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DFT and MP2 study on the electrophilic addition reaction of bromine to exo-tricyclo[3.2.1.0^{2,4}]oct-6-ene

Rza Abbasoglu

Abstract The geometry and electronic structure of exo-tricyclo[3.2.1.0^{2,4}]oct-6-ene (exo-TCO) was investigated using DFT methods. The two faces of the endo-pyramidalised double bond of the molecule are not equivalent. The exo face of the double bond has regions with high electron density ($q_{i,\text{HOMO}}$) and greater negative potential. Molecular complexes of exo-TCO with bromine were investigated using the B3LYP/6-311++G(d,p) method; the exo-TCO…Br$_2$(exo) molecular complex was found to be relatively more stable than the exo-TCO…Br$_2$(endo) complex. The cationic intermediates of the reaction were studied by DFT and MP2 methods. The solvent effect was evaluated using the self-consistent isodensity polarised continuum model (SCI-PCM). The exo-bromonium cation was found to be more stable than the endo-bromonium cation. Exo-facial selectivity due to electronic and steric factors was observed upon addition of bromine to exo-TCO. The multicentre nonclassical delocalised bromocarbonium cation **IV** and the exo-bridged-bromonium cation **I** are more stable than the rearrangement cation **V**. The reaction products are formed via exo-bridged-bromonium **I** and nonclassical **IV** cations, which are the most stable intermediates and whose stabilities barely differ. The mechanism of the addition reaction is also discussed.

Keywords DFT and MP2 calculation · Pyramidalisation · Electrophilic addition · Molecular complex · Multicentre nonclassical cation · Exo-tricyclo[3.2.1.0^{2,4}]oct-6-ene

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Introduction

Electrophilic halogenation of olefins is a classical reaction in organic chemistry, and an important step in the preparation of various synthetic intermediates or products. Therefore, the halogenation of olefins is an important industrial process. The addition of molecular bromine to the carbon–carbon double bond is one of the simplest reactions typical of unsaturated compounds. The nature of the intermediates during this addition depends on temperature, steric factors, torsional effects, π- and σ-participation in the transition state, and the formation of nonclassical ions or the rapid equilibrium of classical ions [1, 2]. The bromination of unsaturated bicyclic systems with molecular bromine leads to rearrangements of the molecular skeleton [3–8]. In order to analyse the reaction mechanism and stereochemistry, some data about the structures and stabilities of the intermediates, such as olefin-halogen molecular complexes, and the cations formed during these reactions are needed. Since the intermediates are characterised by low stability and high reactivity, it is difficult to obtain such data experimentally. Nevertheless, quantum-chemical calculations provide a reliable source of information about the structure and stability of intermediates in the absence of experimental measurements.

The addition reactions of halogens to unsaturated strained molecules, and the corresponding reaction intermediates, have been investigated by quantum chemical methods [9–25]. In this regard, we have recently reported theoretical investigations into the addition of bromine and chlorine to olefins with rigid structure [26 and references therein, 27–33]. Continuing our interest in quantum-chemical studies related to the addition of halogens to unsaturated strained molecules, we report here results obtained from an investigation into the addition of bromine to exo-tricyclo

[3.2.1.0^{2,4}]oct-6-ene (exo-TCO). The reaction of exo-TCO with bromine gave two non-rearranged products, 6-endo-7-exo-dibromo-exo-tricyclo[3.2.1.0^{2,4}]octane (**1**), and 6-exo-7-exo-dibromo-exo-tricyclo[3.2.1.0^{2,4}]octane (**2**); and three rearranged products, 5-exo-bromo-3-exo-bromomethyltricyclo[2.2.1.0^{2,6}]heptane (**3**), 4-exo-6-exo-dibromotricyclo[3.2.1.0^{2,7}]octane (**4**) and 6-exo-bromotricyclo[3.2.1.0^{2,7}]oct-3-ene (**5**) [34]. It is of interest to investigate the reasons underlying the stereoselective properties of this reaction. Generally, electrophilic addition reaction of halogens to alkenes leads to more stable cationic intermediates [1]. In order to carry out any detailed analysis of the formation mechanism and stereochemistry of the products of this reaction, a quantum chemical investigation of the structures and stabilities of the reaction intermediates is crucial. Furthermore, whether formation of the 5-exo-bromo-3-exo-bromomethyltricyclo[2.2.1.0^{2,6}]heptane (**3**) product from the cation proceeds through the Wagner-Meerwein rearrangement or via a nonclassical route is still a subject of discussion (Scheme 1) [34].

Also, although both nonrearranged and rearranged products are obtained in the electrophilic addition reaction of bromine to the exo-TCO molecule, in the bromination reaction of the endo-TCD molecule, only rearranged products are obtained [27, 34]. It is important to explain the reason for this differing behaviour of the exo-TCO and endo-TCO isomer molecules in the reaction medium. Hence, determination of the relationship between the geometrical and electronic structures of these alkenes and their behaviour during the electrophilic addition reaction is vital. In general, the stereochemical regularities of the addition reactions of halogens to unsaturated strained systems have long been the subject of detailed investigation. Stereoselectivity of these reactions depends to a large extent on the electronic structure of the double bonds of strained olefins. The most important factors affecting the structure and stability of olefin-halogen molecular complexes are the structure and properties of olefins. This work describes a theoretical investigation of the electrophilic reaction intermediates such as exo-TCO···Br$_2$ molecular charge-transfer (CT) complexes and cations. The mechanism of formation of the addition products is discussed.

