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ORIGINAL PAPER

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Ab initio and DFT study on the electrophilic addition reaction of bromine to tetracyclo[5.3.0.0^{2,6}.0^{3,10}]deca–4,8–diene

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Abstract The electronic and geometric structures of tetracyclo[5.3.0.0^{2,6}.0^{3,10}]deca-4,8-diene (hypostrophene) have been investigated by *ab initio* and DFT/B3LYP methods using the 6-31G* and 6-311G* basis sets. The double bonds of hypostrophene are *endo*-pyramidalized. The cationic intermediates and products formed in the addition reaction have been investigated using the HF/6-311G*, HF/6-311G**, and B3LYP/6-311G* methods. The bridged bromonium cation was more stable than the 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 *exo*, *exo* and *exo*, *endo* isomers of the N-type dibromide molecule were almost identical. The N-type product was 16.6 kcal mol^{-1} more stable than the U-type product.

Keywords *Ab initio* and DFT calculations · Intramolecular skeletal rearrangement · Electrophilic addition · Parallel face-to-face (juxtaposed) double bonds · Hypostrophene

Introduction

Rigid polycyclic molecules with isolated double bonds in the laticyclic topology [1] and spatially in close proximity have provided suitable frameworks for the study of transannular reactions [2] and orbital interactions [3, 4]. Attack of an electrophile on a molecule with two isolated double bonds in spatial proximity usually leads to transannular bridge formation in either cross (N-type) or paralel (U-type) manners, or both [5–7]. Experimental results of this type of reaction are confusing. In some cases, only the cross or the parallel-bridged product is isolated, while in other cases, both products are formed simultaneously [8–19]. Inagaki et al. advanced a perturbation theory to interpret those cases where preferential cross-bridging takes place [20]. 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. The course of the reaction has been rationalized by Osawa et al. with the aid of empirical force field calculations to depend on the thermodynamic stability of the products [5]. A difference larger than 10 kcal mol^{-1} in calculated strain energies between neutral hydrocarbon skeletons of N-type and U-type adducts would dictate the exclusive formation of the more stable product [5].

In the course of the addition reaction, it is possible for the cyclic bridged halogenium cation, which is formed by the heterolytic splitting of the alkene...halogen molecular complex, to transform into cross- (N-type) and parallel (U-type)-bridged cations as a result of skeletal isomerization (with cross- and parallel bonding of the double bonds). The direction of the flow of these reactions is determined by the direction of the cyclic bridged halogenium cation's skeletal isomerization. Intramolecular skeletal rearrangement occurs so that a stable skeletal structure forms. The determination of the structure and the stability of the addition reaction intermediates (cyclic bridged, N- and U-type cations) and the investigation of the skeletal rearrangements of these are important in learning the inner mechanism and dynamic stereochemistry of the reaction in detail.

The alkene's structure and nature play a vital role for electrophilic addition reactions of the halogens to the face-to-face (juxtaposed) doubly bonded strained alkenes, where they show characteristic features. The investigation of the geometric and electronic structure of alkenes is important for the pyramidization of double bonds, the calculation of the other geometric parameters, and the

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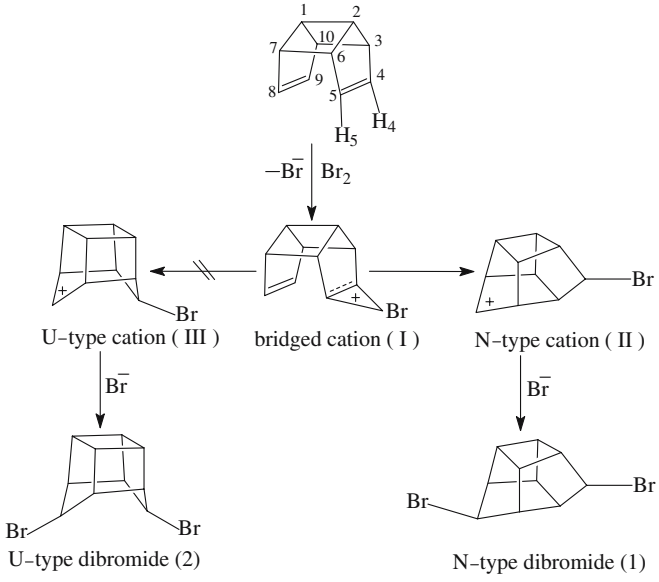
understanding of the mutual interaction of π orbitals. These investigations are also important for the determination of the connections between the structure of the alkenes and their behaviours in electrophilic addition reactions. The investigation of the stability and the stereochemistry of different configurations of the reaction products are necessary to explain the specifics of the electrophilic addition reactions.

