

Density functional theory investigation of electrophilic addition reaction of bromine to tricyclo[4.2.2.2^{2,5}]dodeca-1,5-diene¹

Rza Abbasoglu

Received: 16 September 2008 / Accepted: 27 October 2008 / Published online: 10 December 2008
© Springer-Verlag 2008

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 /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. Potential energy surface (PES) of the TCDD-Br₂ system was studied by B3LYP/6-311++G(d,p) method and the configurations [molecular charge-transfer (CT) complex, transition states (TS1 and TS2), intermediate (INT) and product (P)] corresponding to the stationary points (minima or saddle points) were determined. Initially, a molecular CT-complex forms between Br₂ and TCDD. With a barrier of 22.336 kcal mol⁻¹ the CT-complex can be activated to an intermediate (INT) with energy 15.154 kcal mol⁻¹ higher than that of the CT-complex. The intermediate (INT) then transforms easily (barrier 5.442 kcal mol⁻¹) into the final, N-type product. The total bromination is slightly exothermic. Accompanying the breaking of Br-Br bond, C1-Br, C5-Br and C2-C6 bonds are formed, and C1 = C2 and C5 = C6 double bonds transform into single bonds. The direction of the reaction is determined by the direction of intramolecular skeletal rearrangement that is realized by the formation of C2-C6 bond.

Keywords DFT calculations · Intrinsic reaction coordinate · π - π interactions · Pyramidalization · Transannular reactions · Tricyclo [4.2.2.2^{2,5}]dodeca-1,5-diene

Introduction

Attack of an electrophile on an 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 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 [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 learn the details of the structure and energy changes that are realized during the course of the reactions in question, it is crucial to evaluate the potential energy surface (PES) of the reaction. Hence, this allows the inner mechanism and dynamic stereochemistry of the reaction to be understood in detail. What's more, the determination of the structures and energies of the configurations (molecular

¹Submitted in honor of the 75th birthday of Professor Nikolay F. Stepanov (Moscow State University), our teacher, colleague, and friend.

R. Abbasoglu (✉)
Department of Chemistry, Karadeniz Technical University,
61080 Trabzon, Turkey
e-mail: rabbas@ktu.edu.tr

charge-transfer complexes, transition states, intermediates and products) corresponding to the stationary points (minima or saddle points) by studying the PES of the reaction, is important in order to enlighten the inner mechanism and dynamic stereochemistry of the reaction.

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 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 continuance 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 from the investigation of the mechanism and stereochemistry of addition reaction of bromine 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 study, the potential energy surface (PES) of the TCDD-Br₂ system was investigated by DFT method and hence the structure and energies of the configurations (molecular charge-transfer complex (TCDD...Br₂), transition states (TS1 and TS2), intermediate and product) corresponding to the stationary points (minima or saddle points) were determined and the mechanism of the addition reaction was discussed. The electronic and geometric

structures of TCDD molecule were investigated by DFT methods and the mutual interaction of the π -orbitals were evaluated.