Methods

The geometry and the electronic structure of exo-TCO were investigated at the Becke-style three-parameter level of density functional theory (DFT) [35] with the Lee-Yang-Parr (LYP) correlation function [36] and Perdew-Wang's 91 (PW91) expression [37]. All calculations were performed using the 6-311++G(d,p) and 6-311+G(2df,2pd) [38, 39]

Scheme 1 Mechanism of addition of bromine to exo-tricyclo[3.2.1.0^{2,4}]oct-6-ene (exo-TCO)
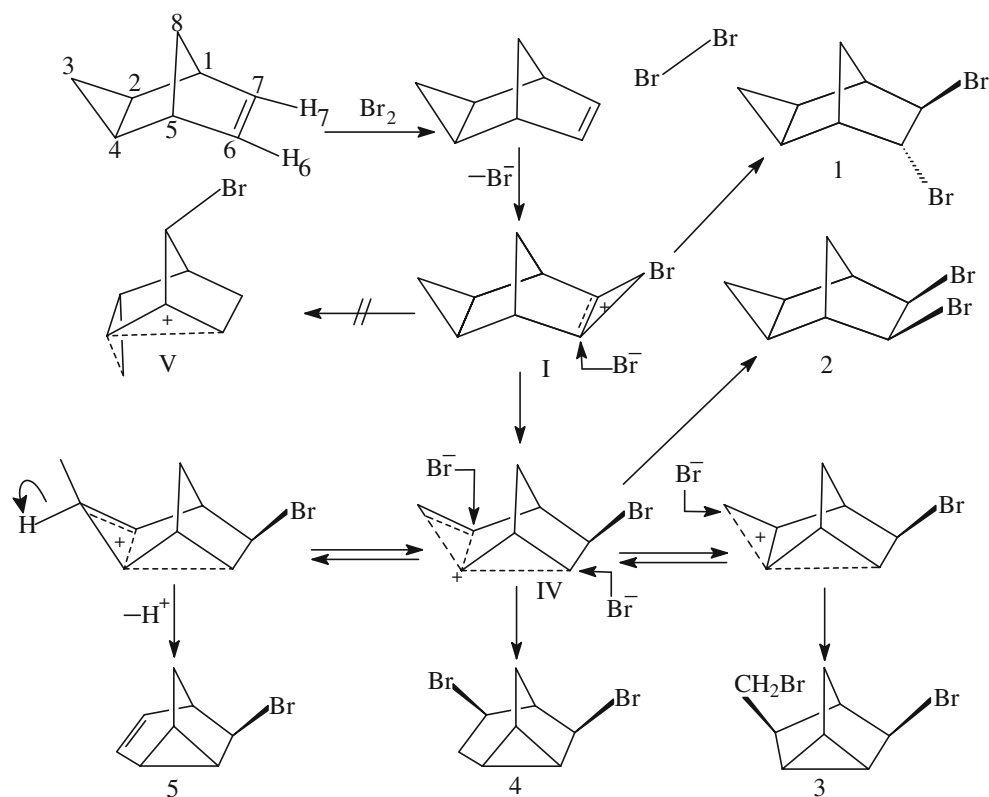
basis sets. The exo-TCO··· Br_2 molecular CT-complexes were studied with B3LYP/6-311++G(d,p) methodology and their stable configurations determined. The structure and stability of cationic intermediates formed in the addition reactions were investigated by B3LYP/6-311++G(d,p), B3LYP/6-311+G(2df,2pd) and MP2 (Møller–Plesset second-order perturbation theory)/6-311+G(2df,2pd) [40] methods. Solvent effects were calculated at the same theory level as the optimisations by performing single-point calculations on the optimised structures using the SCI-PCM (self-consistent isodensity polarised continuum model) [41] in H_2O (ε=78.39). All stationary points were characterised by calculating the vibrational frequencies, and zero point vibrational energies were added for all species. All calculations were performed with Gaussian 03 [42] and HyperChem 8 [43] software on an IBM PC Pentium IV computer.

Results and discussion

Full geometric optimisation of the exo-TCO molecule was performed using DFT/B3LYP and /B3PW91 methods with the 6-311++G(d,p) and 6-311+G(2df,2pd) basis sets, and the structure of the molecule was also investigated in detail. In the light of the results of each method, the pyramidalisation parameters of the molecule were determined in order to establish the structural deformation of the double bond. The calculated values of the pyramidalisation 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) [44] and the out-of-plane bending angle (ψ—out-of-plane angle between the planes C1C7C6C5 and H6C6C7H7 or ψ which is defined as $\psi = 180° - |D|$, D is the dihedral angle C1C7C6H6 as shown in Scheme 1) [45–47] were calculated according to the results of each method. These results are given in Table 1. According to the results, the double bond of the exo-TCO molecule is endo-pyramidalised, and the two faces of the double bond are no longer equivalent. The electron density in the exo direction of the endo-pyramidalised double bond of the molecule must be bigger

than that in the endo direction. This extraordinary geometrical feature causes the very remarkable π-facial stereoselectivity in addition reactions to the double bond [48]. Thus, the addition reaction of bromine to the exo-TCO molecule in which the double bond is endo-pyramidalised should show exo-selectivity. In general, the facial selectivity of attack on a pyramidalised olefin parallels the pyramidalisation [49, 50]. As the pyramidalisation degree of the double bond of olefins increases, so their chemical reactivities also increase [48].