The addition reactions of halogens to unsaturated strained molecules and the reaction intermediates have been investigated quantum-chemically [21–32]. In this connection, we have recently reported the theoretical investigations of the addition of bromine and chlorine to olefins with rigid structures [33]. In the continuation of our interest in quantum-chemical studies related to the addition of halogens to unsaturated strained molecules, we wish to report in this paper the results obtained from the investigation of the mechanism and stereochemistry of addition reactions of bromine to tetracyclo[5.3.0.$0^{2,6}$.$0^{3,10}$] deca-4,8-diene (hypostrophene). Bromination of the hypostrophene molecule gave only the N-type adduct (Scheme 1) [5]. However, the formation of U-type adduct cannot be observed.

In this work, the electrophilic addition of bromine to hypostrophene has been studied theoretically and the structures and stabilities of the cationic reaction intermediates (bridged, N- and U-type cations) and products have been investigated by *ab initio* and density functional theory (DFT) methods. Also, the geometry and the electronic structure of the hypostrophene molecule were calculated by *ab initio* and DFT methods.



Scheme 1 The electrophilic addition reaction of bromine to hypostrophene

Methodology

The geometry and the electronic structure of the hypostrophene molecule were investigated by *ab initio* SCF and DFT/B3LYP [34, 35] methods using the 6-31G* [36] and 6-311G* [37] basis sets. The predicted cationic intermediates and products formed in the addition reaction were investigated using the HF/6-311G*, HF/6-311G**, and B3LYP/6-311G* methods. The electron correlation energy was calculated using Moller–Plesset second-order perturbation theory [38]. 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 0.00001 kcal mol^{-1}) and an RMS gradient of 0.001 kcal $(Å\ mol)^{-1}$. The calculations were performed with the HyperChem 7.5 and Gaussian 98 programs with an IBM PC Pentium IV computer.

Results and discussion

Full geometric optimization of the hypostrophene molecule was performed by *ab initio* SCF and DFT/B3LYP methods with the 6-31G* and 6-311G* basis sets and the structure of the molecule was also investigated in detail. 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 [39] and of the out-of-plane bending angle (χ) (the out-of-plane angle between planes C3C4C5C6 and H4C4C5H5, as shown in Scheme 1) [40] were calculated for each method. The distance (R_u) (distance between mid-point 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 hypostrophene) [41] were determined. These results are given in Table 1. The results show that the double bonds of hypostrophene are *endo*-pyramidalized. Analysis of the frontier orbital (HOMO) showed that the electron density $\left(q_{\mu,HOMO}\right)$ at the *exo* face of the double bond is high (Fig. 1).

Because of the mutual obstruction of the double bonds on the *endo* faces and the higher electron density at the *exo* faces, attack of bromide on hypostrophene should occur from the *exo* face. The polarization of bromine, and, subsequently, the heterolytic splitting of the hypos-

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

Method	E_{tot}	$r_{C=C}$	R_u	θ	ϕ	χ
HF/6-31G*	−241210.629	1.323	2.958	0.0	3.205	3.455
HF/6-311G*	−241251.797	1.322	2.959	0.0	3.324	3.579
B3LYP/6-31G*	−242665.969	1.344	2.966	0.0	3.371	3.635
B3LYP/6-311G*	−242717.245	1.346	2.967	0.0	3.775	4.078

