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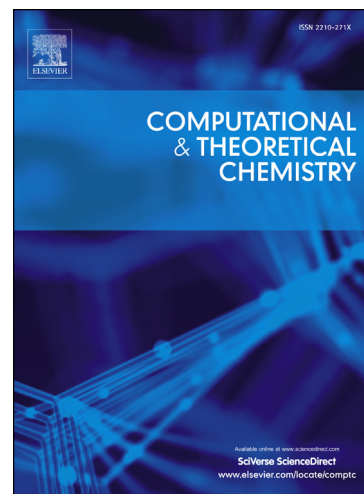
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Peculiar structure of the potential energy surfaces of typical electrocyclic reactions in the areas of the symmetry-forbidden reaction paths

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The mechanisms of the electrocyclic ring opening reactions of cyclobutene to *trans*-1,3-butadiene and 1,3-cyclohexadiene to 1,3,5-hexatriene were computationally studied with the use of B3LYP/6-311++G(d,p), MP2/6-311G++(3df,2p), CCSD/6-311++G(df,p), CCSD/6-311G(df,p) and CCSD(T)/6-311++G(df,p)//CCSD methods. Special attention was paid to the study of the potential energy surfaces (PESs) of both systems in the domains pertaining to the disrotatory movement of the vicinal methylene groups. No symmetry-forbidden disrotatory reaction channel was found within the PES of the cyclobutene – 1,3-butadiene system. Instead of that, disrotatory rotation of two methylene groups of cyclobutene results in elimination of a molecule of dihydrogen giving rise to the formation of a low-stable π -complex H_2 -cyclobutadiene. Similar type π -complex H_2 -benzene was also located on the 1,3-cyclohexadiene - 1,3,5-hexatriene PES along the disrotatory reaction coordinate. The topologies of the PESs of both systems analyzed on the basis of the patterns of the gradient lines are characterized by an existence on both of them of valley-ridge inflection (VRI) points corresponding to the bifurcation of the disrotatory reaction paths leading to the formation of the π -complexes formed upon elimination of a dihydrogen molecule from cyclobutene and 1,3-cyclohexadiene.

Keywords: *ab initio* calculations, density functional theory, potential energy surface, reaction path, valley-ridge inflection point.

1. Introduction

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