

Scientific paper

DFT Study on the Electrophilic Transannular Addition Reaction of Bromine to Tricyclo[4.2.2.2^{2,5}]dodeca-1,5-diene

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Abstract

The geometry and the electronic structure of tricyclo[4.2.2.2^{2,5}]dodeca-1,5-diene (TCDD) molecule were investigated by DFT/B3LYP and DFT/B3PW91 methods using the 6-311G(d,p) and 6-311++G(d,p) basis sets. The double bonds of TCDD molecule are *syn*-pyramidalized. The structure of π -orbitals and their mutual interactions for TCDD molecule were investigated. The cationic intermediates and products formed in the addition reaction have been studied by B3LYP/6-311G(d,p) and B3LYP/6-311++G(2d,p) methods. The solvent effect was evaluated using the conducting polarized continuum model (CPCM). The bridged bromonium cation was more stable than the U-type cation. The N-type products was 18.011 kcal/mol (CPCM-B3LYP/6-311++G(2d,p)//B3LYP/6-311G(d,p)) more stable than the U-type product. The reason for the skeletal structure of U-type being more unstable compared to the N-type is mainly due to the former having highly rigid cyclobutane rings. The configurations (molecular charge-transfer complex, transition states and intermediate) corresponding to the stationary points (minima or saddle points) of potential energy surface of the addition reaction have been investigated using the B3LYP/6-311G(d,p) method. The reaction is realized so as to follow the direction where transannular cross (N-type) bonding of double bonds (formation of C2–C6 bond) occur and more stable skeletal structure (N-type product) is obtained.

Keywords: Density functional theory, intramolecular skeletal rearrangement, transannular reactions, pyramidalization, solvent effects, tricyclo[4.2.2.2^{2,5}]dodeca-1,5-diene

1. Introduction

Attack of an electrophile to unsaturated strained 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.^{1–4} 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.^{5–20} Inagaki *et al.* advanced a perturbation theory to interpret those cases where preferential cross bridging takes place.²¹ While the orbital mixing effect must certainly be applicable 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 Ōsawa *et al.* with the aid of the empirical force field calculations to depend on the thermodynamic stability of the products.¹ 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.¹

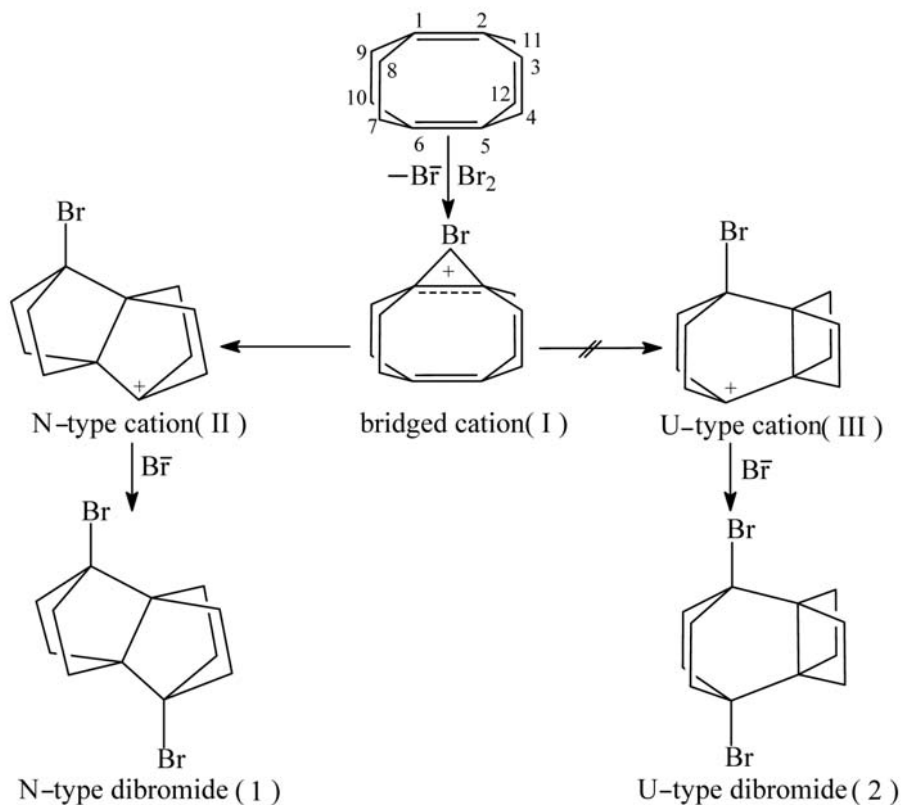
In order to understand the inner mechanism and dynamic stereochemistry of the reactions in question, it is important to identify the structure and stability of the intermediates (cyclic bridged, N- and U-type cations) produced during the reaction's progress and to investigate their skeletal rearrangement. During the course of the addition reaction it is possible for the cyclic bridged halogenium cation, which was produced as a result of the het-

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

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 is important for the pyramidalization of double bonds, the calculation of the other geometric parameters and the understanding of the mutual interaction of orbitals. These investigations are also important for the determination of the connections between the structure of the alkenes and their behaviour in 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.^{22–37} In this connection, the theoretical investigations of the addition of bromine and chlorine to olefins with rigid structure have recently been reported by us.^{38–45} In the continuation of our interest in the quantum-chemical studies related to the addition of halogens to unsaturated strained molecules, we wish to report the results obtained from the investigation of the mechanism and stereochemistry of addition reaction of bromine on tricyclo[4.2.2.2^{2,5}]dodeca-1,5-diene (TCDD). Bromination of the TCDD molecule gives only the adduct of N-type (1,5-addition product) (Scheme 1).^{9–11} However, the formation of U-type (1,6-addition product) adduct cannot be observed.

In this work the electrophilic addition of bromine to TCDD molecule has been studied theoretically and DFT (density functional theory) methods were 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 TCDD molecule. In addition, the potential energy surface (PES) of the TCDD-Br₂ system was investigated by B3LYP/6-311G(d,p) method and hence the structure and energies of the configurations (molecular charge-transfer complex, transition states, intermediate and product) corresponding to the stationary points (minima or saddle points) were determined.



Scheme 1.

2. Methods of Calculation

The geometry and the electronic structure of TCDD molecule have been investigated by using the DFT method at the B3LYP (Becke three-parameter hybrid exchange with Lee–Yang–Parr correlation)^{46,47} and B3PW91 (Becke three-parameter hybrid exchange with Perdew–Wang 1991 gradient corrected correlation)^{47,48} levels with the 6-311G(d,p) and 6-311++G(d,p)⁴⁹ basis sets. The predicted cationic intermediates and products formed in the addition reaction have been investigated using the B3LYP/6-311G(d,p) method. By using the optimized geometries of cations and products by B3LYP/6-311G(d,p) method, their single point energies were calculated at the B3LYP/6-311++G(2d,p)⁴⁹ 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 CPCM (conducting polarized continuum model)^{50,51} method (with UAKS cavities⁵²) in heptane. Also, molecular charge-transfer complex, transition states (TS1 and TS2) and intermediate of the addition reaction have been investigated using the B3LYP/6-311G(d,p) method. 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 performed with Gaussian 03⁵³ and HyperChem 8⁵⁴ program with an IBM PC Pentium IV computer.

3. Results and Discussion

Full geometric optimization of the TCDD molecule was done at the DFT/B3LYP and DFT/B3PW91 levels 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. In order to determine which functional will give results that conform to the experimental results, the geometry of the molecule was optimized by two functionals (B3LYP and B3PW91). The pyramidalization parameters^{55–57} were calculated with the aim of determining the structural deformation of the double bond. The values of the pyramidalization angle (ϕ), the angle between C1–C2 vector and C3C2C11 plane^{55,58} and of the out-of-plane bending angle (ψ) (out-of-plane angle between the planes

C3C2C1C8 and C9C1C2C11 or ψ which is defined as $\psi = 180^\circ - |D|$, D is the dihedral angle C3C2C1C9 as shown in Scheme 1)^{56–58} were calculated according to the results of each method. The distance (R_u) (distance between midpoint of opposing C=C double bonds), the other geometric parameters and the energies of the two highest occupied (HOMO and HOMO-1) MOs of TCDD molecule were calculated. These results, given in Table 1, showed that the double bonds of TCDD molecule are *syn*-pyramidalized. An X-ray structure of TCDD molecule showed C=C double bond lengths of 1.35 Å, pyramidalization angles ϕ and ψ of 27.3° and 35.6°, respectively, and a separation of the two double bonds of 2.395 Å.¹² It is evident that the methods used for the calculation of geometric parameters of the molecule gave similar results to the results obtained by X-ray.

