Indian Journal of Chemistry
Vol. 47B, January 2008, pp. 90-96

Ab initio and DFT investigation of the mechanism and stereochemistry of electrophilic addition reaction of chlorine to bicyclo[3.2.2]nona-6,8-diene

Rza Abbasoglu[1]*, Yaprak Uygur[1] & Abel Magerramov[2]

[1]Department of Chemistry, Karadeniz Technical University, 61080 Trabzon, Turkey

[2]Department of Chemistry, Baku State University, Baku, Azerbaidjan

E-mail: rabbas@ktu.edu.tr

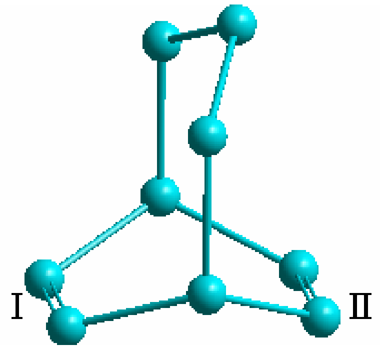
Received 11 January 2007; accepted (revised) 16 July 2007

Full geometric optimization of bicyclo[3.2.2]nona-6,8-diene (BND) is done by *ab initio* and DFT methods and the structure of the molecule is also investigated. The double bond (I) situated in the opposite direction of methylene group in BND molecule is more *exo* pyramidalized than the other double bond (II). The electron density ($q_{i,HOMO}$) of the double bond (I) in HOMO of the molecule is more than that of the double bond (II). *Exo* and *endo* faces of *exo* pyramidalized double bonds of the molecule are not equal and electron density is bigger in *endo* faces. The molecular complexes of BND with chlorine have been investigated by B3LYP/6-311+G* method and their stable configurations have been determined. The reason why *endo* molecular complexes are more stable than *exo* molecular complexes, can be explained by electronic and steric factors. Because of electronic factors, BND...Cl_2(*endo*1) complex is more stable than BND...Cl_2(*endo*2). The *endo*-bridged chloronium cation (I) is relatively more stable than the *endo*-bridged cation (II). *Endo*-facial stereoselectivity and regioselectivity should be observed in the addition of chlorine to BND molecule. *Endo*-facial stereoselectivity is caused by electronic and steric effects, and regioselectivity by electronic effects. The rearranged chlorocarbonium cation (IV) is the most stable among the cationic intermediates and the ionic addition reaction occurs via this cation.

Keywords: Electrophilic addition, bicyclo[3.2.2]nona-6,8-diene, *ab initio* and DFT calculations, stereoselectivity and regioselectivity, pyramidalization

Despite the fact that theoretical and experimental investigation of the electrophilic addition of halogens to olefins have been extensively performed, the mechanism and stereochemistry of these reactions are still under discussion as well as the nature, the structure and the stability of the reaction intermediates. Olefin-halogen molecular complexes detected both experimentally and theoretically are the important intermediates formed in the earlier steps of the addition reaction[1-4]. In order that the role of the complexes may be correctly understood, structural information is required that is difficult to obtain by experimental means because of the fast reactions occurring in the systems. These kind of calculations are also important in terms of stabilities and structures of cationic intermediates formed through the reactions. The experimental investigation of the intermediates is extremely difficult because of their low stabilities and high reactivities. Quantum chemical methods furnish data on the structures and stabilities of the intermediates without being resource to experimental measurements.

The addition reactions of halogens to unsaturated strained molecules and the reaction intermediates have been studied using quantum-chemical methods[5-14]. In this connection, the theoretical investigations of the nonionic and ionic intermediates formed with bromine and chlorine of olefins with rigid structure and sterically encumbered alkens have recently been reported[15-21]. In continuation of our interest in the quantum-chemical studies related to the addition of halogens to rigid and unsaturated bicyclic systems, we wish to report here the results obtained for the investigation of the addition of chlorine to bicyclo[3.2.2]nona-6,8-diene (BND). This work describes a theoretical investigation of the BND…Cl_2 molecular complexes and cationic intermediates. It is interesting to investigate the reasons for the stereo- and regioselectivity properties of this reaction. In order to carry out the detailed analysis of the formation mechanism and stereochemistry of the products in this reaction, a quantum chemical investigation of the structures and the stabilities of the reaction intermediates seem to be very important. In



Scheme I

general, the sterochemical regularities of addition reactions of halogens to bicyclic systems are the subjects of detailed investigation. Stereo- and regio-selectivity of these reactions depend on the geometry and the electron structure of the double bonds of bicyclic olefin to a large extent. The most important factors that affect the structure and the stability of olefin-halogen molecular complexes are the structure and the properties of olefins.

