ORIGINAL PAPER

Ab initio and DFT study of the inner mechanism and dynamic stereochemistry of electrophilic addition reaction of bromine to bisbenzotetracyclo[6.2.2.2^{3,6}.0^{2,7}] tetradeca-4,9,11,13-tetraene

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Abstract The inner mechanism and dynamic stereochemistry of electrophilic addition of bromine to bisbenzotetracyclo[6.2.2.2^{3,6}.0^{2,7}]tetradeca-4,9,11,13-tetraene(BBTT) molecule have been investigated by the methods of quantum chemistry. The structure of the BBTT molecule has been studied by ab initio and DFT/B3LYP methods using the 6-31G(d) and 6-311G(d) basis sets. The double bonds of BBTT molecule are *endo*-pyramidalized. The structure and stability of the cationic intermediates and products of the addition reaction have been investigated by HF/6-311G(d), HF/6-311G(d,p), B3LYP/6-311G(d) and B3LYP/6-311++G(2d,p)//B3LYP/6-311G(d) methods. The bridged bromonium cation isomerized into the more stable nonclassical delocalized N- and U-type cations and the difference between the stability of these cations is small. For the determination of the direction of addition reaction and the stereochemistry of the products, the stability of nonclassical delocalized N- and U-type ions and the structure of their cationic centres play a vital role. Since the cationic centre of the N-type ion is in interaction with the benzene ring from the *exo* face, the nucleofilic attack of the bromide anion to this centre occurs from the *endo* face and the *exo,endo*-isomer of the N-type product is obtained. The attack of bromide anion, towards the cationic centre of U-type ion from the *endo* face is sterically hindered by the hydrogen atom therefore the attack occurs from the *exo* face, which interacts with the benzene ring and the more stable *exo,exo*-isomer of U-type product is formed. Although, the U-type cation was 2.232 kcal mol^{-1} more stable than the N-type cation, the U-type product was 0.587 kcal mol^{-1} less stable than the N-type product.

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Introduction

Rigid polycyclic molecules having isolated double bonds located in the laticyclic topology [1] and spatially in close proximity have provided suitable frameworks for study of transannular reactions [2] and orbital interactions [3–5]. The attack of an electrophile to a molecule having two isolated double bonds in spatial proximity usually leads to the transannular bridge formation in either cross (N-type) or parallel (U-type) manner or both [6–9]. Experimental results on this type of reaction have been confusing. In some cases only the cross or the parallel bridged product is isolated, while in other cases both products are formed simultaneously [10–23]. Recently Inagaki et al. advanced a perturbation theory to interpret those cases where preferential cross bridging takes place [24]. While the orbital mixing effect must certainly be working when cross bridging occurs, a general theory must explain why and to what extent parallel addition takes place in other systems. Osawa et al. suggested that this was due to the thermodynamic stability of the N- and U-type products [6]. According to Osawa, it is possible for both products to form when the difference between the thermodynamic stability of N- and U-type products is less than 10 kcal mol^{-1}. If the difference is more than 10 kcal mol^{-1}, a more stable product is obtained.

In order to learn the inner mechanism and dynamic stereochemistry of these reactions in detail, it is crucial to determine the structure and the stability of the intermediates

(cyclic-bridged, N- and U-type cations) formed during the course of the reaction and investigate their skeletal isomerization. The direction of the flow of these reactions is ascertained by the direction of the skeletal isomerization of the cyclic bridged halogenium cation formed as a result of the heterolytic splitting of the alkene...halogen molecular charge-transfer (CT) complex. The intramolecular skeletal isomerization is realized so as to form the more stable skeletal structure. It is feasible for the cyclic bridged halogenium cation to transform into N- and U-type bridged cations as a result of the transannular cross (N-type) and paralel (U-type) linkage of the double bonds. Therefore, the stability of N- and U-type cations, into which cyclic bridged halogenium cation isomerized, is important in order to ascertain the direction of the flow of the addition reaction. Meanwhile, the investigation of the structure of cationic centres of N- and U-type ions and the possibility of the attack of halogenide anion(X^-) towards these centres is of great significance for the determination of the direction of the addition reaction and the stereochemistry of the products.