Analysis of the frontier orbital (HOMO) of the exo-TCO molecule showed that this orbital is localised principally in the double bond (Fig. 1). As seen in Fig. 1, the exo and endo faces of the endo-pyramidalised double bond of the molecule are not equal. The electron density in the exo face of the double bond is high. Therefore, the bromination reaction of the exo-TCO molecule 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 of determining the direction of the electrophilic attack of a halogen to the double bonds of strained olefins is to calculate the molecular electrostatic potential (MESP). The MESP surfaces show considerable topographical variation, with many minima, saddle points, and maxima. Every π-bond of olefins has a local minimum of electrostatic potential on either face. Because regions with large negative potentials should direct 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 larger on the face with larger integrated volume. These approaches have been used effectively in a number of systems, giving rigorous qualitative results [51–53]. To understand from which direction the double bond of the exo-TCO molecule will be attacked by bromine, the MESP (in kcal mol^{-1}) of the molecule was calculated using the B3LYP/6-311++G(d,p) method (Fig. 2). The electrostatic potential contour maps of the molecule indicate that the electrophilic attack of bromine occurs predominantly on the exo face of the double bond.

Table 1 The calculated energies of frontier molecular orbitals (ε), double bond lengths (r) and pyramidalisation parameters of exo-tricyclo [3.2.1.0^{2,4}]oct-6-ene (exo-TCO). *HOMO* Highest occupied molecular orbital, *LUMO* lowest unoccupied molecular orbital

Method	ε_{HOMO}(eV)	ε_{LUMO}(eV)	$r_{C=C}$(Å)	ϕ (°)	ψ (°)
B3LYP/6-311++G(d,p)	−6.558	0.245	1.339	5.101	5.406
B3LYP/6-311+G(2df,2pd)	−6.586	0.136	1.335	5.093	5.398
B3PW91/6-311++G(d,p)	−6.585	0.155	1.338	5.282	5.589
B3PW91/6-311+G(2df,2pd)	−6.588	0.131	1.334	5.292	5.599

Fig. 1 Electron density distribution [highest occupied molecular orbital (HOMO)] of the exo-tricyclo[$3.2.1.0^{2,4}$]oct-6-ene (exo-TCO) molecule [B3LYP/6-311++G(d,p)]


2D contour   **3D isosurface**
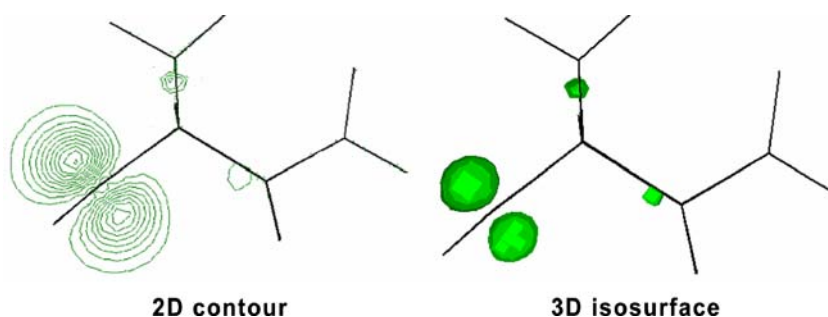
As is known, an olefin-halogen molecular CT-complex is formed in the first step of electrophilic addition of halogens to olefins [11–13, 15–17, 19, 21–23, 26 and references therein, 27, 54]. According to the thermodynamic stability of the molecular CT-complexes, it is possible to determine from which direction the halogen attacks the double bond. Therefore, the stability and electronic structure of the exo-TCO···Br_2(exo) and exo-TCO···Br_2(endo) molecular CT-complexes formed upon addition of bromine from the exo and endo direction to the double bond of the exo-TCO molecule were investigated using B3LYP/6-311++G(d,p) method. The electrophilic attack of bromine on the double bond of the exo-TCO molecule is possible from either the exo or endo side. Moreover, a bromine molecule may approach a carbon–carbon double bond in either axial (the C_∞ axis of the bromine molecule is perpendicular to the double bond plane) or equatorial (the C_∞ axis of the bromine molecule is parallel to the double bond plane) position. By considering these two approaches, the full geometric optimisation of the various configurations of the exo-TCO-Br_2 system was performed and the most stable configuration corresponding to the minimum energy levels was determined. In this regard, two configurations corresponding to the local minima of the exo-TCO-Br_2 system were found. These configurations correspond to the exo-TCO···Br_2(exo) and exo-TCO···Br_2(endo) molecular complexes that are formed by the exo and endo orientation of the Br_2 molecule

to the double bond of the exo-TCO in axial position, respectively (Fig. 3).

