J Mol Model (2006) 12: 290–296
DOI 10.1007/s00894-005-0031-9

ORIGINAL PAPER

Rza Abbasoglu · Sevil Savaskan Yilmaz

Ab initio and DFT study on the electrophilic addition of bromine to *endo*-tricyclo[3.2.1.0^{2,4}]oct-6-ene

Received: 19 December 2004 / Accepted: 5 July 2005 / Published online: 26 October 2005

Abstract Full geometric optimization of *endo*-tricyclo[3.2.1.0^{2,4}]oct-6-ene (*endo*-TCO) by ab initio and DFT methods allowed us to investigate the structure of the molecule. The double bond is *endo*-pyramidalized and its two faces are no longer found to be equivalent. The *exo* face of the double bond has regions with far more electron density ($q_{i,HOMO}$) and more negative electrostatic potential. The *endo*-TCO-Br_2 system was investigated at the B3LYP/6-311+G** level and the *endo*-TCO···Br_2(*exo*) molecular complex was found to be relatively more stable than the *endo*-TCO···Br_2(*endo*) complex. The cationic intermediates of the reaction were studied by ab initio and DFT methods. The bridged *exo*-bromonium cation(**I**) is relatively more stable than the *endo*-bromonium cation(**II**). An absolute *exo*-facial selectivity should be observed in the addition reaction of Br_2 to *endo*-TCO, which is caused by steric and electronic factors. The nonclassical rearranged cation **IV** was found to be the most stable ion among the cationic intermediates and the ionic addition occurs via the formation of this cation. The mechanism of the addition reaction is also discussed.

Keywords Ab initio and DFT calculations · Molecular complexes · Nonclassical cation · Pyramidalization · *Endo*-tricyclo[3.2.1.0^{2,4}]oct-6-ene

Introduction

In addition to all the numerous industrial applications as pesticides, plastics, fire retardants and pharmaceutical chemicals, the halogen derivatives of a compound are also valuable as a model for synthesizing other derivatives. Therefore, the halogenation of organic compounds is an important process. Electrophilic addition reactions of halogens to unsaturated molecules have been studied extensively both theoretically and experimentally but the mechanism and stereochemistry of these reactions are still under discussion as well as the nature, the structure and the stability of the intermediates formed during addition. Olefin–halogen molecular complexes are important intermediates formed in the earlier steps of the addition reaction [1–9]. The determination of the structure and the stability of olefin–halogen molecular complexes and cationic intermediates plays an important role in the investigation of the addition reactions' mechanism and stereochemistry. Since the intermediates possess low stabilities and high reactivities, it is difficult to obtain such experimental data. However, quantum-chemical calculations provide a reliable source for these data.

The addition reactions of halogens to unsaturated strained molecules and the reaction intermediates have been investigated quantum chemically [1–7,10–14]. In this connection, we have recently reported theoretical investigations of the addition of bromine and chlorine to olefins with rigid structure [15]. In continuation of our interest in quantum-chemical studies related to the addition of halogens to unsaturated strained molecules, we wish to report here the results obtained from the investigation of the addition of bromine to *endo*-tricyclo[3.2.1.0^{2,4}]oct-6-ene. Reaction of *endo*-tricyclo[3.2.1.0^{2,4}] oct-6-ene (*endo*-TCO) with bromine gave two rearranged products; 6-*exo*-8-*anti*-dibromo-*exo*-tricyclo[3.2.1.0^{2,4}]octane(**1**) and 5-*exo*-bromo-3-*endo* bromomethyltricyclo[2.2.1.0^{2,6}]heptane(**2**) [16]. In order to carry out a 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 seems to be very important. On the other hand, the formation of 5-*exo*-bromo-3-*endo*-bromomethyltricyclo[2.2.1.0^{2,6}]heptane(**2**) product from the nonclassical cation **IV** or *exo*-classical bromocarbonium cation **III** is still a subject of

R. Abbasoglu (✉) · S. S. Yilmaz
Department of Chemistry, Karadeniz Technical University, 61080 Trabzon, Turkey
E-mail: rabbas@ktu.edu.tr
E-mail: sevily@ktu.edu.tr
Fax: +90-462-3253195