Methodology

The geometry and the electronic structure of the bicyclo[3.2.2]nona-6,8-diene (BND) molecule are investigated by *ab initio* and DFT/B3LYP[22,23] methods in 6-31G* [24], 6-311G* [25] and 6-311+G* [26] basis sets. The theoretical investigation of BND...Cl_2 molecular complexes has been performed by using the B3LYP/6-311+G* method. The predicted cationic intermediates formed in the addition reactions have been investigated through the HF/6-311G*, B3LYP/6-311G* and B3LYP/6-311+G* methods. Full geometry optimization was carried out employing the Polak-Ribiere (conjugate gradient) algorithm (convergence of 0.00001 kcal mol^{-1}) and an RMS gradient at 0.001 kcal $(Å\ mol)^{-1}$. All the calculations have been carried out by using the HYPERCHEM 7.5 and Gaussian 03 program on an IBM Pentium IV computer.

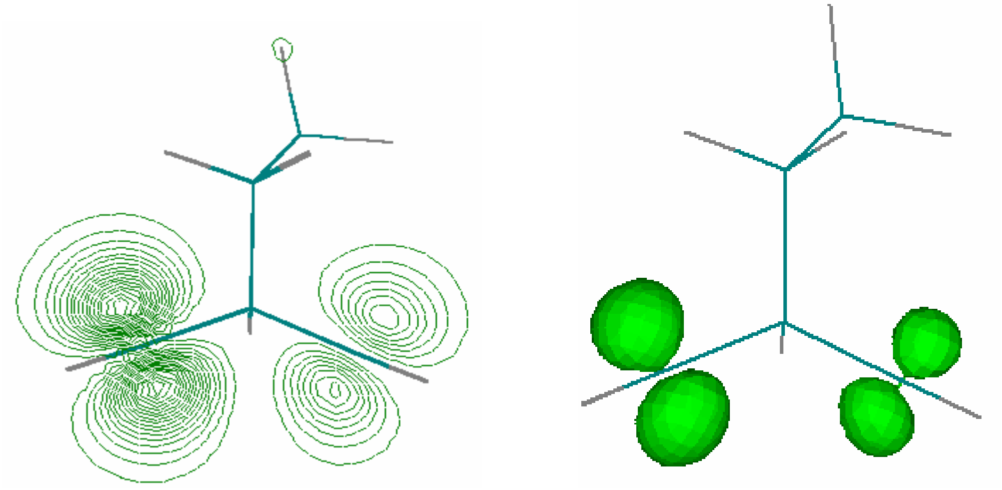
Results and Discussion

Full geometric optimization of the BND molecule is done by *ab initio* SCF and DFT methods in 6-31G*, 6-311G* and 6-311+G* basis sets and the structure of the molecule is also investigated in detail. In the light of the results of each method, the pyramidalization parameters[27,28] of the molecule are evaluated with the aim of determining the structural deformation of double bonds. The values of the pyramidalization angle (ϕ)[27], of twisting (torsion) angle (ϕ_D)[28] and of out-of-plane bending angle (χ)[28] are calculated according to the results of each method of the double bonds which are opposite (I) and same (II) direction (**Scheme I**) with the methylene group in the middle of bridged methylene chain of the BND molecule, given in **Table I**. According to the determined results, the structural deformation of the double bond (I), shown by the values of pyramidalization parameters, is more than that of the double bond (II). Therefore, the double bond (I) of the BND molecule is more *exo* pyramidalized than the double bond (II). Since the double bonds of the BND molecule is *exo* pyramidalized, *endo* selectivity should be observed in the addition reaction to the molecule. In general, the facial selectivity of attack on a pyramidalized olefin parallels the pyramidalization[29,30]. When the pyramidalization degree of the double bond of olefins increases, their chemical reactivities increase[31]. Hence, the addition possibility of chlorine to BND molecule from the double bond (I) is higher.

