

Scientific paper

Ab Initio and DFT Investigation of Electrophilic Addition Reaction of Chlorine to Tetracyclo[5.3.0.0^{2,6}.0^{3,10}]deca-4,8-diene

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Abstract

The geometry and the electronic structure of tetracyclo[5.3.0.0^{2,6}.0^{3,10}]deca-4,8-diene (hypostrophene) molecule were investigated by *ab initio* and DFT/B3LYP methods using the 6-31G(d) and 6-311G(d) basis sets. The double bonds of hypostrophene molecule are *endo* pyramidalized. The cationic intermediates and products formed in the addition reaction have been studied 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 solvent effect was evaluated using the conducting polarized continuum model (CPCM). The bridged chloronium cation was more stable than the U-type cation. Considering that the bridged cation does not isomerize into the more unstable U-type cation, it is not possible for U-type product to be obtained in the reaction. The bridged chloronium 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 dichloride molecule were almost identical. The N-type product was 12.201 kcal/mol (CPCM-B3LYP/6-311++G(2d,p)//B3LYP/6-311G(d)) more stable than the U-type product.

Keywords: Ab initio and DFT calculations, electrophilic addition, transannular reactions, intramolecular skeletal rearrangement, pyramidalization, hypostrophene

1. Introduction

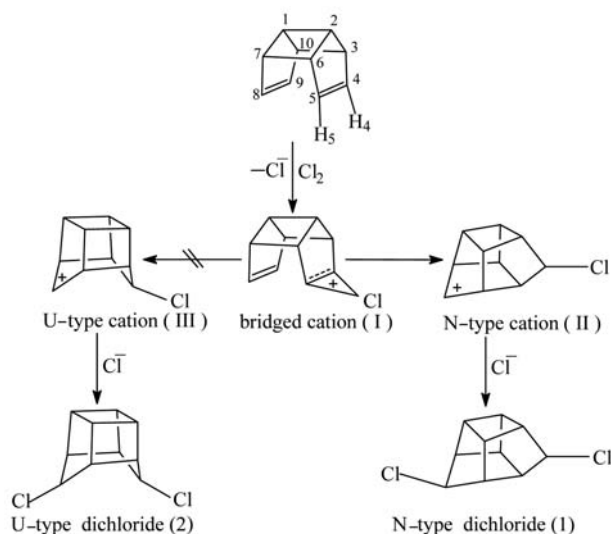
Rigid polycyclic molecules having isolated double bonds located in the laticyclic topology¹ and spatially in close proximity have provided suitable frameworks for the study of orbital interactions^{2–3} and transannular reactions.⁴ Attack of an electrophile to a molecule having two isolated double bonds in spatial proximity usually leads to transannular bridge formation, for which two formal possibilities, cross (N-type) and parallel (U-type), exist.^{5–7} 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.^{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 reaction has been rationalized by

Osawa et al. with the aid of the empirical force field calculations to depend on the thermodynamic stability of the products.⁵ A difference larger than 10 kcal/mol 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 the skeletal isomerization (with the 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 in the way 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 order to learn the inner mechanism and dynamic stereochemistry of the reaction in detail. The alkene's structure and nature play a vital role for the electrophilic addition reactions of the halogens into the face-to-face (juxtaposed) double bonded strained alkenes where they show characteristic features. The investigation of the geometric and electronic structure of alkenes are important for the pyramidalization of double bonds, the calculation of the other geometric parameters and the 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 substantial in order to explain the specifics of the electrophilic addition reactions.

The addition reactions of halogens to unsaturated strained molecule and the reaction intermediates have been quantum chemically investigated.^{21–32} In this connection, the theoretical investigations of the addition of bromine and chlorine to olefins with rigid structure have recently been reported by us.^{33–35} 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 chlorine to tetracyclo[5.3.0.0^{2,6}.0^{3,10}]deca-4,8-diene (hypostrophene) (Scheme 1).



Scheme 1.

In this work, the electrophilic addition of chlorine to hypostrophene has been studied theoretically and the structures and stabilities of the reaction cationic intermediates (bridged, N- and U-type cations) and products have been investigated by ab initio and DFT methods. Also, the

geometry and the electronic structure of the hypostrophene molecule were calculated by ab initio and DFT methods.

2. Methods of Calculation

The geometry and the electronic structure of the hypostrophene molecule have been investigated by ab initio SCF method with 6-31G(d)³⁶ and 6-311G(d)³⁷ basis sets. The calculations of the molecule have been also performed by using the density functional theory (DFT) method at the B3LYP/6-31G(d)^{38–39} and /6-311G(d) levels. 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/6-311G(d) method, their single point energies were calculated at the B3LYP/6-311++G(2d,p)³⁹ level. 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)^{40–41} method in cyclohexane ($\epsilon=2.023$). All stationary points have been characterized by calculating the vibrational frequencies and zero point vibrational energies have been added for all species. Full geometry optimization was carried out employing the *Polak-Ribiere* (conjugate gradient) algorithm⁴² (convergence of $0.00001 \text{ kcal mol}^{-1}$) and an RMS gradient at $0.001 \text{ kcal}(\text{\AA} \text{ mol})^{-1}$. The calculations have been performed with HyperChem 7.5 and Gaussian 03 program with an IBM PC Pentium IV computer.