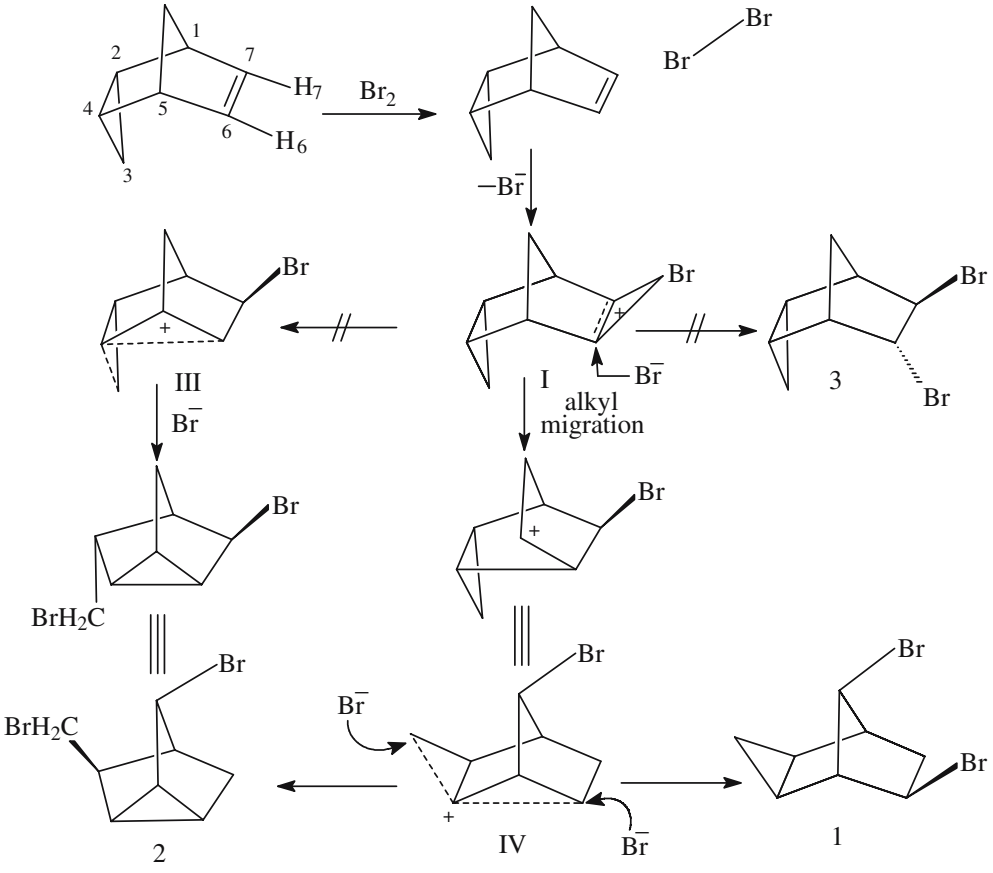
discussion (Scheme 1) [16]. These two reasonable routes to product **2** are not differentiated by experiment. [16].

Although nonrearranged *trans*- and *cis*-adducts are formed in the addition reaction of bromine to *exo*-TCO, nonrearranged products are not formed in the bromination of *endo*-TCO [16]. In general, the stereochemical regularities of the addition reactions of halogens to unsaturated strained molecules are the subjects of detailed investigation. The bromination of unsaturated bi- and tricyclic systems with molecular bromine leads to rearrangements of the molecular skeleton [16–21]. The stereoselectivity of these reactions depends substantially on the electronic and the geometrical structures of the double bonds of the strained olefins. The most important factors that affect the structure and stability of olefin–halogen molecular complexes are the structure and the properties of the olefins.

In this study, the geometry and the electronic structure of the *endo*-tricyclo[3.2.1.$0^{2,4}$] oct-6-ene have been investigated in detail by ab initio and density-functional theory (DFT) methods. *Endo*-TCO···Br_2 molecular complexes have been studied using DFT and their stable configurations have been determined. The structure and the stability of cations and their isomers have also been investigated by ab initio and DFT methods. The formation mechanism of the addition products is discussed.