The structure and the nature of the alkene plays an important role in the display of characteristic features by the electrophilic addition reaction of halogens to paralel face-to-face (juxtaposed) double bonded strained alkens. The investigation of geometric and electronic structure of alkenes by calculating the pyramidilization of the double bonds and other geometric parameters determines the relationship between the structure of the alkenes and their behaviours in electrophilic addition reactions. The study of the structure of different configurations of reaction products, their stability and stereochemistry provides an insight to the many features of the electrophilic addition reactions.

The addition reactions of halogens to alkenes with rigid structure and their intermediates have been investigated by the methods of quantum chemistry [25–38]. In our previous studies, the addition of chlorine and bromine to many olefins with rigid structure have been studied theoretically [39–43]. In order to continue these investigations, the inner mechanism and dynamic stereochemistry of the electrophilic addition of bromine to bisbenzotetracyclo [$6.2.2.2^{3,6}.0^{2,7}$]tetradeca-4,9,11,13-tetraen (BBTT) molecule has been investigated. A mixture of N-type *exo,endo*-dibromide (62% yield) and U-type *exo,exo*-dibromide (11% yield) products was obtained in the electrophilic addition of bromine to BBTT molecule (Scheme 1) [7]. However, the *exo,exo*-dibromide isomer of N-type product was not obtained hence the reason for this should be explained.

Methodology

The geometry and the electronic structure of the bisbenzo-tetracyclo[$6.2.2.2^{3,6}.0^{2,7}$]tetradeca-4,9,11,13-tetraen

Scheme 1 The electrophilic addition reaction of bromine to BBTT molecule
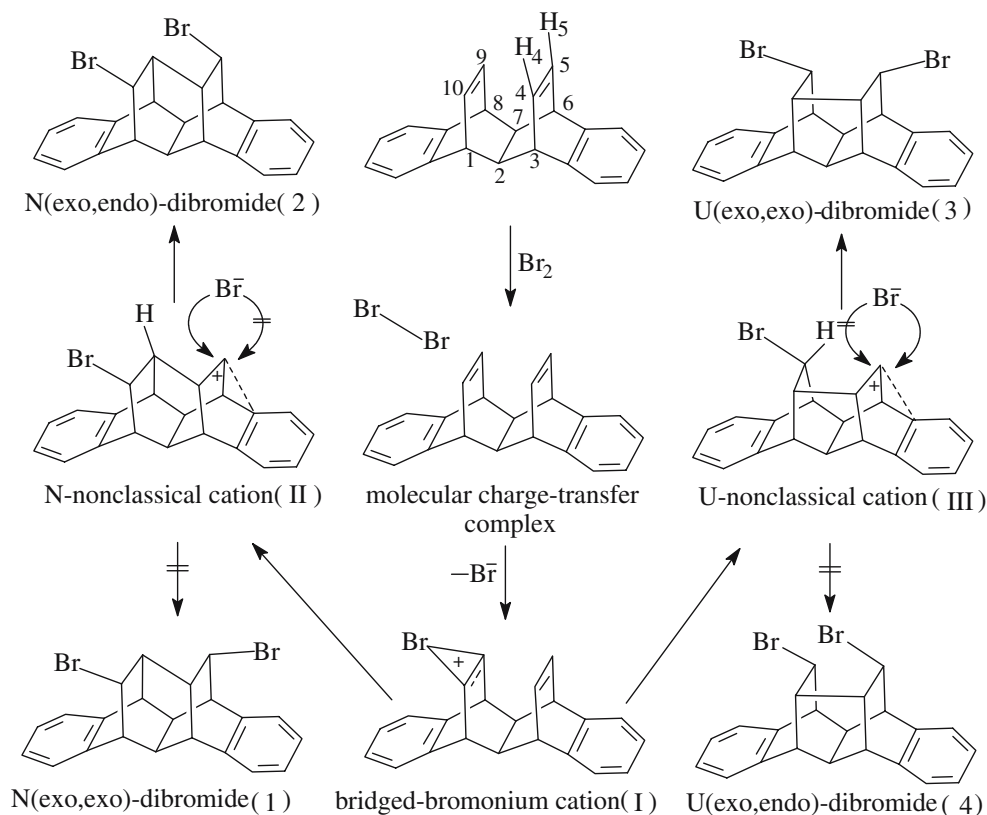
(BBTT) molecule have been investigated by ab initio SCF and DFT/B3LYP (density functional theory with B3LYP-the hybrid Becke's three parameter functional and Lee-Young-Parr exchange-correlation potential) [44, 45] methods using the 6-31G(d) [46] and 6-311G(d) [47] basis sets. The predicted cationic intermediates and products formed in the addition reaction have been investigated using the HF/6-311G(d), HF/6-311G(d,p) and B3LYP/6-311G(d) methods. By using the optimized geometries of cations and products by B3LYP/6-311(d) method, their single point energies were calculated at the B3LYP/6-311++G(2d,p) [47] level. All stationary points have been characterized by calculating the vibrational frequncies and zero-point vibrational energies have been 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(Å mol)$^{-1}$. The calculations have been perfomed with Gaussian 03 and HyperChem 7.5 program with an IBM PC Pentium IV computer.