3. Results and Discussion

Full geometric optimization of the hypostrophene molecule was performed 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 the light of the results of each method, the pyramidalization parameters^{43–44} of the molecule were evaluated with the aim of determining the structural deformation of 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)⁴³ and of the out-of-plane bending angle (χ) (out of plane angle: between plane C3C4C5C6 and plane H4C4C5H5 as seen Scheme 1)⁴⁴ 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 hypostrophene molecule)⁴⁵ were determined. These results are

Table 1. The calculated total energies (kcal/mol), double bond lengths (Å), distance (Å) and orientation (degree) between two double bonds and pyramidalization parameters (degrees) of hypostrophene.

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

given in Table 1. According to the determined results, the double bonds of hypostrophene molecule was endo pyramidalized. The analysis of frontier orbital (HOMO) of the molecule showed that the electron density ($q_{\mu, \text{HOMO}}$) in exo face of double bond was high (Fig. 1).

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 hypostrophene molecule should occur from the exo face. The polarization of chlorine and, subsequently, the heterolytic splitting of hypostrophene...Cl₂ (HS...Cl₂) molecular complex results in the formation of the bridged cation (I) (Scheme 2). This cation and its isomers were the possible intermediates of the addition reactions of chlorine to hypostrophene in gas phase and solvent medium (Scheme 2).

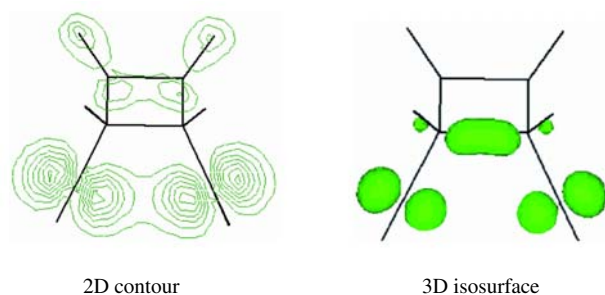


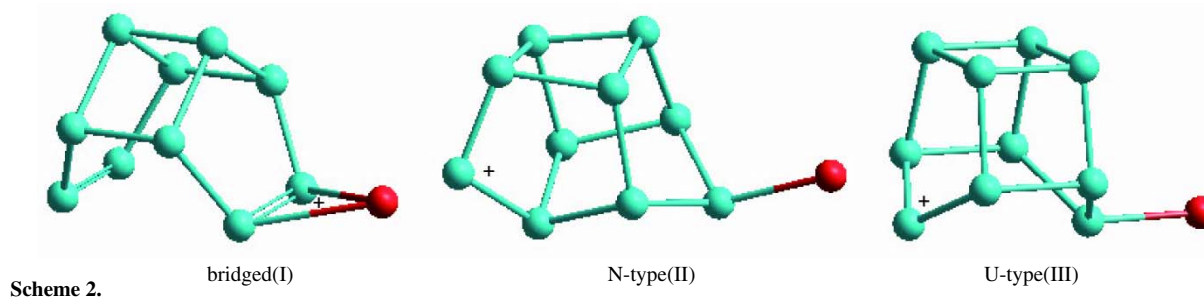
Figure 1. Electron density distribution (HOMO) of the hypostrophene (B3LYP/6-311G(d)).

In order to determine the structures and the relative stabilities of the predicted cationic intermediates, their full geometry optimization was performed using HF/6-311G(d), HF/6-311G(d,p) and B3LYP/6-311G(d) methods and the total energies (E_{tot}) were 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 each method, bridged chloronium 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 chloronium 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 chloronium cation to isomerize skeletally to the unstable U-type cation. As a result, the direction of the electrophilic addition reaction of chlorine to hypostrophene is determined by the direction of the skeletal isomerization of the bridged chloronium cation into N-type cation and N-type reaction product is obtained over N-type cation (a cation N-type-Cl⁻ couple was assumed as the transition form). Thus, theoretical investigations show that the ionic addition of the chlorine molecule to hypostrophene follows these steps: formation of the HS...Cl₂ molecular complex and decomposition of this complex to the bridged-chloronium ion; rearrange-

Table 2. The calculated relative energies of cations

Cations	Relative energy (kcal/mol)			
	HF/6-311G(d)	HF/6-311G(d,p)	B3LYP/6-311G(d)	B3LYP/6-311++G(2d,p)// B3LYP/6-311G(d)
I	14.072	13.814	7.792	6.078
II	0.0	0.0	0.0	0.0
III	17.286	17.202	11.737	11.718



ment of bridged-chloronium ion to the N-type cation; and nucleophilic attack of the chloride ion (Cl^-) on this cation.

