DFT Investigation of the Mecahanism and Stereochemistry of Electrophilic Transannular Addition Reaction of Bromine to Tricyclo[4.2.2.0²,⁵]Deca-3,7-Diene

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Abstract

Full geometric optimization of tricyclo[4.2.2.0²,⁵]deca-3,7-diene (TDD) has been done by DFT/B3LYP methods and the structure of the molecule was investigated. Cyclobuten double bond (I) of molecule is *syn* pyramidalized, and bicyclookten double bond (II) is also *exo* pyramidalized. The double bond (I) is more pyramidalized than the double bond (II) and it has higher reactivity. The TDD-Br$_2$ system has been investigated by B3LYP/6-311++G(d,p) method and their stable configurations have been determined. The cationic intermediates and products obtained as a result of the addition reaction has been studied using B3LYP/6-311G(d,p) and B3LYP/6-311++G(d,p) methods. Bridged bromonium cation is more stable than *U*-type cation. Considering that the bridged cation does not isomerize to the less stable *U*-type cation, it is not possible for the *U*-type product to be obtained in the reaction. The bridged bromonium cation transformed into the more stable N-type cation and the *N*-type product was obtained via this cation. The thermodynamic stability of the *anti, exo* and *anti, endo* isomers of *N*-type dibromide molecule were almost identical. N-type product is 11.759 kcal mol more stable than U-type product.

Keywords: DFT calculations, transannular interaction, intramolecular skeletal rearrangement, pyramidalization, tricyclo[4.2.2.0²,⁵]deca-3,7-diene.

1. 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] 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.[10–24] Recently Inagaki et al. advanced a perturbation theory to interpret those cases where preferential cross bridging takes place.[25] 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 41.84 kJ mol^{-1}. If the difference is more than 10 kcal mol^{-1}, 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 isomeriz (*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.

The structure and the nature of the alkene play an important role in the display of characteristic behavior of the electrophilic addition reactions of the halogens to parallel face-to-face (juxtaposed) double bonded strained alkenes. The investigation of the geometrical and electronical 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 behaviors 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 quantum chemically investigated.[26–40] Accordingly, the theoretical investigations of the addition of bromine and chlorine to olefins with rigid structure have recently been reported by us.[41–50] In continuation of our interest in the quantum-chemical studies related to the addition of halogens to unsaturated strained molecules, we wish to report here the results obtained for the investigation of the mechanism and stereochemistry of addition reaction of bromine to tricyclo[4.2.2.0²,⁵]deca-3,7-diene(TDD). Bromination of the TDD molecule gives only the adduct of *N*-type (Scheme 1).[6,11] But, the formation of *U*-type adduct can't be observed.

