

Ab initio and DFT investigation of electrophilic addition reaction of bromine to *endo,endo*-tetracyclo[4.2.1.1^{3,6}.0^{2,7}]dodeca-4,9-diene

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Abstract Full geometric optimization of *endo,endo*-tetracyclo[4.2.1.1^{3,6}.0^{2,7}]dodeca-4,9-diene (TTDD) has been carried out by *ab initio* and DFT/B3LYP methods and the structure of the molecule investigated. The double bonds of TTDD molecule are *endo* pyramidalized. The structure of π -orbitals and their mutual interactions for TTDD molecule were investigated. The cationic intermediates and products obtained as a result of the addition reaction have been studied using the HF/6-311G(d), HF/6-311G(d,p) and B3LYP/6-311G(d) methods. The bridged bromonium cation isomerized into the more stable N- and U-type cations and the difference between the stability of these cations is small. The N- and U-type reaction products are obtained as a result of the reaction, which takes place *via* the cations in question. The stability of *exo,exo* and *exo,endo* isomers of N-type product are nearly the same and the formation of both isomers is feasible. The U-type product basically formed from the *exo,exo*-isomer. Although the U-type cation was 0.68 kcal mol⁻¹ more stable than the N-type cation, the U-type product was 4.79 kcal mol⁻¹ less stable than the N-type product.

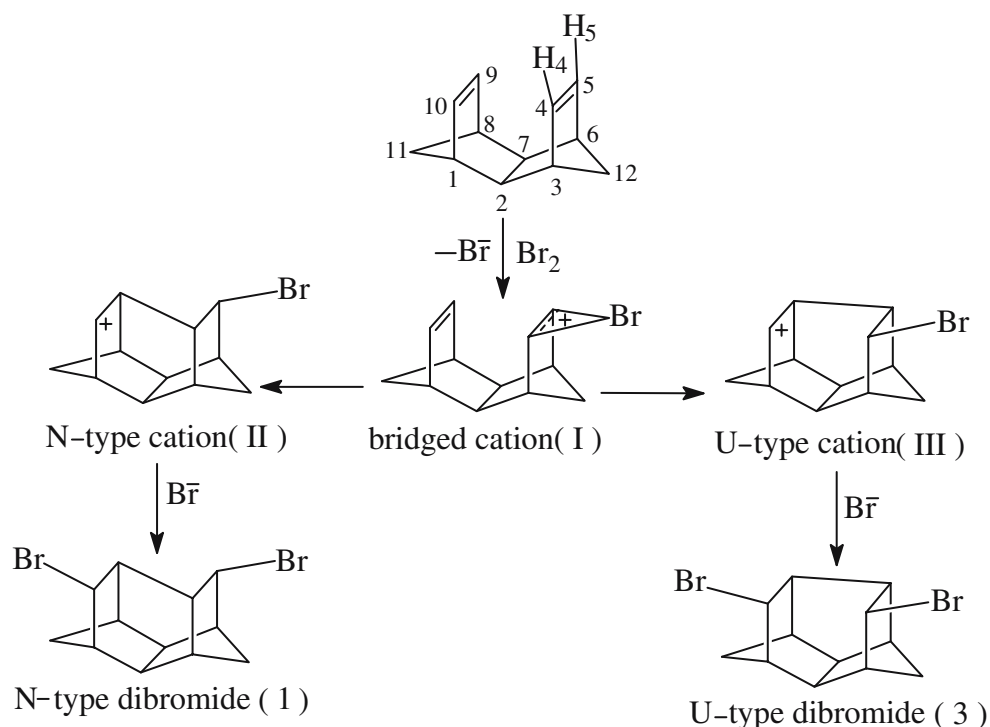
Keywords *Ab initio* and DFT calculations · Transannular interaction · Intramolecular skeletal rearrangement · Pyramidalization · *Endo-endo*-tetracyclo[4.2.1.1^{3,6}.0^{2,7}]dodeca-4,9-diene

