

Notes

Density functional theory investigation of electrophilic addition reaction of chlorine to 3,4-benzobicyclo[3.2.1]-octadiene

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Full geometric optimization of 3,4-benzobicyclo[3.2.1]-octadiene (BBOD) has been carried out by DFT/B3LYP method using the 6-311G(d), 6-311G(d,p) and 6-311+G(d,p) basis sets. The double bond is endo-pyramidalized and its two faces are not equivalent. The BBOD-Cl₂ system have been investigated by B3LYP/6-311+G(d,p) method and stable configurations determined. The stable configurations of the BBOD-Cl₂ system correspond to BBOD...Cl₂(*exo*) and BBOD...Cl₂(*endo*) molecular complexes which are formed by the *exo* and *endo* orientation respectively of Cl₂ molecule to the double bond of BBOD in axial position. *Exo*-complex is relatively more stable than the *endo*-complex. *Exo*-chloronium cation was found to be more stable than *endo*-chloronium cation by the DFT method. *Exo*-facial selectivity is expected in the addition reaction to BBOD of chlorine. The non-classical delocalized chlorocarbonium cation(IV) is the most stable ion among the cationic intermediates, and the ionic addition reaction occurs via this cation. The mechanism of the addition reaction is also discussed.

Keywords: Theoretical chemistry, Electrophilic additions, Density functional calculations, Addition reactions, Geometric optimization

Despite the fact that the theoretical and experimental investigation of the electrophilic addition of halogens to olefins has been extensively studied, 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, investigated both experimentally and theoretically, are the important intermediates formed in the earlier steps of the addition reaction¹⁻⁵. In order that the role of the complexes in these reactions may be correctly understood, structural information is required, which difficult to obtain by experimental means because of the fast reactions occurring in the systems. These kinds 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 recourse to experimental measurements.

The addition reactions of halogens to unsaturated strained molecules and the reaction intermediates have been quantum chemically investigated¹⁻⁵. In this connection, the theoretical investigations of the addition of bromine and chlorine to olefins with rigid structure have recently been reported by us⁶⁻⁹. In continuation of our interest in quantum-chemical studies related to the addition of halogens to rigid and unsaturated strained molecules, we wish to report here the results obtained for the investigation of the addition of chlorine to 3,4-benzobicyclo[3.2.1]octadiene (BBOD). Chlorination of the BBOD molecule having a rigid structure gives only the ordered product 2-*exo*-8-*anti*-dichloro-6,7-benzobicyclo[3.2.1]octa-6-ene at room temperature. Thus, it is interesting to investigate the reasons for the high stereoselectivity properties of this reaction. Stereoselectivity of these reactions depends on the electronic structure of the double bonds of strained olefins to a large extent. In order to do the detailed analysis of the formation mechanism and stereochemistry of the product in this reaction, a quantum-chemical investigation of the structure and stability of the reaction intermediates seems to be very important. The present work describes a theoretical investigation of the electrophilic reaction intermediates such as BBOD...Cl₂ molecular complexes and the cations.

Methodology

The geometry and the electronic structure of the 3,4-benzobicyclo[3.2.1]octadiene (BBOD) were investigated by DFT/B3LYP¹⁰⁻¹¹ method in 6-311G(d)¹², 6-311G(d,p)¹² and 6-311+G(d,p)¹³ basis. The theoretical calculation related to 3,4-benzobicyclo[3.2.1]octadiene-chlorine (BBOD...Cl₂) molecular complexes were performed by using the B3LYP/6-311+G(d,p) method. Basis-set

superposition error (BSSE) was estimated using the counterpoise method¹⁴ for the van der Waals complex produced in the reactant region. The cationic intermediates predicted in the reactions have been searched by B3LYP/6-311G(d), B3LYP/6-311G(d,p) and B3LYP/6-311+G(d,p) methods. All stationary points were characterized by calculating the vibrational frequency and zero point vibrational energies were added for all species. Full geometry optimization was carried out employing the Polak-Ribiere (conjugate gradient) algorithm¹⁵ (convergence of 0.00001 kcal mol⁻¹) and an RMS gradient at 0.001 kcal(Å mol)⁻¹. All the calculations were performed with HyperChem 7.5¹⁶ and Gaussian 03¹⁷ program with an IBM Pentium IV computer.