The stabilisation energies of the molecular CT-complexes, the equilibrium distance $R_{X–Br}$(X is midpoint of the C=C bond of exo-TCO), and other calculated properties are given in Table 2. The exo-complex is 1.547 kcal mol^{-1} relatively more stable than the endo-complex. The results obtained indicate that an exo selectivity must be considered in the electrophilic addition of the bromine molecule to exo-TCO. The π-facial selectivity observed in [2.2.1] systems parallels the double bond pyramidalisation and also results in the minimisation of steric interactions by approaching from the same face as the methano bridge rather than the ethano bridge. On the other hand, as we pointed out, the electron density ($q_{i,HOMO}$) in the exo face of the endo-pyramidalised double bond of the exo-TCO molecule is higher (Fig. 1). That is, the HOMO$_{TCO}$–LUMO$_{brom}$ interaction realised from the exo face of the double bond in the formation of the exo-molecular CT-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 the olefin-halogen complex [55]. So, because of electronic and steric factors, the exo-molecular CT-complex is more stable than the endo-molecular CT-complex (Table 2). Thus, the exo-facial stereoselectivity of the electrophilic addition reaction

Fig. 2 Molecular electrostatic potential (MESP) contour map of exo-TCO molecule [B3LYP/6-311++G(d,p)]
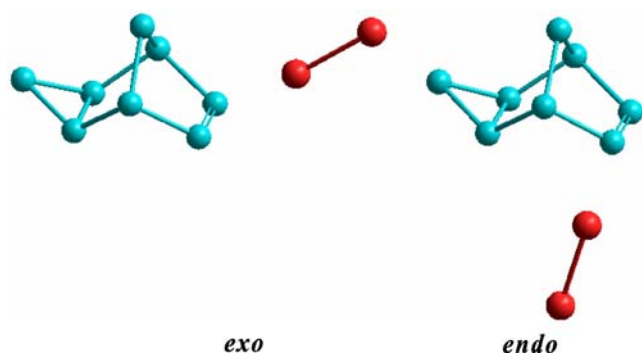

2D contour   **3D isosurface**
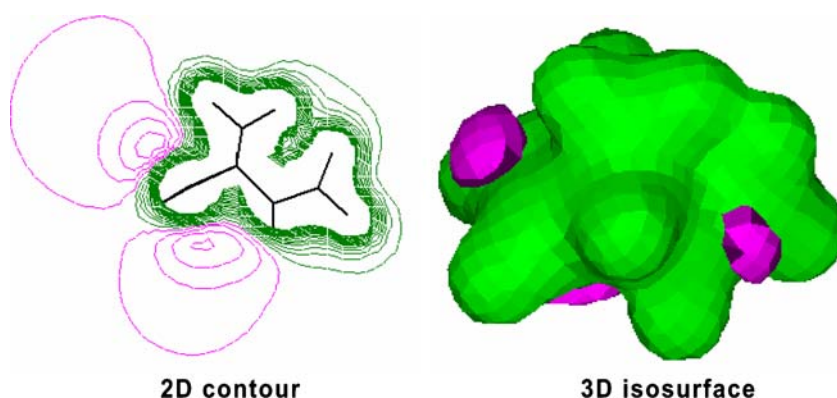
Fig. 3 Optimised geometries of the exo-TCO···Br$_2$(exo) and exo-TCO···Br$_2$(endo) molecular charge-transfer (CT)-complexes [B3LYP/6-311++G(d,p)]

of bromine to exo-TCO is caused by electronic and steric effects. It is obvious that exo-selectivity must be taken into consideration in this addition.

The bromine molecule is partly polarised in the exo-TCO···Br$_2$(exo) molecular complex, and the bromine atom near the double bond has a partial positive charge while the other has a partial negative charge (Table 2). The bond length of the bromine molecule in the molecular complex is relatively longer than that in the neutral bromine molecule. The results obtained reveal that the exo-TCO···Br$_2$(exo) molecular complex plays an important role in the heterolytic splitting of the bromine molecule leading to an ionic addition. It should be noted that the entropy of the exo-TCO···Br$_2$(exo) complex is 27.634 cal mol^{-1} K^{-1} higher than that of the exo-TCO-Br$_2$ system. Therefore, during dissociation of the exo-TCO···Br$_2$(exo) molecular complex, entropy plays an important role. Studying the structures and stabilities of molecular complexes is very important in the determination of stereoselectivity of the addition reaction of halogens to strained olefins. Also, investigation of the molecular complexes has been shown to be very important in the overall reaction coordinates of brominations due to the autocatalytic action of bromine.

It is known that an olefin–halogen molecular complex is more stable in a solvent than in a gas phase medium, and the stabilisation energy of the complex becomes higher as the solvent polarity increases [56].

As a result, in the first step of the addition of bromine to exo-TCO, the exo-TCO···Br$_2$(exo) molecular complex must be formed either in a gas or a solvent medium. Subsequently, splitting of this complex is predicted to occur, and the cations and their isomers shown in Scheme 2 are formed as the possible cationic intermediates of the reaction.