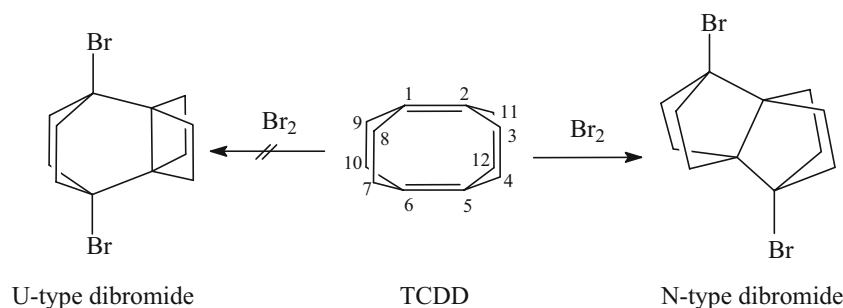
Methodology

The geometry and the electronic structure of the tricyclo[4.2.2.2^{2,5}]dodeca-1,5-diene (TCDD) molecule have been investigated by using the DFT (density functional theory) method at the B3LYP (Becke 3-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 configurations (molecular charge-transfer complex, transition states, intermediate and product) corresponding to the stationary points (minima or saddle points) of potential energy surface of the addition reaction have been investigated using the B3LYP/6-311++G(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 reactants, molecular charge-transfer complex and intermediate were characterized by all the real frequencies. The transition state has only one imaginary frequency. Connections of the transition states between two local minima have been confirmed by intrinsic reaction coordinate (IRC) [50–52] calculations at the B3LYP/6-311++G(d,p) level. The intrinsic reaction coordinates were followed to verify the energy profiles connecting each transition state to the correct local minima. The calculations have been performed with Gaussian 03 and HyperChem 8 program with an IBM PC Pentium IV computer.

Results and discussion

Full geometric optimization of the TCDD molecule was performed at the DFT/B3LYP and /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. The pyramidalization parameters [53–56] were determined with

Scheme 1 The electrophilic addition reaction of bromine to TCDD



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 [53, 56] 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) [54–56] 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 are given in Table 1. The results 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, a pyramidalization angles φ and ψ , respectively, of 27.3° and 35.6° and a separation 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.

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. The molecules for whom the distance (R_u) between its double bonds is less than 3 Å, the interaction of the π -orbitals is efficient through space, hence for the TCDD molecule, there must be strong through-space interaction between its double bonds [57, 58]. On the other hand, for the TCDD molecule, the interaction between the π -orbital of the highly pyramidalized double bond and the σ -orbital of the four allyl group is also strong hence the through-bond interaction among the π -orbitals is strong. For the TCDD molecule, whose double bonds were separated by an odd number of ($m=3$) σ bonds, the mutual interaction of the π -orbitals through-space and through the three σ bonds weakens each other and the splitting of the energy levels of the orbitals becomes less [57, 58]. The splitting of the energy levels ($\Delta\varepsilon = \varepsilon_{\text{HOMO}} - \varepsilon_{\text{HOMO-1}}$), which is a measure of the mutual interaction of

the orbitals, were calculated and are given in Table 1. The small value of $\Delta\varepsilon$ implies that for the TCDD molecule, the through-space and through-bond interaction of the π -orbitals are equal and opposite to each other. The HOMO and HOMO-1 of TCDD consists 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 considerable strain molecule [57–59].

The optimized structures at the B3LYP/6-311++G (d,p) level for the TCDD molecule and all stationary points (TCDD...Br₂ molecular CT-complex, transition states (TS1 and TS2) intermediate (INT) and product (P) are given in Scheme 2. Selected structural parameters (bond lengths) are listed in Table 2. The total energies (E_{tot}) and relative energies (E_r) at B3LYP/6-311++G(d,p) level for all the involved stationary points are summarized in Table 3. The potential energy surface (PES) for the TCDD + Br₂ electrophilic addition reaction is illustrated in Fig. 2.

As known, olefin-halogen molecular CT-complexes are formed in the first step of electrophilic addition of halogens to olefins [24–26, 28–30, 32, 34, 35]. 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 TCDD...Br₂ molecular CT-complex formed by the approach of a Br₂ molecule to the double bond in the axial position (Scheme 2). The molecular CT-complex (TCDD...Br₂) is of C_{2v} symmetry. The stabilization energy of the complex is 10.222 kcal mol⁻¹ (Fig. 2) and the equilibrium distance R_{X-Br} (X is the midpoint of the C = C bond of TCDD) is 2.567 Å (Scheme 2). The bond length of the bromine atoms ($R_{Br-Br}=2.487$ Å) in the molecular complex is longer than that of the isolated Br₂ molecule (2.332 Å). The bromine molecule in the TCDD...Br₂ complex is partially polarized. The bromine atom near the double bond has a partial positive charge(+0.031e) and the other one has a partial negative charge(-0.153 e). The results obtained for the

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

Metod	$r_{C=C}$	R_u	φ	ψ	$\varepsilon_{\text{HOMO}}$	$\varepsilon_{\text{HOMO-1}}$	$\Delta\varepsilon^a$
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 $\Delta\varepsilon = \varepsilon_{\text{HOMO}} - \varepsilon_{\text{HOMO-1}}$ energy gap