Results and discussion

Full geometric optimization of BBOD molecule was done by B3LYP/6-311G(d), B3LYP/6-311G(d,p) and B3LYP/6-311+G(d,p) methods, and the structure of the molecule was also investigated in detail. In the light of the results of each method, the pyramidalization parameters^{18,19} of the molecule were determined with the aim of determining the structural deformation of double bond. According to the results of each method of the double bond of BBOD molecule, the calculated values of the pyramidalization angle (ϕ)¹⁸ and out-of-plane bending angle (χ)¹⁹ are given in Table 1. According to the

determined results, the double bond of BBOD molecule is *endo* pyramidalized and the two faces of double bond are no longer equivalent. The electron density in *exo* direction of *endo* pyramidalized double bond of the molecule must be higher than that in *endo* direction. This extraordinary geometrical feature causes a very noticeable π -facial stereoselectivity in addition reactions to double bond²⁰. Also, the addition reaction of chlorine to BBOD molecule for which the double bond is *endo* pyramidalized, should show the *exo*-selectivity. In general, the facial selectivity of attack on a pyramidalized olefin parallels the pyramidalization^{21,22}. When the pyramidalization degree of the double bond of olefins increases, their chemical reactivities also increase²⁰.

The analysis of frontier orbital (HOMO) of BBOD molecule shows that *exo* and *endo* faces of *endo* pyramidalized double bond of the molecule are not equal. The electron density in *exo* face of double bond is high (Fig. 1). Therefore, the chlorination reaction of the BBOD molecule should show the stereoselectivity property, and the addition of chlorine should be realized from *exo* direction where the electron density of the double bond is higher.

As known, olefin-halogen molecular complex is formed in the first step of electrophilic addition of halogens to olefins. According to the thermodynamic stability of the molecular complexes, it is possible to determine the direction from which the halogen

Table 1 – Calculated total energies, energies of frontier molecular orbitals, double bond lengths and pyramidalization parameters of 3,4-benzobicyclo[3.2.1]octadiene

Method	E_{tot} (kcal/ mol)	ϵ_{HOMO} (ev)	ϵ_{LUMO} (ev)	$r_{\text{C=C}}$ (Å)	ϕ (deg.)	χ
B3LYP/6-311G(d)	-291526.436	-6.286	0.218	1.333	5.897	6.392
B3LYP/6-311G(d,p)	-291538.063	-6.289	0.244	1.333	5.900	6.396
B3LYP/6-311+G(d,p)	-291540.480	-6.367	0.335	1.334	5.904	6.402

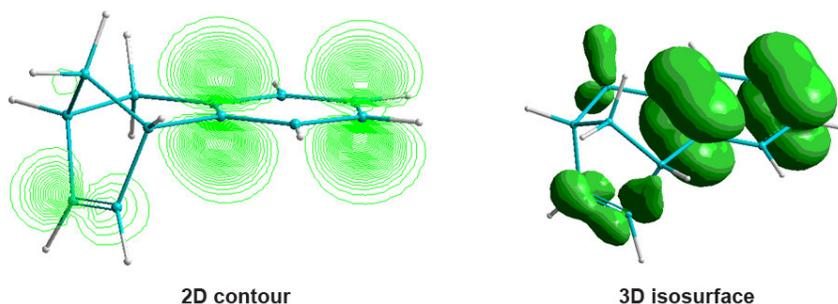


Fig. 1 – Electron density distribution (HOMO) of the BBOD molecule from B3LYP/6-311G(d).