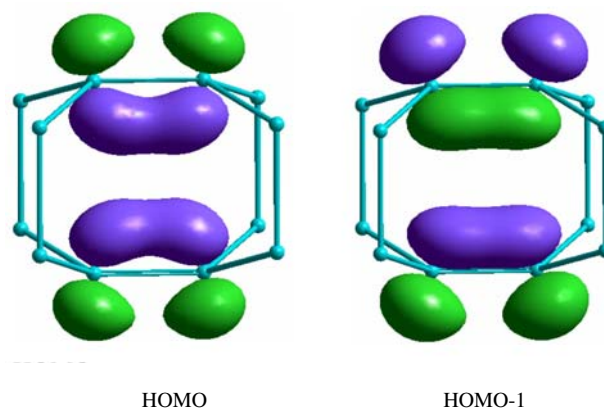


Figure 1. Electron distribution of the two highest occupied molecular orbitals (HOMO and HOMO-1) of the TCDD molecule (B3LYP/6-311G(d,p)).

The structure of the π -orbitals of the TCDD molecule and their mutual interactions were investigated. The double bonds of TCDD molecule are constrained to interact through-space and they may also be important for through-bond interactions. For the molecules having the distance (R_u) between their double-bonds less than 3Å, the interaction of the π -orbitals is efficient through space, hence for the TCDD molecule there must be a strong through-space interaction between its double bonds.^{59,60} On the other hand, for

Table 1. The calculated bond lengths (Å), distance (Å) between two double bonds, pyramidalization parameters (degrees) and energies (eV) of the two highest occupied (HOMO and HOMO-1) MOs of TCDD molecule.

Method	$r_{C=C}$	R_u	ϕ	ψ	ϵ_{HOMO}	ϵ_{HOMO-1}	$\Delta\epsilon^a$
B3LYP/6-311G(d,p)	1.350	2.411	27.306	35.981	-6.095	-6.150	0.035
B3LYP/6-311++G(d,p)	1.351	2.410	27.272	35.917	-6.177	-6.259	0.082
B3PW91/6-311G(d,p)	1.349	2.394	27.225	35.763	-6.068	-6.177	0.109
B3PW91/6-311++G(d,p)	1.350	2.393	27.272	35.715	-6.123	-6.231	0.108

^a $\Delta\epsilon = \epsilon_{HOMO} - \epsilon_{HOMO-1}$ energy gap

the TCDD molecule, the interaction between the π -orbital of the highly pyramidalized double bond and the σ -orbital of the four allyl groups is also strong, hence the through-bond interaction among the π -orbitals is strong. For the TCDD molecule whose double bonds were separated by odd number of σ bonds ($m = 3$) the mutual interactions of the π -orbitals through-space and through three σ bonds weaken each other and the splitting of the energy levels of the orbitals becomes lesser.^{57,58} The splittings of the energy levels ($\Delta\varepsilon = \varepsilon_{\text{HOMO}} - \varepsilon_{\text{HOMO-1}}$), which are a measure of the mutual interaction of the orbitals, were calculated and are given in Table 1. The HOMO and HOMO-1 of TCDD consist of the out-of-phase combination of, respectively, the a_g skeletal orbital and π^+ (in-phase) and the b_{1u} skeletal orbital and π^- (out-of-phase) (Fig. 1). It must be noted that the short transannular distance between the π bonds (the transannular interaction of the π -orbitals), leads to high pyramidalization of the double bond and a rise in the chemical activity of the considerably strained molecule.⁵⁹⁻⁶¹