In this work, the electrophilic addition of bromine to TDD molecule has been studied theoretically and DFT methods have been used to investigate the structures and
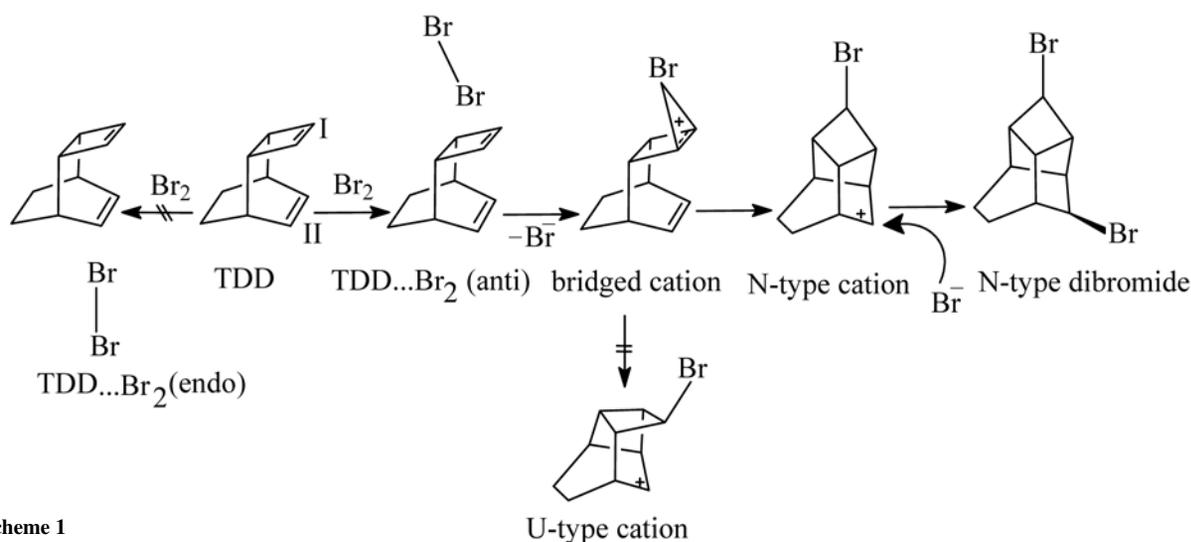
stabilities of the reaction cationic intermediates (bridged, *N*- and *U*-type cations) and reaction products. These methods were also used to calculate the geometry and the electronic structure of the TDD molecule. Also, various models (geometric distortions, electron density, orbital effects, electrostatic effects and intermediates stabilities) have been used for prediction and interpretation of π-facial selectivity and regioselectivity of the electrphilic addition reaction to TDD of bromine.

2. Computational Methods

The geometry and the electronic structure of the tricyclo[4.2.2.0²,⁵]deca-3,7-diene (TDD) molecule have been investigated by DFT/B3LYP[51,52] method using the 6-311G(d,p) and 6-311++G(d,p)[53] basis sets. The predicted cationic intermediates and products formed in the addition reaction have been investigated using the B3LYP/6-311G(d,p) and B3LYP/6-311++G(d,p) methods. Solvent effects were calculated at the same theory level as the optimizations by performing single-point calculations on the optimized structures using the CPCM (conducting polarized continuum model)[54,55] method (with UAKS cavities[56]) in $CHCl_3$ ($\varepsilon = 4.9$). All stationary points have been characterized by calculating the vibrational frequencies and zero-point vibrational energies have been added for all species. The calculations have been perfomed with Gaussian 03[57] program with an IBM PC Pentium IV computer.

3. Results and Discussion

Full geometric optimization of the TDD molecule was done by DFT/B3LYP method with the 6-311G(d,p) and 6-311++G(d,p) basis sets and the structure of the molecule was also investigated in detail. The pyramidalization parameters[58,59] were determined so as to determine

Scheme 1

Method	cyclobuten double bond(I)				bicyclookten double bond(II)			
	$r_{C=C}$	ϕ	χ	$q_{i,\ HOMO}$	$r_{C=C}$	ϕ	χ	$q_{i,\ HOMO}$
B3LYP/6-311G(d,p)	0.1338	0.322	0.277	0.464	0.1334	0.090	0.107	0.369
B3LYP/6-311++G(d,p)	0.1339	0.331	0.287	0.468	0.1336	0.094	0.108	0.372

the structural deformation of the double bond. The values of the pyramidalization angle (ϕ)[58] and of the out-of-plane bending angle (χ)[59] were calculated according to the results of each method of cyclobuten (I) (the double bond of cyclobuten fragment) and bicyclookten (II) (the double bond of bicyclookten fragment) dauble bonds (Scheme 1) and are given in Table 1. According to obtained results, cyclobuten double bond (I) is *syn* pyramidalized and bicyclookten double bond (II) is also *exo* pyramidalized. Also, cyclobuten double bond (I) had greater structural deformation as compared to bicyclookten double bond (II). That is, the double bond (I) of TDD molecule is more pyramidalized than the double bond (II). Therefore, cyclobuten double bond (I) in TDD molecule has higher reactivity than that of bicyclookten double bond (II). On the other hand, the attack of the bromine molecule on the cyclobutane double bond (I) was not sterically hindered. Hence, the possibility of addition of bromine to TDD molecule at the double bond (I) is higher. That is, the addition of bromine to TDD molecule is realized on the cyclobutane double bond (I). So, the regioselectivity in the electrophilic addition reactions of bromine to TDD molecule should be evident.