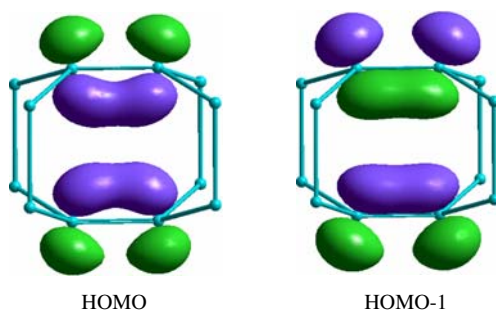


Fig. 1 Electron distribution of the two highest occupied molecular orbitals (HOMO and HOMO-1) of the TCDD molecule (B3LYP/6-311++G(d,p))

stability and geometric parameters of the TCDD...Br₂ complex shows that the π interaction between Br₂ and the highly pyramidalized double bond of the TCDD molecule is strong.

The second step of the reaction takes place over the transformation of CT-complex (TCDD...Br₂) into intermediate (INT) over TS1. According to the calculation of the IRC of TS1 and the further optimization calculation of the IRC results, TS1 connects CT-complex (TCDD...Br₂) and intermediate (INT). In this step, the C1-Br bond forms, the Br-Br bond breaks, the C2-C6 distance shortens, and C1 = C2 double bond transforms into single bond. As the system is activated to transition states TS1, considerable structural

change occurs. First, when the bromine approaches to double bond, R_{C1-Br} is shortened from 2.568 to 2.090 Å, where R_{Br-Br} is lengthened from 2.487 to 3.897 Å, indicating that the partial C1-Br bond formation and Br-Br bond breaking happen in a concerted way. For TS1, the bromine atom in the three-membered ring has positive charge (+0.134), the other bromine atom has negative charge (-0.763 e). Second, the C2-C6 distance is shortened from 2.754 to 2.682 Å and the C1-C2 bond distance is lengthened from 1.379 to 1.478 Å, indicating that the C1-C2 bond partly transforms from double bond to single bond. These results imply that at the same time, the interaction in the system transforms from π character into σ character. It should be emphasized that the structure of TS1 is similar to the structure of the bridged bromonium cation.

To activate CT-complex to TS1, 22.336 kcal mol⁻¹ are required. Over this barrier, the system goes to the intermediate (INT). The energy of INT is 15.154 kcal mol⁻¹ relative to CT-complex. The transformation of the TS1 to INT involves the shortening of the C2-C6 distance from 2.682 to 2.435 Å, the increase in C1-C2 bond length from 1.478 to 1.505 Å and the lengthening of the Br-Br distance from 3.897 to 5.912 Å. For INT, the C1-C2 bond is single and the positive charge(+0.117 e) is localized over C2 atom. As the transannular interaction between the C2 cation centre and C5 = C6 double bond increases, for INT,

Scheme 2 Optimized geometries of reactant (TCDD), charge-transfer complex (TCDD...Br₂), transition states (TS1 and TS2), intermediate (INT) and product (P) at B3LYP/6311++G(d,p) level. Bond lengths are in Å. Point group in paranthesis