Results and discussion

Full geometric optimization of the BBTT molecule was obtained by ab initio SCF and DFT/B3LYP methods with the 6-31G(d) and 6-311G(d) basis sets and the structure of the molecule was also investigated in detail. In light of the results of each method, the pyramidalization parameters [48, 49] of the molecule were evaluated with the aim of determining the structural deformation of the double bond. The values of the pyramidalization angle (ϕ)(ϕ is 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) [48] and of the out-of-plane

Table 1 The calculated double bond lengths (Å), distance (Å) and orientation angle (degree) between two double bonds and pyramidalization parameters (degrees) of BBTT molecule

Metod	$r_{C=C}$	R_u	θ	ϕ	χ
HF/6-31G(d)	1.317	3.097	0.0	1.278	1.535
HF/6-311G(d)	1.315	3.099	0.0	1.394	1.587
B3LYP/6-31G(d)	1.332	3.082	0.0	1.750	1.991
B3LYP/6-311G(d)	1.331	3.081	0.0	1.809	2.028

bending angle (χ)(out of plane angle: between plane C3C4C5C6 and plane H4C4C5H5 as seen in Scheme 1) [49] were calculated according to the results of each method. The distance (R_u) (distance between midpoint of opposing C=C double bonds) and the orientation angle (θ) (dihedral angle between two planes containing four unsaturated carbon atoms in the minimum energy structure of the BBTT molecule) [50] were determined. These results are given in Table 1. According to the results obtained, the double bond of the BBTT molecule is *endo*-pyramidalized.

Because of the mutual obstruction of the double bonds in *endo* faces and the higher electron density in *exo* faces, the attack of bromine to BBTT molecule from its *endo* face was sterically hindered. The addition of bromine to the BBTT molecule occurs from the *exo* face, where the electron density of the double bond is higher. As known, olefin-halogen molecular CT-complex is formed in the first step of electrophilic addition to olefins of halogens [27–29, 31–33, 35, 38]. The polarization of bromine and the subsequent heterolytic splitting of BBTT...Br$_2$ molecular CT-complex results in the formation of the bridged (I) cation (Scheme 1). This cation and its isomers are the possible intermediates of the addition reactions of bromine to the BBTT molecule in gas phase and solvent medium (Scheme 2).

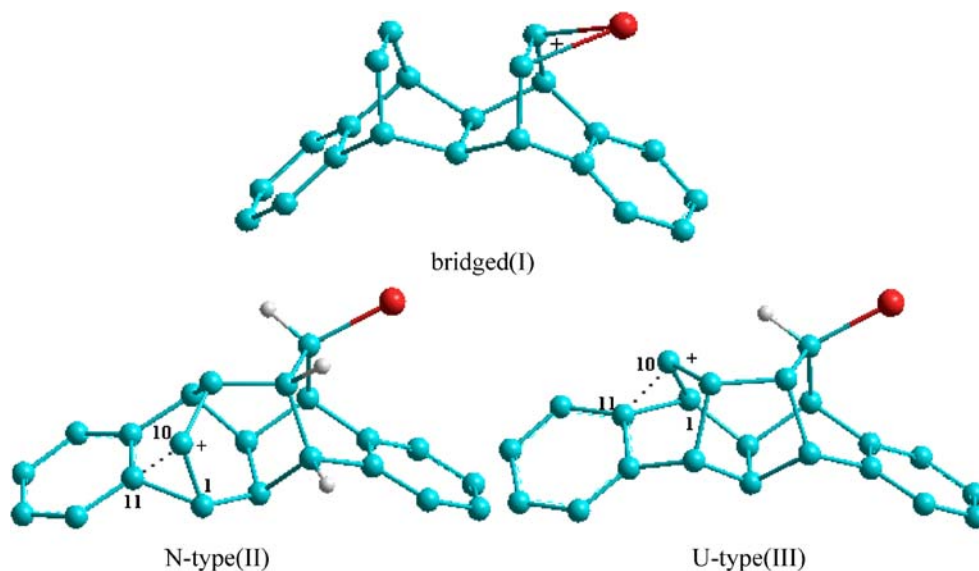**Scheme 2** The optimized geometries of cations (B3LYP/6-311G(d))

bridged(I)

