The quantum chemical investigation of the addition reactions of Br2 to homocubyllidenehomocubane and its derivatives

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The electronic and geometric structures of homocubyllidenehomocubane (HC), trans-(1-methyl-2-homocubyliden)-1-methylhomohomocubane (DMHC) and trans-(1-tert-butyl-2-homocubyliden)-1-tert-butylhomocubane (DBHC) molecules have been investigated by B3LYP/6-311G* method. These results agree with X-ray results and show that the double bond of HC molecule has a planar structure, while the double bonds in DMHC and DBHC molecule are almost planar. The complexes (1:1 π complexes) of the molecules with Br2 have been investigated by B3LYP/6-311+G* method and it is observed that the stable configurations have an axial structure. The electronic and the steric factors affecting the structure and the stability of the molecular complexes have been studied. It is observed that the DMHC...Br2 complex is more stable than HC...Br2 complex. The DBHC...Br2 complex containing the bulky tert-butyl group has stability of sterically encumbered olefin-bromocomplex and it depends on the nature of 'eage' substituents on the double bond carbons. The bridged bromonium cation is the more stable cation among the cationic intermediates formed in the addition reaction of bromine to HC and the reaction occurs via this cation. The nucleophilic attack by bromide ion is not sterically prevented to HC-Br+ bridged bromonium cation and as a result, normal 9, 9'-dibromide product is formed. The nucleophilic attack by bromide ion is sterically prevented to AD-Br+ bridged bromonium cation.

Electrophilic halogenation of olefins is one of the classical reactions in organic chemistry and have been studied extensively theoretically and experimentally. However, the mechanism of this reaction as well as the nature, the structure and the stability of the reaction intermediates is still under discussion. In order to analyze the reaction mechanism and stereochemistry, detailed data about the structures and stabilities of the intermediates such as olefin-halogen molecular complexes and cations formed during the reactions are needed. Olefin-halogen molecular complexes are important intermediates formed in the earlier steps of the addition reaction. Since the intermediates have low stabilities and high reactivities, it is difficult to obtain information about their structure and the stability experimentally. In fact, quantum chemical calculations might help in obtaining of detailed information about the structure and stability of intermediates.

Addition reactions of halogens to unsaturated strained molecule and the reaction intermediates have been quantum chemically investigated. We have recently reported the theoretical investigations on the addition of bromine and chlorine to olefins with rigid structure.

The electrophilic addition reaction of Br2 molecule to sterically encumbered homocubyllidenehomocubane (HC) having 'eage' structure and its derivatives have been investigated experimentally. It has been determined that normal dibromide product is formed in the addition reaction. Due to the inherent symmetry in homocubyllidenehomocubane, it is not possible to deduce the stereochemistry of electrophilic addition (i.e., syn or anti) across the C=C double bond from only knowledge of the structure of the adduct. Hence, determination of the structure and the stability of the intermediates formed in the addition reaction is important. On the other hand, although the normal dibromide addition product is formed in the bromination reaction of HC molecule, the bromination of sterically encumbered adamantylidenecadamanth (AD) cannot proceed beyond the stage of the bromonium ion. In explaining the structures of the cation, intermediates formed in the bromination of each olefin is important. Mainly the structure of the olefin determines the stability of the complex and the intermediates.

In this study, the geometry and the electronic structure of homocubyllidenehomocubane (HC), trans-(1-methyl-2-homocubyliden)-1-methylhomocubane
(DMHC) and trans-(1-tert-butyl-2-homocubyliden)-1-tert-butylhomocubane (DBHC) molecules (as shown in Scheme 1) have been investigated by DFT method. Olefin-Br2 molecular complexes have been studied using DFT method. The relationship between the quantum chemical parameters of olefins and the stability and properties of molecular complexes have also been studied. Also, the splitting of HC..Br2 molecular complex results in the forming of cyclic three-membered bromonium ion (HC-Br+) and its isomers geometric and electronic properties have been investigated by ab initio method. The geometric parameters of HC-Br+ and AD-Br+ bromonium ions have been compared.

