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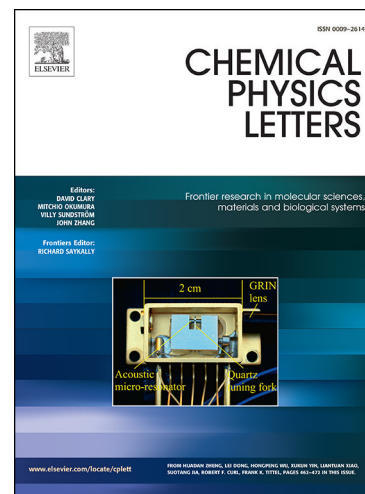
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The transition state of the automerization reaction of cyclobutadiene: a theoretical approach using the Restricted Active Space Self Consistent Field method[†]

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Abstract

The application of the Restricted Active Space Self Consistent Field (RASSCF) quantum chemical method using an extended active space and including σ - σ , π - σ and π - π dynamical electron correlation shows that the transition state structure for the automerization reaction of cyclobutadiene is an isosceles trapezium. This transition state is obtained without any symmetry constraints. The calculated energy barrier height involving the zero point vibrational energy corrections is $9.62 \text{ kcal}\cdot\text{mol}^{-1}$ (0.417 eV), with the corresponding rate constant being equal to $0.18 \times 10^9 \text{ s}^{-1}$ (or $7.1 \times 10^{10} \text{ s}^{-1}$ in case of using the vibrational energy splitting tunneling method).

Keywords:

Cyclobutadiene Transition State
Cyclobutadiene Automerization
Cyclobutadiene RASSCF

1. Introduction

Cyclobutadiene (CBD) is a fascinating molecule that has puzzled experimental and theoretical chemists for more than 80 years [1-3]. It has been characterized as the Mona Lisa of organic chemistry [4] due to its extreme chemical instability and consequently to its fleeting existence and because it has stimulated the scientific imagination by challenging the interpretive instincts. After its synthesis in 1965 by Petit and coworkers [5], it was found that the molecule is stable in matrices at very low temperatures, usually below 35 K [6,7], and inside the cavity of a hemicarcerand [4] where it was found to be very stable for months even at room temperatures. In both cases the molecules remain far apart from each other, no other molecules can enter the cavity and thus no reaction can take place. Its ground state (S_0) structure has been proved both theoretically [8] and experimentally [9-11] to be a rectangular singlet (D_{2h} symmetry) with two alternating pairs of equal single and double bonds.

One of the most studied problems concerning cyclobutadiene is the mechanism of the automerization reaction which involves the interconversion of the two equivalent rectangular structures via a transition structure. The geometry of this transition structure, characterized by one negative frequency, is always assumed to be a perfect square of D_{4h} symmetry which is found by

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[†] This paper is dedicated to our teacher, Professor

Antonios K. Zarkadis (University of Ioannina, Greece)

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