The different configurations of the N-type dichloride molecule (exo, exo and exo, endo) and the geometric structure of exo,exo isomer (Scheme 3) of U-type dichloride molecule were optimized by HF/6-311G(d), HF/6-311G(d,p) and B3LYP/6-311G(d) methods and their total energies (E_{tot}) were calculated and their stereochemistries 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 the N-type dichloride molecule differed very little and their stabilities are nearly the same. Thus, thermodynamically, the possibility of the formation of both of these isomers was almost the same and feasible. The structure of the cation centre of N-type cation was investigated and it was determined that the attack of chloride ion to the centre, towards exo and endo faces, was not hindered sterically. This implies the possible sterical formation of both isomers. Therefore, as a result of the electrophilic addition reaction of chlorine to hypostrophene molecule,



Scheme 3.

Table 3. The calculated relative energies of products

Products	Relative energy (kcal/mol)			
	HF/6-311G(d)	HF/6-311G(d,p)	B3LYP/6-311G(d)	B3LYP/6-311++G(2d,p)// B3LYP/6-311G(d)
1	0.0	0.0	0.0	0.0
2	0.381	0.374	0.381	0.361
3	14.191	14.134	12.217	12.201

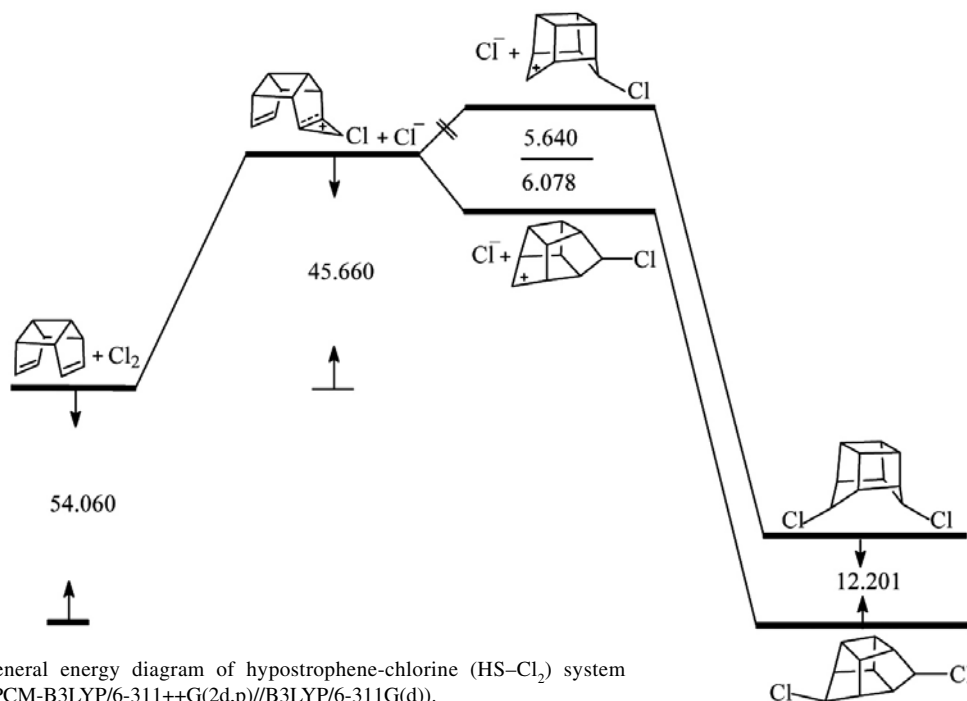


Figure 2. General energy diagram of hypostrophene-chlorine ($\text{HS}-\text{Cl}_2$) system (kcal/mol) (CPCM-B3LYP/6-311++G(2d,p)//B3LYP/6-311G(d)).

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Povzetek

Prispevek obravnava študijo elektronske strukture in geometrijo tetraciklo [5.3.0.0^{2,6}.0^{3,10}]deka-4,8-diena (hipostrofena) z uporabo *ab initio* in DFT/B3LYP kvantnokemijskih metod ter 6-31G(d) in 6-311G(d) baznih setov. Dvojne vezi v molekuli hipostrofena so *endo* piramidalizirane. Pri študiju kationskih intermediatov in produktov, ki nastanejo pri reakciji adicije molekule klora na hipostrofen, so bile uporabljene HF/6-311G(d), HF/6-311G(d,p), B3LYP/6-311G(d) in B3LYP/6-311++G(2d,p)//B3LYP/6-311G(d) metode. Vpliv topila je bil študiran z uporabo prevodnega polarizacijskega kontinuum modela (CPCM). Rezultati študije kažejo, da je premosteni kloronijev kation bolj stabilen kot kation U-tipa. Upošteva se, da premosteni kation ne izomerizira v manj stabilen kation U-tipa, ni verjetno, da bi pri reakciji nastajal produkt U-tipa. Premosteni kloronijev kation se pretvori v bolj stabilen kation N-tipa, kar vodi do ustreznega produkta N-tipa. Termodinamska stabilnost *ekso,ekso* in *ekso,endo* izomerov dikloridne molekule produkta N-tipa je skoraj identična. Produkt N-tipa je za 12.2 kcal/mol (CPCM-B3LYP/6-311++G(2d,p)//B3LYP/6-311G(d)) bolj stabilen od produkta U-tipa.