Methodology

The geometry and the electronic structure of the HC molecule and its derivative (DMHC, DBHC) (Scheme 1) were investigated by the DFT method at the B3LYP/6-311G* [20, 21] level. The theoretical investigation of olefin-Br2 molecular complexes was performed by using the B3LYP/6-311+G* method. Basis-set superposition error (BSSE) energies are corrected. The structure and the stability of cyclic three-membered bromonium ion of (HC-Br+) and its isomers were investigated by HF/6-311G* (ref. 23) method. 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) algorithm (convergence of 0.00001 kcal mol⁻¹) and an RMS gradient at 0.001 kcal (A mol)⁻¹. The calculations were performed with HyperChem 7.5 and Gaussian98 program with an IBM PC Pentium IV computer.

Full geometric optimizations of HC molecule and its derivatives (DMHC, DBHC shown in Scheme 1) were done by B3LYP/6-311G* method and the structure of the molecules were also investigated in detail (Fig. 1). The total energy (Eₚₚ), the energies (Eₓₓ, Eₓₓ, Eₓₓ, Eₓₓ) of frontier molecular orbitals, the double bond length (rCc) of each molecule, the distance (r₈₁₁) between the hydrogen atoms situated in β-positions to the double bond in different homocubane moieties, and the distance (r₈₁₁) between R group (Scheme 1) and hydrogen atom in the α-positions to the double bond have been calculated. The values of the out-of-plane bending angle²⁴ (χ) of each molecule were calculated according to the results of B3LYP/6-311G* calculations to determine the structural deformation of double bond. The volumes of R groups²⁵ were also calculated. These results are given in Table 1.

![Scheme 1](image)

**Fig. 1—**The optimized geometry of the investigated molecules by the B3LYP/6-311G* method. [HC (1); DMHC (2) and DBHC (3)].

**Table 1—**The calculated total energies (hartree), the energies of frontier molecular orbitals (eV), the double bond lengths (Å), the distances between the hydrogen atoms in the β-positions (Å), the distances between the R group and the hydrogen atom in the α-positions (Å), the out-of-plane bending angle (deg) (B3LYP/6-311G*) and the calculated volumes (Å³) of R substituents.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Point groups</th>
<th>Eₚₚ</th>
<th>Eₓₓ</th>
<th>Eₓₓ</th>
<th>Eₓₓ</th>
<th>rCc</th>
<th>r₈₁₁</th>
<th>r₈₁₁</th>
<th>χ</th>
<th>V</th>
</tr>
</thead>
<tbody>
<tr>
<td>HC</td>
<td>D₂h</td>
<td>-694.929</td>
<td>-6.203</td>
<td>0.308</td>
<td>1.332</td>
<td>5.561</td>
<td>2.520²⁴</td>
<td>0.000</td>
<td>71.7</td>
<td></td>
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<tr>
<td>DMHC</td>
<td>C₃₀</td>
<td>-772.565</td>
<td>-6.154</td>
<td>0.348</td>
<td>1.338</td>
<td>5.580</td>
<td>2.288²⁴</td>
<td>0.010</td>
<td>150.3</td>
<td></td>
</tr>
<tr>
<td>DBHC</td>
<td>C₃₀</td>
<td>-1005.444</td>
<td>-6.126</td>
<td>0.356</td>
<td>1.348</td>
<td>5.646</td>
<td>2.005²⁵</td>
<td>0.015</td>
<td>311.3</td>
<td></td>
</tr>
</tbody>
</table>

² Distance between the hydrogen atoms in the α-positions.
²² Average distance between α-hydrogen and hyrogens of R group.
Results and Discussion

The B3LYP/6-311G* results show that although there are bulky 'cage' groups attached to the double bonded carbons in HC molecule, the carbon-carbon double bond has essentially a planar structure and the point group of the molecule is $D_{2h}$. These results are in full agreement with the experimental X-ray results. The surrounding of the double bond in DMHC and DBHC molecules is almost planar and the molecules have $C_{2v}$ point group. The double bond distance, $(r_{C=C})$, and the distance, $(r_{H-H})$, between hydrogen atoms situated in $\beta$-positions increase with increasing volume of R group (Table 1). On the other hand, HOMO energy level of the molecule increases and the ionization potential (IP=$-\epsilon_{\text{HOMO}}$) decreases with increasing electron donor property of R group as shown in Table 1. Thus, the ionization potentials of molecules 1-3 (Scheme 1) decrease and the electron-donating ability increases with respect to R group.