The analysis of frontier orbital (HOMO) of TDD molecule showed that this orbital is principally localized in the double bonds. In the case of HOMO, the electron density($q_{i,\ HOMO}$) in the doubl bond (I) is higher than that of the double bond (II) (Table 1), as shown in Figure 1. The analysis of HOMO of the molecule showed that the electrophilic attack of bromine occurs on *anti* face the cyclobutane double bond (I), which has higher electron density.

2D contour   **3D isosurface**
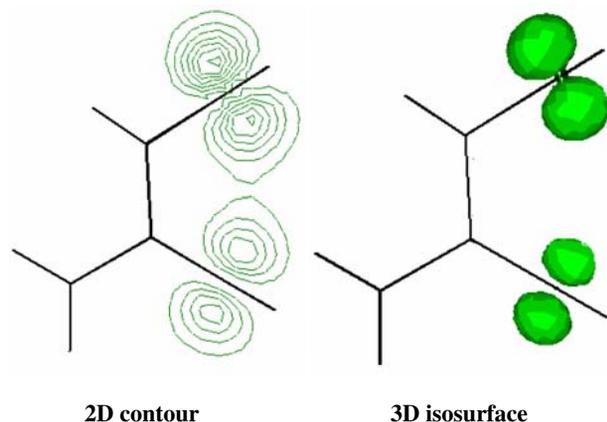
Figure 1: Electron density distribution (HOMO) of the tricyclo[4.2.2.0²,⁵]deca-3,7-diene molecule [B3LYP/6-311++G(d,p)].

In order to determine the possible center of attack of bromine to TDD molecule, the molecular electrostatic potential (MESP) (in kcal mol⁻¹) of the molecule was also calculated by means of B3LYP/6-311++G(d,p) method. The electrostatic potential contour maps (Fig. 2) of the molecule, also reveal that the electrophilic attack of bromine is realized on *anti* face of the cyclobutane double bond (I), which has larger integrated volume of a certain negative potential.

2D contour   **3D isosurface**
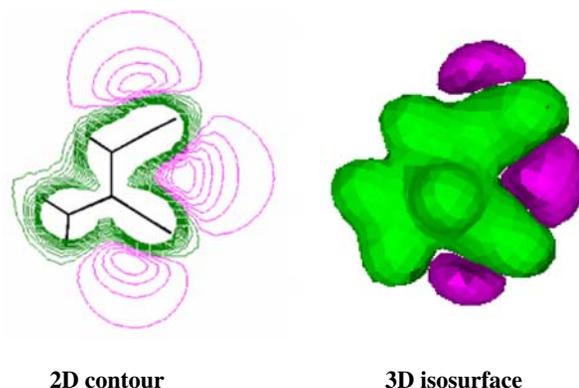
Figure 2: Molecular electrostatic potential contour map of tricyclo[4.2.2.0²,⁵]deca-3,7 diene molecule [B3LYP/6-311++G(d,p)].