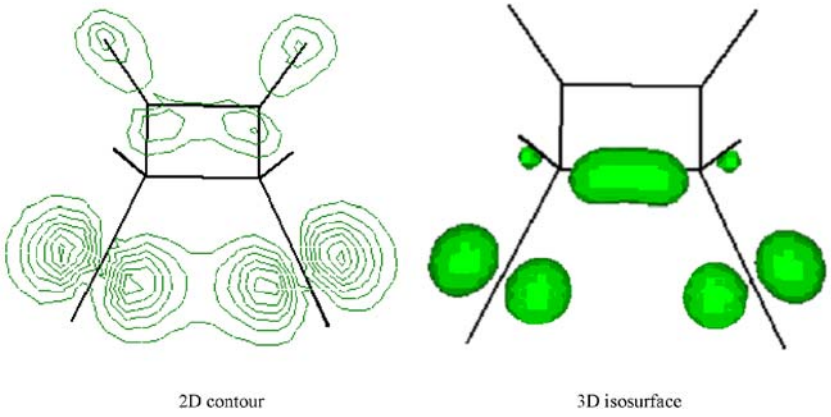


Fig. 1 Electron density distribution (HOMO) of the hypostrophene (B3LYP/6-311G*)

trophene...Br_2 (HS...Br_2) molecular complex, result in the formation of the bridged cation (I) (Scheme 1). This cation and its isomers were the possible intermediates of the addition reactions of bromine to hypostrophene in the 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*, HF/6-311G**, and B3LYP/6-311G* methods, and the total energies (E_{tot}) were also calculated. Single-point energy calculations at the MP2/6-311G*//HF/6-311G* 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.

Each method suggests that the bridged bromonium cation (I) is more stable than the U-type cation (III) and less stable than the N-type cation (II) (Table 2). In other words, the bridged bromonium cation transforms into the 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 isomerize skeletally to the unstable U-type cation. As a result, the direction of the electrophilic addition reaction of bromine to hypostrophene is determined by the direction of the skeletal isomerization of the bridged bromonium cation into the N-type cation and N-type reaction product is prefered 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 hipostrophene follows these steps: formation of the HS...Br_2 molecular complex and decomposition of this complex to the bridged-bromonium ion; rearrangement of bridged-bromonium ion to the N-type cation; and nucleophilic attack of the bromide ion (Br^-) on this cation.

The different configurations of the N-type dibromide molecule (*exo*, *exo* and *exo*, *endo*) and the geometric structure of the *exo*, *exo* isomer (Scheme 3) U-type dibromide molecule were optimized using the HF/6-311G*, HF/6-311G**, and B3LYP/6-311G* methods and their total energies (E_{tot}) were calculated and their stereochemistries investigated. The correlation energies of the molecules were evaluated using the MP2/6-311G*// HF/6-311G* method The calculated relative energies are given in Table 3.

The total energies of the *exo*, *exo* and *exo*, *endo* isomers of the N-type dibromide molecule differ very little and their stabilities are almost the same. Thus, thermodynamically, the possibilities of formation of both of these isomers are similar. The structure of the cation center of the N-type cation was investigated, and it was determined that the attack of the bromide ion on the center, towards *exo* and *endo* faces, was not sterically hindered. This implies that it is possible for both isomers to form sterically. Therefore, as a result of the electrophilic addition reaction of bromine to hypostrophene, a mixture of the *exo*, *exo* and *exo*, *endo* isomers should be obtained. The N-type dibromide molecule was more stable than U-type dibromide molecule (Table 3). In other words, parallelism exists between the cation and the corresponding product (Fig. 2).