Methodology

The geometry and the electronic structure of *endo*-tricyclo[3.2.1.$0^{2,4}$]oct-6-ene(*endo*-TCO) was investigated by the ab initio SCF method using the 6-31G*, [22] 6-311G* and 6-311G** [23] basis sets and with DFT at the B3LYP/6-31G* [24, 25] level. The theoretical investigation of *endo*-TCO···Br_2 molecular complexes used the B3LYP/6-311 + G** method [26]. Basis-set superposition error (BSSE) energies are corrected. The predicted cationic intermediates formed in the addition reactions have been investigated at the HF/6-311G*, HF/6-311G** and B3LYP/6-311G** levels. The electron-correlation energy was calculated using Moller–Plesset second-order perturbation theory [27]. All stationary points were characterized by calculating the vibrational freqencies and zero-point vibrational energies were added for all species. The calculations were carried out with different basis sets and the results compared. Full geometry optimizations were carried out using the Polak–Ribiere (conjugate gradient) algorithm (convergence of 0.00001 kcal mol^{-1}) and an RMS gradient at 0.001 kcal $(Å\ mol)^{-1}$. The calculations were perfomed with the HyperChem 7.5 and Gaussian98 programs with an IBM PC Pentium IV computer.



Scheme 1 The mechanism of the addition of bromine to *endo*-TCO

Results and discussion

Full geometry optimization of *exo*-TCO molecule was performed at the HF/6-31G*, HF/6-311G*, HF/6-311G**, B3LYP/6-31G* and B3LYP/6-311 + G** levels and the structure of the molecule was also investigated in detail. In the light of the results obtained from each method, the pyramidalization parameters of each molecule were evaluated with the aim of determining the structural deformation of the double bond. The values of the pyramidalization angle (ϕ) (the angle between the plane containing one of the double bonded carbons and the two substituents attached to it and the extension of the double bond) [28] and of the out-of-plane bending angle (χ) (out of plane angle: between plane C1C7C6C5 and plane H6C6C7H7 as seen in Scheme 1) [29] were calculated for each method. These results are given in Table 1. According to the results obtained, the double bond of *endo*-TCO is *endo*-pyramidalized. The two faces of the double bond are not equivalent and the electron density in the *exo*-direction must be larger than that in the *endo*-direction. This extraordinary geometrical feature causes the very remarkable π-facial selectivity in the addition reactions to the double bond [30]. Thus, the addition reaction of bromine to *endo*-TCO, in which the double bond is *endo*-pyramidalized, should be seen as *exo*-selectivity. In general, the facial selectivity of an attack on a pyramidalized olefin parallels the pyramidalization [31, 32]. When the pyramidalization degree of the double bond of olefins increases, their chemical reactivity also increases [30].

An analysis of the frontier orbital (HOMO) of *endo*-TCO showed that this orbital is principally localized on the double bond (Fig. 1). As seen in Fig. 1, *exo*- and *endo*-faces of the *endo*-pyramidalized double bond of the molecule are nonequivalent and the electron density in *exo*-face is large. Therefore, the bromination reaction of *endo*-TCO should show facial selectivity. The addition of bromine should occur from the *exo*-side, which has higher electron density.

One of the most accurate methods for determining the direction of electrophilic attack of halogens on double bonds of strained olefins is calculating the molecular electrostatic potentials (MESP) of the molecule. The MESP surfaces show considerable topographical variation with many saddle points, minima and maxima. Every π-bond of olefins has a local minimum of the electrostatic potential on either face. Since the regions with large negative potential should direct

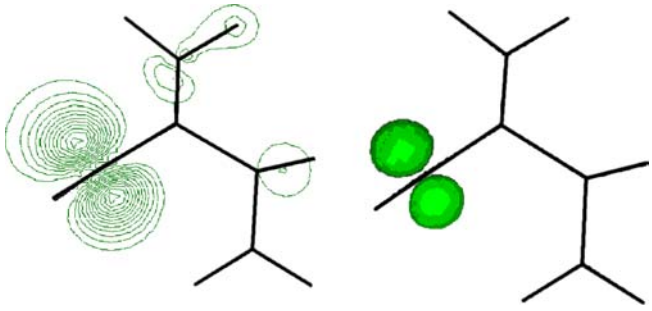


Fig. 1 Electron density distribution (HOMO) of the *endo*-tricyclo[3.2.1.$0^{2,4}$]oct-6-ene(HF/6-311G*)

the initial approach of an electrophile, the relative depths of the two minima can be used to predict the preferred facial selectivity. Alternatively, integrated volumes of a certain negative potential can be obtained for the two faces. Electrophilic attack is predicted to be more favorable on the face with larger integrated volume. These approaches have been used effectively in a number of systems, qualitatively as well as rigorously [33–35]. In order to understand from which side of the double bond the bromine attacks, the molecular electrostatic potential (MESP) (in kcal mol^{-1}) of the molecule was calculated by HF/6-311G* level (Fig. 2). The electrostatic potential contour maps of the molecule reveal that the electrophilic attack of bromine occurs predominantly on the *exo*-face of the double bond.

As known, olefin-halogen molecular complexes are 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 side from which the halogen attacks. In order to find out or investigate Br_2 attack on *endo*-TCO, the *endo*-TCO-Br_2 system was investigated in detail at the B3LYP/6-311 + G** level. The orientation of halogens to the double bond of unsaturated bi- and tricyclic compounds is generally possible from the *exo*- or *endo*-sides. Furthermore, the approach of a halogen molecule to the double bond may occur either in axial (the C_∞ axis of halogen molecule is perpendicular to double bond plane) or equatorial (the C_∞ axis of halogen is parallel to double bond plane) position. Hence, the full geometry optimization of the various configurations of the *endo*-TCO-Br_2 system was performed and stable configurations corresponding to the minimum energy levels determined. In this connection, two configurations corresponding to the minima of the *endo*-TCO-Br_2 system were identified. A local minimum was found for the

Table 1 The calculated total energies (kcal mol^{-1}), energies of frontier molecular orbitals (eV), double bond lengths (Å) and pyramidalization parameters (degrees) of *endo*-tricyclo[3.2.1.$0^{2,4}$]oct-6-ene

Method	E_{tot}	ε_{HOMO}	ε_{LUMO}	$r_{C=C}$	ϕ	χ
HF/6-31G*	−193698.4810	−9.189	4.997	1.323	4.856	5.145
HF/6-311G*	−193731.7395	−9.296	4.213	1.322	5.105	5.432
HF/6-311G**	−193741.7798	−9.298	4.211	1.321	5.201	5.493
B3LYP/6-31G*	−194886.1317	−6.290	0.635	1.344	5.248	5.573
B3LYP/6-311 + G**	−194928.1252	−6.292	0.634	1.344	5.514	5.865

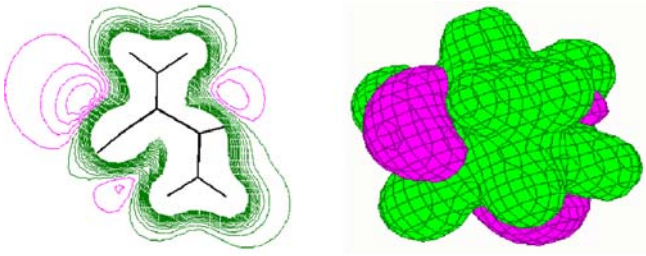


Fig. 2 Molecular electrostatic potential contour map of *endo*-tricyclo[3.2.1.$0^{2,4}$]oct-6-ene (HF/6-311G*)

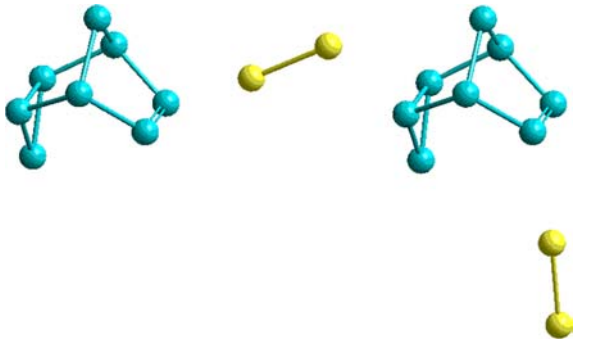


Fig. 3 The optimized geometries of *endo*-TCO···Br_2 (*exo*) and *endo*-TCO···Br_2 (*endo*) molecular complexes (B3LYP/6-311 + G**)

endo-TCO···Br_2 (*exo*) molecular complex, which is formed by the *exo*-orientation of the Br_2 molecule to the double bond of *endo*-TCO in the axial position (Fig. 3) A shallow minimum was found for the *endo*-TCO···Br_2 (*endo*) molecular complex formed by the approach of a Br_2 molecule to the double bond in the axial position and in an *endo*-orientation (Fig. 3). The properties of the molecular complexes are shown in Table 2. In *endo*-TCO···Br_2(*endo*), the equilibrium distance $R_{X\text{-}Br}$ (X is the midpoint of the C = C bond of *endo*-TCO) is 4.549 Å and the stabilization energy of the complex is low (0.084 kcal mol^{-1}). The molecular geometry of the *endo*-TCO···Br_2 (*endo*) complex is in agreement with the geometry of the isolated *endo*-TCO and bromine molecules. This situation indicates that the molecular interaction on the *endo*-side is very low. Furthermore, the values of equilibrium distances and stabilization energies of the *endo*-TCO···Br_2 (*endo*) system reveal that the approach of the Br_2 molecule to the double bond on the *endo*-side is difficult and not effective. This difficulty can be attributed mainly to the steric hindrance of the cyclopropane ring of *endo*-TCO.