Introduction

Rigid polycyclic molecules with two isolated double bonds located in the laticyclic topology [1] and spatially in close proximity have provided suitable frameworks for the study of transannular interactions and reactions [2–5]. 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]. Previously, although the formation of N-type products was ascribed to the mutual interaction of the orbitals, the reason for the formation of U-type product was not explained [24]. Later on, 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, the more stable product is obtained. In order to understand the inner mechanism and dynamic stereochemistry of the reactions in question, it is important to identify the structure and stability of the intermediates (cyclic bridged, N- and U-type cations) produced during the reaction's progress and to investigate their skeletal rearrangement. During the course of the addition reaction, it is possible for the cyclic bridged halogenium cation, which was produced as a result of the heterolytic separation of the alkene...halogen molecular complex, to transform into cross (N-type) and parallel (U-type) bridged cations by skeletal isomerization (the bonding of the double bonds crosswise and parallel). The direction of the flow of these reactions is

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Scheme 1 The electrophilic addition reaction of bromine to TTDD



determined by the direction of the skeletal isomerization of the cyclic bridged halogenium cation. The intramolecular skeletal rearrangement occurs in the direction of more stable skeletal structure.

The structure and the nature of the alkene play an important role in the display of characteristic behaviour of the electrophilic addition reactions of the halogens to parallel face-to-face (juxtaposed) double bonded strained alkenes. The investigation of the geometrical and electronic structure of alkenes is important in order to evaluate the pyramidalization and the other geometrical parameters of the double bonds, and the mutual interactions of the π -orbitals. 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 vital so as to interpret the many features of the electrophilic addition reactions.

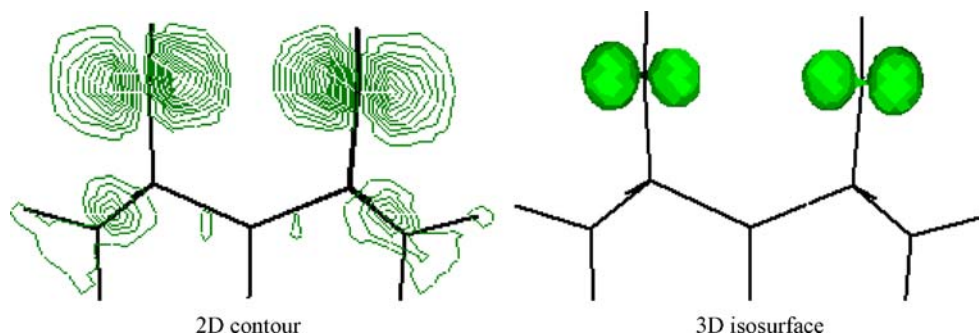
The addition reactions of halogens to unsaturated strained molecule and the reaction intermediates have been investigated quantum chemically [25–36]. In this connection, theoretical investigations of the addition of bromine and chlorine to olefins with rigid structure have recently been reported by us [37–39]. In continuance 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 mechanism and stereochemistry of the addition reaction of bromine to *endo,endo*-tetracyclo[4.2.1.1^{3,6}.0^{2,7}]dodeca-4,9-diene (TTDD). Bromination of the TTDD molecule gave the N- and U-type adducts (Scheme 1) [10].

In this work, the electrophilic addition of bromine to the TTDD molecule has been studied theoretically and *ab initio* and DFT methods were used to investigate the structures and stabilities of the cationic reaction intermediates (bridged, N- and U-type cations) and reaction products.