The TCDD...Br₂ molecular charge-transfer (CT) complex is formed in the first step of electrophilic addition of bromine to TCDD molecule.^{24-26,28-30,32,34,35} The polarization of bromine and the subsequent heterolytic splitting of TCDD...Br₂ molecular CT-complex results in the formation of the bridged (I) cation (Scheme 1). This cation and its isomers are the possible intermediates of the addition reactions of bromine to TCDD 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 B3LYP/6-311G(d,p) method and the total energies (E_{tot}) were also calculated. By using the op-

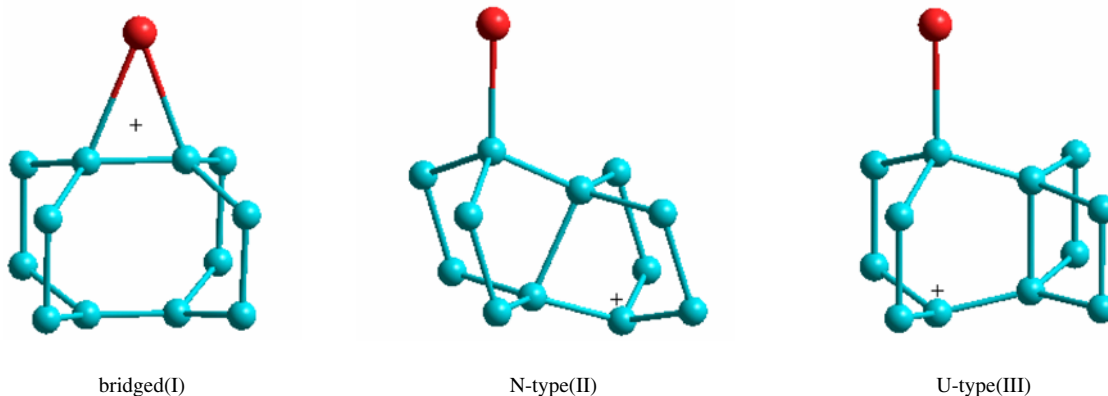
timized geometries of cations at the B3LYP/6-311G(d,p) level, their single point energies have been computed using B3LYP/6-311++G(2d,p) and CPCM-B3LYP/6-311++G(2d,p) methods. The calculated relative energies are given in Table 2.

According to the results of each method 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 TCDD 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 obtained over N-type cation.

The stereochemistry and the stable configurations of the reaction products were investigated by DFT method. The geometrical structure of the N- and U-type products (Scheme 3) were optimized by B3LYP/6-311G(d,p) method and their total energies were evaluated. The single point energies of products were calculated by using B3LYP/6-311++G(2d,p)//B3LYP/6-311G(d,p) and CPCM-B3LYP/6-311++G(2d,p)//B3LYP/6-311G(d,p) methods. The calculated relative energies are given in Table 3. According to the results of each method, 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 (Table 2 and Table 3).

Table 2. The calculated relative energies of cations.

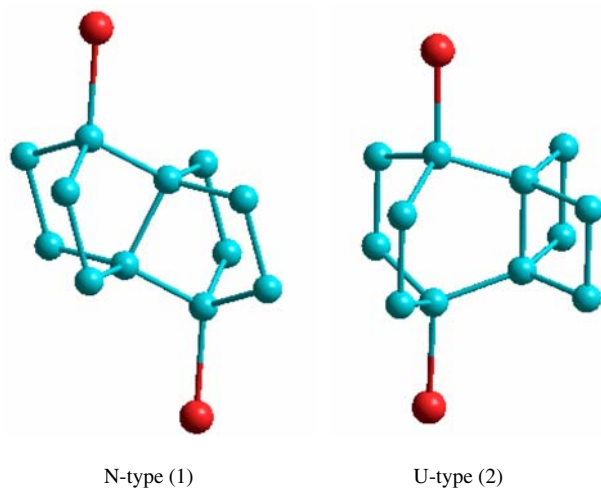
Cations	Relative energy (kcal mol ⁻¹)		
	B3LYP/6-311G(d,p)	B3LYP/6-311++G(2d,p) //B3LYP/6-311G(d,p)	CPCM-B3LYP/6-311++G(2d,p) //B3LYP/6-311G(d,p)
I	4.308	3.451	3.699
II	0.0	0.0	0.0
III	16.344	16.676	16.503



Scheme 2.

