

# Formation and isomerization of dicyclopenta[*de,mn*]anthracene. Electronic Structure Study

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**Abstract** The formation of dicyclopenta[*de,mn*]anthracene (P1) and its isomerization into dicyclopenta[*jk,mn*]phenanthrene (P3) was investigated using density functional theory. It was shown that P1 is formed from 1,4-diethynylanthracene, but due to its instability, it undergoes further transformation. This transformation involves rearrangements of some hydrogen atoms and ring contraction/ring expansion process, yielding as a final product the isomer P3. The energies of activation for the P1→P3 intraconversion show that this reaction is competitive to the other, previously investigated isomerization of P1 into dicyclopenta[*de,kl*]anthracene (P2). In addition, our investigation shows that the formation of P3 from P1 is energetically more favorable than the formation of P3 from P2. Thus, the presence of the isomer P3 in the reaction mixtures could also be caused by the isomerization of the very unstable isomer P1.

**Keywords** Density functional calculations · Energy profile · Reaction mechanism · Thermal rearrangement

## Introduction

The thermal isomerizations of some cyclopenta-fused polycyclic aromatic hydrocarbons (CP-PAHs) has been a subject of many semiempirical [1–3] and DFT [3–9] studies. One of the reasons for this lies in the fact that CP-PAHs are

considered to be responsible for the genotoxicity of mixtures produced by incomplete combustion of various hydrocarbon-containing fuel sources [10–12]. In order to obtain various CP-PAHs in high yields, many flash vacuum pyrolysis (FVP) experiments were performed using appropriate starting compounds [1, 2, 13–17]. For example, Scott et al. [13] exposed 1,4-bis(1-chlorovinyl)anthracene to high temperatures in the FVP experiments to produce dicyclopenta[*de,mn*]anthracene (P1). However, their attempts failed, and dicyclopenta[*de,kl*]anthracene (P2) was detected at 900 °C. In addition, at even higher temperatures (1100 °C) the mixture of P2 and dicyclopenta[*jk,mn*]phenanthrene (P3) was obtained. Although they never succeeded to detect P1, Scott et al. suggested that P1 did form *via* 1,4-diethynylanthracene (I1) and 5-ethynylaceanthrylene (I3), but due to its low stability, it underwent isomerization into P2. The structures of P1, P2, P3, I1 and I3 are shown in Fig. 1. The results of our recent computational study [7] were in agreement with the unsuccessful syntheses of P1, stability of P2 at higher temperatures, and formation of P3 under extreme temperature regime in the FVP processes. However, it was suggested that P3 was formed only at the expense of P2.

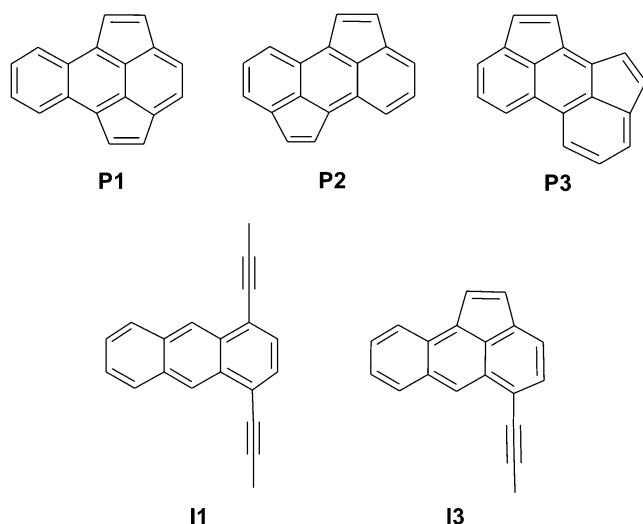
The aim of this paper is to show that the isomerization of P1 into P3 is not less likely to occur *via* a different mechanism that excludes the isomer P2 as a precursor. The energetically competitive way of forming the isomer P3 from P1 is presented. The mechanism of the formation of P1 *via* I1 and I3 is also studied, indicating again that P1 is a precursor that should not be neglected in this kind of isomerization processes.