As is known, olefin-halogen molecular charge-transfer (CT) complexe is formed in the first step of electrophilic addition of halogens to olefins.[33,34,36,38] According to the thermodynamic stability of the moleculer CT-complexes, it is possible to determine from which direction the halogen attacks the double bond. Therefore, the stability and electron structure of the TDD...Br$_2$ (*anti*) and TDD...Br$_2$ (*endo*) molecular CT-complexes (Scheme 1, Fig. 3) were investigated by using B3LYP/6-311++G(d,p) method. The stabilization energies of the molecular CT-complexes, the equilibrium distance $R_{X–Br}$ (X is midpoint of the C = C bond of TDD), and the other calculated properties are given in Table 2. The *anti* complex is 0.392 kcal mol⁻¹ relatively more stable than the *endo* complex. Hence, according to the stability of the molecular complexes too, regioselectivity should be observed in the electrophilic addition of bromine to TDD molecule. The electrophilic attack of bromine occurs on the cyclobutane double bond (I). The bromine molecule is partly polarized in the TDD...Br$_2$ (*anti*) molecular complex and 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 molecule in the molecular complex is relatively longer than the one in the neutral bromine molecule. The obtained results reveal that TDD...Br$_2$ (*anti*) molecular complex plays an important part in the heterolytic splitting of the bromine molecule leading to an ionic addition. Subsequently, the heterolytic splitting of the TDD...Br$_2$ (*anti*) molecular complex, result in the formation of the bridged cation (Scheme 1). This cation and its isomers were the possible intermediates of the addition reactions of bromine to TDD molecule in the gas phase and solvent medium (Scheme 2).
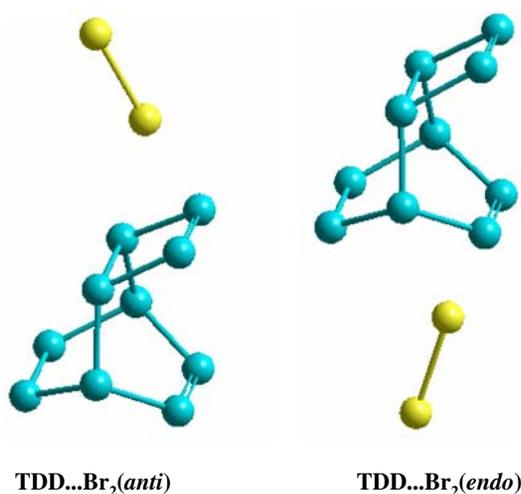
In order to determine the structures and relative stabilities of the predicted cationic intermediates (Scheme 2), their full geometry optimization was performed at the B3LYP/6-311G(p,d) and B3LYP/6-311++G(p,d) levels and the totol energies (E$_{tot}$) were also calculated. By using the optimized geometries of cations at the B3LYP/6-311++G(d,p) level, their single point energies have been computed using CPCM-B3LYP/6-311++G(d,p) method. The calculated relative energies are given in Table 3.

According to the results of each method, bridged bromonium cation is more stable than *U*-type (III) cation and less stable than *N*-type (II) cation (Table 3). In other words, bridged bromonium cation transforms into more stable N-type cation by cross-bonding (cross mechanism) of the double bonds (Scheme 1). It is not possible for the bridged bromonium cation to isomerizes skeletally to the unstable *U*-type cation. As a result, the direction of the electrophilic addition reaction of bromine to TDD molecule is determined by the direction of the skeletal isomerization of the bridged bromonium cation into *N*-type cation and *N*-type reaction product is perfered over the *N*-type cation (a cation *N*-type-Br$^-$ couple was assumed as the transition form). Thus, theoretical investigations show that the ionic addition of the bromine molecule to TDD follows these steps: formation of the TDD…Br$_2$ (*anti*) molecular complex and decomposition of this complex to the bridged-bromonium ion; rearrangemet bridged-bromonium ion to *N*-type cation; and nucleophilic attack of bromide ion (Br$^-$) on this cation.

The different configurations of *N*-type dibromide molecule (*anti, exo* and *anti, endo*) and the geometric structure of *anti,exo* isomere (Scheme 3) *U*-type dibromi-

Figure 3: The optimized geometries of the TDD...Br$_2$ (*anti*) and TDD...Br$_2$ (*endo*) molecular CT-complexes [B3LYP/6-311++G(d,p)].

Table 2: The properties of TDD...Br$_2$(*anti*) and TDD...Br$_2$ (*endo*) molecular complexes [B3LYP/6-311++G(d,p)].

Molecular complex	Stabilization energy (kJ mol^{-1})[a]	Equilibrium distance, R(nm)	r$_{Br-Br}$ (nm)	Charge transferred from TCO to Br$_2$,(e)
TDD…Br$_2$ (*anti*)	19.029	0.2844	0.2397	0.262[b]
TDD…Br$_2$ (*endo*)	17.389	0.2921	0.2394	0.157[b]

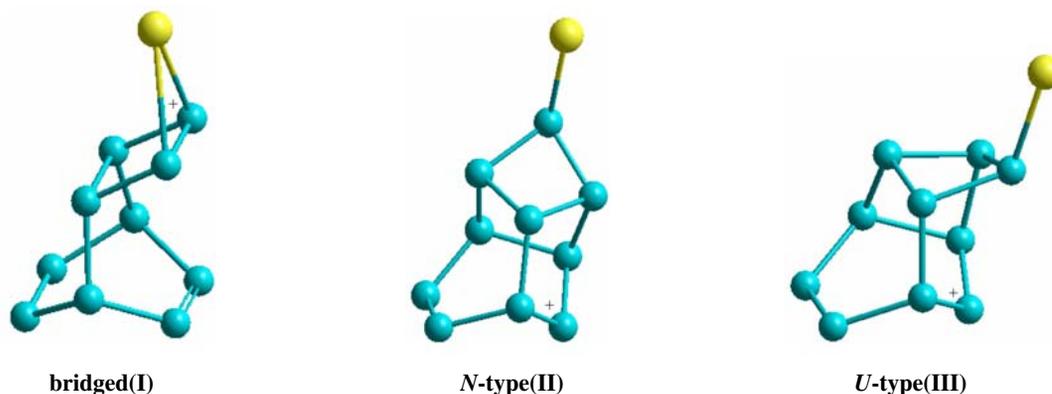[a] Without zero point energy (ZPE) corrections   [b] Mulliken charges

bridged(I)   ***N*-type(II)**   ***U*-type(III)**

Figure 4: The optimized geometries of cations [B3LYP/6-311++G(d,p)].

Table 3: The calculated relative energies of cations.

Cations	Relative energy (kJ mol^{-1})		
	B3LYP/6-311G(d,p) B	B3LYP/6-311++G(d,p)	CPCM-B3LYP/6-311++G(d,p)//B3LYP/6-311++G(d,p)
I	19.999	10.895	25.468
II	0.0	0.0	0.0
III	37.300	25.259	41.673

de molecule were optimized by B3LYP/6-311G(p,d) and B3LYP/6-311++G(p,d) methods and their total energies (E_{tot}) were calculated and their stereochemistries investigated. By using the optimized geometries of products at the B3LYP/6-311++G(d,p) level, their single point energies were computed using CPCM-B3LYP/6-311+G(d,p) method. The calculated relative energies are given in Table 4. The total energies of the *anti, exo* and *anti, endo* isomers of *N*-type dibromide molecule differ very little and their stabilities are nearly the same. Thus, thermodynamically, the possibilities of the formation of both of these isomers is the same and feasible. The *N*-type dibromide molecule was more stable than *U*-type dibromide molecule (Table 4). In other words, parallelism exists between the cation and the corresponding product (Fig. 6).

tion and finally an *N*-type product was obtained. Thus, the reaction occurs by the formation of the most stable intermediate combination (*N*-type cation). The empirical rule suggested by Osawa is valid for the above reaction. The *N*-type product is 11.059 kcal mol^{-1}

[CPCM-B3LYP/6-311++G(d,p)//B3LYP/6-311++G(d,p)] more stable than the *U*-type product. In solvent medium (CHCl$_3$), the energy barrier (Fig. 6) between the reactants and intermediates is reduced and the reaction takes place easily. On the other hand, the rule (Abbasoglu rule)[49,50] 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