Table 3. The calculated relative energies of products.

Products	Relative energy (kcal mol ⁻¹)		
	B3LYP/6-311G(d,p)	B3LYP/6-311++G(2d,p) B//B3LYP/6-311G(d,p)	CPCM-B3LYP/6-311++G(2d,p) //B3LYP/6-311G(d,p)
1	0.0	0.0	0.0
2	18.266	17.966	18.011

**Scheme 3.**

For better determination of the direction of addition of bromine to TCDD molecule, molecular charge-transfer complex (TCDD...Br₂), transition states (TS1, TS-N and TS-U) and intermediate were also investigated. The optimized structures at the B3LYP/6-311G(d,p) level for the TCDD molecule, molecular charge-transfer complex (TCDD...Br₂), transition states (TS1, TS-N and TS-U), intermediate (INT) and products [P(N-type and U-type)] are given in Figure 2. The potential energy surface (PES) for the TCDD+Br₂ electrophilic addition reaction is illustrated in Figure 3. The addition reaction of bromine to TCDD starts with the exothermic formation of reactive, essential 1:1 TCDD...Br₂ complex, which is lower in energy than the reagents. The structure of the TS1, TS-N and TS-U resembles bridged bromonium cation, N-type cation and U-type cation, respectively. For TS1, the bromine atom in the three-membered ring has a positive charge (+0.133 e), the other bromine atom has a negative charge (-0.762 e). The C2–C6 distance is 2.672 Å and the C1–C2 bond distance is 1.477 Å, indicating that the C1–C2 bond partially transforms from a double bond to a single bond. These results imply that at the same time the interaction in the system transforms from π character to σ character. It should be emphasized that the structure of TS1 is similar to the structure of the bridged bromonium cation. For INT, the C1–C2 bond is single and the positive charge (+0.116 e) is localized over C2 atom. As the transannular interaction between the C2 cation centre and C5=C6 double bond increases, for INT C2–C6 distance

shortens. The distance between the bromide ion (Br⁻) is formed as a result of the lengthening of Br–Br distance to 5.931 Å. During the transition of the system from INT to TS-N, the decrease from 2.446 to 2.347 Å in the C2–C6 distance proves that for TS-N the transannular interaction increases.

One of the remarkable changes during the transition is the increase in the interaction between the C5 atom and the bromide ion (Br⁻) and the decrease in the C5–Br distance ($R_{C5-Br} = 3.861$ Å). With the reaction going the distances C2–C6 (INT: 2.446 Å, TS-N: 2.347 Å, P(N-type): 1.560 Å) and the C5–Br (INT: 4.394 Å, TS-N: 3.861 Å, P(N-type): 1.981 Å) gradually shorten, the angle C1C2C6 (INT: 72.929°, TS-N: 74.282°, P(N-type): 92.826°) gradually increases and the C5–C6 bond (INT: 1.366 Å, TS-N: 1.377 Å, P(N-type): 1.531 Å) gradually elongates, where finally the INT transforms into the N-type product via the transition state (TS-N). Thus, the intramolecular skeletal isomerisation of the INT into product (N-type) over TS-N is realized through the formation of C2–C6 bond over transannular cross-mechanism. In this step C5–Br bond is also formed and C5=C6 double bond transforms into a single bond. The reaction is realized through the transannular cross (N-type) bonding of the double bonds (formation of C2–C6 bond) and formation of the more stable skeletal structure. Therefore, the direction of the reaction is determined by the direction of the intramolecular skeletal isomerisation. The intramolecular skeletal rearrangement occurs in the direction of the more stable skeletal structure. The reaction progress is accompanied by shortening of the C2–C6 distance along the reaction pathway, eventually resulting in bond formation and (from TCDD+Br₂ to N-type product) C1C2C6 angle gradually increases (Figure 3). On the other hand, the reaction cannot take place through TS-U transition state because it has a higher energy barrier as compared to TS-N transition state. Therefore, addition reaction through TS-U transition state does not take place and U-type reaction product is not formed.

