cyclobutene and 1, 2-dihydroazete

Levels of calculation	Cyclobutene	1,2-Dihydroazete
MP2/6-311+G**	34.0	35.0
B3LYP/6-311+G**	33.3	35.5
Experimental Values	32.9	-

B. NUCLEUS-INDEPENDENT CHEMICAL SHIFT (NICS)

For ERO the choice of the points to calculate NICS is not so obvious in the center of the forming ring and/or 1 A° above or below this point to avoid spurious effects associated to σ bonds[53] for that reason we decided to calculate NICS not only in a particular point but in a set of points defined by a line, which passes through the geometrical center of the four-membered ring. This calculation was done for the transition state (TS) and for the reactant to observe the differences between them. The results are presented in Figure 2 shows the enhanced aromaticity, which takes place at the transition state. When comparing the NICS data of transition state and reactant, we can conclude that the transition state shows a greater aromaticity, which normally takes place at the transition state for pericyclic reaction. Comparing the NICS profile of ERO of 1, 2-dihydroazete with and without LLPE by hydrogen bonding on Nitrogen atom conforms lone pair of electron on N_1 not involve in ERO. From the Figure 2 comparing the NICS value of reactant and TS of with and without LLPE in nitrogen atom shows enhanced aromaticity in TS it conform pericyclic nature. Comparing the NICS value of both TS of with and without LLPE shows no contribution of lone pair electrons during the ERO reaction.
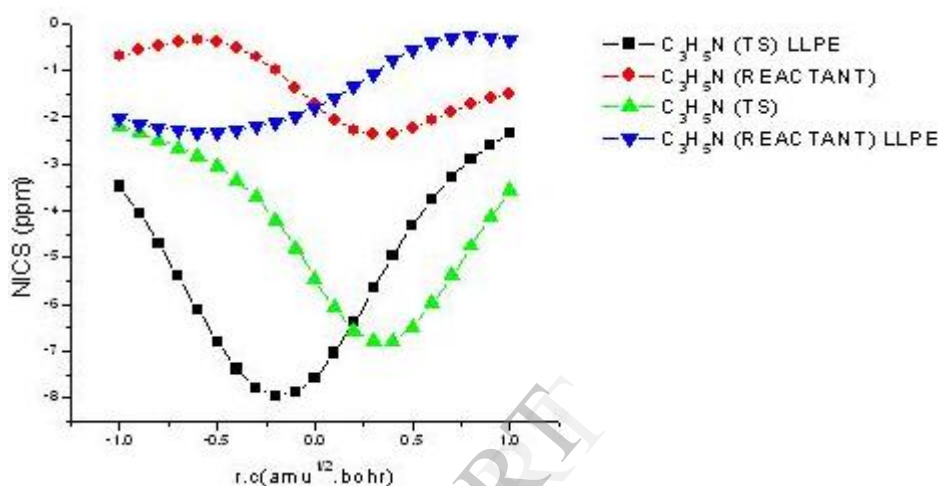

FIGURE 2. VARIATION OF NICS ALONG THE REACTION COORDINATES

C. LOCKING OF LONE PAIR OF ELECTRONS (LLPE)

The ring opening of 1, 2-dihydroazete can takes place by two modes. The first possibility is the shifting of the double bond at C_2-C_3 to form a double bond at C_2-N_1. Synchronously the bond-pair of electrons from C_4-N_1 migrates to C_4-C_3 to form a double bond at C_4-C_3. In this mode the lone-pair of electrons on the Nitrogen atom cannot get involved. In the second mode double bond at C_2-C_3 is shifted to C_3-C_4 to form a double bond at C_3-C_4. Simultaneously the bond-pair of electrons from C_4-N_1 is shifted to N_1-C_2 to form a double bond there. The lone-pair of electrons on the Nitrogen atom N_1 competes with the above process in getting shifted to the bond at N_1-C_2 to form a double bond. The competition of electron pair shifting from either the bond-pair of electrons at C_4-N_1 or the lone-pair of electrons on the Nitrogen atom N_1 to the bond at C_2-N_1 to form a double bond is the cause of the pseudopericyclic nature of the transformation. When the lone-pair of electrons on the Nitrogen atom N_1 is locked by hydrogen bonding to a molecule of water by LLPE method the percentage of reaction gets altered substantially, indicating the involvement of the lone-pair of electrons and also the direction of the flow of electrons.

TABLE 4. PERCENTAGE REACTION OF 1, 2-DIHYDROAZETE WITH AND WITHOUT LLPE

BY H_2O COMPUTED AT B3LYP/6-311+G**

Bond order between	Percentage of reaction without H_2O	Percentage of reaction with H_2O
C_4-C_3	20.7	21.1
C_3-C_2	24.2	24.1
C_2-N_1	30.7	32.9
C_4-N_1	29.5	27.2

Percentage of reaction for ERO reaction of 1, 2-dihydroazete with locking of lone pair electron and without

locking of lone pair electron shows below 50% presented in Table 4. This shows that the transition state is closer to the reactant, thus characterizing an exothermic reaction. In the absence of hydrogen bonding by water molecule the percentage of reaction at C_2-N_1 is found to be

30.7. When hydrogen bonded by a molecule of water the percentage of reaction is increase to 32.9 as presented in Table 4. This indicates that the reaction is pericyclic. When locking the lone pair of electrons on the nitrogen atom, it increases the percentage of reaction by almost 2.2. This shows the lone pair of electron present on N_1 not involves in ERO reaction of 1, 2-dihydroazete. Hence the reaction is pericyclic nature.

IV   CONCLUSION

ERO reaction of 1, 2-dihydroazete was studied using *ab initio* molecular orbital and density functional theory. Transition state for this reaction was located and the energy barrier (35.0 – 73.7 kcal mol^{-1}) of this reaction was calculated at different levels of theory. When comparing the ring opening of 1, 2-dihydroazete with cyclobutene the ring opening of 1, 2-dihydroazete was found to be pericyclic in nature, even though it has more planar transition state. To investigate the behavior of aromaticity in ring opening of 1, 2-dihydroazete, we have computed the NICS profiles which show enhanced aromaticity in transition state when compared with reactant. This normally takes place at the transition state for pericyclic reaction. LLPE method also used to confirm the pericyclic/Pseudopericyclic nature of ERO reaction. From NICS profile and LLPE method we concluded the ERO reaction of 1, 2-dihydroazete is pericyclic in nature.

ACKNOWLEDGMENTS

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