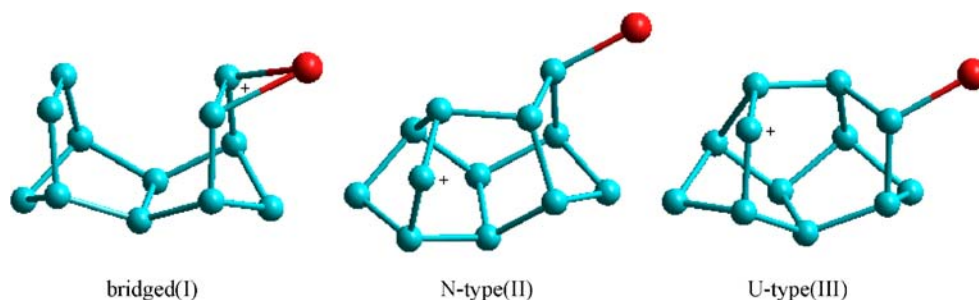
Table 1 The calculated total energies (kcal mol^{-1}), double bond lengths (\AA), distance (\AA) and orientation angle (degree) between two double bonds and pyramidalization parameters (degrees) of TTDD molecule

Method	E_{tot}	$r_{\text{C}=\text{C}}$	R_{u}	θ	φ	χ
HF/6-31G(d)	-290,208.07692	1.321	3.020	0.0	5.538	5.872
HF/6-311G(d)	-290,257.96881	1.319	3.022	0.0	5.648	5.925
B3LYP/6-31G(d)	-291,982.37076	1.342	3.027	0.0	5.683	5.966
B3LYP/6-311G(d)	-292,045.14208	1.343	3.028	0.0	5.795	6.110

Fig. 1 Electron density distribution (HOMO) of the TTDD molecule [B3LYP/6-311G(d)]



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



These methods were also used to calculate the geometry and the electronic structure of the TTDD molecule.

Methodology

The geometry and electronic structure of the *endo,endo*-tetracyclo[4.2.1.1^{3,6}.0^{2,7}]dodeca-4,9-diene (TTDD) molecule have been investigated by *ab initio* SCF and DFT/B3LYP [40, 41] methods using the 6-31G(d) [42] and 6-311G(d) [43] 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. The energy of electron correlation was calculated using Møller–Plesset second-order perturbation theory [44]. All stationary points were characterized by calculating the vibrational frequencies and zero-point vibrational energies were added for all species. Full

geometry optimization was 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)⁻¹. The calculations were performed with the HyperChem 7.5 and Gaussian 03 programs with an IBM PC Pentium IV computer.

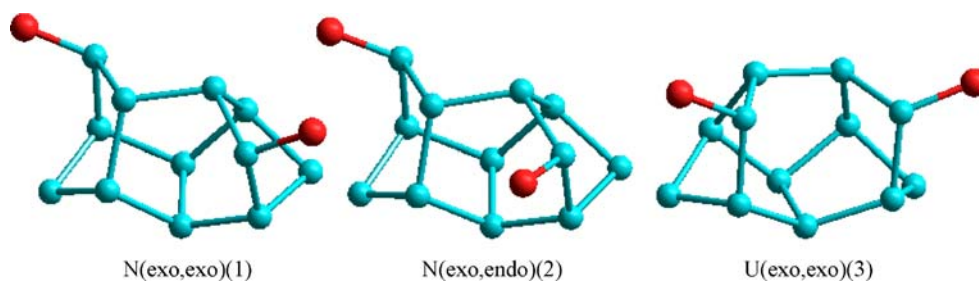
Results and discussion

Full geometric optimization of the TTDD molecule was carried out with *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. The pyramidalization parameters [45, 46] were determined 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 [45] and of the out-of-plane bending angle (χ) (out-of-plane angle between plane C3C4C5C6 and plane H4C4C5H5, as shown in Scheme 1) [46] 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 TTDD molecule) [47] were determined. These results are given in Table 1. The results show that the double bonds of the TTDD molecule are *endo*-pyramidal-

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)	MP2/6-311G(d)//HF/6-311G(d)
I	21.36	21.13	13.38	15.24
II	3.39	3.64	2.96	0.68
III	0.0	0.0	0.0	0.0

Scheme 3 The optimized geometries of products [B3LYP/6-311G(d)]



ized. Analysis of frontier orbital (HOMO) of the molecule showed that the electron density ($q_{\mu, \text{HOMO}}$) on the *exo*-face of double bonds is higher than the electron density on the *endo*-face (Fig. 1).