It should be noted that the stability of the N- and U-type structures (cations, transition states and products), is based on the transannular cross (N-type) and parallel (U-type) bonding of the double bonds and on the stability and thus, the type of the new rings formed from the skeletal structures (N- and U-type structures) into which the bridged cation (i.e. TS1) isomerized. On the other hand, the type of the new rings originates from the bonding type

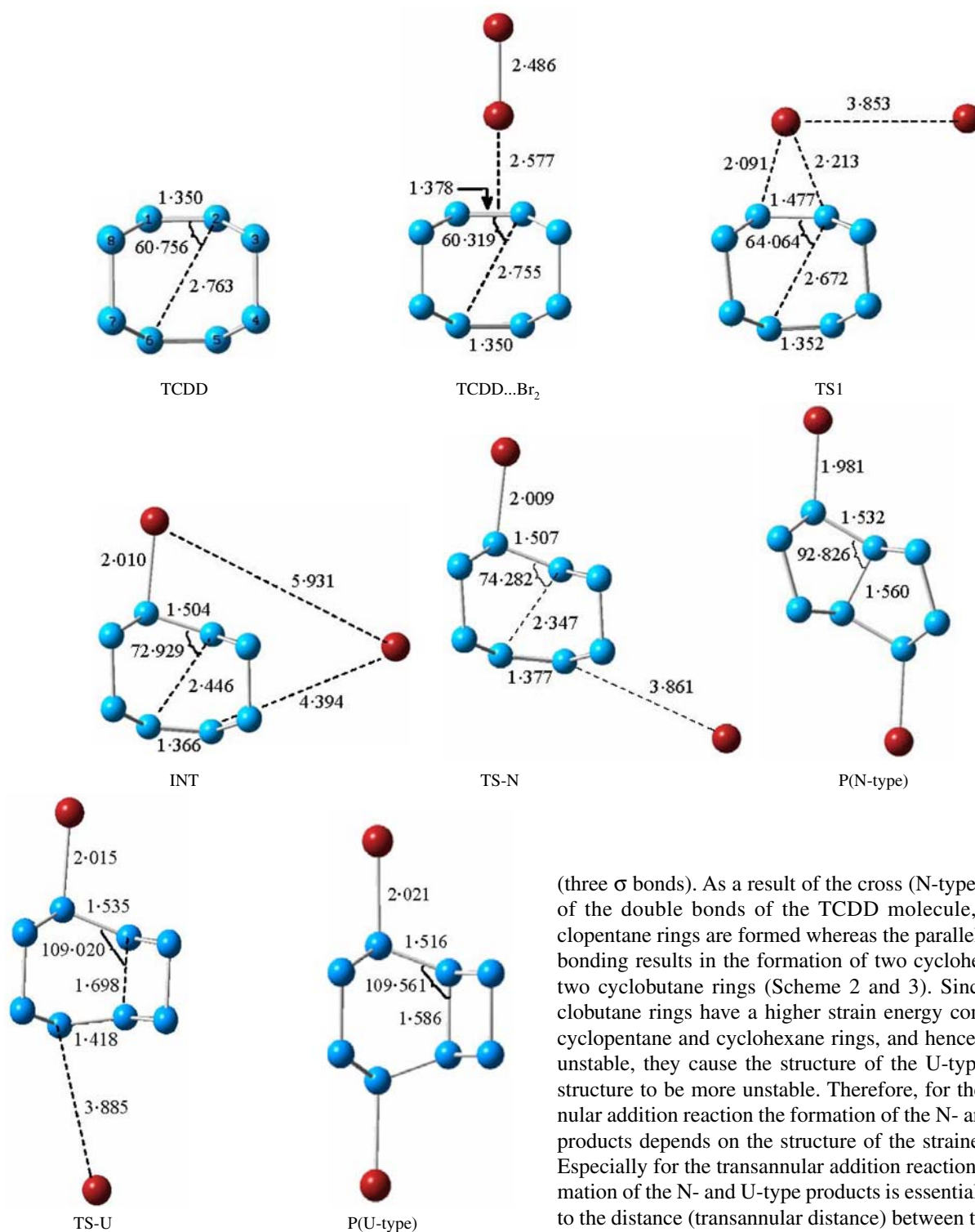


Figure 2. Optimized geometries of reactant (TCDD), molecular CT-complex (TCDD...Br₂), transition states (TS1, TS-U and TS-N), intermediate (INT) and products [P(N-type) and P(U-type)] at B3LYP/6-311G(d,p) level. Bond lengths are in Å and angles are in degrees.

(N- and U-type) and the number of the σ bonds connecting them to each other. For the TCDD molecule, the two double bonds were connected by four ethano bridges

(three σ bonds). As a result of the cross (N-type) bonding of the double bonds of the TCDD molecule, four cyclopentane rings are formed whereas the parallel (U-type) bonding results in the formation of two cyclohexane and two cyclobutane rings (Scheme 2 and 3). Since the cyclobutane rings have a higher strain energy compared to cyclopentane and cyclohexane rings, and hence are more unstable, they cause the structure of the U-type skeletal structure to be more unstable. Therefore, for the transannular addition reaction the formation of the N- and U-type products depends on the structure of the strained alkene. Especially for the transannular addition reactions, the formation of the N- and U-type products is essentially related to the distance (transannular distance) between the double bonds and number of the σ bonds (m) (the number of the carbon atoms of the bridge connecting the double bonds). For the reaction to take place, generally, the distance between the double bonds must be less than 3Å .^{1,12,18,62} The transannular addition reaction of the halogens to strained alkenes, which have 3 σ bonds ($m = 3$) connecting the double bonds, basically realizes in order to form N-type product and when $m = 4$, N- and U-type products are obtained.^{1,41–45}

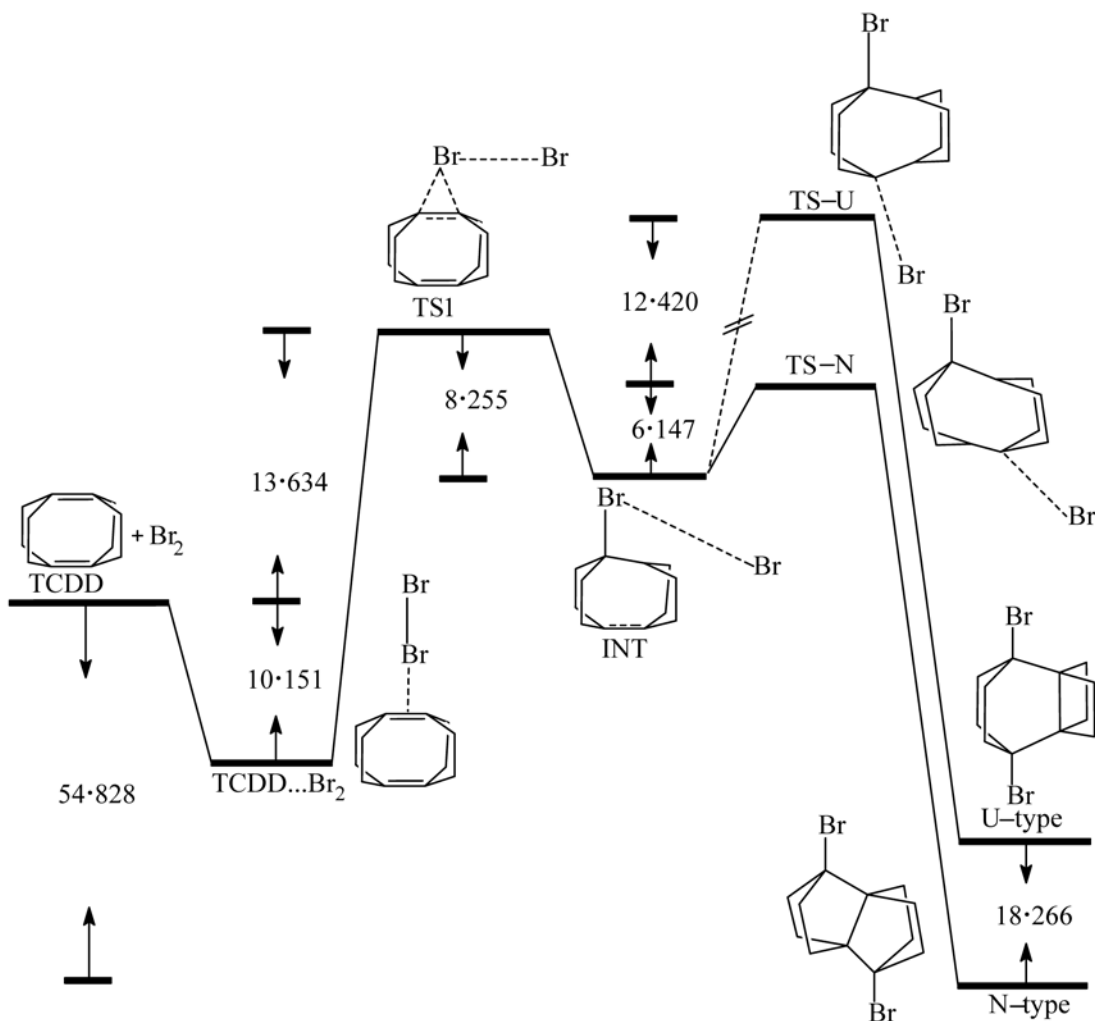


Figure 3. The potential energy surface for the electrophilic transannular addition reaction of bromine to TCDD. The energy values are given in kcal mol⁻¹ at B3LYP/6-311G(d,p) level.

4. Conclusions

The double bonds of TCDD molecule are *syn*-pyramidalized. The bridged bromonium cation is less stable than the N-type cation and more stable than the U-type cation. The N-type cation was 16.503 kcal/mol (CPCM-B3LYP/6-311++G(2d,p)//B3LYP/6-311G(d,p)) more stable than the U-type cation. The U-type cation and product being less stable than N-type cation and