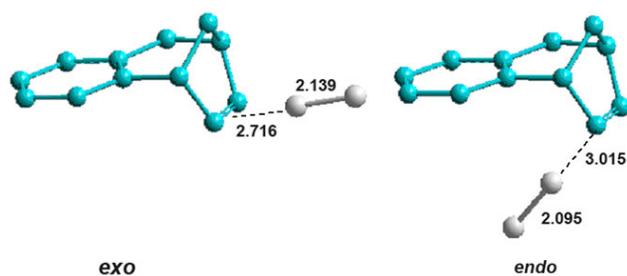


Fig. 2 – The optimized geometries of the BBOD...Cl₂(*exo*) and BBOD...Cl₂(*endo*) molecular complexes from B3LYP/6-311+G(d, p). [Distances are in Å].

attacks the double bond. Therefore, the stability and the electron structure of BBOD...Cl₂(*exo*) and BBOD...Cl₂(*endo*) molecular complexes formed by the addition of chlorine from *exo* and *endo* direction to double bond of BBOD molecule were investigated by using B3LYP/6-311+G(d,p) method. The electrophilic attack of chlorine to double bond of BBOD molecule is possible either from *exo* or *endo* side. Moreover, a chlorine molecule may approach the carbon-carbon 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. By considering these, the full geometric optimization of the various configurations of BBOD-Cl₂ system was performed and the stable configuration corresponding to the minimum energy levels was determined. Two configurations corresponding to the local minima of the BBOD-Cl₂ system were found (Fig. 2).

These configurations correspond to BBOD...Cl₂(*exo*) and BBOD...Cl₂(*endo*) molecular complexes, which are formed by the *exo* and *endo* orientation of Cl₂ molecule to the double bond of BBOD in axial position, respectively. The stabilization energies { $\Delta E = (E_{\text{BBOD}} + E_{\text{Cl}_2}) - E_{\text{BBOD}\dots\text{Cl}_2}$ } of the *exo* and *endo* molecular complexes, the equilibrium distance $R_{\text{X-Cl}}$ (X is midpoint of the C=C bond of BBOD), and the other calculated properties are given in Table 2. The *exo* complex is 1.751 kcal/mol more stable than the *endo* complex. The results obtained indicate that an *exo* selectivity must be considered in the electrophilic addition of chlorine molecule to 3,4-benzobicyclo[3.2.1]-octadiene. On the other hand, as we pointed out, the electron density (q_i , HOMO) in *exo* face of *endo* pyramidalized double bond of BBOD molecule is higher, that is, HOMO_{BBOD}-LUMO_{chlor} interaction realized from *exo* face of the double bond in the formation of *exo*

Table 2 – Properties of BBOD...Cl₂ molecular complexes. [B3LYP/6-311+G(d,p)]

Molecular complex	Stabilization energy (kcal/mol)	Equil. distance, R _e (Å)	r _{Cl-Cl} (Å)	Transferred charge from BBOD to Cl ₂ (e)
BBOD...Cl ₂ (<i>exo</i>)	4.969	2.716	2.139	0.046
BBOD...Cl ₂ (<i>endo</i>)	3.218	3.015	2.095	0.025

molecular complex is more effective than that of *endo* face and should be optimal. According to the frontier molecular orbital theory, HOMO_{olef}-LUMO_{halogen} interaction is the decisive factor in the formation of olefin-halogen complex²³. Hence, facial selectivity in the addition reaction of chlorine to BBOD molecule is caused by electronic effect to an important degree.

The chlorine molecule in the BBOD...Cl₂(*exo*) complex is partially polarized; the chlorine atom near the double bond has a partial positive charge (natural bond orbitals charges) while the other chlorine atom has a partial negative charge. The bond length of the chlorine molecule in the complex is relatively longer than that of the neutral chlorine molecule (Table 2). These results indicate that the BBOD...Cl₂(*exo*) molecular complex plays an important part for the heterolytic splitting of chlorine molecule leading to an ionic addition. The studies of the structures and the stabilities of the molecular complexes are very important in the determination of stereoselectivity of the addition reaction of halogens to strained olefins.

It is known that an olefin-halogen molecular complex is more stable in a solvent compared to a gas phase medium and the stabilization energy of the complex becomes higher as the solvent polarity increases²⁴. As a result, in the first step of the addition of chlorine to BBOD, the BBOD...Cl₂(*exo*) molecular complex must essentially be formed either in a gas or a solvent medium. The polarization of chlorine and subsequently the heterolytic splitting of BBOD...Cl₂(*exo*) molecular complex result in the formation of a cation. This cation and its isomers are the possible intermediates of the addition reactions of chlorine to BBOD in gas phase and solvent medium (Fig. 3). In order to determine the structures and relative stabilities of the predicted cationic intermediates, their full geometry optimization was performed using B3LYP/6-311G(d), B3LYP/6-311G(d,p) and B3LYP/6-311+G(d,p) methods, and the total energies (E_{tot}) were calculated. The calculated relative energies are given in Table 3.