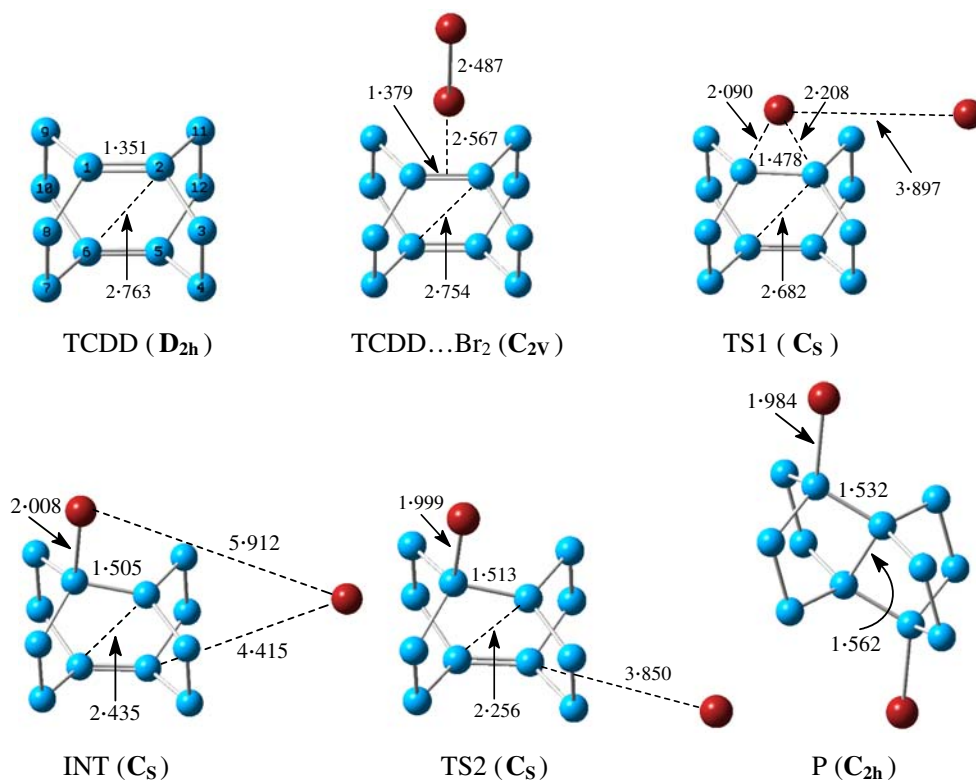


Table 2 Selected structural parameters of the TCDD-Br₂ stationary points^a

Geometry	TCDD + Br ₂	TCDD...Br ₂	TS1	INT	TS2	Product (P)
C1 = C2	1.351	1.379	1.478	1.505	1.513	1.532
C5 = C6	1.351	1.351	1.353	1.368	1.384	1.532
Br-Br	2.333	2.487	3.897	5.912	7.774	7.095
C1-Br	-	2.658	2.090	2.008	1.999	1.984
C5-Br	-	-	-	4.415	3.850	1.984
C2-C6	2.763	2.754	2.682	2.435	2.256	1.562
∠C1C2C6	60.282	60.716	63.622	73.109	76.291	92.761

^a Bond lengths are in Å and angles are in degrees. The numbers of the C atoms are shown in Scheme 2.

C2-C6 distance shortens. The distance between the bromide ion (Br⁻), which is formed as a result of the lengthening of Br-Br distance to 5.912 Å, and C5 atom is 4.415 Å.

Starting from INT, the system can be easily activated to the second transition state (TS2), which leads to the final product. According to the calculation of the IRC of TS2 and the further optimization calculation of the IRC results, TS2 connects intermediate (INT) and product (P). The energy barrier of the third step is 5.442 kcal mol⁻¹. It is obvious that from CT-complex across TS1 to INT, the second step along the reaction path, is rate limiting. The structure of INT is similar to that of TS2, with R_{C2-C6} further shortened (Scheme 2). During the transition of the system from INT to TS2, the decrease from 2.435 to 2.256 Å in the C2-C6 distance proves that for TS2 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} = 3.850 Å). With the reaction going, the distances C2-C6 (INT: 2.435 Å, TS2: 2.256 Å, P: 1.562 Å) and the C5-Br (INT: 4.415 Å, TS2: 3.885 Å, P: 1.984 Å) gradually shorten, the angle C1C2C6 (INT: 73.109°, TS2: 76.291°, P: 92.761°) gradually increases and the C5-C6 bond (INT: 1.368 Å, TS2: 1.379 Å, P: 1.532 Å) gradually elongates, where finally the INT transforms into the product (P) via

the transition state (TS2), with a low barrier of 5.442 kcal mol⁻¹. Thus, the intramolecular skeletal isomerisation of the INT into product (P) over TS2 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 single bond. Since serious geometric changes occur in the system in this step of the reaction, remarkable energy change is realized (Fig. 2).