N(anti,exo)(1)   *N(anti,endo)*(2)   *U(anti,exo)*(3)
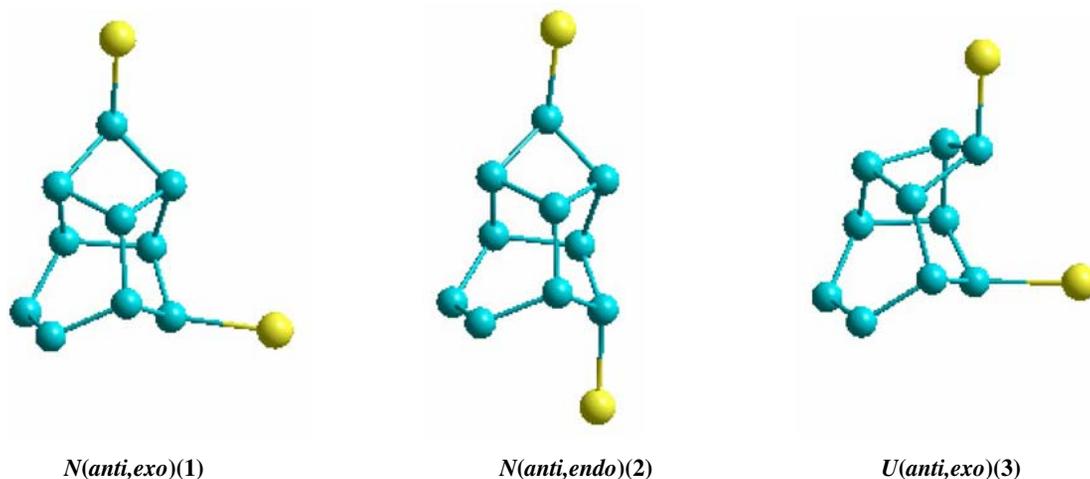
Figure 5: The optimized geometries of products [B3LYP/6-311++G(d,p)].

Table 4: The calculated relative energies of products.

Products	Relative energy (kJ mol^{-1})		
	B3LYP/6-311G(d,p)	B3LYP/6-311+G(d,p)	CPCM-B3LYP/6-311+G(d,p)//B3LYP/6-311+G(d,p)
1	0.0	0.0	0.0
2	17.753	8.399	9.205
3	44.961	45.162	46.271

In Figure 6, the energy diagram of electrophilic addition reaction of bromine to TDD molecule is given. As can be seen from the energy diagram, the reaction progresses in the direction of the more stable cation and the skeletal isomerisaton of the bridged cation into N-type cation and the bridged cation into N-type cation reaction realizes in the direction that leads to *N*-type product, if m = 4, it realizes in the direction that leads to *N*- and *U*-type products. In TDD molecule, there are three σ bonds between double bonds and hence N-type product is obtained.
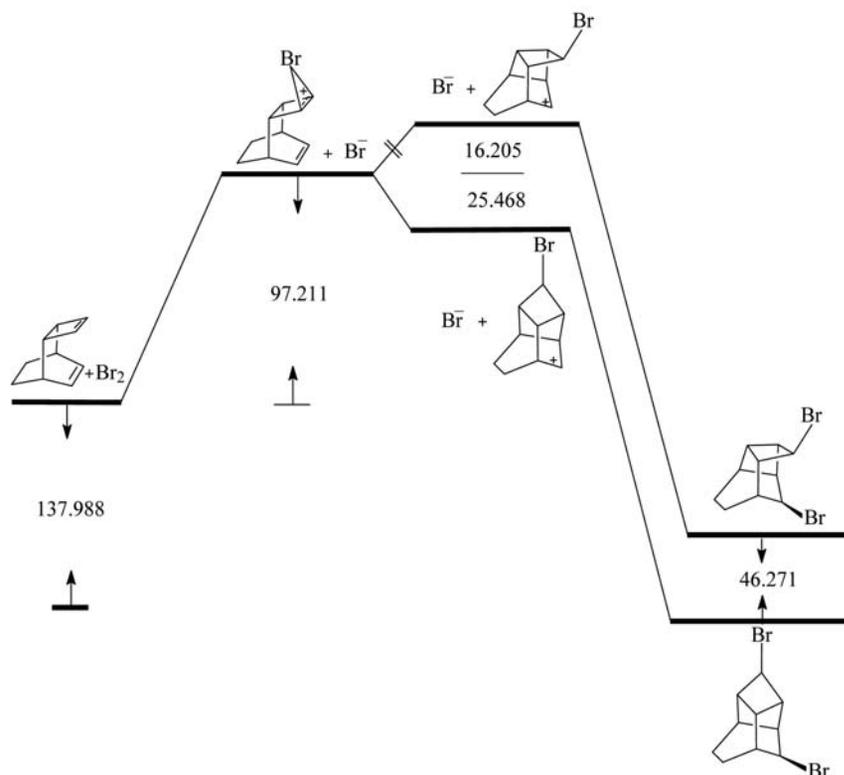
Figure 6: The energy diagram of TDD-Br$_2$ system (kJ mol^{-1}) [CPCM-B3LYP/6-311++G(d,p)//B3LYP/6-311++G(d,p)].