In order to determine the structure and the stability of HC...Br$_2$, DMHC...Br$_2$(II) and DBHC...Br$_2$(III) molecular complexes (1:1 $\pi$-complexes), olefin-Br$_2$ systems were investigated in detail at B3LYP/6-311+G* level. It is possible that the bromine molecule approaches to the double bond of the olefin in axial (the $C_\alpha$ axis of the Br$_2$ molecule is perpendicular to the plane of double bond) and equatorial (the $C_\alpha$ axis of Br$_2$ is parallel to the plane of double bond) positions. By considering these, the full geometric optimization of the various configurations of HC...Br$_2$, DMHC...Br$_2$ and DBHC...Br$_2$ systems were performed and the stable configurations corresponding to the minimum energy were determined. Br$_2$ molecule is in axial position to the double bond plane of olefin in the stable configuration corresponding to the minimum energy of the $\pi$-complex for each system. The optimized geometries of the molecular complexes are given in Fig. 2. The stabilization energies of the molecular complexes ($\Delta E$) were calculated and the equilibrium distance $R_{X-H}$ (X is midpoint of the C=C bond of olefins), the distance $(r_{H-H})$ between the hydrogen atoms in the $\beta$-positions of the double bond, in the different homocubane moiety, the distance $(r_{H-H})$ between R group and hydrogen atom in $\alpha$-positions and the other calculated properties are given in Table 2. The out-of-plane bending angle (\( \gamma \)) of the complexes in olefins have been also calculated according to the results of B3LYP/6-311+G* method (Table 2).

![Image](image-url)

**Fig. 2**—The optimized geometries of HC...Br$_2$(I), DMHC...Br$_2$(II) and DBHC...Br$_2$(III) molecular complexes by the B3LYP/6-311+G* method.

**Table 2**—The properties of HC...Br$_2$(I), DMHC...Br$_2$(II) and DBHC...Br$_2$(III) molecular complexes (B3LYP/6-311+G*). (Geometric parameters are in Á; the out-of-plane bending angle is also in degree unit.)

| Molecular complex | $\Delta E$ (kcal/mol) | $R_{X-H}$ | $r_{H-H}$ | Transferred charge olefins to Br$_2$(e) | Charge on bromines, (e) | $\gamma$ | $|\Delta|^{a}$ |
|-------------------|-----------------------|-----------|-----------|------------------------------------------|---------------------------|-------|----------|
| I                 | 2.61                  | 2.910     | 2.375     | 0.047                                    | 0.021                     | -0.068| 6.038    | 2.516 | 8.42  | 10.885 |
| II                | 8.04                  | 2.840     | 2.377     | 0.049                                    | 0.020                     | -0.069| 6.070    | 2.341 | 8.86  | 10.833 |
| III               | 5.84                  | 3.173     | 2.371     | 0.032                                    | 0.016                     | -0.048| 5.951    | 2.004 | 5.68  | 10.805 |

$^a$ $\Delta$= HOMO$_{\text{olefin}}$ - LUMO$_{\text{olefin}}$ energy gap.
Electron transfer from olefin to the bromine molecule is observed in each complex. For that reason, bromine in the charge transfer complexes (CTC) is partially polarized. The bromine atom near the double bond has a partial positive charge and the other bromine has a partial negative charge (Table 2). The DMHC...Br₂ (II) complex have the largest stabilization energy and the smallest equilibrium distance among the molecular complexes, i.e., DMHC makes the most stable molecular complex with Br₂ molecule compared to HC and DBHC molecules. DBHC...Br₂ (III) molecular complex is more unstable than HC...Br₂ (I).