The structure of the π -orbitals of the TTDD molecule and their mutual interactions were investigated. For the TTDD molecule, whose double bonds were separated by an even number of ($m=4$) σ bonds, the mutual interaction of the π -orbitals through space and through the four σ bonds strengthen each other and the splitting of the energy levels of the orbitals increases. Hence the energy level of HOMO increases, the ionization potential of the molecule decreases and the chemical activity increases [1–4, 48].

The attack of bromine to TTDD molecule from its *endo* face was sterically hindered. The addition of bromine to TTDD molecule occurs from the *exo* face, where the electron density of the double bond is higher. The polarization of bromine and the subsequent heterolytic splitting of the TTDD...Br₂ molecular complex, results in the formation of the bridged cation (I) (Scheme 2). This cation and its isomers are the possible intermediates of the addition reactions of bromine to TTDD molecule in gas phase and solvent medium (Scheme 2).

The structures and relative stabilities of these cations were determined by carrying out geometrical optimization using the HF/6-311G(d), HF/6-311G(d,p) and B3LYP/6-311G(d) methods and the total energies (E_{tot}) were also calculated. Single-point energy calculations at the MP2/6-311G(d)//HF/6-311G(d) level were used to evaluate the electron correlation effect on the energies and the order of

stability of the cations. The calculated relative energies are given in Table 2.

The results showed that the N- and U-type cations are more stable than the bridged bromonium cation. The skeletal isomerization of the bridged bromonium 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 0.68 kcal mol⁻¹ (MP2/6-311G(d)//HF/6-311G(d)) more stable than the N-type cation. Hence, the bridged bromonium cation transforms into the appropriate N- and U-type cations as a result of skeletal isomerization, where crosswise and parallel mechanisms take place. The direction of the addition reaction is determined by the direction of the rearrangement of the bridged bromonium ion into the N- and U-type cations. The reaction takes place over the N- and U-type cations (cation N-type-Br⁻ and cation U-type-Br⁻ couple were assumed as the transition forms) in the parallel direction and finally, the N- and U-type reaction products are obtained.

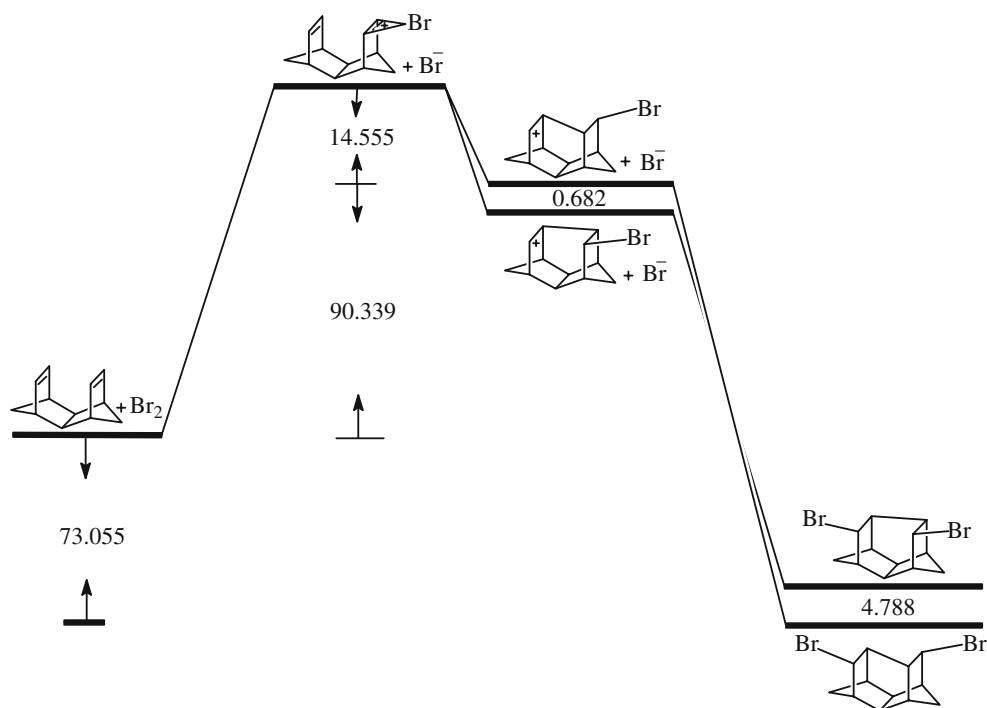
The stereochemistry and the stable configurations of the reaction products were investigated by *ab initio* and DFT methods. The geometrical structure of the different configurations of the N- and U-type products (Scheme 3) were optimized by HF/6-311G(d), HF/6-311G(d,p) and B3LYP/6-311G(d) methods and their total energies were evaluated. The electron correlation energies of the molecules were calculated by MP2/6-311G(d)//HF/6-311G(d) method. The calculated relative energies are given in Table 3.