The *exo*-form of the *endo*-TCO···Br_2 (*exo*) molecular complex is more stable than the *endo*-form (Table 2). It is reasonable to consider that the orientation of the Br_2 molecule to the double bond may essentially occur on the *exo*-side because of the steric hindrance of the cyclopropane ring of *endo*-TCO. Hence, an absolute *exo*-selectivity must be taken into consideration. On the other hand, as we pointed out, the electron density ($q_{i,HOMO}$) on the *exo*-face of the *endo*-pyramidalized double bond of *endo*-TCO is higher than on the *endo*-face (Fig. 1). In other words, the $HOMO_{TCO}$–$LUMO_{brom}$ interaction possible from the *exo*-face of the double bond in the formation of the *exo*-molecular complex is more effective than that of the *endo*-face and should be optimal. According to frontier molecular orbital theory, the $HOMO_{olf}$–$LUMO_{halogen}$ interaction is the decisive factor in the formation of olefin–halogen complexes [36]. Thus, because of steric and electronic factors, the *exo*-molecular complex is more stable than the *endo*-molecular complex (Table 2). In a similar manner, *exo*-facial selectivity is caused by steric and electronic effects. As a result, *endo*-TCO···Br_2 (*exo*) molecular complex must be formed as an essential and important intermediate during the ionic addition of Br_2 to *endo*-TCO. Studies of the structures and stabilities of the molecular complexes are very important in the determination of facial selectivity and regioselectivity of the addition reactions.

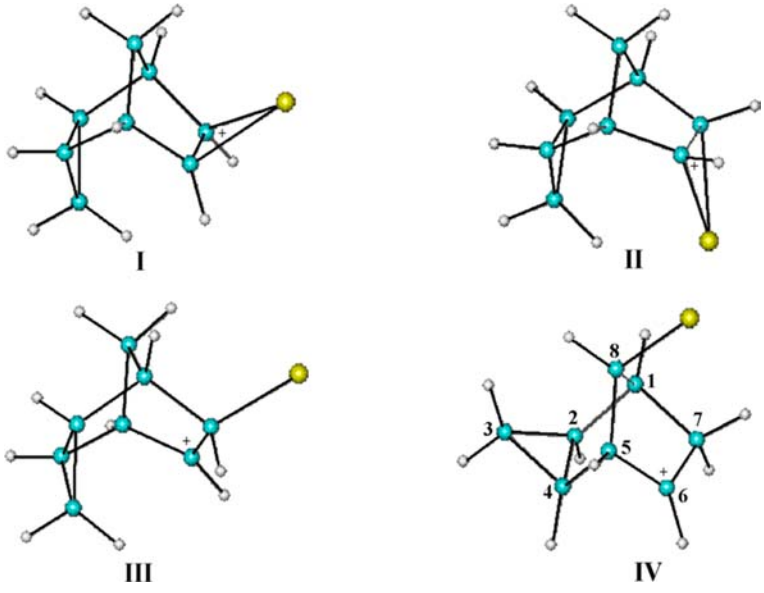
The bromine molecule in the *endo*-TCO···Br_2 (*exo*) complex is partially polarized. The bromine atom near the double bond has a partial positive charge and the other one has a partial negative charge (Table 2). The bond length of the bromine atoms in the complex is longer than that of the neutral bromine molecule (Table 2). These results indicate that the *endo*-TCO···Br_2 (*exo*) form plays an important part for the heterolytic splitting of the bromine molecule leading to an ionic addition. Theoretical investigations show that molecular complexes are essential and important intermediates of the addition reactions.

Molecular complexes are more stable in a solvent medium than in the gas phase, and their stabilization energies become higher as the solvent polarity increases [37]. The polarization of bromine and subsequent heterolytic splitting of the *endo*-TCO···Br_2 (*exo*) molecular complex results in the formation of the *exo*-bridged bromonium cation. This cation and its isomers are possible intermediates in the addition reactions of bromine to *endo*-TCO in the gas phase and solvent medium (Scheme 2).