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## Computational methods

In order to provide compatibility of the results of this work with the findings of our previous investigation [7], we used



**Fig. 1** The structures of dicyclopenta[*de,mn*]anthracene (P1), dicyclopenta[*de,kl*]anthracene (P2), dicyclopenta[*jk,mn*]phenanthrene (P3), 1,4-diethynylantracene (I1) and 5-ethynylaceanthrylene (I3)

the same computational methods. Thus, geometrical parameters of all stationary points and transition states for the formation and isomerization of dicyclopenta[*de,mn*]anthracene were optimized in vacuum, at the B3LYP/6-311G(d,p) level of theory [18–20], using the GAUSSIAN 03 program package [21]. All calculated structures were confirmed to be local minima (all positive eigenvalues) for ground state structures, or first-order saddle points (one negative eigenvalue) for transition state structures, by frequency calculations. The intrinsic reaction coordinates (IRCs), from the transition states down to the two lower energy structures, were traced using the IRC routine in Gaussian in order to verify that each saddle point is linked with two putative minima. Evolution of relevant bonds along the reaction pathway was estimated using the natural bond orbital analysis [22].

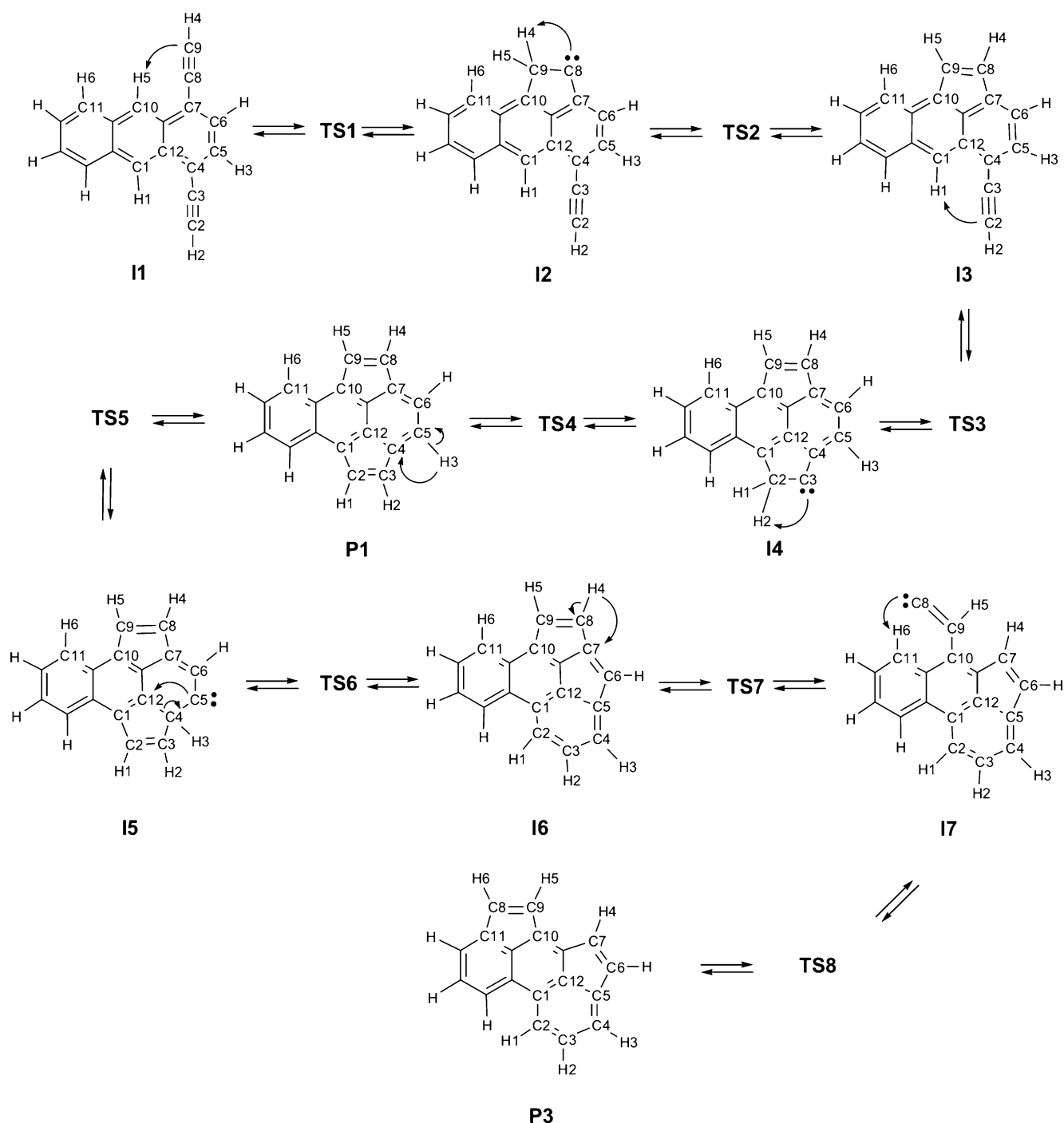
## Results and discussion

The first part of our work is devoted to the formation of P1 from 1,4-diethynylantracene (I1), and the second part examines the isomerization of P1 into P3. The reactions proceed *via* the intermediates I2 – I7 and transition states TS1 – TS8 (Fig. 2). The optimized geometries of all transition states are presented in Fig. 3. Table 1 contains bond distances that undergo significant changes during the isomerization of I1 into P1, whereas Table 2 represents bond distances in the P1→P3 isomerization process. The energetic diagram of the transformation of I1 into P3 is presented in Fig. 4, and the total energies, enthalpies, and free energies of all relevant species are provided as [Electronic supplementary material](#).