As seen in **Figure 1**, *exo* and *endo* faces of *exo* pyramidalized double bonds of the molecule are not equal. The electron density in *endo* face of each double bond is high. The chlorination reaction of the BND molecule should show regio- and stereoselective property, hence the addition of chlorine should be realized from *endo* direction which has higher electron density of the double bond (I).

Table I — The calculated double bond lengths (Å), pyramidalization parameters (degrees) and values of electron densities ($q_{i,\ HOMO}$) of bicyclo[3.2.2]nona-6,8-diene

Method	Double bond (I)					Double bond (II)				
	$r_{C=C}$	ϕ	ϕ_D	χ	$q_{i,HOMO}$	$r_{C=C}$	ϕ	ϕ_D	χ	$q_{i,HOMO}$
HF/6-31G*	1.315	2.503	0.0	2.817	0.460	1.319	1.831	0.0	2.052	0.311
HF/6-311G*	1.314	2.524	0.0	2.844	0.465	1.317	1.911	0.0	2.169	0.317
B3LYP/6-31G*	1.333	2.554	0.0	2.887	0.394	1.337	1.973	0.0	2.226	0.295
B3LYP/6-311G*	1.335	2.578	0.0	2.950	0.399	1.339	1.991	0.0	2.234	0.299
B3LYP/6-311+G*	1.329	2.562	0.0	2.914	0.391	1.333	1.982	0.0	2.230	0.293

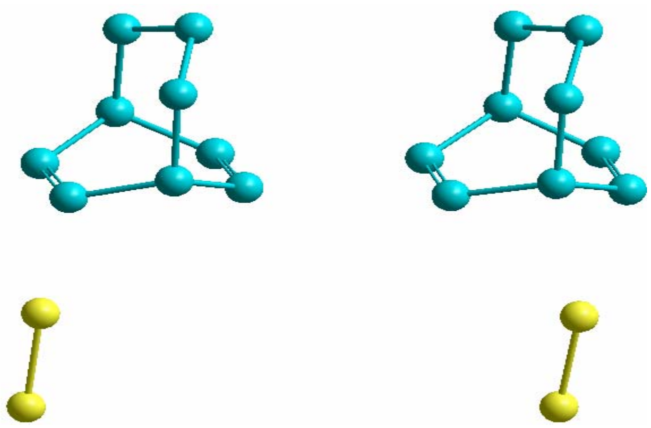


2D contours **3D isosurface**

Figure 1 — Electron density distribution (HOMO) of the bicyclo[3.2.2]nona-6,8-diene molecule (HF/6-311G*).

Table II — The properties of BND...Cl_2 molecular complexes (B3LPY/6-311+G*)

Molecular complex	Stabilization energy (kcal/mol)	Equilibrium distance R_e (Å)	$r_{Cl\text{-}Cl}$ (Å)	Transferred charge from BND to Cl_2 (e)
BND...Cl_2(*endo* 1)	2.176	2.837	2.099	0.054
BND...Cl_2(*exo* 1)	1.624	2.983	2.094	0.041
BND...Cl_2(*endo* 2)	2.126	2.851	2.098	0.053



***endo* 1** ***endo* 2**

Figure 2 — The optimized geometries of BND...Cl_2(*endo*1) and BND...Cl_2(*endo*2) molecular complexes (B3LYP/6-311+G*).