Table 2 The properties of *endo*-TCO...Br_2 (*exo*) and *endo*-TCO...Br_2 (*endo*) molecular complexes (B3LYP/6-311 + G**)

Molecular complex	Stabilization energy (kcal mol^{-1})	Equilibrium distance R_e (Å)	$r_{Br\text{-}Br}$ (Å)	Charge on bromines (e)		Transferred charge from *endo* TCO to Br_2 (e)
				near	far	
endo-TCO···Br_2(*exo*)	1.976	2.947	2.375	0.021	-0.069	0.048
endo-TCO···Br_2(*endo*)	0.084	4.549	2.367	0.006	-0.025	0.019

Scheme 2 The optimized geometries of cations (HF/6-311G**)



In order to determine the structures and relative stabilities of the predicted cationic intermediates (Scheme 2), their full geometry optimization was performed at the HF/6-311G*, HF/6-311G** and B3LYP/6-311G** levels and the total energies (E_{tot}) calculated. Single-point energy calculations at the MP2/6-311G**//HF/6-311G** level were used to evaluate the electron-correlation effect on the energies and the order of stability of cations. The calculated relative energies are given in Table 3.

Because of the steric hindrance (Scheme 2, cation **II**) caused by the cyclopropane ring, the *endo*-bridged-bromonium cation **II** is unstable. In *endo*-bridge cation **II**, the steric interaction of the bromine with the hydrogen atom of methylene group is at a maximum. *Endo*-bromonium cation **II** is relatively less stable than *exo*-bromonium cation **I** and the formation probability of cation **II** is low. In other words, an *exo*-bridged cation formed by the splitting of the *exo*-molecular complex is more stable than an *endo*-bridged cation. This reveals that absolute *exo*-facial selectivity must be considered in the mechanism of the electrophilic addition of Br_2 to *endo*-TCO. The *exo*-bromonium cation is relatively more stable than the classical bromocarbonium cation **III**. For this reason, the conversion of cation **I** to ion **III** is not easy. The relative stabilities of bridged halogenium and the classical halogenocarbonium cations are still under discussion in the literature [38, 39]. According to calculations performed by ab initio and DFT methods, bridged bromonium cations are more stable than the corresponding classical bromocarbonium cations [38, 39]. Among the cationic intermediates, the most stable one is the nonclassical rearranged cation **IV**. These results are consistent with those calculated for the 2-norbornyl, *exo*-2-bromo-3-benzonorbornenyl and 6-tricyclo[3.2.1.$0^{2,4}$]octyl cations using various quantum-chemical methods [10, 40–43]. The nonclassical cation **IV** is probably formed by a Wagner–Meerwein rearrangement involving an alkyl migration from *exo*-bridged-bromonium cation **I**. It is reasonable to consider that the ionic addition of bromine to *endo*-TCO proceeds via the formation of nonclassical rearranged cation **IV** because of its higher stability.

The cyclopropyl group has long been considered to be similar to a double bond and so can stabilize cations even at remote positions [44]. The positive charge of rearranged cation **IV** (Scheme 1, cation **IV**) is delocalized and the cation is rendered more stable by the interaction of the positive center and the electron clouds of the cyclopropane ring. On the other hand, it is possible that the rearranged cation **IV** is a σ/π no-bond homoconjugated species in which there is no bond path between C4 and C6 (Scheme 2, cation **IV**). No bond path was found between C4 and C6, so the rearranged cation **IV** is a classical cation without pentacoordinated carbon atoms. Compared with the C1–C2 bond, which

Table 3 The calculated relative energies of cations

Cations	Relative Energy (kcal mol^{-1})			
	HF/6-311G*	HF/6-311G**	B3LYP/6-311G**	MP2/6-311G**/ /HF/6-311G**
I	9.413	5.917	4.985	9.022
II	32.263	29.942	22.746	30.378
III	11.922	9.221	10.124	19.078
IV	0.0	0.0	0.0	0.0

we take as a normal single bond, the bonds between C4 and C3, C5 are weak. The C3–C4 and C4–C5 internuclear distances increased while the C2–C3 and C5–C6 distances decreased, suggesting that double bond character developed at these centers. According to ab initio HF/6-311G**, the lengths of the C1–C2, C2–C3,C3–C4, C4–C5 and C5–C6 bonds are found to be 1.534, 1.417, 1.630, 1.560, and 1.439 Å, respectively (Scheme 2, cation **IV**). Also, the C4–C6 internuclear distance is 1.733 Å (HF/6-311G**).