In Fig. 2, the energy diagram of the electrophilic addition of bromine to hypostrophene is given. As can be seen from the energy diagram, the reaction progresses in the direction of the more stable cation and the skeletal isomerization of the bridged cation into the N-type cation and finally an N-type product was obtained. Thus, the reaction occurs by the formation of the most stable intermediate combination (N-

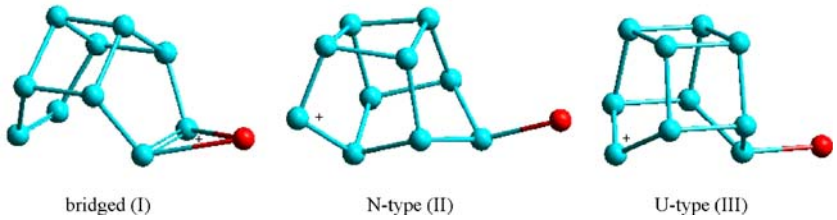
Table 2 The calculated relative energies of cations

Cations	Relative energy (kcal mol^{-1})			
	HF/ 6-311G*	HF/ 6-311G**	B3LYP/ 6-311G*	MP2/6-311G*// HF/ 6-311G*
I	5.899	5.585	5.961	8.056
II	0.0	0.0	0.0	0.0
III	15.814	15.751	17.257	18.324

Table 3 The calculated relative energies of products

Products	Relative energy (kcal mol^{-1})			
	HF/ 6-311G*	HF/ 6-311G**	B3LYP/ 6-311G*	MP2/6-311G*//HF/ 6-311G*
1	0.0	0.0	0.0	0.0
2	14.182	14.119	12.362	16.550
3	0.056	0.502	0.678	0.690

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



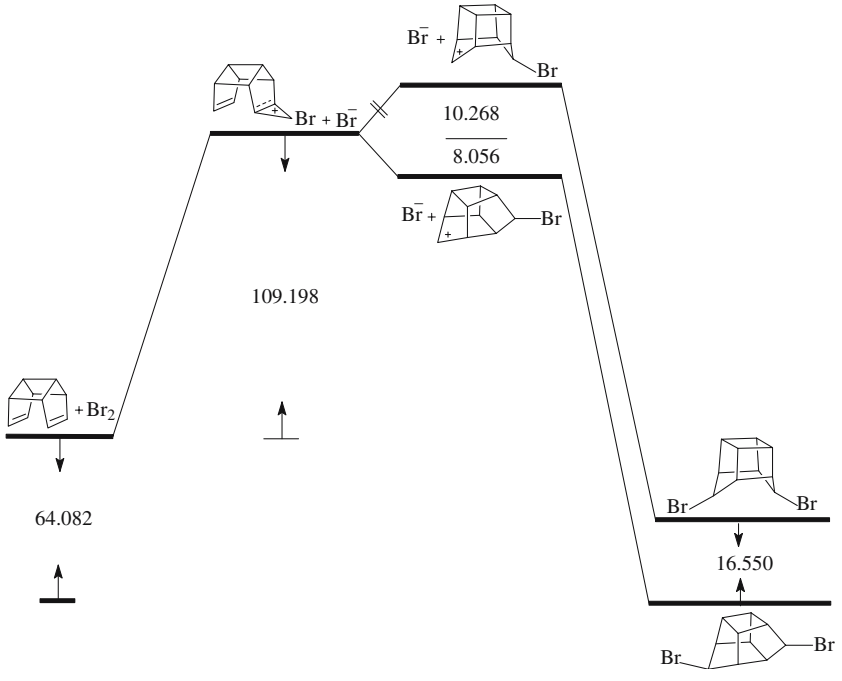
Scheme 3 The optimized geometries of products (B3LYP/6-311G*)

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 N-type product was 16.6 kcal mol^{-1} (MP2/6-311G*// HF/6-311G*) more stable than the U-type product.

Conclusions

Our investigations show that the double bonds of hypostrophene are *endo*-pyramidalized. The bridged bromonium cation was less stable than the N-type cation and more stable than the 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 isomerize into the less stable U-type cation, it is not possible for U-type products to be obtained in the reaction. The thermodynamic stability of the N-type dibromide products (*exo*, *exo* and *exo*, *endo* isomers) were almost identical. The U-type product was less stable than the N-type product.

Fig. 2 General energy diagram of the hypostrophene–bromine ($HS–Br_2$) system (kcal mol^{-1}) (MP2/6-311G*//HF/6-311G*)



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