In order to make these results clear, it is important to determine the electronic and steric factors affecting the formation of the molecular complexes. According to the frontier molecular orbital theory, the formation of olefin-bromine molecular complex occurs when the HOMO orbital of olefin (donor) and LUMO orbital of bromine (acceptor) mutually interact²⁶. For effective and optimal HOMO₂₂-LUMO₂₉ interaction, it is necessary that the energies of the orbitals are close and HOMO₂₂-LUMO₂₉ energy gap is small. Consequently, the electron-donating ability of olefin (ionization potential value, IP = -½HOMO) is important in the formation of olefin-bromine molecular complex. The electron-donor groups (R) situated in the surrounding of the olefin double bond enhance HOMO energy level of alkene²⁷ and affect the formation and stability of olefin-bromine molecular complexes positively. In other words, the electron-donor groups reduce the value of HOMO₂₂-LUMO₂₉ energy gap that makes the change transfer to bromine from olefin easy leading to increase in the stability of olefin-bromine complex (Table 2). Therefore, the stability of the molecular complex with bromine molecule increases when the electron-donating ability of olefin increases. That is, with respect to electronic effect, the stability of the complexes increases as: HC...Br₂ > DMHC...Br₂ > DBHC...Br₂. However, the electronic effect alone is not sufficient to explain the stability of complexes. For example, the DBHC...Br₂ complex containing the bulky tert-butyl groups is more unstable than the other two complexes, indicating that the steric effect should also be taken into account along with the electronic effects in determining stability of the complexes.

In order to achieve the optimal olefin-Br₂ interaction in the formation of the molecular complex, the approach of bromine toward the double bond of olefin in a certain position should not be hindered sterically. In the HC type of molecules, four hydrogen atoms are situated in β-positions on both sides of the double bond. The distance (r₁₁) between hydrogen atoms that are situated in β-positions of the double bond in the molecules and in π-complexes are given Tables 1 and 2. The distance (r₁₁) between β-hydrogen atoms (hydrogen atoms situated in β-positions) that prevent the bromine molecule from approaching the double bond in each olefin increased with the formation of the complex and reached a maximum in the stable configuration of the π-complex. The formation of olefin-bromine molecular complexes was achieved by increasing the distance (r₁₁) between the β-hydrogens and by the pyramidalization of the double bond (Table 2). When the pyramidalization degree of the olefins increases; their chemical reactivities increase and their steric strains decrease²⁸. Thus, the factors that increase the distance between β-hydrogen atoms and ease the pyramidalization of the double bond positively affect the formation of molecular complexes and increase their stability. Among the complexes investigated, the best double bond pyramidalization and the largest distance (r₁₁) between β-hydrogen atoms is found in the DMHC...Br₂ (II) complex (Table 2). Methyl groups attached to the allylic carbon atoms in DMHC molecule affect the pyramidalization of the double bond in DMHC...Br₂ complex positively and also increase the distance between β-hydrogen atoms. The distances (r₁₁) between the hydrogen atoms and methyl groups in DMHC...Br₂ complex are much larger than those in DMHC (Tables 1 and 2). Hence, the steric interaction between methyl groups and the hydrogen atoms in DMHC...Br₂ complex is smaller as compared to that in DMHC molecule. Thus, the electronic and steric factors positively affect the formation of DMHC...Br₂ complex and the increase its stability (Tables 1 and 2).

The complex undergoing the least structural deformation of the double bond is DBHC...Br₂ complex (Table 2). The distances (r₁₁) between α-hydrogen atoms and tert-butyl groups in the complex and in the molecule are almost the same (Tables 1 and 2). Hence, the strain caused by the interaction between hydrogen atoms and tert-butyl groups in DBHC molecule is not lowered much in the DBHC...Br₂ complex. Therefore, the bulky tert-butyl groups protect the double bond in DBHC...Br₂ system, making the olefin inert towards the addition
Table 3—The calculated central C-C bond lengths ($r_{CC}$), the C-Br bond lengths ($r_{CB}$), the distances between the hydrogen atoms in the $\alpha$-positions of the central bond, in the different cage moiety ($r_{\alpha \beta}$), the distances between the hydrogen atoms in the $\beta$-positions ($r_{\beta \beta}$), the diagonal distances between the $\alpha$- and $\beta$-hydrogens ($R_{\alpha}$) and the diagonal distances between the $\beta$- and $\beta$-hydrogens ($R_{\beta}$). (The geometric parameters are in Å) (11F/6-311G*).