The mechanism of the ionic addition of Br_2 to *endo*-TCO can occur as shown in Scheme 1. The ionic addition of bromine to *endo*-TCO is predicted to proceed via rearranged ion **IV** since this cation is the most stable of the cations studied. In this reaction, the nucleophilic attack of the initially formed bromide (Br^-) ion on the cationic center C-6 may occur from the opposite side of cyclopropane ring, because of the interaction between this cationic center and the electron clouds of the cyclopropane ring in the cation **IV**, and so, 6-*exo*-8-*anti*-dibromo-*exo*-tricyclo[3.2.1.$0^{2,4}$]octane(**1**) is formed as a Wagner–Meerwein rearrangement product. In the ionic addition of Br_2 to *endo*-TCO, the formation of 6-*endo*-8-*anti*-dibromo-*exo*-tricyclo[3.2.1.$0^{2,4}$]octane is not possible due to the electronic interaction. On the other hand, as a consequence of the attack of bromide(Br^-) ion to cation **IV**, its C3–C4 cyclopropyl bond became weak and broke and 5-*exo*-bromo-3-*endo*-bromomethyltricyclo[2.2.1.$0^{2,6}$]heptane(**2**) product results in the formation of the C4–C6 bond. Thus, theoretical investigations show that the formation of 5-*exo*-bromo-3-*endo*-bromomethyltricyclo[2.2.1.$0^{2,6}$]heptane(**2**) occurs via nonclassical cation **IV** not via *exo* classical bromocarbonium cation **III**.

As known, the *trans*-adducts are formed via bridged-halogenium ions in the addition of halogens to olefins [45]. Because of steric hindrance of the cyclopropane ring in *exo*-bridged bromonium cation (Scheme 2, cation **I**), it is impossible to make a nucleophilic *endo*-attack. Thus, the formation of non-rearranged *trans*-adduct **3** (an *exo*, *endo*-dibromide) (Scheme 1, product 3) in the addition reaction of bromine to *endo*-TCO is sterically hindered. Fundamentally, *cis*-adducts occur out of classical halogenocarbonium cations in the addition reaction of halogens to unsaturated strained molecules [45]. Classical bromocarbonium cation **III** (Scheme 1) is no more stable than the *exo*-bridged-bromonium cation and hence, the probability of their formation is small. Therefore, the formation probability of *cis*-adducts (an *exo*, *exo*-dibromide) are small in the addition reaction of bromine to *endo*-TCO.

Conclusions

Our investigations of bromine addition to *endo*-tricyclo[3.2.1.$0^{2,4}$]oct-6-ene (*endo*-TCO) by ab initio and DFT methods give some important results, as mentioned below. The double bond of *endo*-TCO is *endo*-pyramidalized. The electron density ($q_{i,HOMO}$) on the *exo*- and *endo*-faces of the double bond is not equivalent and is larger on the *exo*-face. The *exo*-face of the double bond of the molecule is an area with more negative potential. The *exo*-molecular complex is more stable than the *endo*-complex. The bridged *exo*-bromonium cation **I** is relatively more stable than the *endo*-bromonium cation (**II**). An absolute *exo*-facial selectivity should be observed in the addition reaction of Br_2 to *endo*-TCO, which is caused by steric and electronic factors. Classical bromocarbonium cation **III** is relatively less stable than the bridged *exo*-bromonium cation **I**. The nonclassical rearranged cation **IV** is the most stable ion among the cationic intermediates and the ionic addition occurs via the formation of this cation. The C3–C4 and C4–C6 internuclear distances of the rearranged cation **IV** optimized at the ab initio HF/6-311G** level are 1.630 and 1.733 Å, respectively. Since the cyclopropane ring forms a steric hindrance in the *exo*-bridged-bromonium cation, it is impossible to form the nonrearranged *trans*-adduct.

