Nature of the ring-closure process along the rearrangement of octa-1,3,5,7-tetraene to cycloocta-1,3,5-triene from the perspective of the electron localization function and catastrophe theory.

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Streszczenie

We analyze the behavior of the energy profile of the ring-closure process for the transformation of (3Z,5Z)-octa-1,3,5,7-tetraene 5 to (1Z,3Z,5Z)-cycloocta-1,3,5-triene 6 through a combination of electron localization function (ELF) and catastrophe theory (CT). From this analysis, concepts such as bond breaking/forming processes, formation/annihilation of lone pairs, and other electron pair rearrangements arise naturally through the reaction progress simply in terms of the different ways of pairing up the electrons. A relationship between the topology and the nature of the bond breaking/forming processes along this rearrangement is reported. The different domains of structural stability of the ELF occurring along the intrinsic reaction path have been identified. The reaction mechanism consists of six steps separated by fold and cusp catastrophes. The transition structure is observed in the third step, d(C1-C8) = 2.342 Å, where all bonds have topological signature of single bonds (C-C). The "new" C1-C8 single bond is not formed in transition state and respective catastrophe of the ELF field (cusp) is localized in the last step, d(C1-C8) ≈ 1.97 Å, where the two monosynaptic nonbonding basins V(C1) and V(C8) are joined into single disynaptic bonding basin V(C1,C8). The V(C1,C8) basin corresponds to classical picture of the C1-C8 bond in the Lewis formula. In cycloocta-1,3,5-triene 6 the single C1-C8 bond is characterized by relatively small basin population 1.72e, which is much smaller than other single bonds with 2.03 and 2.26e.

Słowa kluczowe

electron localization function, catastrophe theory, chemical bond, ring-closure process, electrocyclic reactions, cyclooctatriene, octatetraene