To find out the possible way of approach and the determination of the center of attack for Cl_2 to BND molecule, the BND-Cl_2 system was investigated in detail at the B3LYP/6-311+G* level. In general, the *exo* or *endo* orientation of halogens to the double bond of unsaturated bicyclic systems is possible. On the other hand, a chlorine molecule may approach the double bond in either axial (the C∞ axis of chlorine molecule is perpendicular to the double bond plane) or equatorial (C∞ axis of chlorine molecule is parallel to the double bond plane) position. Thus, the full geometry optimization of BND-Cl_2 system has been performed taking into consideration the fact that the BND molecule involves two double bonds in different positions, and the stable configurations of the system corresponding to the minimum energy level have been determined. So, it has been found that the BND...Cl_2(*endo*1) molecular complex formed by the approach of Cl_2 molecule to the double bond (I) (**Scheme I**) in axial position and in an *endo* orientation correspond to the most stable configuration of BND-Cl_2 system (**Figure 2**, *endo*1). The stabilization energies of the BND...Cl_2 (*endo*1) molecular complex is 2.176 kcal/mol and the equilibrium distance $R_{X\text{-}Cl}$ (X is midpoint of the C=C bond of BND) is 2.837 Å. The other (second) stable configuration corresponds to BND...Cl_2 (*endo*2) (**Figure 2**, *endo2*) molecular complex formed by the *endo* orientation of Cl_2 molecule to the double bond (II) in axial position. The stabilization energy and equilibrium distance of BND...Cl_2(*endo*2) complex has been calculated as 2.126 kcal/mol and 2.851 Å, respectively. The properties of molecular complexes are compiled in **Table II**. On the other hand, the results obtained reveal that the predicted molecular complexes formed by the *exo* approach of Cl_2 molecule to the double bond (I) and double bond (II) (**Scheme I**) in axial position are less stable than the BND…Cl_2(*endo*1) and BND...Cl_2(*endo*2) molecular complexes. Due to the steric hindrance of bridged methylene chains of the BND molecule, the *exo* attack of chlorine molecule on both double bonds is difficult. Thus, the *exo* complexes have become unstable. Since the steric hindrance forming the bridge methylene chain in the double bond (II) direction is higher, BND...Cl_2(*exo*2) complex is more unstable. On the other hand, as it is pointed out that, the electron density ($q_{i,HOMO}$) in *endo* face of *exo* pyramidalized double bonds is higher (**Figure 1**). That is, $HOMO_{BND}$-$LUMO_{chlor}$ interaction realized from *endo* face of the double bond in the formation of *endo* molecular complexes is more effective than that of *exo* face and should be optimal. According to the frontier molecular orbital theory, $HOMO_{olef.}$-$LUMO_{halogen}$ interaction is a decisive factor in the formation of olefin-halogen complex[32]. So, because of electronic and steric factors, *endo* molecular complexes are more stable than *exo* molecular complexes. The double bond (I) of the BND molecule is much more *exo* pyramidalized than double bond (II) and the electron density ($q_{i,HOMO}$) in *endo* face of the bond (I) is bigger than the bond (II) (**Table I** and **Figure 1**). That is, $HOMO_{BND}$-$LUMO_{chlor}$ interaction is more effective in the formation of BND...Cl_2(*endo*1) complex and it causes an increase in the stability of the complex. Therefore, the electronic factor causes BND...Cl_2(*endo*1) complex to be more stable than BND...Cl_2(*endo*2) complex (**Table II**). So, *endo*-facial stereoselectivity is caused by electronic and steric effects, regioselectivity is also basically caused by electronic effects.