The structures and relative stabilities of these cations were determined by carrying out geometrical optimisations using B3LYP/6-311++G(p,d), B3LYP/6-311+G(2df,2pd) and MP2/6-311+G(2df,2pd) methods, and then the total energies (E_{tot}) were calculated. By using the optimised geometries of cations at the B3LYP/6-311+G(2df,2pd) level, their single point energies were computed by SCI-PCM-B3LYP/6-311+G(2df,2pd) methods. The calculated relative energies are given in Table 3.

According to the results of each method, the exo-bridged-bromonium cation **I** is more stable than the endo-bridged cation **II**. This confirms that Br$_2$ prefers to attack the exo side, rather than the endo side. Therefore, these results confirm the exo-facial selectivity of the addition reaction. The exo-bridged cation **I** is relatively more stable than the classical bromocarbonium cation **III**. The relative stabilities of the bridged halogenium and the classical halogenocarbonium cations are still under discussion in the literature [57, 58]. According to calculations performed by ab initio and DFT methods, the bridged bromonium cations are more stable than the corresponding classical bromocarbonium cations [56, 57]. The formation of the rearranged cation **V** can be expected by a Wagner-Meerwen rearrangement from cation **I**. But, according to the DFT methods, cation **I** is more stable than cation **V**. In other words, the conversion of cation **I** to ion **V** is not easy. The stabilities of the exo-bridged-bromonium (**I**) and the nonclassical (**IV**) cations are close to each other.

As shown in Table 3, the most stable cation intermediate is the nonclassical cation **IV**. These results are consistent with those calculated for the 2-norbornyl, 2-exo-bromo-3-benzonorbornenyl, 3-exo-chloro-2-homobenzonorbornenyl, 6-tricyclo[3.2.1.0^{2,4}]octyl, an 8-anti-bromo-6-tricyclo[3.2.1.0^{2,4}]octyl cations using various quantum chemical methods [26 and references therein, 27, 59–62]. On the other hand, in the solvent medium, the nonclassical cation

Table 2 Properties of exo-TCO···Br$_2$(exo) and exo-TCO···Br$_2$(endo) molecular complexes [B3LYP/6-311++G(d,p)]

Molecular complex	Stabilisation energy (kcal mol^{-1})[a]	Equilibrium distance, R(Å)	r_{Br-Br} (Å)	Charge transferred from TCO to Br$_2$,(e)
exo-TCO···Br$_2$(exo)	5.049	2.822	2.407	0.286[b]
exo-TCO···Br$_2$(endo)	3.502	3.013	2.384	0.194[b]

[a] Without zero point energy (ZPE) corrections

[b] Mulliken charges

Scheme 2 Optimised geometries of cations [B3LYP/ 6-311++G(d,p)]
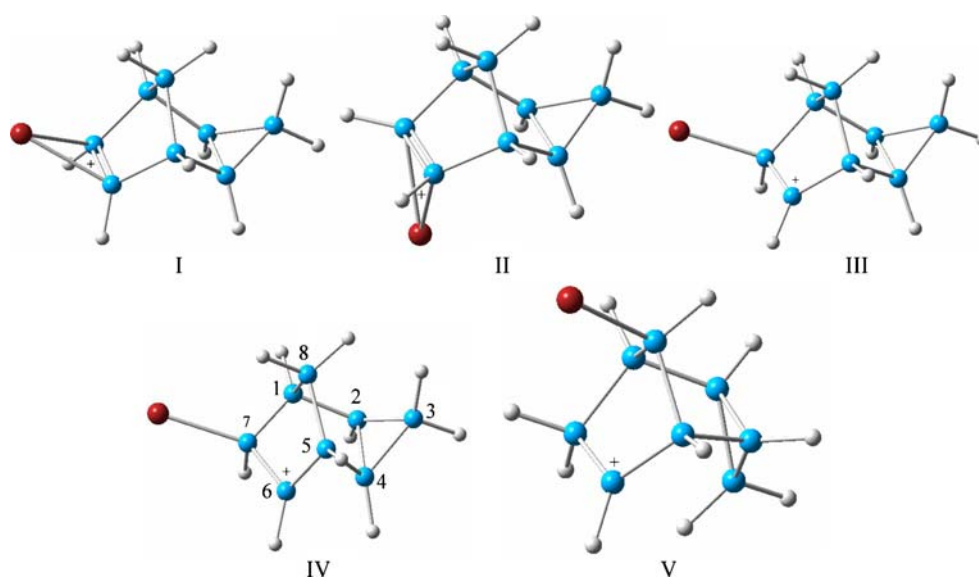
is stabilised more than the other ions (Table 3). The cyclopropyl group has long been considered to be similar to a double bond and so can stabilise cations even at remote positions [63]. The positive charge of the nonclassical cation **IV** (Scheme 2) is delocalised, and the cation is rendered more stable by the interaction of the positive centre and the electron clouds of the cyclopropane ring. On the other hand, it is possible that the nonclassical cation **IV** is a π/π or σ/π no-bond homoconjugated species in which there is no bond path between C4 and C6 (Scheme 2, cation **IV**). The atoms in molecules (AIM) [64, 65] analysis of the nonclassical cation (**IV**) by the MP2/6-311+G(2df,2pd) method shows that the bond order of the C4···C6 bond is 0.621. No bond path was found between C4 and C6, so the nonclassical cation **IV** is a classical cation without pentacoordinated carbon atoms. The calculated geometrical parameters of the nonclassical cation **IV** are given in Table 4. Compared with the C1–C2 bond, which we take as a normal single bond, the bonds between C4 and C2, C3 and C5 are weak. The C2–C4, C3–C4 and C4–C5