N-type(II)

U-type(III)

Table 2 The calculated relative energies of cations

Cations	Relative energy (kcal mol^{-1})			
	HF/6-311G (d)	HF/6-311G (d,p)	B3LYP/6-311G(d)	B3LYP/6-311++G(2d, p)//B3LYP/6-311G (d)
I	26.590	26.887	19.659	18.110
II	3.159	3.179	2.279	2.232
III	0.0	0.0	0.0	0.0

In order to determine the structures and relative stabilities of the predicted cationic intermediates (Scheme 2), their full geometry optimization has been performed using HF/6-311G (d), HF/6-311G(d,p) and B3LYP/6-311G(d) methods and the total energies (E_{tot}) have been calculated. By using the optimized geometries of cations at the B3LYP/6-311G(d) level, their single point energies have been computed using B3LYP/6-311++G(2d,p) method. The calculated relative energies are given in Table 2.

According to the results of the ab initio and DFT calculations, the N- and U-type cations are more stable than the bridged (I) cation. The skeletal isomerization of the bridged(1) cation into N- and U-type cations is thermodynamically feasible. The total energies of N- and U-type cations differ little and their stabilities are nearly the same. The U-type cation is 2.232 kcal mol^{-1} (B3LYP/6-311++G (2d,p)//B3LYP/6-311G(d)) more stable than the N-type cation. The analysis of electronic and geometric structures of N- and U-type cations showed that there was an anchimeric interaction of σ character between the vacant p orbital of the cationic centre and π-orbitals of the benzene ring of these ions (Scheme 2). On the other hand, it is

possible that the N- and U-type cations are σ/π no-bond homoconjugated species in which there is no bond path between C10 and C11 (Scheme 2, cation II and III). As a result of this interaction, the positive charge of the cations becomes delocalized by partially transferring to the benzene ring and this causes an increase in the stability of the ions. Hence, the interaction, which takes place for the nonclassical delocalized N- and U-type cations, causes the ions to become more stable by bringing about specific changes in the electronic and geometric structure of the ions. For nonclassical delocalized N- and U-type cations, the bond length of C1-C10 decreased and the bond length of C1-C11 increased (Scheme 2). According to the results obtained by B3LYP/6-311G(d) method, the bond lengths of C1-C10 and C1-C11 were 1.437 Å and 1.722 Å, respectively for N-type cation and 1.437 Å and 1.663 Å, respectively for U-type cation. Also, for N- and U-type cations, the C10-C11 internuclear distances were 1.593 Å and 1.618 Å, respectively (B3LYP/6-311G(d)). Therefore, for the determination of the stability of N- and U-type ions, the skeletal structure of the cation and the interaction between the cationic centre and benzene ring are important.

Hence, the direction of the electrophilic addition reaction of bromine to the BBTT molecule is determined by the direction of the skeletal isomerization of bridged (I) ion into N- and U- type nonclassical delocalized cations according to the cross and parallel mechanism. The addition reaction is realized over the N- and U- type nonclassical delocalized cations in the parallel direction and as a result, N- and U- type reaction products are formed.