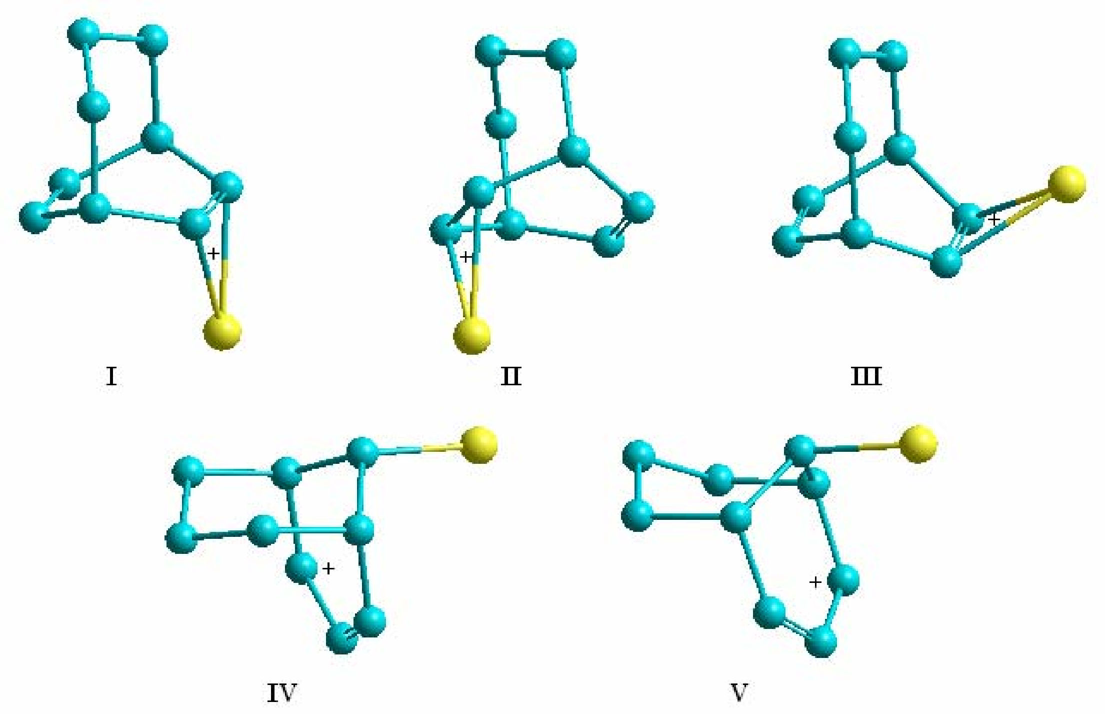
As seen from **Table II**, the stabilities of BND...Cl_2(*endo*1) and BND...Cl_2(*endo*2) molecular complexes are close to each other, and so, both of the complexes may be formed in the first step of the addition of chlorine to BND. However, BND...Cl_2(*endo*1) complex is observed to be favoured. The chlorine molecule has been partially polarized in both of the molecular complexes, the chlorine atom close to the double bond has a partial positive charge and the other one has a partial negative charge. The bond length between the chlorine atoms in the molecular complexes is relatively longer than that of the neutral chlorine molecule. The results obtained indicate that the molecular complexes play an important role in the heterolytic splitting of chlorine molecule, leading to an ionic addition. The investigation of the molecular complexes have been shown to be very important on the overall reaction coordinate of chlorinations due to autocatalytic action of chlorine. The studies of the structures and the stabilities of the molecular complexes are very important in the determination of stereo- and regioselectivity of the addition reaction to bicyclic olefins of halogens.

As a result of the polarization of chlorine and the cationic intermediates of the ionic addition reaction are formed, subsequently. The possible cationic intermediates and their isomers have been studied by *ab initio* and DFT methods and shown in **Scheme II**. In order to determine the structure and the relative stabilities of these cations, the optimized geometries have been found by HF/6-311G*, B3LYP/6-311G* and B3LYP/6-311+G* methods and the total energies (E_{tot}) have been calculated. The calculated relative energies are given in **Table III**. As seen in **Table III**, *endo* bridged chloronium cations (I and II) are more stable than *exo* cation (III). These results confirm that Cl_2 prefers to attack the *endo* side, rather than *exo* side. Thefore, these results showed that *endo*-facial selectivity is formed in the addition reaction.

Nevertheless, it has been found that the stability of bridged *endo* chloronium cations (I) and (II) are close

Table III — The calculated relative energies of cations

Cations	Relative energy (kcal/mol)		
	HF/6-311G*	B3LYP/6-311G*	B3LYP/6-311+G*
I	29.434	21.209	21.093
II	30.338	22.952	22.820
III	36.083	26.899	26.701
IV	0.0	0.0	0.0
V	7.835	8.063	8.059



Scheme II

to each other and it is possible for both to occur. However, there has been fewer selectivity in the bridged chloronium cation (I). The most stable cation, among the investigated ions by using these m9lethods, is the rearranged cation (IV) which is formed by 1,2-migration of the trimethylene bridge of an *endo* bridged chloronium cation (I and II). The conversion of *endo*-bridged chloronium cation (II) into the rearranged cation (IV) is realized by 1,2-migration of the trimethylene bridge and by inversion of the methylene group in the middle of these bridges. Cation (V) is computed to be less stable than cation (IV) by 7.835 kcal/mol at HF/6-311G* and 8.059 kcal/mol at B3LYP/6-311+G*. Interconversion of cations (V) and (IV) is predicted to be facile proceeding through a transition state with a planar trimethylene bridge and an activation barrier (B3LYP/6-311+G*) of only ~2.088 kcal/mol.

According to the theoretical results, rearranged cation (IV) is the most stable cation among the other cations formed during the addition reaction and the reaction must be completed via this cation. For this reason, the rearranged products are predicted to form in the addition reaction. The cationic center of the ion (IV) has a planar structure similar to allylic cation. The anionic chloride (Cl^-) attacks the cationic center through *endo* and *exo* directions to form two rearranged addition products.