The NBO analysis of I1 shows that C9 and C2 bear partial negative charges, while H5 and H1 are partially positively charged (Fig. 5). Our calculations reveal a nucleophilic attack of C9 on H5, where the carbene intermediate I2 is formed *via* the transition state TS1. An activation energy ( $E_a$ ) of 310.71 kJ mol<sup>-1</sup> is required for this step of the reaction. In TS1 the C10-H5 bond is being broken, whereas the C9-H5 and C9-C10 bonds are being formed (Fig. 3 and Table 1). The results of the IRC calculation for TS1 are given in the [Electronic supplementary material](#). The NBO analysis of the carbene I2 reveals a lone pair in the sp<sup>1.17</sup> orbital on C8. In addition, the greatest contribution to the HOMO of I2 comes from C8 (Fig. 5). These facts indicate that C8 will perform a nucleophilic attack on a partially positively charged H4 or H5 (the NBO charge=0.250). This attack leads to the formation of I3 *via* TS2 (Fig. 2), requiring  $E_a$  of 36.63 kJ mol<sup>-1</sup>. In TS2 (Fig. 3) the C8, C9 and H4 atoms form a three-membered cycle where H4 lies over the molecular plane. As the C9-H4 bond is broken and the C8-H4 bond is formed (Table 1), the intermediate I3 is produced. This intermediate contains one closed five-membered ring. This feature can be attributed to its particular stability (Table 1 in [Electronic supplementary material](#) and Fig. 4). In a similar manner, C2 in I3 invokes a cleavage of the C1-H1 bond, with the simultaneous formation of the C1-C2 and C2-H1 bonds (Fig. 2). This step occurs *via* TS3 with  $E_a$  of 339.76 kJ mol<sup>-1</sup>, giving the intermediate I4. A lone electron pair in the sp<sup>1.13</sup> orbital on C3 of I4 causes a shift of H2 from C2 to C3, building P1 *via* TS4 (Fig. 2) with  $E_a$  of 49.25 kJ mol<sup>-1</sup>.

Table 1 in [Electronic supplementary material](#) and Fig. 4 show that the formations of TS1 and TS3 are energetically most demanding steps in the I1→P1 isomerization. If we examine the reverse reaction, i.e., the P1→I1 isomerization, we see that the conversions of P1 into I4 ( $E_a$ =294.59 kJ mol<sup>-1</sup>) and I3 into I2 ( $E_a$ =300.29 kJ mol<sup>-1</sup>) are the steps that require the highest energies of activation (see Table 1 in [Electronic supplementary material](#)). Obviously, these activation barriers are slightly lower than those required for the formations of TS1 from I1 and TS3 from I3, and indicate that the isomerization P1→I1 is likely to occur. However, we assume that low stability of I1 shifts the reaction to the direction of the formation of P1, which is by 153.98 kJ mol<sup>-1</sup> more stable than I1.

