DFT Study on the Electrophilic Addition Reaction of Chlorine to Tricyclo[4.2.2.2.5]dodeca-1,5-diene

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Halogenation of the tricyclo[4.2.2.2.5]dodeca-1,5-diene (TCDD) molecule gives only the adduct of N-type\(^1\). However, the formation of U-type adduct can’t be observed.

In this study, the electronic and geometric structures of TTDD molecule were investigated by B3LYP/6-311+G(d) method and the mutual interaction of the π-orbitals were evaluated. Potential energy surface (PES) of the TCDD-Cl\(_2\) system was studied by B3LYP/6-311+G(d) method and the configurations (molecular TCDD...Cl\(_2\) complex, transition states (TS1 and TS2), intermediate (INT) and product (P) corresponding to the stationary points (minima or saddle points) were determined. All energy minima and TS's were characterized by frequency analysis. The intrinsic reaction coordinate (IRC) were followed to verify the energy profiles connecting each TS to the correct local minima. When the CT-complex is highly stable, the high pyramidalization of the double bond and the interactions of the π-orbitals are important. The structure of TS1 is similar to the structure of the bridged bromonium cation. The N-type product is obtained over TS2, which has a similar structure to the N-type cation. The direction of the flow of this reaction is determined by the direction of the intramolecular skeletal isomerization. The intramolecular skeletal rearrangement occurs in the direction of more stable skeletal structure.

Energetic profile (kcal/mol) for the potential energy surface of the TCDD+Cl\(_2\) reaction

Reference: