

Scientific paper

DFT Investigation of the Mechanism and Stereochemistry of Electrophilic Transannular Addition Reaction of Chlorine to Bisbenzotetracyclo[6.2.2.2^{3,6}.0^{2,7}]tetradeca-4,9,11,13-tetraene

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Abstract

The mechanism and stereochemistry of electrophilic addition of chlorine to bisbenzotetracyclo[6.2.2.2^{3,6}.0^{2,7}]tetradeca-4,9,11,13-tetraene (BBTT) molecule were investigated by DFT methods. The geometry and the electronic structure of BBTT molecule was studied by DFT/B3LYP method using the 6-311G(d) and 6-311++G(d,p) 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 were investigated by B3LYP/6-311G(d) and B3LYP/6-311++G(2d,p) methods. The solvent effect was evaluated using SCI-PCM method. The bridged chloronium cation is 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 for the determination of the direction of addition reaction and the stereochemistry of the products. Since the cationic centre of the *N*-type ion is in interaction with the benzene ring from the *exo* face, the nucleophilic attack of the chloride anion to this centre occurs from the *endo* face, and the *exo,endo*-isomer of the *N*-type product is obtained. The attack of chloride 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 3.485 kcal mol⁻¹ more stable than the *N*-type cation, the *U*-type product was 1.886 kcal mol⁻¹ [SCI-PCM-B3LYP/6-311++G(2d,p)// B3LYP/6-311G(d)] less stable than the *N*-type product.

Keywords: DFT calculations, intramolecular skeletal rearrangement, transannular reactions, nonclassical cation, solvent effects, bisbenzotetracyclo[6.2.2.2^{3,6}.0^{2,7}]tetradeca-4,9,11,13-tetraene

1. Introduction

Rigid polycyclic molecules having isolated double bonds located in the laticyclic topology¹ and spatially in close proximity have provided suitable frameworks for study of transannular reactions² 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 was isolated, while in other cases both products were 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.

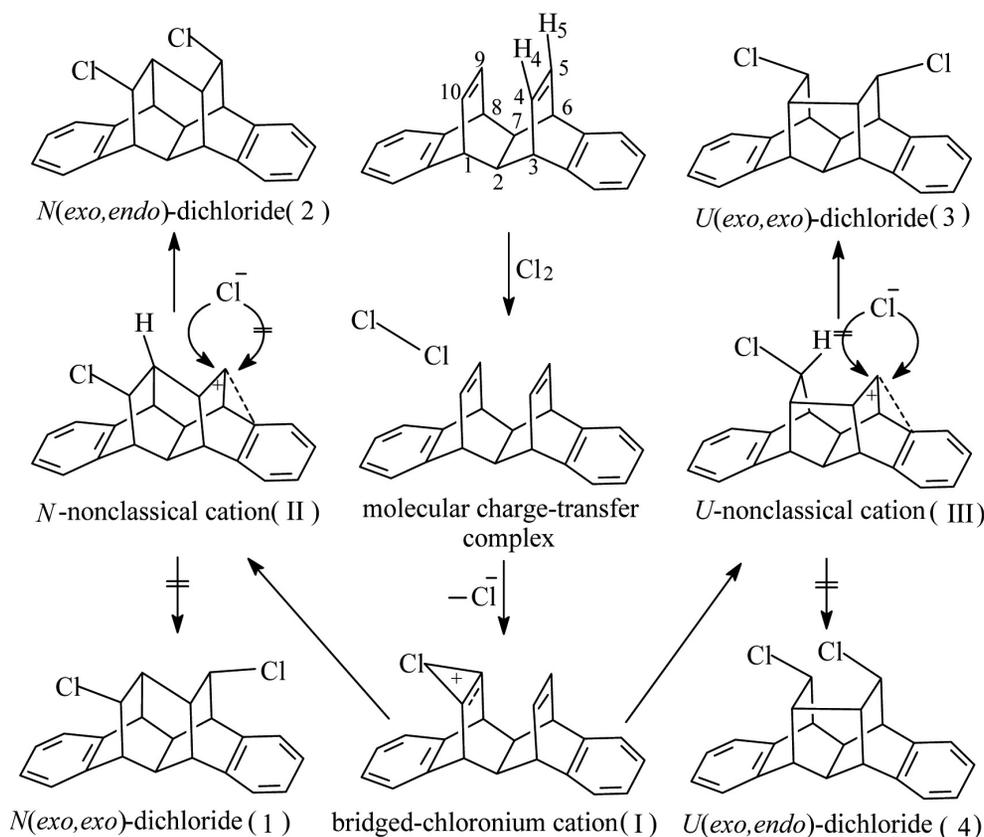
In order to learn the inner mechanism and dynamic stereochemistry of these reactions in detail, it is crucial to

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 parallel (*U*-type) linkage of the double bonds. Therefore, the stability of *N*- and *U*-type cations, into which cyclic bridged halogenium cation is isomerized, is important in order to ascertain the direction 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 play an important role in the display of characteristic features by the electrophilic addition reaction of halogens to parallel face-to-face (juxtaposed) double bonded strained alkenes. The investigation of geometric and electronic structure of alkenes by calculating the pyramidalization of the double bonds and other geometric parameters determines the rela-

tionship between the structure of the alkenes and their behaviours in electrophilic addition reactions. It is crucial to investigate the structure of the strained alkenes and calculate the reactivity indices ("relative electrophilicity" and "relative nucleophilicity") with the intention of locating their preferable reactive sites and centres.²⁵ These investigations are also necessary to resolve the link between the structure of the alkenes and their behaviours during the electrophilic addition reactions. The study of the stability and stereochemistry of the different configurations of the reaction products is fundamental so as to interpret the many characteristics 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.^{26–44} In our previous studies, the addition of chlorine and bromine to many olefins with rigid structure have been studied theoretically.^{45–56} As a follow-up to these investigations, the mechanism and stereochemistry of the electrophilic addition of chlorine to bisbenzotetracyclo[6.2.2.2^{3,6}.0^{2,7}]tetradeca-4,9,11,13-tetraene (BBTT) molecule were investigated (Scheme 1). In this work, the electrophilic addition of chlorine to BBTT molecule was studied theoretically, and the structures and stabilities of the reaction cationic intermediates (bridged, *N*- and *U*-type cations) and products were investigated by DFT methods. The geometry and the electronic structure of BBTT molecule were also computed by DFT methods.



Scheme 1.

2. Methods of Calculation

The geometry and the electronic structure of BBTT molecule were investigated by DFT/B3LYP (density functional theory with B3LYP – the hybrid Becke's three parameter functional and Lee–Yang–Parr exchange–correlation potential)^{57,58} method using the 6-311G(d) and 6-311++G(d,p)⁵⁹ basis sets. The predicted cationic intermediates and the products formed in the addition reaction were investigated using the B3LYP/6-311G(d) method. By using the geometries of cations and products optimized by B3LYP/6-311G(d) method, their single point energies were calculated at the B3LYP/6-311++G(2d,2p)⁵⁹ level. Solvent effects were calculated at the same theory level as the optimizations were performed by single-point calculations on the optimized structures using the SCI-PCM (self-consistent isodensity polarized continuum model)⁶⁰ method in cyclohexane ($\epsilon = 2.023$). All stationary points were characterized by calculating the vibrational frequencies, and zero-point vibrational energies were added for all species. The calculations were performed with Gaussian 03⁶¹ program with an IBM PC Pentium IV computer.

3. Results and Discussion

Full geometric optimization of BBTT molecule was obtained by DFT/B3LYP method with the 6-311G(d) and 6-311++G(d,p) basis sets and the structure of the molecule was investigated in detail. Based on the results of each method, the pyramidalization parameters^{62,63} of the molecule were evaluated with the aim of determining the structural deformation of double bond. The values of 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,⁶² and of the out-of-plane bending angle (χ), the angle between plane C3C4C5C6 and plane H4C4C5H5 as shown in Scheme 1,⁶³ were calculated according to the results of each method. The distance R_u , the distance between midpoint of opposing C=C double bonds and the orientation angle θ , the dihedral angle between two planes containing four unsaturated carbon atoms in the minimum energy structure of the BBTT molecule,⁶⁴ were determined. The 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 chlorine to BBTT molecule from its *endo* face was sterically hindered. The addition of chlorine to 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.^{28–30,32–34,36,39} The polarization of chlorine and the subsequent heterolytic splitting of BBTT...Cl₂ molecular CT-complex results in the formation of the bridged cation (I) (Scheme 1). This cation and its isomers are the possible intermediates of the addition reactions of chlorine to BBTT molecule in gas phase and in solution (Fig. 1).

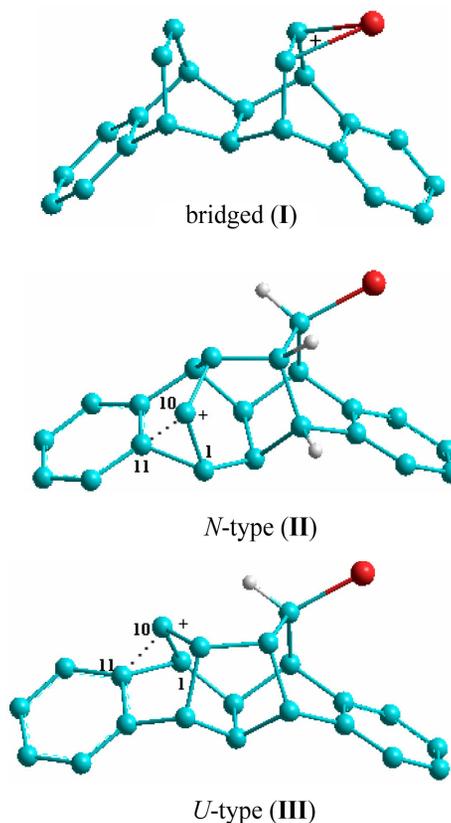


Figure 1: The optimized geometries of cations [B3LYP/6-311G(d)]

So as to determine the structures and relative stabilities of the predicted cationic intermediates (Fig. 1), the optimizations of their full geometries were performed using B3LYP/6-311G(d) method, and the total energies (E_{tot}) were calculated. By using the optimized geometries of cations at the B3LYP/6-311G(d) level, their single

Table 1: The calculated double bond lengths (r), distance (R) and orientation angle (θ) between two double bonds and pyramidalization parameters of BBTT molecule.

Metod	$r_{\text{C=C}}$ (Å)	R_u (Å)	θ (°)	ϕ (°)	χ (°)
B3LYP/6-311G(d)	1.331	3.081	0.0	1.809	2.028
B3LYP/6-311++G(d,p)	1.332	3.088	0.0	1.813	2.054

Table 2: The calculated relative energies of cations.

Cations	Relative energy (kcal mol ⁻¹)		
	B3LYP/6-311G(d)	B3LYP/6-311++G(2d,p) //B3LYP/6-311G(d)	SCI-PCM-B3LYP/6311++G(2d,p) //B3LYP/6-311G(d)
I	25.991	24.297	27.523
II	2.049	2.094	3.485
III	0.0	0.0	0.0

point energies were computed using B3LYP/6-311++G(2d,p) and SCI-PCM-B3LYP/6-311++G(2d,p) methods. The calculated relative energies are given in Table 2.

According to the results of the DFT calculations, the *N*- and *U*-type cations are more stable than the bridged cation (**I**). The skeletal isomerization of the bridged cation (**I**) into *N*- and *U*-type cations is thermodynamically feasible. The difference between the total energies of *N*- and *U*-type cations is very small, and their stabilities are nearly the same. The *U*-type cation is 3.485 kcal mol⁻¹ [SCI-PCM-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 cationic centre and π -orbitals of the benzene ring of these ions (Fig. 1). 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 (Fig. 1, 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 (Fig. 1). 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 1.436 Å and 1.663 Å, respectively, for *U*-type cation. Also, for *N*- and *U*-type cations, the C10–C11 internuclear distances were 1.592 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 BBTT molecule is determined by the direction of the skeletal isomerization of bridged ion (**I**) 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 (Scheme 1).

By fully optimizing the geometric structures of different configurations (Fig. 2) of *N*- and *U*-type reaction products by B3LYP/6-311G(d) method, their total energies were calculated and their stereochemistry were investigated. The single point energies of the products were calculated by using B3LYP/6-311++G(2d,p)//B3LYP/6-311G(d) and SCI-PCM-B3LYP/6-311++G(2d,p)//B3LYP/6-311G(d) methods. The calculated relative energies are given in Table 3.

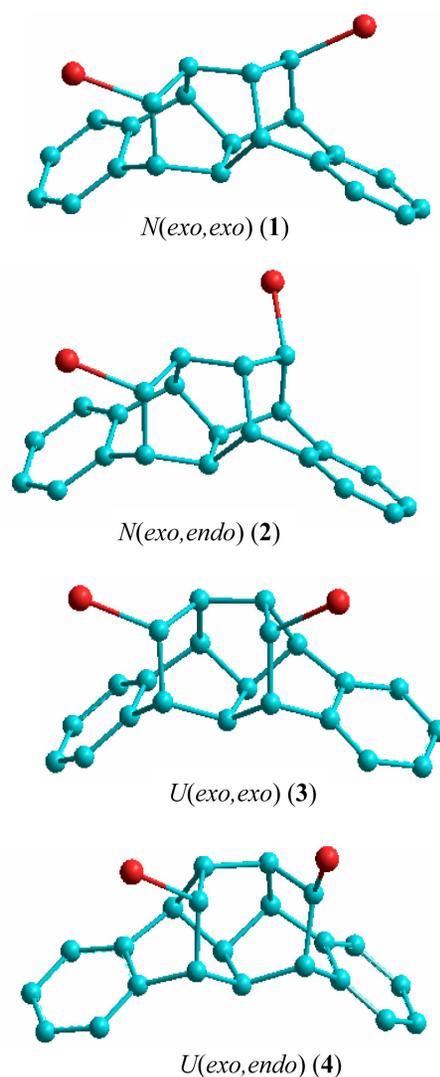
**Figure 2:** The optimized geometries of products (B3LYP/6-311G(d))

Table 3: The calculated relative energies of products.

Products	Relative energy (kcal mol ⁻¹)		
	B3LYP/6-311G(d)	B3LYP/6-311++G(2d,p) //B3LYP/6-311G(d)	SCI-PCM-B3LYP/6311++G(2d,p) //B3LYP/6-311G(d)
1	0.270	0.324	0.549
2	0.0	0.0	0.0
3	0.476	0.696	1.886
4	3.343	3.431	3.765

The total energies of the *exo,exo*- and *exo,endo*-isomers of *N*-type dichloride molecule differed very little, and their stabilities were nearly the same (Table 3). Among the thermodynamically feasible *exo,exo*- and *exo,endo*-dichlorides, only the second isomer is produced (Scheme 1). The *exo,exo*-isomer of the *U*-type dichloride molecule is more stable than *exo,endo*-isomer (Table 3), and the first dichloride is produced. Although *N(exo,endo)* dichloride is more stable than *N(exo,exo)* dichloride, the *exo,exo*-isomer of the *N*-type product, which is formed as a result of addition of chlorine 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.⁵¹ This is most probably due to the steric characteristic.

In Scheme 1, the mechanism of the electrophilic addition reaction of chlorine to BBTT molecule is given. The electronic and steric factors are important for the determination of the direction of the attack of chloride anion (Cl⁻) 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 chloride anion to this centre occurs on the *endo* face, and thus, the more stable *exo,endo*-dichloride isomer of *N*-type product is obtained. The attack of chloride anion towards the cationic centre of *N*-type ion from the *endo* face is not sterically prevented by the hydrogen atoms (Fig. 1, 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 chloride anion is realized on the *exo* face. Because the attack of chloride anion towards the cationic centre from the *endo* face is sterically hindered by the hydrogen atom (Fig. 1, cation **III**), therefore, the *exo,exo*-isomer of *U*-type product is formed. The stability of *N*- and *U*-type nonclassical delocalized ions and the structure of their cationic centres are effective in the determination of the direction of addition reaction and the stereochemistry of products.

The energy diagram of the addition reaction of chlorine to BBTT molecule is given in Figure 3. As can

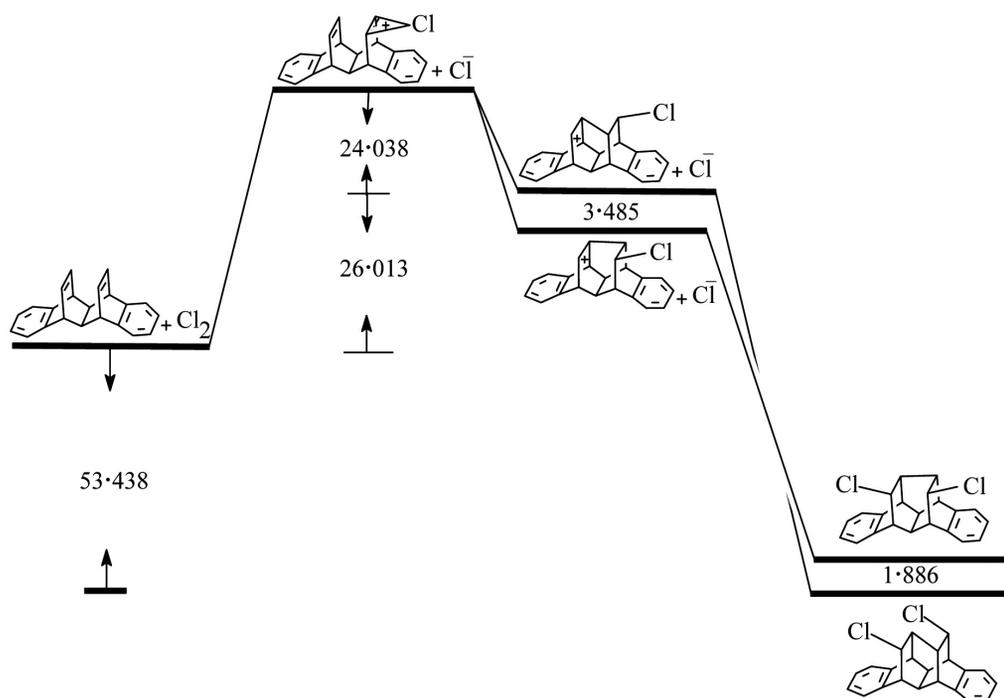


Figure 3: The energy diagram of BBTT-Cl₂ system. The energy values are given in kcal mol⁻¹ at SCI-PCM-B3LYP/6-311++G(2d,p)//B3LYP/6-311G(d) level.

be seen from the energy diagram of BBTT-Cl₂ system, the reaction is realized over the transformation of bridged cation (**I**) into slightly different *N*- and *U*-type nonclassical delocalized cations. The *exo,endo*-dichloride product is obtained over *N*-type cation, and *exo,exo*-dichloride product is obtained over *U*-type cation. In addition, the reaction products are kinetically controlled. The empirical rule suggested by Osawa is also valid for the above reaction. The difference between the stability of *N*- and *U*-type products is small and *N*-type product is 1.886 kcal mol⁻¹ (SCI-PCM-B3LYP/6-311++G(2d,p)//B3LYP/6-311G(d)) more stable than *U*-type product. On the other hand, the rule (Abbasoglu rule)⁵⁵ also applies for this reaction, i.e. transannular electrophilic addition reaction of halogens to strained alkenes with two isolated double bonds. This rule states that if the number of σ bonds between double bonds of the alkene is three ($m = 3$), the reaction takes place in the direction that leads to *N*-type product, if $m = 4$, it occurs in the direction that leads to *N*- and *U*-type products. In BBTT molecule, there are four σ bonds between double bonds and hence *N*- and *U*-type products are obtained.

4. 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 cation (**I**). The addition reaction of chlorine to BBTT molecule takes place over *N*- and *U*-type nonclassical delocalized cations, which are obtained as a result of the skeletal isomerization of bridged ion (**I**). 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 chloride anion (Cl⁻) to this centre occurs on the *endo* face, and as a result, the more stable *exo,endo*-dichloro 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 chloride anion towards the centre from the *endo* face is sterically hindered; hence, the addition occurs on the *exo* face, and the more stable *exo,exo*-isomer of *U*-type product is 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.

5. References

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Povzetek

Z DFT metodo smo raziskali mehanizem in stereokemijo reakcije elektrofilnega transanularnega adiranja klora na molekulo bisbenzotetraciklo[6.2.2.^{3,6}.0^{2,7}]tetradeka-4,9,11,13-tetraena (BBTT). Geometrijo in elektronsko strukturo molekule BBTT smo raziskali z metodo DFT/B3LYP z uporabo baznih setov 6-311G(d) in 6-311++G(d,p). Dvojne vezi v molekuli BBTT so *endo*-piramidalizirane. Strukturo in stabilnost kationskih intermediatov ter produktov adicije smo raziskali z metodama B3LYP/6-311G(d) in B3LYP/6-311++G(2d,p). Vpliv topila smo ovrednotili z metodo SCI-PCM. Premosteni kloronijev kation se lahko namreč izomerizira v bolj stabilna, neklasično delokalizirana, kationa tipa *N* in *U*, vendar je razlika v stabilnosti med njima majhna. Za določitev usmerjanja adicije in stereokemije nastalih produktov, je bistvena stabilnost neklasično delokaliziranih ionov tipa *N* in *U* ter struktura njihovih kationskih centrov. Ker je kation-ski center v ionu tipa *N* v interakciji z benzenskim obročem na *ekso* strani, je nukleofilni napad kloridnega aniona na ta center mogoč zgolj z *endo* strani, zato kot produkt nastane *ekso,endo* izomer tipa *N*. Napad kloridnega aniona na kation-ski center v ionu tipa *U* je z *endo* strani onemogočen z vodikovim atomom; zato napad poteče z *ekso* strani, ki je v interakciji z benzenskim obročem, in tako nastane bolj stabilen *ekso,ekso* izomer tipa *U*. Čeprav je kation tipa *U* za 3.485 kcal mol⁻¹ bolj stabilen od kationa tipa *N*, je produkt tipa *U* za 1.886 kcal mol⁻¹ [XPCM-B3LYP/6-311++G(2d,p)//B3LYP/6-311G(d)] manj stabilen od produkta tipa *N*.