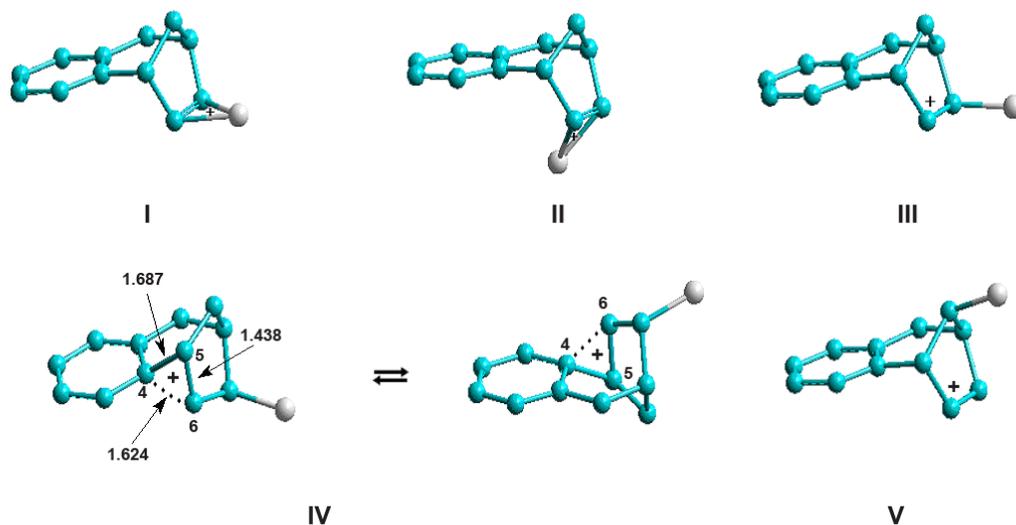


Fig. 3 – The optimized geometries of cations by B3LYP/6-311+G(d, p). [Bond lengths are in Å].

Table 3 – Calculated relative energies of cations

Cations	Relative energy (kcal/mol)		
	B3LYP/ 6-311G(d)	B3LYP/ 6-311G(d,p)	B3LYP/ 6-311+G(d,p)
(I)	16.204	16.311	15.603
(II)	26.402	26.491	25.725
(III)	16.256	16.383	16.007
(IV)	0.0	0.0	0.0
(V)	7.389	7.427	7.168

Exo-chloronium cation (I) is relatively more stable than *endo*-chloronium cation (II) according to DFT methods. In other words, *exo*-bridged cation formed by the splitting of the *exo*-molecular complex is more stable than *endo*-bridged cation. This reveals that an absolute *exo*-selectivity must be considered in the mechanism of the electrophilic addition of Cl₂ to BBOD. As shown in Table 3, the most stable cationic intermediate is the non-classical delocalized chlorocarbonium ion (IV) among the possible cationic intermediates (I)-(V). These results are consistent with those reported for the 2-norbornyl, 2-*exo*-bromo-3-benzonorbornenyl, and 6-tricyclo[3.2.1.0^{2,4}]octyl cations using various quantum chemical methods²⁵⁻²⁸. Classical rearranged cation (V) (Fig. 3) is not more stable than non-classical delocalized chlorocarbonium cation (IV) and, thus, the probability of the formation of cation (V) is small. In the non-classical delocalized chloro-carbonium ion (IV) the positive charge is partially transferred to the benzene ring and the ion