The energy diagram of the electrophilic addition reaction of chlorine to BND molecule is shown in **Figure 3**. As seen from the diagram, the reaction takes place by the transformation of the bridged *endo* chloronium cations (I) and (II) in to the rearranged cation (IV). As the reaction progresses over the rearranged cation (IV), the rearranged products are obtained.

Thus theoretical study shows that the ionic addition of the chlorine molecule to BND follows the following steps: formation of the *endo* molecular complexes and decomposition of these complexes to bridged *endo*-chloronium ions; rearrangement of chloronium ions to chlorocarbonium (IV) cation; and nucleophilic attack of chloride ion (Cl^-) to cationic center through *exo* and *endo* directions of this cation, respectively (**Scheme III** and **Figure 3**).

Consequently, the investigation of chlorine addition to bicyclo[3.2.2]nona-6,8-diene by *ab initio* and DFT methods give some important results. The double bond (I) situated in the opposite direction of methylene group in BND molecule is more pyramidalized than the other double bond (II). The electron density ($q_{i,HOMO}$) of the double bond (I) in

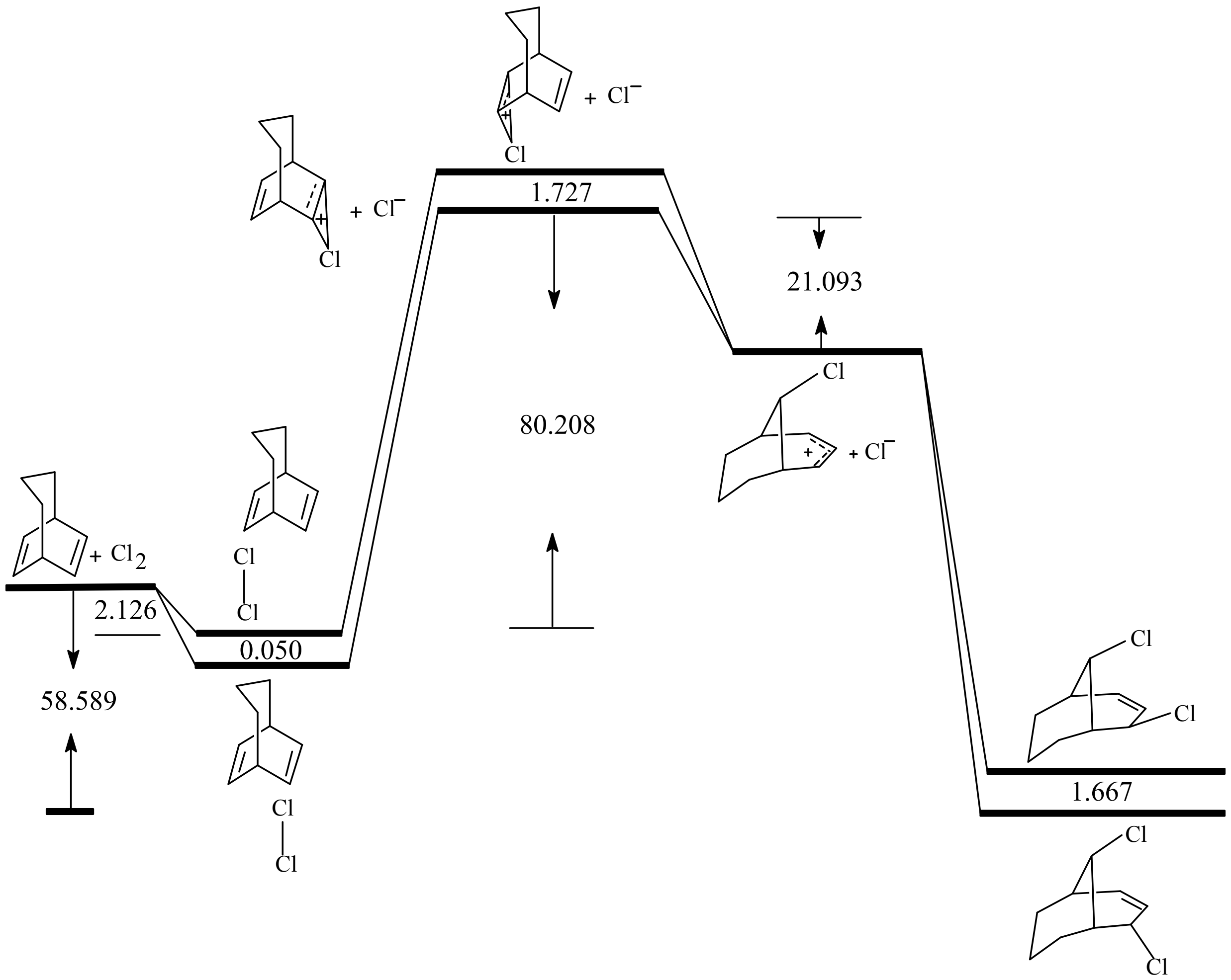
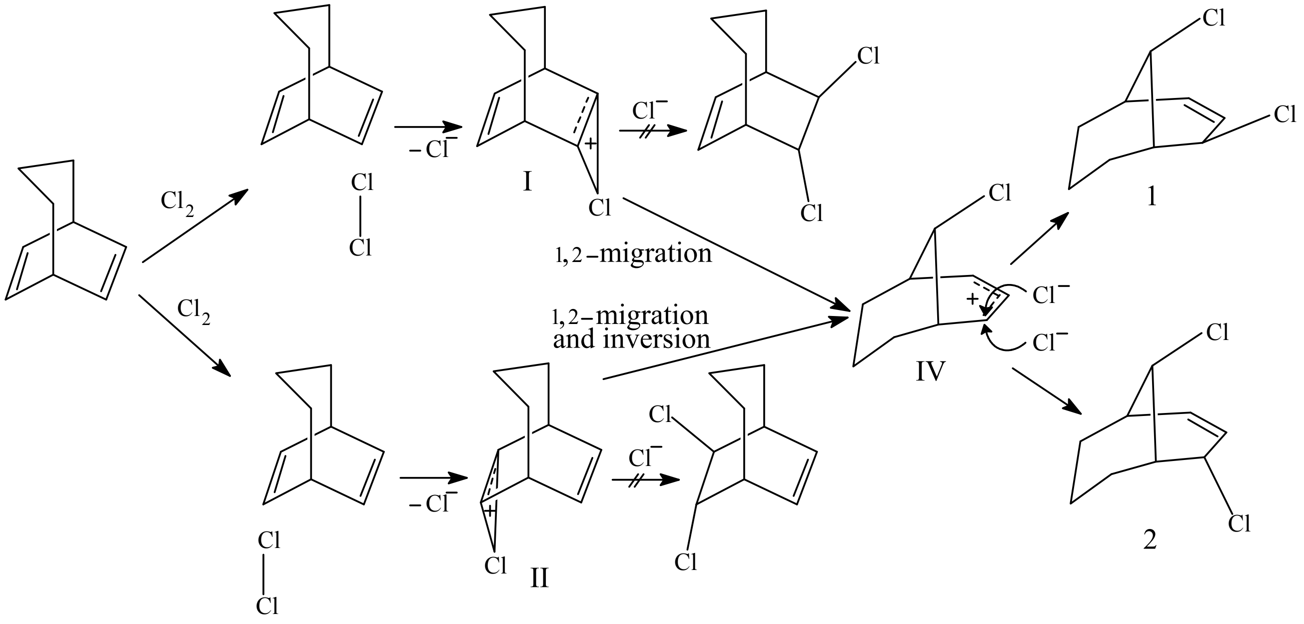


Figure 3 — The energy diagram of BND-Cl_2 system (kcal mol^{-1}) (B3LYP/6-311+G*).



Scheme III

HOMO of the molecule is bigger than that of the double bond (II). The electron density in *exo* and *endo* faces of the double bonds is not equal and is bigger in *endo* faces. Cl_2 molecule should attack from *endo* face to the double bonds. This attack is on the double bond (I) precedently. The reason of *endo* molecular complexes being more stable than *exo* molecular complexes, is due to electronic and steric factors. Because of electronic factors, BND... Cl_2(*endo* 1) complex is more stable than BND...Cl_2 (*endo* 2). *Endo*-bridged chloronium cations are more stable than *exo* cations. The *endo*-bridged chloronium cation (I) is relatively more stable than the *endo*-bridged cation (II). *Endo*-facial stereoselectivity and regioselectivity should be observed in the addition reaction of chlorine to BND molecule. *Endo*-facial stereoselectivity is caused by electronic and steric effects, regioselectivity is also principally caused by electronic effects. The rearranged cation (IV) is one of the most stable among the cationic intermediates and the reaction must be completed via this cation. The activation barriers for the interconversion of (V) and (IV) cations are calculated to be relatively low ($\Delta H^*\sim 2.088$ kcal/mol).