Hence, the reaction takes place through the formation of three bonds (C1-Br, C2-Br and C2-C6), the splitting of one bond (Br-Br) and the transformation of two double bonds (C1 = C2 and C5 = C6) into single bonds. C1-Br bond is formed from TCDD..Br₂ to INT, Br-Br bond breaks and the C1 = C2 bond transforms into single bond and from INT to product (P), C2-C6 and C2-Br bonds are formed and C5 = C6 bond transforms into single bond. During the course of the reaction, the change in the bond order for selected bonds is given in Table 4. The calculated bond order values also confirm that in the second step of the reaction, (from TCDD..Br₂ to INT), C1-Br bond is formed, Br-Br bond breaks and C5 = C6 bond transforms into a single bond. At the same time, according to the results of these calculations, in the third step of the reaction (from INT to product) C2-C6, C2-Br bonds are formed and the C5 = C6 bond transforms into C5-C6 bond.

The energy of the product (P) is -54.123 kcal mol⁻¹ relative to the initial reactants (TCDD + Br₂), the bromination is thermodynamically favored (Fig. 2). The N-type product was 18.011 kcal mol⁻¹ [B3LYP/6-311++G (d,p)] more stable than the U-type product. The reaction is realized through the transannular cross (N-type) bonding of the double bonds (formation of C2-C6 bond) and formation of more stable skeletal structure. Therefore, the direction of the reaction is determined by the direction of the intramolecular skeletal isomerisation. The reaction progress is accompanied by shortening of C2-C6 distance along the reaction pathway, eventually resulting in bond formation and [from TCDD+Br₂ to product (P)] C1C2C6 angle gradually increases (Fig. 2).

Table 3 Total energies E_{tot} and relative energies E_r of various species involved in the reaction of Br₂ with TCDD using B3LYP/6-311++G (d,p) level of theory

Species	E _{tot} (hartree)	E _r (kcal mol ⁻¹)
TCDD+Br ₂	-5615.217042	0.0
TCDD...Br ₂	-5615.233173	-10.112
TS1	-5615.197562	12.224
INT	-6615.209006	5.042
TS2	-5615.200333	10.484
Product (P)	-5615.303292	-54.123

Table 4 Bond order of selected bonds of the TCDD-Br₂ stationary points^a

Bond	TCDD + Br ₂	TCDD...Br ₂	TS1	INT	TS2	Product (P)
C1 = C2	1.854	1.707	1.022	0.995	0.978	0.956
C5 = C6	1.854	1.853	1.852	1.744	1.494	0.956
Br-Br	1.000	0.856	0.075	0.029	0.0	0.0
C1-Br	-	0.085	0.803	0.912	0.927	0.949
C5-Br	-	-	-	0.007	0.007	0.949
C2-C6	-	-	0.002	0.055	0.216	0.940