There is little difference between the stabilities of the *exo, exo*- and *exo, endo*-isomers of N-type reaction product (Scheme 3) and it is likely that both isomers form. The analysis of cationic center of the N-type ion (Scheme 2) showed that bromide (Br⁻) ion's attack from *exo* and *endo* faces was not sterically prevented. Thus, it is possible that the N-type product is a mixture of these two isomers (*exo, exo* and *exo, endo*). The *exo, endo*-isomer of U-type product is 6.14 kcal mol⁻¹ (MP2/6-311G(d)//HF/6-311G(d)) less stable than the *exo, exo*-isomer, however, the attack of bromide (Br⁻) anion to cationic center of U-type ion from its *endo* face was sterically hindered by the hydrogen atom. Hence, the U-type product, essentially, should be composed of *exo, exo*-isomer. The results

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)	MP2/6-311G(d)//HF/6-311G(d)
1	0.0	0.0	0.0	0.0
2	2.27	2.28	2.14	1.63
3	4.88	4.71	3.79	4.79

Fig. 2 The energy diagram of TTDD-Br₂ system (kcal mol⁻¹) [MP2/6-311G(d)//HF/6-311G(d)]



indicated that although the U-type cation is more stable than the N-type cation, the U-type product is less stable than the N-type product.

Figure 2 shows the energy diagram of the electrophilic addition reaction of bromine to the TTDD molecule. As seen from the diagram, the reaction takes place by the transformation of the bridged bromonium cation into the N- and U-type cations. As the reaction progresses over the N- and U-type cations, the N- and U-type products are obtained. The stabilities of the N- and U-type cation differ little and the stabilities of the N- and U-type products are very close to each other. The N-type product is 4.79 kcal mol⁻¹ [MP2/6-311G(d)//HF/6-311G(d)] more stable than the U-type product. In addition to this, the reaction's products are kinetically controlled. The empirical rule suggested by Osawa is also valid for the above reaction.

Conclusions

The double bonds of TTDD are *endo*-pyramidalized. The N- and U-type cations are more stable than the bridged bromonium cation and their thermodynamic stabilities are very similar. The bridged bromonium cation that was formed as a result of the heterolytic splitting of the TTDD...Br₂ molecular complex transforms into the more stable N- and U-type cations and the reaction takes place *via* these cations. The reaction product is basically composed of *exo*, *exo*- and *exo*, *endo*-isomers of the N-

type product and *exo*, *exo*-isomer of the U-type product. There is little difference between the stabilities of the reaction products. Despite the higher stability of the U-type cation compared to the N-type cation, the N-type product is more stable than the U-type product.

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