

Hydrogen-mediated Stone-Wales isomerization of dicyclopenta[*de,mn*]anthracene

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Abstract The mechanism of transformation of two radicals (R1p and R1i) obtained by addition of a hydrogen atom to an external and internal carbon atom of dicyclopenta[*de,mn*]anthracene (P1) was investigated. Two pathways were revealed. The first mechanism is a one-step process, whereas the second mechanism includes two transition states and a cyclobutyl intermediate. The formation of R1p and R1i and the homolytic cleavage of the radicals obtained during the isomerization processes were also examined. In both pathways the addition of a hydrogen atom to the internal carbon significantly lowers the activation energy for hydrogen-mediated isomerization of P1 to acefluoranthene. This finding could be explained by the specific electronic structures of the transition states and intermediates participating in the isomerization processes.

Keywords Activation energy lowering ·
Density functional theory · Electronic structure ·
Radical mechanism

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Introduction

Polycyclic aromatic compounds (PAHs) are generated during incomplete combustion of hydrocarbon-containing materials. They are considered as environmental pollutants, and some of them are responsible for the genotoxicity of combustion products. The genotoxicity of these PAHs is attributed to their specific structure, which usually includes the presence of five-membered rings (CP-PAHs) [1–3]. It was found that at high temperatures CP-PAHs undergo various isomerization and intraconversion processes, whereas many other reactions do not even occur [4–11]. It was suggested that CP-PAHs, when exposed to high temperatures, undergo consecutive ring-contraction/ring expansion processes, involving 1,2-C/1,2-H shifts [5, 8–12]. In addition, CP-PAHs have been a subject of numerous graph-theoretical [13, 14], semiempirical [5, 10, 11] and density functional theoretical (DFT) [11, 15, 16] investigations.

Scott et al. performed a series of flash vacuum pyrolysis (FVP) [17] experiments aimed at preparing dicyclopenta[*de,mn*]anthracene (P1) under various experimental conditions [4]. However, the products of these reactions were always mixtures of isomeric dicyclopenta[*de,kl*]anthracene (P2) and dicyclopenta[*jk,mn*]phenanthrene (P3). It was suggested that P1 did form, but, due to its instability, it underwent isomerization to P2 *via* ethynylaceanthrylene (I0) [4] (Fig. 1).

This assumption was recently confirmed using a DFT approach [18]. It was found that I0 can be transformed to both P1 and P2. The energetics of the investigated reactions indicates that P1 isomerizes to P2. The mechanism for a P2→P3 transformation is based on a ring contraction/ring conversion process, and requires extremely high temperatures. A mechanistic pathway for the P1→P3 isomerization was also revealed [19]. This transformation involves rear-