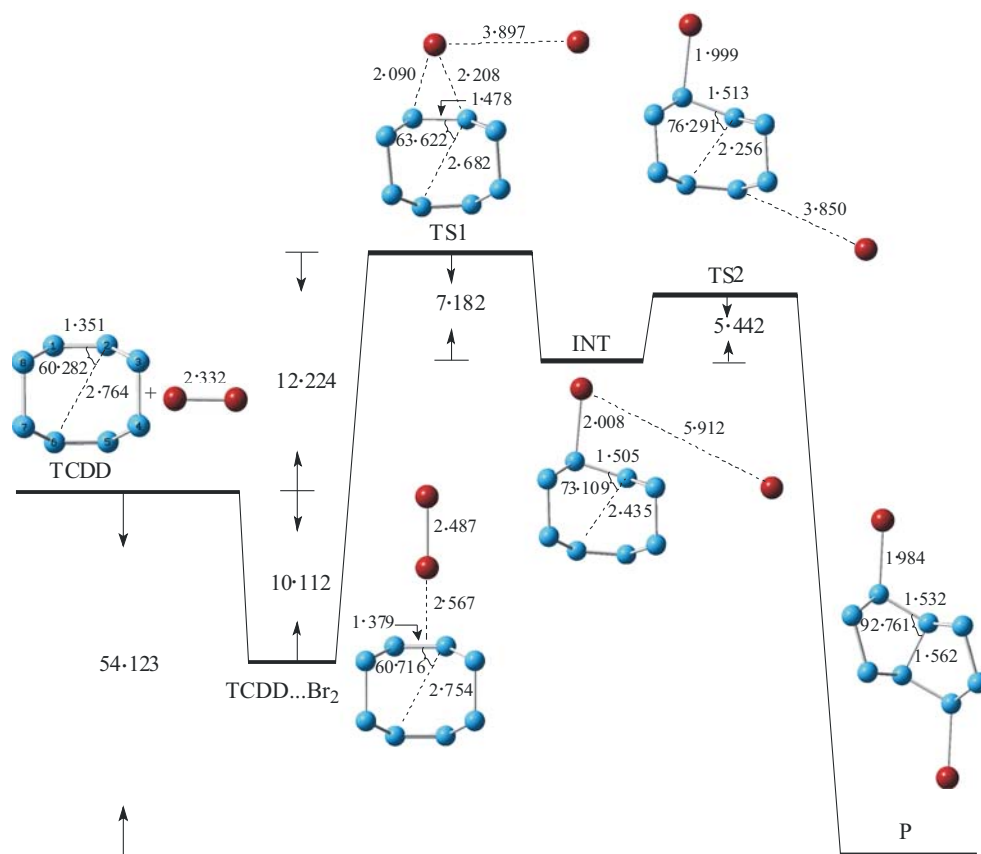
^a The numbers of the C atoms are shown in Scheme 2.

Conclusions

The bromination of tricyclo[4.2.2.2^{2,5}]dodeca-1,5-diene is a typical electrophilic transannular addition reaction. The present reaction pathway can be divided into three steps. First, the exothermic formation of reactive, essential 1:1 TCDD...Br₂ molecular CT-complex, for which the stabilization energy is 10.112 kcal mol⁻¹. Second, the prereactive CT-complex is activated to an intermediate (INT) 15.154 kcal mol⁻¹ higher in energy, the barrier of the rate-limiting step is 22.336 kcal mol⁻¹. Third, the intermediate

(INT) transforms into the final product (P) with a barrier of 5.442 kcal mol⁻¹. Accompanying the C1-Br bond formation, Br-Br bond splits and C1 = C2 bond transforms into C1-C2 in the second step and C2-C6, C2-Br bonds are formed and C5 = C6 bond transforms into C5-C6 bond in the third step. The direction of the reaction pathway is determined by the direction of the intramolecular skeletal isomerisation. 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 a more stable skeletal structure (N-type product) is obtained.

Fig. 2 Potential energy profile along the minimal energy pathway for the stepwise mechanisms of the electrophilic transannular addition reaction of bromine to TCDD. The energy values are given in kcal mol⁻¹ at B3LYP/6311++G(d,p) level. Bond lengths are in Å and angles are in degrees