References

1 Stepanov N F, Grikina D E, Sergeev G B & Smirnov V V, *Adv Mol Relax Inter Proces,* 12, **1978**, 325.
2 Brown R S, *Acc Chem Res,* 30(3), **1997**, 131.
3 Chiappe C, Rubertis A D, Lemmen D & Lenoir D, *J Org Chem,* 65, **2000**, 273.
4 Legon A C & Thumwood J M A, *Phy Chem Chem Phys,* 3(8), **2001**, 1397.
5 Belluci G, Chiappe C, Bianchini R, Lenoir D & Herges R J, *J Am Chem Soc,* 117, **1995**, 1**2001**.
6 Herges R, *Angew Chem Int Ed Engl,* 34, **1995**, 51.
7 Ruiz E, Dennis R, Salahub R & Vela A, *J Phys Chem,* 100, **1996**,12265.
8 Bianchini R, Chiappe C, Lenoir D, Lammeu R, Herges R & Grunenber J, *Angew Chem Int Ed Engl,* 36, **1997**, 1284.
9 Smith W B, *J Org Chem*, 63, **1998**, 2661.
10 Bianchini R, Chiappe C, Moro LG, Lenoir D, Lemmen P & Goldberg N, *Chem Eur J,* 5, **1999**, 1570.
11 Chiappe C, Rubertis A D, Detert H, Lenoir D, Wannere C & Schleyer R P, *Chem Eur J,* 8, **2002**, 967.
12 Rathere R, Lindeman S V, Zhu CJ, Mori T, Schleyer R & Kochi J K, *J Org Chem*, 67, **2002**, 5106.
13 Lenoir D & Chiappe C, *Chem Eur J*, 9, **2003**,1037.
14 Chiappe C, Detert H, Lenoir D, Pamelli C S & Ruasse M F, *J Am Chem Soc*, 11125, **2003**, 2864.
15 Abbasoglu R, *J Mol Struct (Theochem)*, 686, **2004**, 1.
16 Abbasoglu R, *Indian J Chem,* 44B, **2005**, 1708.
17 Abbasoglu R, Yilmaz S & Gök Y, *Indian J Chem,* 44A, **2005**, 221.
18 Abbasoglu R &Yilmaz S, *J Mol Model,* 12, **2006**, 290.
19 Abbasoglu R, *J Mol Model*, 12, **2006**, 991.
20 Abbasoglu R & Yilmaz S, *Indian J Chem,* 45B, **2006**, 1721.
21 Abbasoglu R & Uygur Y, *Indian J Chem,* 46A, **2007**, 396.
22 Lee C, Yang W & Parr R G, *Phys Rev* B 37, **1988**, 785.
23 Becke A D, *J Chem Phys,* 98, **1993**, 5648.
24 Hehre W J, Ditchfield R & Pople J A, *Chem Phys,* 56, **1972**, 2257.
25 Krishnan R, Binkley J S, Seeger R & Pople J A, *J Chem Phys,* 72, **1980**, 650.
26 Perdew J P & Wang Y, *Phys Rev*, B 45, **1992**, 13244.
27 Borden W T, *Chem Rev,* 89, **1989**,1095.
28 Ermer O, Bell P & Mason S A, *Angew Chem Int Ed Engl,* 28, **1989**,1239.
29 Houk K N, Rondon N G, Brown F K, Jorgensen W L, Madura J D & Spellmeyer D C, *J Am Chem Soc,* 105, **1983**, 5980.
30 Gandolfi R, Tonoletti G, Rastelli A & Bagatti M, *J Org Chem,* 58, **1993**, 6038.
31 Watson W, *Stereochemistry and Reactivity of Systems Containing π Electrons*, (Verlag Chemie International, Deerfield Beach, Florida), **1983**.
32 Fleming I, Frontier Orbitals and Organic Chemical Reactions (Wiley, New York), **2002**, 5.