By fully optimizing the geometric structures of different configurations (Scheme 3) of N- and U-type reaction products by HF/6-311G(d) , HF/6-311G(d,p) and B3LYP/
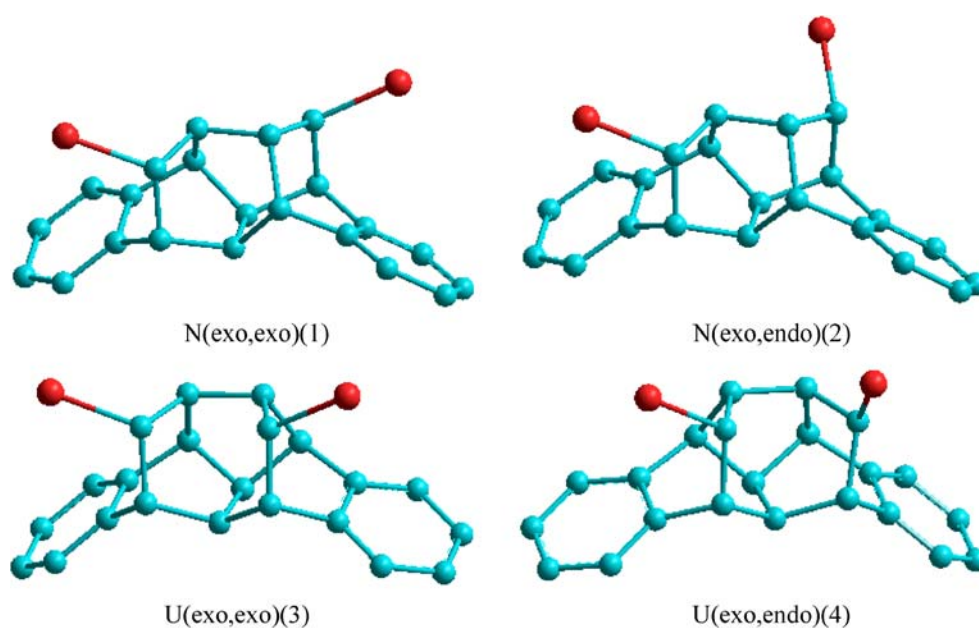
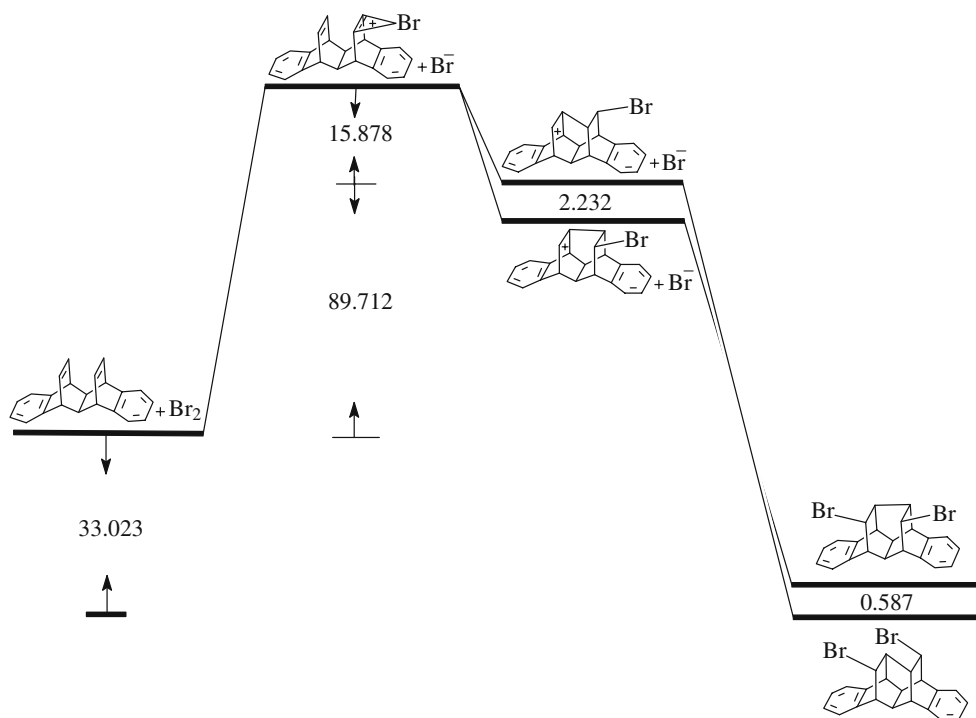**Scheme 3** The optimized geometries of products (B3LYP/6-311G(d))

N(exo,exo)(1)

N(exo,endo)(2)

U(exo,exo)(3)

U(exo,endo)(4)

Table 3 The calculated relative energies of products

Products	Relative energy (kcal mol^{-1})			
	HF/6-311G (d)	HF/6-311G(d, p)	B3LYP/6-311G (d)	B3LYP/6-311++G(2d, p)//B3LYP/6-311G(d)
1	0.297	0.310	0.433	0.177
2	0.0	0.0	0.0	0.0
3	2.191	2.116	0.932	0.587
4	5.505	5.456	3.588	3.428

6-311G(d) methods, their total energies were calculated and their stereochemistry were investigated. The single point energies of products were calculated by using B3LYP/6-311++G(2d,p)//B3LYP/6-311G(d) method. The calculated relative energies are given in Table 3.