References

1. Belluci G, Chappe C, Bianchini R, Lenoir D, Herges R (1995) J Am Chem Soc 117:12001–12002
2. Herges R (1995) Angew Chem Int Ed Engl 34:51–53
3. Ruiz E, Dennis R, Salahub R, Vela A (1996) J Phys Chem 100:12265–12276
4. Brown RS (1997) Acc Chem Res 30:131–137
5. Bianchini R, Chappe C, Lenoir D, Lammeu R, Herges R, Grunenber J (1997) Angew Chem Int Ed Engl 36:1284–1287
6. Bianchini R, Chiappe C, Moro LG, Lenoir D, Lemmen P, Goldberg N (1999) Chem Eur J 5:1570–1580
7. Chiappe C, Rubertis AD, Lemmen P, Lenoir D (2000) J Org Chem 65:1273–1279
8. Legon AC, Thumwood JMA (2001) Phys Chem Chem Phys 3:1397–1403
9. Chiappe C, Rubertis AD, Lemmen D, Jaber A, Lenoir D, Watteubochi C, Ponelli CS (2002) J Org Chem 67:7066–7074
10. Smith WB (1998) J Org Chem 63:2661–2664
11. Chiappe C, Rubertis DA, Detert H, Lenoir D, Wannere C, Schleyer RP (2002) Chem Eur J 8:967–978
12. Rathere R, Lindeman SV, Zhu CJ, Mori T, Schleyer RP, Kochi JK (2002) J Org Chem 67:5106–5116
13. Lenoir D, Chiappe C (2003) Chem Eur J 9:1037–1044
14. Chiappe C, Detert H, Lenoir D, Pamelli CS, Ruasse MF (2003) J Am Chem Soc 125:2864–2865
15. Abbasoglu R (2004) J Mol Struct (Theochem) 686:1–5 and references therein
16. Coxon JM, Steel PJ, Burritt A, Whittington BI (1995) Tetrahedron 51:8057–8072
17. Dastan A, Demir U, Balci M (1999) J Org Chem 59:6534–6538
18. Burritt A, Coxon JM, Steel PJ (1996) J Org Chem 61:4328–4335
19. Satake K, Hikasa K, Itoh H, Okamoto H, Kimura M, Morosawa S (1996) Bull Chem Soc Jap 69:453–457
20. Dastan A (2001) Tetrahedron 57:8725–8732
21. Horasan N, Kara Y, Azizoglu A, Balci M (2003) Tetrahedron 59:3691–3699
22. Hehre WJ, Ditchfield R, Pople JA (1972) J Chem Phys 56:2257–2261
23. Krishnan R, Binkley JS, Seeger R, Pople JA (1980) J Chem Phys 72:650–654
24. Becke AD (1993) J Chem Phys 98:5648–5652

25. Lee C, Yang W, Parr RG (1988) Phys Rev B 37:785–789
26. Frisch MJ, Pople JA, Binkley JS (1984) J Chem Phys 80:3265–3269
27. Krishnan R, Frisch MJ, Pople JA, (1980) J Chem Phys 72:4244–4249
28. Borden WT (1989) Chem Rev 89:1095–1109
29. Ermer O, Bell P, Mason SA (1989) Angew Chem Int Ed Engl 28:1239–1241
30. Watson WH (1983) Stereochemistry and reactivity of systems containing (electrons. Verlag Chemie International, Deerfield beach, Florida
31. Houk KN, Rondon NG, Brown FK, Jorgensen WL, Madura JD, Spellmeyer DC (1983) J Am Chem Soc 105:5980–5988
32. Gandalfi R, Tonaletti G, Rostelli A, Bagatti M (1993) J Org Chem 58:6038–6048
33. Royer J (1978) Tetrahedron Lett 1343–1346
34. Paguette LA, Belliamy F, Wells GJ, Bohm MC, Gleiter R (1981) J Am Chem Soc 103:7122–7133
35. Broughton HB, Green SM, Rzepa HS (1992) J Am Chem Soc, Chem Commun 998–1001
36. Fleming I (1976) Frontier orbitals and organic chemical reactions. Wiley, New York, pp 5–33
37. Smirnov VV, Tihomirov VA, Cudinov GE (1993) Zh Struct Chem 34:14–18
38. Teberekidis VI, Sigalas MP (2002) Tetrahedron 58:6171–6178
39. Teberekidis VI, Sigalas MP (2003) Tetrahedron 59:4749–4751
40. Perera SA, Bartlett RJ (1996) J Am Chem Soc 1118:7849–7850
41. Werstiuk NH, Muchall HM (1999) J Mol Struct (Theochem) 463:225–229
42. Werstiuk NH, Muchall HM (2000) J Phys Chem 104A: 2054–2060
43. Werstiuk NH, Wang YG (2001) J Phys Chem 105A:11515–1152
44. Cremer D, Childs RL, Kraka E (1995) In the chemistry of the cyclopropyl group. In: Rappoport Z (ed) Wiley, New York, 2:339–410
45. de la Mare PBD, Bolton R (1982) Electrophilic additions to unsaturated systems, 2nd edn. Elsevier, New York, pp 135–197