4. Conclusions

Our investigations show that cyclobuten double bond (I) of TDD molecule is *syn* pyramidalized, and bicyclookten double bond (II) is *exo* pyramidalized. Cyclobuten double bond (I) is more pyramidalized as compared to that of bicyclookten double bond (II) and it also has higer reactivity. The electron density ($q_{i, HOMO}$) of the cyclobuten double bond (I) in the HOMO of the molecule is greater than that of the bicyclookten double bond (II). *Anti* face of cyclobuten double bond (I) of the molecule is region has much more negative potential.

Anti molecular complex is more stable than *endo* complex. Regioselectivity should be observed in the addition reaction. Regioselectivity of investigated addition reaction is parallel with the pyramidalization of the double bond. The bridged bromonium cation was less stable than the *N*-type cation and more stable than *U*-type cation. The bridged bromonium cation transformed into the more stable *N*-type cation by a cross (*N*-type) mechanism and over this cation the *N*-type product was obtained. Considering that the bridged cation does not isomerizes into the less stable *U*-type cation, it is not possible for *U*-type product to be obtained in the reaction. The thermodynamic stability of the *N*-type dibromide products (*anti,exo* and *exo,endo* isomers) were almost identical. The *U*-type product was less stable than the *N*-type product.

5. References

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Povzetek

Z uporabo Beckejevega triparametričnega Lee-Yang-Parrovega gostotnega funcionala (DFT/B3LYP) smo izvedli popolno geometrijsko optimizacijo triciklo[4.2.0^{2,5}]deka-3,7-diena (TDD) in preučevali strukturo molekule. Ugotovili smo, da je *sin* piramidalizirana dvojna vez v ciklobutenu (I) bolj piramidalizirana in reaktivna od *ekso* piramidalizirane dvojne vezi v biciklooktenu (II).

S popolno geometrijsko optimizacijo na B3LYP/6-311++G(d,p) nivoju smo za reakcijo adicije Br$_2$ na TDD določili stabilne konfiguracije reaktantov, kationskih intermediatov in produktov. Ugotovili smo, da mostni bromonijev kation, zaradi večje stabilnosti, ne izomerizira v U-obliko, tako da U-oblika produkta pri tej reakciji ne more nastati. Nasprotno pa mostni bromonijev kation izomerizira v stabilnejšo N-obliko kationa, zato nastane N-oblika produkta. Ugotovili smo tudi, da je termodinamska stabilnost anti, ekso in anti, endo izomerov N-oblike dibromidov skoraj enaka in da je N-oblika produkta 11.759 kcal mol^{-1} stabilnejša kot U-oblika.