References

- Osawa E, Aigami K, Inamoto Y (1978) *Tetrahedron* 34:509–515. doi:10.1016/0040-4020(78)80044-1
- Lin CT, Wang NJ, Yeh YL, Chou TC (1995) *Tetrahedron* 51:2907–2928. doi:10.1016/0040-4020(95)00041-6
- Lin CT, Wang NJ, Tseng HZ, Chou TC (1997) *J Org Chem* 62:4857–4861. doi:10.1021/jo970299c
- Lin CT, Hsu HC, Chou TC (1999) *J Org Chem* 64:7260–7264. doi:10.1021/jo990569 m
- Soloway SB, Damiana AM, Sim JW, Bluestone H, Lidov RE (1960) *J Am Chem Soc* 82:5377–5385. doi:10.1021/ja01505a024
- Franz HJ, Hobold W, Hohn R, Muller-Hagen G, Muller R, Pritzkow R et al. (1970) *J Prakt Chem* 320:622–634. doi:10.1002/prac.19703120412
- Sasaki T, Kanematsu K, Kondo A (1974) *J Org Chem* 39:2247–2251
- Haufe G, Kleinpeter E, Muhlstadt M, Graefe J (1978) *Monatshfte f. Chem (Kyoto)* 109:575–585
- Matturro MG, Adams RD, Wiberg KB (1981) *Chem Commun* 17:878–879
- Uemura S, Fukuzawa S, Toshimitsu A, Masaya O (1983) *J Org Chem* 48:270–273. doi:10.1021/jo00150a029
- Wiberg KB, Matturro MG, Okarma PJ, Jason ME (1984) *J Am Chem Soc* 6:2194–2200. doi:10.1021/ja00319a047
- Wiberg KB, Adams RD, Okarma PJ, Matturro MG, Segmiller B (1984) *J Am Chem Soc* 6:2200–2206
- Kimura M, Morossawa S (1985) *J Org Chem* 50:1532–1534. doi:10.1021/jo00209a035
- Shea KJ, Greeley AC, Nguyen S, Beauchamp PD, Aue DH, Witzeman JS (1986) *J Am C Chem Soc* 108:5901–5908. doi:10.1021/ja00279a040
- Haufe G, Alvernhe G, Laurent A (1986) *Tetrahedron Lett* :4449–4452. doi:10.1016/S0040-4039(00)84975-8
- Murty BARC, Pinkos R, Spurr PR, Fessner WD, Lutz G, Fritz H et al. (1992) *Chem Ber* 125:1719–1739. doi:10.1002/cber.19921250728
- Pinkos R, Melder JP, Weber K, Hunkler D, Prinzbach H (1993) *J Am Chem Soc* 115:7173–7191. doi:10.1021/ja00069a015
- Herges R, Neumann H (1995) *Liebigs Ann* :1283–1289. doi:10.1002/jlac.1995199507170
- Robinson RE, Myers DY (1999) *Tetrahedron Lett* :1099–1100. doi:10.1016/S0040-4039(98)02643-4
- Günbas DD, Algi F, Hökelek T, Watson WH, Balci M (2005) *Tetrahedron* 61:11177–11183. doi:10.1016/j.tet.2005.09.019
- Inagaki S, Fujimoto H, Fukui K (1976) *J Am Chem Soc* 98:4054–4061. doi:10.1021/ja00430a006
- Belluci G, Chiappe C, Bianchini R, Lenoir D, Herges RJ (1995) *J Am Chem Soc* 117:12001–12002. doi:10.1021/ja00153a025
- Herges R (1995) *Angew Chem Int Ed Engl* 34:51–53. doi:10.1002/anie.199500511
- Ruiz E, Dennis R, Salahub R, Vela A (1996) *J Phys Chem* 100:12265–12276. doi:10.1021/jp9533077
- Brown RS (1997) *Acc Chem Res* 30(3):131–137. doi:10.1021/ar960088e
- Bianchini R, Chiappe C, Lenoir D, Lemmen P, Herges R, Grunenberg J (1997) *Angew Chem Int Ed Engl* 36:1284–1287. doi:10.1002/anie.199712841
- Smith WB (1998) *J Org Chem* 63:2661–2664. doi:10.1021/jo9722459
- Bianchini R, Chiappe C, Moro LG, Lenoir D, Lemmen P, Goldberg N (1999) *Chem Eur J* 5:1570–1580. doi:10.1002/(SICI)1521-3765(19990503)5:5<1570::AID-CHEM1570>3.0.CO;2-A