internuclear distances increased while the C2–C3 and C5–C6 distances decreased, suggesting that a double bond character developed at these centres. Thus, the cyclopropyl group underwent large geometrical changes. Compared with the C1–C2 distance, the C2–C4 and C3–C4 distances increased by 0.107 and 0.093 Å, respectively, while the C2–C3 distance shortened by 0.109 Å [B3LYP/6-311+G (2df,2pd)]. For the nonclassical cation **IV,** the C2–C4 and C3–C4 bonds tend to break, the C4–C6 bond tends to form, and the C2–C3 bond has double bond character. The mechanism of the ionic addition of Br_2 to exo-TCO can occur as shown in Scheme 1. It is known that trans-adducts are formed via bridged-halogenium ions upon the addition of halogens to olefins [66]. As shown in Scheme 2, the nonrearranged trans-adduct **1** is also formed via the bridged exo-bromonium ion **I**, and the bromine atoms in adduct **1** are in exo and endo configurations, respectively. Furthermore, the nonrearranged cis-adduct **2** (an exo, exo-dibromide) is formed by the exo attack of bromide ion on the C6 centre of nonclassical cation **IV**. The nonclassical

Table 3 Calculated relative energies of cations. *MP2* Møller–Plesset second-order perturbation theory, *SCI-PCM* self-consistent isodensity polarised continuum model

Cation	Relative energy (kcal mol^{-1})			
	B3LYP/6-311 ++G(d,p)	B3LYP/6-311 +G(2df,2pd)	MP2/6-311 +G(2df,2pd)	SCI-PCM-B3LYP/6311+ G(2df, 2pd)//B3LYP/6-311+G(2df,2pd)
I	1.885	1.412	3.918	4.115
II	9.659	9.193	12.465	11.781
III	7.231	7.012	9.864	10.201
IV	0.0	0.0	0.0	0.0
V	14.751	13.213	16.125	13.943

Table 4 Selected internuclear distances (Å) of nonclassical cation **IV** optimised at various levels with the 6-311+G (2df,2pd) basis set

| Level of theory	C1–C2	C2–C3	C2–C4	C3–C4	C4–C5	C4–C6	C5–C6
B3LYP	1.533	1.424	1.640	1.626	1.562	1.730	1.449
MP2	1.523	1.425	1.628	1.630	1.556	1.682	1.452

cation **IV** possesses three effective cationic centres as C2, C3 and C6 (Scheme 2, cation **IV**). An analysis of the LUMO of the nonclassical cation **IV** showed that this orbital is localised principally on the C2, C-3 and C6 carbon atoms (Fig. 4).

Hence, the widest distribution of the lobes of the LUMO of nonclassical cation **IV** are on carbon atoms C6, C3 and C2, respectively. Therefore, the attack of the nucleophile (bromide ion) towards the multicentre nonclassical cation **IV** occurs from these carbon atoms. Consequently, during the attack of the bromide (Br^-) ion on the C3 centre of the nonclassical cation **IV**, the weak C3–C4 cyclopropyl bond is broken and the 5-exo-bromo-3-exo-bromomethyltricyclo [2.2.1.0^{2,6}]heptane (**3**) product is formed by forming a C4–C6 bond. Also, during the attack of the bromide ion on the C2 centre of the nonclassical cation **IV**, the weak C2–C4 cyclopropyl bond is broken and this attack gives the rearrangement product **4** by forming a C4–C6 bond. On the one hand, for the nonclassical cation **IV**, the length of the C3–H bond (Scheme 1) and the charge of the hydrogen atom increases, meaning that the possibility of the separation of hydrogen as proton (H^+) increases. On the other hand, C2–C3 has a double-bond character. The 6-exo-bromotricyclo[3.2.1.0^{2,7}]oct-3-ene (**5**) product is obtained by deprotonation of the nonclassical cation **IV**. Hence, the products are formed over stable ions, i.e. nonclassical **IV** and exo-bridged-bromonium **I**, whose stabilities differ little. As a result, in the electrophilic addition reactions of halogens to strained alkenes, in cases where there is little difference between the stabilities of the bridged-halogenium cation and the cation that is formed from the isomerisation of the bridged-halogenium cation, it is possible to obtain products of normal and skeletal isomerisation. In cases where there is too much difference between the stabilities of the bridged-halogenium cation and the cation that is formed

from the isomerisation of the bridged-halogenium cation, the reaction takes place over the more stable cation (skeletal isomerisation cation) and actually, the products of skeletal isomerisation are obtained [26 and references therein, 27, 32].