Our investigation reveals that, under the extreme temperature regime of the FVP experiments, P1 suffers further transformations, thus yielding P3. The P1→P3 isomerization starts with hydrogen (H3) transfer from C5 to C4 (Fig. 2), which is a common case in electron rich cyclic conjugated systems [1–4, 13–17, 23–25]. The formation of TS5, where H3 lies between the C4 and C5 atoms (Fig. 3), requires  $E_a$  of 354.89 kJ mol<sup>-1</sup>. As a result of this shift, C4 changes its hybridization from sp<sup>2</sup> in P1 to

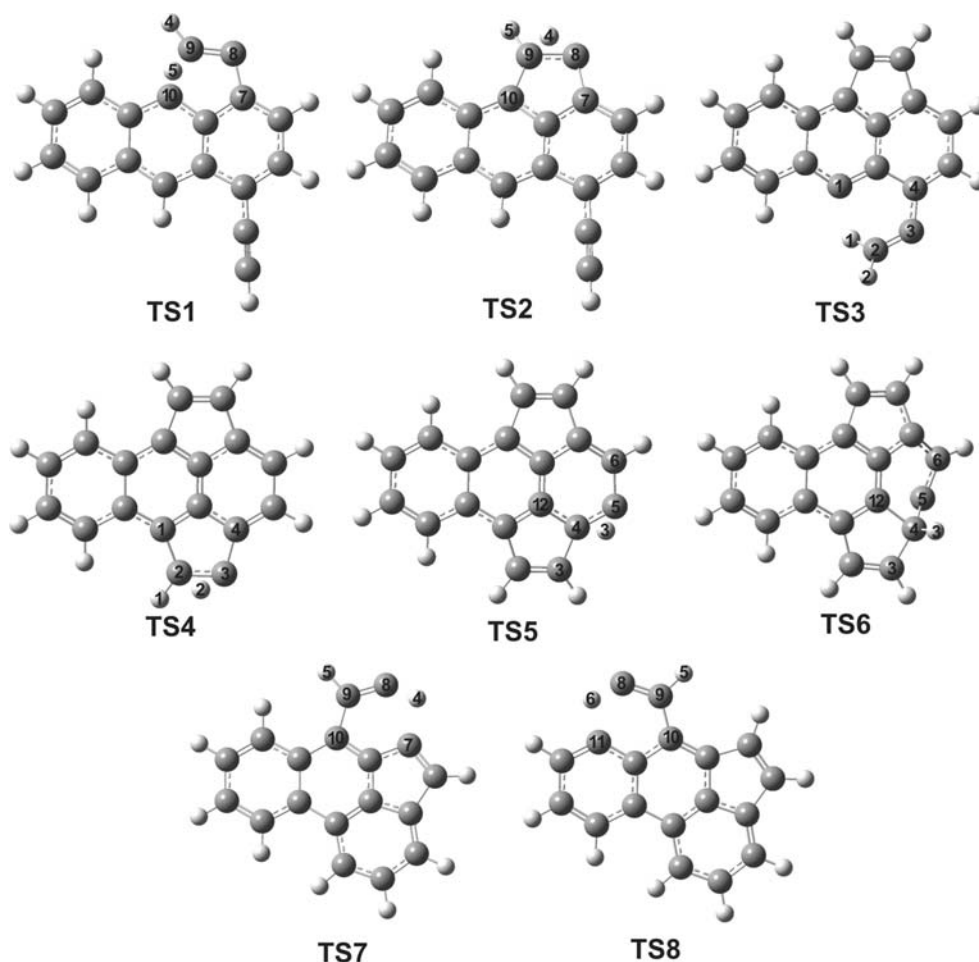


**Fig. 2** Mechanism of the formation of dicyclopenta[de,mn]anthracene (P1) from 1,4-diethynylanthracene (I1), and its isomerization into dicyclopenta[jk,mn]phenanthrene (P3). I2 - I7 denote intermediates, whereas TS1 - TS8 are transition states