<table>
<thead>
<tr>
<th>Bromonium cation</th>
<th>Point groups</th>
<th>$r_{CC}$</th>
<th>$r_{CB}$</th>
<th>$r_{\alpha \beta}$</th>
<th>$r_{\beta \beta}$</th>
<th>$R_{\alpha}$</th>
<th>$R_{\beta}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>AD-Br$^+$</td>
<td>C$_{2v}$</td>
<td>1.484</td>
<td>2.167</td>
<td>1.993</td>
<td>2.155</td>
<td>3.258</td>
<td>3.339</td>
</tr>
<tr>
<td>HC-Br$^+$</td>
<td>C$_{2v}$</td>
<td>1.445</td>
<td>2.149</td>
<td>2.515</td>
<td>3.721</td>
<td>4.052</td>
<td>4.558</td>
</tr>
</tbody>
</table>

$^a$ The X-ray diffraction data indicate that the bromonium ion of AD-Br$^+$ is essentially symmetrical with the following averaged structural parameters $r_{CC} = 1.49(Å)$ and $r_{CB} = 2.11(Å)$ (ref. 29).
reaction. These groups also prevent the optimal interaction of bromine molecule with the double bond in π-complex and reduce the stability of the complex.

The polarization of bromine and subsequently the heterolytic splitting of HC...Br₂ molecular complex results in the formation of cyclic three-membered bromonium cation (HC-Br⁺). This cation and its isomers are the predicted cationic intermediates of the addition reaction (Scheme 2). In order to determine the structures and relative stabilities of the cations, their full geometry optimization has been performed by HF/6-311G* method. The electronic properties and the geometric parameters have been calculated.

The most stable cation among the investigated ions (Scheme 2) by using HF/6-311G* method is the cyclic three-membered bromonium cation (I). According to HF/6-311G* method, cations (II) and (III) are 4.228 kcal/mol and 8.074 kcal/mol less stable than cation (I), respectively. The ionic addition of bromine to homocubylidenohomocubane is predicted to proceed via the cyclic three-membered bromonium ion (I) (cation-I-Br) couple is assumed to be in the transition form), since this cation is the most stable one among the cationic intermediates (Scheme 2). However, by analogy to the electrophilic bromination of adamantylidenadamantane, it is likely that bromination of HC proceeds anti-stereospecifically via the bromonium ion (I). It is known that bromination of HC molecule gives the normal dibromide addition product. The bromination of AD molecule cannot proceed beyond the stage of the cyclic three-membered bromonium ion (AD-Br⁺). To explain the reason for this, the full geometric optimization of AD-Br⁺ ions was done by HF6-311G* method and the electronic and the geometric properties were calculated. The results are compared with those of HC-Br⁺ ions (Table 3).

The values of $R_a$ (the diagonal distances between the α- and β-hydrogens), $R_b$ (the diagonal distances between the α- and β-hydrogens) calculated by the HF6-311G* method are also in agreement with each bromonium ion as shown in Table 3. The average values of $R_a$ and $R_b$ for AD-Br⁺ ion are 3.258 Å and 3.339 Å, respectively. These values for HC-Br⁺ ion are 4.052 Å and 4.558 Å, respectively. The nucleophilic attack of the initially formed bromide ion (Br⁻) on the cationic center of bromonium ion occurs from the opposite side of the three-membered ring. For such a nucleophilic attack, the average values of the cavity radii $R_a$ and $R_b$ formed by the hydrogen atoms of bromonium ion must be larger than the average value of the ion radii ($R_a \sim 3.64$ Å) of bromide ion (Br⁻). Since the average $R_a$ and $R_b$ values for AD-Br⁺ ion are smaller than the average $R_{ ave}$ value, in AD-Br⁺ the nucleophilic attack of Br⁻ ion is sterically prevented as shown in Scheme 3. For the HC-Br⁺ ion, the average $R_a$ and $R_b$ values are larger than the average $R_{ave}$ value, the nucleophilic attack to bromonium ion of Br⁻ ion is not sterically prevented and normal dibromide addition product is obtained.

References