Conclusions

The present investigation by DFT and MP2 methods into the addition of bromine to exo-TCO gave some important results, which can be summarised as follows. The double bond of the exo-TCO molecule is endo pyramidalised. The electron density ($q_{i,HOMO}$) in exo and endo faces of the double bond is not equal, being greater in the exo face. 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**. Exo-facial selectivity caused by electronic and steric factors should be observed in the addition reaction of bromine to the exo-TCO molecule. The bridged exo-bromonium cation **I** is more stable than the rearranged cation **V**. For this reason, the conversion of cation **I** to ion **V** is not easy. The stabilities of the exo-bridged-bromonium **I** and nonclassical **IV** cations differ little. The reaction products are formed over these stable cations. In electrophilic addition reactions of halogens to strained alkenes, in cases where there is little difference between the stabilities of the bridged-halogenium cation and the cation that is formed as a result of the isomerisation of the bridged-halogenium cation, products of normal and skeletal isomerisation are formed with progress of the reaction over both cations. The C2–C3, C2–C4, C3–C4 and C4–C6 internuclear distances of the nonclassical cation **IV** optimised at the B3LYP/6-311+G(2df,2pd) level are 1.424, 1.640, 1.626 and 1.730 Å, respectively.

Fig. 4 Electron density distribution [lowest unoccupied molecular orbital (LUMO)] of the nonclassical cation **IV** [B3LYP/6-311++G(d,p)]