approximately  $sp^3$  in I5. Since C4 is bonded to the  $sp^2$  hybridized carbon atoms, the planarity of I5 is significantly disturbed, and the intermediate is under significant strain. As a consequence, I5 is particularly unstable (Table 1 in Electronic supplementary material and Fig. 4). This intermediate is a carbene species with a lone electron pair

in the  $sp^{1.66}$  orbital on C5. In addition, the HOMO map of I5 indicates that C5 is most electron-sufficient (Fig. 5). This lone pair attacks C12 forming TS6 with  $E_a$  of  $17.44 \text{ kJ mol}^{-1}$ . This reaction step includes the cleavage of the C4-C12 bond and the formation of the C5-C12 bond, i.e., a simultaneous ring contraction/ring expansion

**Fig. 3** Optimized geometries of transition states in the mechanism depicted in Fig. 2



process. The intermediate I6, whose structure slightly deviates from planarity, is formed. In the further course of the reaction, H4 transfers from C8 to C7 with a simultaneous cleavage of the C7-C8 bond, thus forming

I7. This process requires  $E_a$  of  $312.08 \text{ kJ mol}^{-1}$ . I7 is a carbene with a lone electron pair in the  $sp^{0.54}$  orbital on C8. The last step of the reaction comprises the nucleophilic attack of C8 on the partially positively charged H6

**Table 1** Bond distances that undergo significant changes during the isomerization of 1,4-diethynylantracene into dicyclopenta[de,mn]anthracene

Distance (Å)	I1	TS1	I2	TS2	I3	TS3	I4	TS4
C7-C8	1.424	1.461	1.450	1.489	1.465	1.460	1.470	1.485
C8-C9	1.205	1.363	1.524	1.445	1.364	1.369	1.374	1.366
C9-H4	1.062	1.080	1.099	1.242	2.184	2.187	2.185	2.178
C9-H5	3.003	1.351	1.099	1.086	1.081	1.082	1.082	1.081
C9-C10	3.689	1.667	1.526	1.494	1.470	1.473	1.480	1.489
C10-H5	1.084	1.239	2.208	2.285	2.274	2.277	2.288	2.295
C8-H4	2.267	2.243	2.141	1.400	1.081	1.081	1.081	1.081
C1-H1	1.084	1.084	1.084	1.085	1.084	2.102	2.222	2.308
C1-C2	3.689	3.797	3.798	3.806	3.809	2.448	1.541	1.515
C2-C3	1.205	1.205	1.205	1.205	1.205	1.328	1.542	1.445
C2-H1	3.003	3.199	3.213	3.220	3.220	1.110	1.098	1.086
C2-H2	1.062	1.063	1.063	1.063	1.062	1.082	1.098	1.253
C3-C4	1.424	1.422	1.422	1.424	1.423	1.410	1.456	1.507
C3-H2	2.267	2.268	2.268	2.267	2.268	2.166	2.155	1.391



## Summary

Our study revealed two isomerization pathways: the formation and the isomerization of P1. The suggestion of Scott et al. that P1 is formed from 1,4-diethynylanthracene is again confirmed through a thoroughly examined mechanism. The energetics of this isomerization is in agreement with the high-temperature regime of the FVP experiments. In our previous study [7], it was established that the extreme temperature of 1100 °C provokes the mutual isomerization of P2 and P3, thus forming an isomeric mixture. The RDS for the P2→P3 process requires an activation energy of 361.03 kJ mol<sup>-1</sup>. The present study shows that the isomerization of P1 into P3 is energetically more favorable than the isomerization of P2 into P3, and is competitive to the isomerization of P1 into P2. We also predict that higher stability of P3 over P1 is responsible for directing the mechanism toward the formation of P3, and thus disabling the detection of the molecule P1. Concerning this, the presence of P3 in reaction mixtures is caused not only by the transformation of P2, but also by the intraconversion of the very unstable isomer P1.

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