- Chiappe C, Rubertis AD, Lemmen P, Lenoir D (2000) *J Org Chem* 65:1273–1279. doi:10.1021/jo9910076
- Chiappe C, Rubertis AD, Detert H, Lenoir D, Wannere C, Schleyer RP (2002) *Chem Eur J* 8:967–978. doi:10.1002/1521-3765(20020215)8:4<967::AID-CHEM967>3.0.CO;2-I
- Rathere R, Lindeman SV, Zhu CJ, Mori T, Schleyer RP, Kochi JK (2002) *J Org Chem* 67:5106–5116. doi:10.1021/jo0200724
- Lenoir D, Chiappe C (2003) *Chem Eur J* 9:1037–1044. doi:10.1002/chem.200390097
- Chiappe C, Detert H, Lenoir D, Pomelli CS, Ruasse MF (2003) *J Am Chem Soc* 125:2864–2865. doi:10.1021/ja027630 g
- Herges R, Papaflippopoulos A, Hess K, Chiappe C, Lenoir D, Detert H (2005) *Angew Chem Int Ed* 44:1412–1416. doi:10.1002/anie.200461632
- Chiappe C, Pomelli CS, Lenoir D, Wattenbach C (2006) *J Mol Model* 12:631–639. doi:10.1007/s00894-005-0038-2
- Wang SC, Tantillo DJ (2006) *Eur J Org Chem* 738–745. doi:10.1002/ejoc.200500742
- Balci M, Güney M, Daştan A, Azizoglu A (2007) *J Org Chem* 72:4756–4762. doi:10.1021/jo070253b
- Abbasoglu R (2004) *J Mol Struct THEOCHEM* 686:1–5. doi:10.1016/j.theochem.2004.06.054, and references therein
- Abbasoglu R, Yilmaz S, Gök Y (2005) *Indian J Chem* 44A:221–226
- Abbasoglu R, Yilmaz S (2006) *J Mol Model* 12:290–296. doi:10.1007/s00894-005-0031-9
- Abbasoglu R (2006) *J Mol Model* 12:991–995. doi:10.1007/s00894-006-0113-3
- Abbasoglu R (2007) *J Mol Model* 13:425–430. doi:10.1007/s00894-006-0161-8
- Abbasoglu R (2007) *J Mol Model* 13:1215–1220. doi:10.1007/s00894-007-0236-1
- Abbasoglu R, Uygur Y (2007) *Indian J Chem* 46A:396–400
- Abbasoglu R, Magerramov A (2007) *Acta Chim Slov* 54:882–887
- Lee C, Yang W, Parr RG (1988) *Phys Rev B* 37:785–789. doi:10.1103/PhysRevB.37.785
- Becke AD (1993) *J Chem Phys* 98:5648–5652. doi:10.1063/1.464913
- Perdew JP, Wang Y (1992) *Phys Rev B* 45:244–249. doi:10.1103/PhysRevB.45.13244
- Krishnan R, Binkley JS, Seeger R, Pople JA (1980) *J Chem Phys* 72:650–654. doi:10.1063/1.438955
- Page M, Mclver JW Jr (1988) *J Chem Phys* 88:922–935. doi:10.1063/1.454172
- Gonzalez C, Schlegel HB (1989) *J Chem Phys* 90:2154–2161. doi:10.1063/1.456010
- Gonzalez C, Schlegel HB (1990) *J Phys Chem* 94:5523–5527. doi:10.1021/j100377a021
- Borden WT (1989) *Chem Rev* 89:1095–1109. doi:10.1021/cr00095a008
- Ermer O, Bell P, Mason SA (1989) *Angew Chem Int Ed Engl* 28:1239–1241. doi:10.1002/anie.198912391
- Margtic D, Williams VR, Warrenner R (2003) *J Org Chem* 68:9186–9190. doi:10.1021/jo035110d
- Vazquez S, Camps P (2005) *Tetrahedron* 61:5147–5208. doi:10.1016/j.tet.2005.02.007
- Hoffmann R, Imamura A, Hehre WJ (1968) *J Am Chem Soc* 90:1499–1509. doi:10.1021/ja01008a018
- Hoffmann R (1971) *Acc Chem Res* 4:1–9. doi:10.1021/ar50037a001
- Watson WH (1983) *Stereochemistry and reactivity of systems containing π electrons*. Verlag Chemie International, Deerfield beach, Florida
- Camps P, Perez F, Vazquez S (1997) *Tetrahedron* 53:9727–9734. doi:10.1016/S0040-4020(97)00595-4