The total energies of the *exo,exo* and *exo,endo* isomers of N-type dibromide molecule differed very little and their stabilities were nearly the same (Table 3). Among the thermodynamically feasible *exo,exo*- and *exo,endo*-dibromides, only the second isomer is produced [7]. The *exo,exo*-isomer of the U-type dibromide molecule, is more stable than *exo,endo*-isomer (Table 3) and the first dibromide is produced [7]. Although N(*exo,endo*) dibromide is more stable than N(*exo,exo*) dibromide, the *exo,exo* isomer of the N-type product, which is formed as a result of addition of bromine to TTDD (*endo,endo*-tetracyclo[4.2.1.1^{3,6}.0^{2,7}]dodeca-4,9-diene) molecule, is more stable than *exo,endo* isomer [43]. This is most probably due to the steric feature.

In Scheme 1, the mechanism of the electrophilic addition reaction of bromine to the BBTT molecule is given. The electronic and steric factors are important for the determination of the direction of the attack of the bromide anion (Br$^-$) towards the cationic centres of N- and U- type nonclassical delocalized cations. Since the cationic centre of N-type cation is in interaction with the electron cloud of benzene ring from the *exo* face, the nucleophilic attack of bromide (Br$^-$) anion to this centre occurs on the *endo* face and as a result, the more stable *exo,endo*-dibromide isomer of N-type product is obtained. The attack of bromide (Br$^-$) anion towards the the cationic centre of N-type ion from the *endo* face was not sterically prevented by the hydrogen atoms (Scheme 2, cation II). Although the cationic centre of U-type ion is in interaction with the electron cloud of benzene ring from the *exo* face, the nucleophilic attack of bromide anion is realized on the *exo* face. Because, the attack of bromide anion towards the cationic centre from the *endo* face was sterically hindered by the hydrogen atom (Scheme 2, cation III). Therefore, the *exo,exo*-isomer of U-type product is formed. As can be seen, the stability of N- and U-type nonclassical delocalized ions and the structure of their cationic centres are effective on the determination of the direction of the addition reaction and the stereochemistry of products.

The energy diagram of the addition reaction of bromine to the BBTT molecule is given in Fig. 1. As can be seen from the energy diagram of BBTT-Br$_2$ system, the reaction is realized over the transformation of bridged (I) cation into slightly different N- and U-type nonclassical delocalized

Fig. 1 The energy diagram of BBTT-Br$_2$ system (kcal mol^{-1}) [B3LYP/6-311++G(2d,p)//B3LYP/6-311G(d)]

cations. The *exo,endo*-dibromide product is obtained over N-type cation and *exo,exo*-dibromide product is obtained over U-type cation. In addition to this, the reaction's products are kinetically controlled. The empirical rule suggested by Osawa is also valid for the above reaction. The stability of N- and U-type products differ little and N- type product is 0.587 kcal mol^{-1}(B3LYP/6-311++G (2d,p)//B3LYP/6-311G(d)) more stable than U-type product.

Conclusions

The double bonds of BBTT molecule are *endo*-pyramidalized. The nonclassical delocalized N- and U-type cations, whose thermodynamical stabilities differ little, are more stable than the bridged (I) cation. The addition reaction of bromine to the BBTT molecule takes place over N- and U- type nonclassical delocalized cations, which are obtained as a result of the skeletal isomerization of bridged (I) ion. The structure of the cationic centres of N- and U-type ions plays an important role on the facial selectivity in the addition reaction and the stereochemistry of the products. Since the cationic centre of N-type cation is in interaction with the benzene ring from the *exo* face, the nucleophilic attack of bromide (Br$^-$) anion to this centre realizes on the *endo* face and as a result, the more stable *exo,endo*-dibromide isomer of N-type product is obtained. Although the cationic centre of U-type ion is in interaction with the electron cloud of benzene ring from the *exo* face, the attack of the bromide anion towards the centre from the *endo* face was sterically hindered, hence the additon realizes on the *exo* face and the more stable *exo,exo*-isomer of U-type product is obtained. The theoretical investigations were in agreement with the experimental results and showed that the *exo,endo* isomer of N-type product and *exo, exo*-isomer of U-type product were obtained. The difference between the stability of the reaction products is little. Even though, the U-type cation is more stable than the N-type cation, the N-type product is more stable than the U-type product.

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