becomes more stable due to the overlapping of the π orbitals of aromatic ring. The length of the C₄-C₅, C₄-C₆ and C₅-C₆ bonds of the non-classical chlorocarbonium ion (IV) (Fig. 3) optimized by B3LYP/6-311+G(d,p) method are 1.687Å, 1.624Å and 1.438Å, respectively. The ionic addition of chlorine to BBOD molecule is predicted to proceed via non-classical chlorocarbonium ion (IV) (cation IV-Cl⁻ couple is assumed as the transition form) since this cation is the most stable among the cations studied. The C-5 atom of the non-classical delocalized cation IV (Fig. 3) has the maximum positive charge, i.e., because of aryl shift, the cationic centre is shifted to the C-5 atom. Due to the interaction between the C-5 cationic centre and the π -electron clouds of the benzene ring, the nucleophilic attack of the initially formed chloride ion (Cl⁻) to the cationic center occurs from the opposite side of the benzene ring, and only one rearrangement product, 2-*exo*-8-*anti*-dichloro-6,7-benzobicyclo[3.2.1]octa-6-ene, is formed. In the ionic addition of Cl₂ to BBOD, the formation of 2-*endo*-8-*anti*-dichloro-6,7-benzobicyclo[3.2.1]octa-6-ene is not possible due to the electronic interaction.

The energy diagram of the addition reaction of chlorine to BBOD molecule is given in Fig. 4. As can be seen from the energy diagram of BBOD-Cl₂ system, the reaction takes place by formation of the BBOD...Cl₂(*exo*) molecular complex and decomposition of this complex to bridged *exo*-chloronium ion (I) and following this ion transforms into the

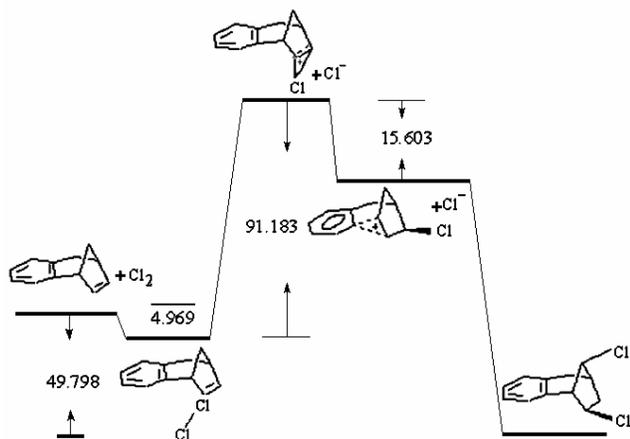


Fig. 4 – Energy diagram of BBOD-Cl₂ system (kcal/mol) by B3LYP/6-311+G(d, p) method.

cation (**IV**). As the reaction progresses over the cation (**IV**), the rearranged product is obtained.

The theoretical results are in agreement with those obtained by the experimental investigation of the addition of chlorine to BBOD^{29,30}. Thus, theoretical study shows that the ionic addition of the chlorine molecule to BBOD follows these steps: formation of the *exo*-molecular complex and decomposition of this complex to bridged *exo*-chloronium ion (**I**); rearranging of chloronium ion to non-classical delocalized chlorocarbonium cation (**IV**); and nucleophilic attack of chloride ion (Cl⁻) on this cation, respectively.

The present study shows that the double bond of BBOD molecule is *endo* pyramidalized. The electron densities ($q_{i,HOMO}$) in *exo* and *endo* faces of the double bond are not equal and is larger in *exo* face. BBOD...Cl₂(*exo*) molecular complex is more stable than BBOD...Cl₂(*endo*) complex, and an essentially *exo* complex is formed throughout the reaction. *Exo* complex plays an important role in heterolytic splitting of chlorine molecule. The bridged *exo*-chloronium cation (**I**) is relatively more stable than the *endo*-chloronium cation (**II**). *Exo*-facial selectivity should be observed in the addition reaction to BBOD molecule of chlorine. The most stable cation of cationic intermediates is the non-classical delocalized chlorocarbonium (**IV**), and the ionic addition reaction occurs via this cation. Only one Wagner-Meerwein rearrangement product 2-*exo*-8-*anti*-dichloro-6,7-benzobicyclo[3.2.1]octa-6-ene is formed in the

reaction. The non-classical delocalized cation (**IV**) is more stable than the classical rearranged cation (**V**). Thus, the conversion of the cation (**IV**) to ion (**V**) is not easy.

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