2D contour

3D isosurface
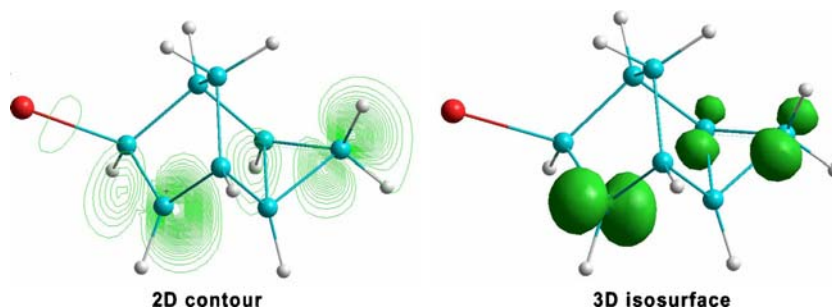
References

1. Barkhash VA (1984) Top Curr Chem 16(17):1–265
2. Cakmak O, Balci M (1989) J Org Chem 54:181–187
3. Dastan A, Demir U, Balci M (1994) J Org Chem 59:6534–6538
4. Burritt A, Cxon JM, Stell PJ (1996) J Org Chem 61:4328–4335
5. Tutar A, Taskesenligil Y, Cakmak O, Abbasoglu R, Balci M (1996) J Org Chem 61:8297–8300
6. Menzek A, Saracoglu N, Dastan A, Balci M, Abbasoglu R (1997) J Org Chem 53:14451–14462
7. Dastan A (2001) Tetrahedron 57:8725–8732
8. Horasan N, Kara Y, Azizoglu A, Balci M (2003) Tetrahedron 59:3691–3699
9. Belluci G, Chappe C, Bianchini R, Lenoir D, Herges R (1995) J Am Chem Soc 117:12001–1200
10. Herges R (1995) Angew Chem Int Ed Engl 34:51–53
11. Ruiz E, Dennis R, Salahub R, Vela A (1996) J Phys Chem 100:12265–12276
12. Brown RS (1997) Acc Chem Res 30(3):131–137
13. Bianchini R, Chiappe C, Lenoir D, Lemmen P, Herges R, Grunenberg J (1997) Angew Chem Int Ed Engl 36:1284–1287
14. Smith WB (1998) J Org Chem 63:2661–2664
15. Bianchini R, Chiappe C, Moro LG, Lenoir D, Lemmen P, Goldberg N (1999) Chem Eur J 5:1570–1580
16. Chiappe C, Rubertis AD, Lemmen P, Lenoir D (2000) J Org Chem 65:1273–1279
17. Chiappe C, Rubertis AD, Detert H, Lenoir D, Wannere C, Schleyer PvR (2002) Chem Eur J 8:967–978
18. Rathere R, Lindeman SV, Zhu CJ, Mori T, Schleyer PvR, Kochi JK (2002) J Org Chem 67:5106–5116
19. Chiappe C, Rubertis AD, Lemmen D, Jaber A, Lenoir D, Watteubochi C, Ponelli CS (2002) J Org Chem 67:7066–7074
20. Chiappe C, Detert H, Lenoir D, Pamelli CS, Ruasse MF (2003) J Am Chem Soc 125:2864–2865
21. Lenoir D, Chiappe C (2003) Chem Eur J 9:1037–1044
22. Herges R, Papafilippopoulos A, Hess K, Chiappe C, Lenoir D, Detert H (2005) Angew Chem Int Ed 44:1412–1416
23. Chiappe C, Pomelli CS, Lenoir D, Wattenbach C (2006) J Mol Model 12:631–639
24. Wang SC, Tantillo DJ (2006) Eur J Org Chem 2006(3):738–745
25. Balci M, Güney M, Daştan A, Azizoglu A (2007) J Org Chem 72:4756–4762
26. Abbasoglu R (2004) THEOCHEM 686:1–5
27. Abbasoglu R, Yilmaz S (2006) J Mol Model 12:290–296
28. Abbasoglu R (2006) J Mol Model 12:991–995
29. Abbasoglu R (2007) J Mol Model 13:425–430
30. Abbasoglu R (2007) J Mol Model 13:1215–1220
31. Abbasoglu R, Magerramov A (2007) Acta Chim Slov 54:882–887
32. Abbasoglu R, Uygur Y, Magerramov A (2008) Indian J Chem 47B:90–96
33. Abbasoglu R (2009) J Mol Model 15:397–403
34. Coxon JM, Steel PY, Burritt A, Whittington BI (1995) Tetrahedron 51:8057–8072
35. Becke AD (1993) J Chem Phys 98:5648–5652
36. Lee C, Yang W, Parr RG (1988) Phys Rev B 37:785–789
37. Perdew JP, Wang Y (1992) Phys Rev B45:244–249
38. Krishnan R, Binkley JS, Seeger R, Pople JA (1980) J Chem Phys 72:650–654
39. McGrath MP, Radom L (1991) J Chem Phys 94:511–516
40. Moller C, Plesset MS (1934) Phys Rev 46:618–622
41. Foresman JB, Keith TA, Wiberg KB, Snoonian J, Frisch MJ (1996) J Phys Chem 100:16098–16104
42. Frisch MJ, Trucks GW, Schlegel HB, Scuseria GE, Robb MA, Cheeseman JR, Montgomery JAJ, Vreven T, Kudin KN, Burant JC, Millam JM, Iyengar SS, Tomasi J, Barone V, Mennuci B, Cossi M, Scalmani G, Rega N, Petersson GA, Nakatsuji H, Hada M, Ehara M, Toyota K, Fukuda R, Hasegawa J, Ishida M, Nakajima T, Honda Y, Kitao O, Nakai H, Klene M, Li X, Knox JE, Hratchian HP, Cross JB, Adamo C, Jaramillo J, Gomperts R, Stratmann RE, Yazyev O, Austin AJ, Cammi R, Pomelli C, Ochterski JW, Ayala PY, Morokuma K, Voth GA, Salvador P, Dannenberg JJ, Zakrzewski VG, Dapprich S, Daniels AD, Strain MC, Farkas O, Malick DK, Rabuck AD, Raghavachari K, Foresman JB, Ortiz JV, Cui Q, Baboul A, Clifford GS, Cioslowski J, Stefanov BB, Liu G, Liashenko A, Piskorz P, Komaromi I, Martin RL, Fox DJ, Keith T, Al-Laham MA, Peng CY, Nanayakkara A, Challacombe M, Gill PMW, Johnson B, Chen W, Wong MW, Gonzalez C, Pople JA (2003) Gaussian 03, Rev B.03. Gaussian, Pittsburgh, PA
43. HyperChem Release 8 for Windows, Hypercube, Inc (2007), www.hyper.com/
44. Borden WT (1989) Chem Rev 89:1095–1109
45. Ermer O, Bell P, Mason SA (1989) Angew Chem Int Ed Engl 28:1239–1241
46. Margtic D, Williams VR, Warrener NR (2003) J Org Chem 68:9186–9190
47. Vazquez S, Camps P (2005) Tetrahedron 61:5147–5208
48. Watson WH (1983) Stereochemistry and reactivity of systems containing π electrons. Chemie International, Deerfield Beach, FL
49. Houk KN, Rondon NG, Brown FK, Jorgensen WL, Madura JD, Spellmeyer DC (1983) J Am Chem Soc 105:5980–5988
50. Gandalfi R, Tonaletti G, Rostelli A, Bagatti M (1993) J Org Chem 58:6038–6048
51. Royer J (1978) Tetrahedron Lett 1978:1343–1346
52. Paguette LA, Belliamy F, Wells GJ, Bohm MC, Gleiter R (1981) J Am Chem Soc 103:7122–7133
53. Broughton HB, Green SM, Rzepa HS (1992) J Am Chem Soc Chem Commun 998-1001
54. Legon AC, Thumwood JMA (2001) Phys Chem Chem Phys 3 (8):1397–1403
55. Fleming I (2002) Frontier orbitals and organic chemical reactions. Wiley, New York, pp 5–33
56. Smirnov VV, Tikhomirov VA, Chudinov GE (1994) J Struct Chem 34:14–18, Translated from Zh Strukt Khim 34:14–18 (1993)
57. Teberekidis VI, Sigalas MP (2002) Tetrahedron 58:6171–6178
58. Teberekidis VI, Sigalas MP (2003) Tetrahedron 59:4749–4751
59. Perera SA, Bartlett RJ (1996) J Am Chem Soc 1118:7849–7850
60. Werstiuk NH, Muchall HM (1999) THEOCHEM 463:225–229
61. Werstiuk NH, Muchall HM (2000) J Phys Chem 104A:2054–2060
62. Werstiuk NH, Wang YG (2001) J Phys Chem 105A:11515–1152
63. Cremer D, Childs RL, Kraka E (1995) In: Rappoport Z (ed) The chemistry of the cyclopropyl group, vol 2. Wiley, New York, pp 339–410
64. Bader RFW (1990) Atoms in molecules—a quantum theory. Clarendon, Oxford
65. Bader RFW (1998) J Phys Chem 102A:7314–7323
66. De la Mare PBD, Bolton R (1982) Electrophilic additions to unsaturated systems, 2nd edn. Elsevier, New York, pp 135–197