product, can be attributed to the U-type skeletal structure having highly strained cyclobutane rings. The direction of the reaction is determined by the direction of the intramolecular skeletal rearrangement that is realized by the formation of C2–C6 bond. The reaction progress is accompanied by shortening of C2–C6 distance along the reaction pathway, eventually resulting in bond formation and C1C2C6 angle gradually increases. The reaction is realized so as to follow the direction where transannular cross (N-type) bonding of double bonds (formation of C2–C6 bond) occurs and more stable skeletal structure (N-type product) is obtained.

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Povzetek

S pomočjo metod DFT/B3LYP in DFT/B3PW91 z baznima setoma 6-311G(d,p) in 6-311++G(d,p) smo raziskali geometrijo in elektronsko strukturo molekule triciklo[4.2.2.2^{2,5}]dodeka-1,5-diena (TCDD). Dvojni vezi v molekuli TCDD sta *sin*-piramidalizirani. Raziskali smo tudi strukturo π -orbital in njihove medsebojne interakcije. S pomočjo metod B3LYP/6-311G(d,p) in B3LYP/6-311++G(2d,p) smo raziskali kationske intermedie in produkte, nastale z adicijsko reakcijo. Vpliv topila smo določili s pomočjo kontinuirnega modela topila kot polarizabilnega prevodnika (CPCM). Premosten bromonijev kation je bil bolj stabilen kot kation U-tipa. Produkt N-tipa je bil za 18.011 kcal/mol (CPCM-B3LYP/6-311++G(2d,p)//B3LYP/6-311G(d,p)) bolj stabilen od produkta U-tipa. Razlog, da je skeletna struktura produkta U-tipa manj stabilna od produkta N-tipa, je predvsem dejstvo, da U-tip vsebuje več zelo rigidnih ciklobutanskih obročev. S pomočjo metode B3LYP/6-311G(d,p) smo raziskali konfiguracije (molekulske komplekse s prenosom naboja, prehodna stanja in intermedie), ki ustrezajo stacionarnim točkam (minimumi ali sedla) površja potencialne energije za adicijsko reakcijo. Reakcija poteka tako, da sledi smeri transanularne (N-tip) vezave dvojnih vezi (tvorba vezi C2–C6) in s tem nastane bolj stabilna skeletna struktura (produkt N-tipa).