Electronic Structure Study of Thermal Intraconversions of Some Dicyclopenta-Fused Polycyclic Aromatic Compounds

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The electronic structure of dicyclopenta[*de,mn*]anthracene (P1), dicyclopenta[*de,kl*]anthracene (P2), and dicyclopenta[*jk,mn*]phenanthrene (P3) and their mutual isomerization processes are investigated using density functional theory. Two mechanisms for the thermal intraconversion of P1 to P2 were found. The first mechanism occurs via ethynylaceanthrylene (I0), and the second involves a 1,2-hydrogen shift. It is supposed that I0 is initially formed during the flash vacuum pyrolysis experiments, eventually rearranging to P2 on high temperatures. The energetics of the latter mechanism also indicate that P1 isomerizes to P2. The mechanism for a transformation of P2 to P3 is based on a ring contraction/ring conversion process and requires extremely high temperatures. Our investigation is in accord with the experimental results: unsuccessful synthesis of P1, stability of P2 at high temperature, and formation of P3 under extreme temperature regime.

INTRODUCTION

Polycyclic aromatic compounds (PAHs) constitute an important group of environmental pollutants and are generated during incomplete combustion of hydrocarbon-containing fuel sources. Among the variety of possible PAHs, a relatively small number of them is considered to be responsible for the genotoxicity of combustion products. In addition, this property is prescribed to their specific structure, which, in most cases, implies the presence of five-membered rings as part of PAHs.[1−3] Many thermodynamic properties of various cyclopenta-fused PAHs (CP-PAHs) have been established.[4]

Flash vacuum pyrolisis (FVP)[5] appears to be a good method for obtaining CP-PAHs in high yields. As FVP involves high-temperature and high vacuum conditions, this kind of treatment influences different thermal rearrangements of ethynylarenes to CP-PAHs as well as thermal intraconversions of CP-PAHs under various experimental conditions.[6−11,14] Experimental examination of these FVP processes attracted great attention from theoretical chemists.

A strong evidence is available suggesting that the thermal intraconversions of CP-PAHs under high-temperature conditions take place by consecutive ring-contraction/ring expansion process, involving 1,2-C/1,2-H shifts.[6,11−15] AM1 semiempirical[6,14,15] and DFT[15−17] calculations have been employed to provide better insight into the stepwise rearrangement through respective transition states and intermediates of possible isomerization paths of various mono CP-PAHs. In addition, the pyracylene-type rearrangement, also known as the Stone-Wales rearrangement, has been widely discussed, and various mechanisms have been proposed.[18−21] However, until now, these isomerization pathways have not been experimentally sustained.

In this work we are studying possible mechanisms of mutual intraconversions of three isomers: dicyclopenta[*de,mn*]-anthracene (P1), dicyclopenta[*de,kl*]anthracene (P2), and dicyclopenta[*jk,mn*]phenanthrene (P3) (Chart 1). These three isomers have been the subject of some experimental studies.[4,7,9] To test the viability of the Stone-Wales rearrangement Scott et al.[7] performed a series of FVP experiments to prepare P1. They supposed that thermal cyclization of 9,10-diethynylanthracene would yield the target compound P1 and/or the isomeric P2. In an experiment performed at 900 °C only P2 was produced. At temperatures above 1000 °C P3 was also obtained, at the expense of P2. In similar experiments, Scott et al. never succeeded to produce P1 but obtained P2 at 900 °C and the same mixture of P2 and P3 at 1100 °C. It was suggested[7] that P1 did form, but, due to its instability, it underwent isomerization to P2 via ethynylaceanthrylene (I0 in Chart 1). Recently, a rationalization of the stability order of these three CP-PAHs was offered using a pertinent graph-theoretical method.[22] This study again confirmed the greater stability of P2 and P3 in comparison to P1.

Our attention is devoted to the examination of possible mechanisms embracing the three dicyclopenta-fused PAHs mentioned above and their mutual intraconversions. Mechanisms involving free radicals are not discussed here because they would include bimolecular reactions. Such reactions are less likely to occur, in view of the low pressure conditions of the FVP experiments. We hope that our findings will elucidate the reasons for the unsuccessful synthesis of P1, the stability of P2 at 900 °C, and the formation of P3 at even higher temperatures.

COMPUTATIONAL METHODS

All calculations were conducted using Gaussian03[23] with the B3LYP hybrid functional.[24−26] The triple split valence basis set 6−311G(d,p) was used. This polarized basis set adds p functions to hydrogen atoms in addition to the d functions on heavy atoms. The suitability of this level of theory for studies of reactions involving arenes and carbenes

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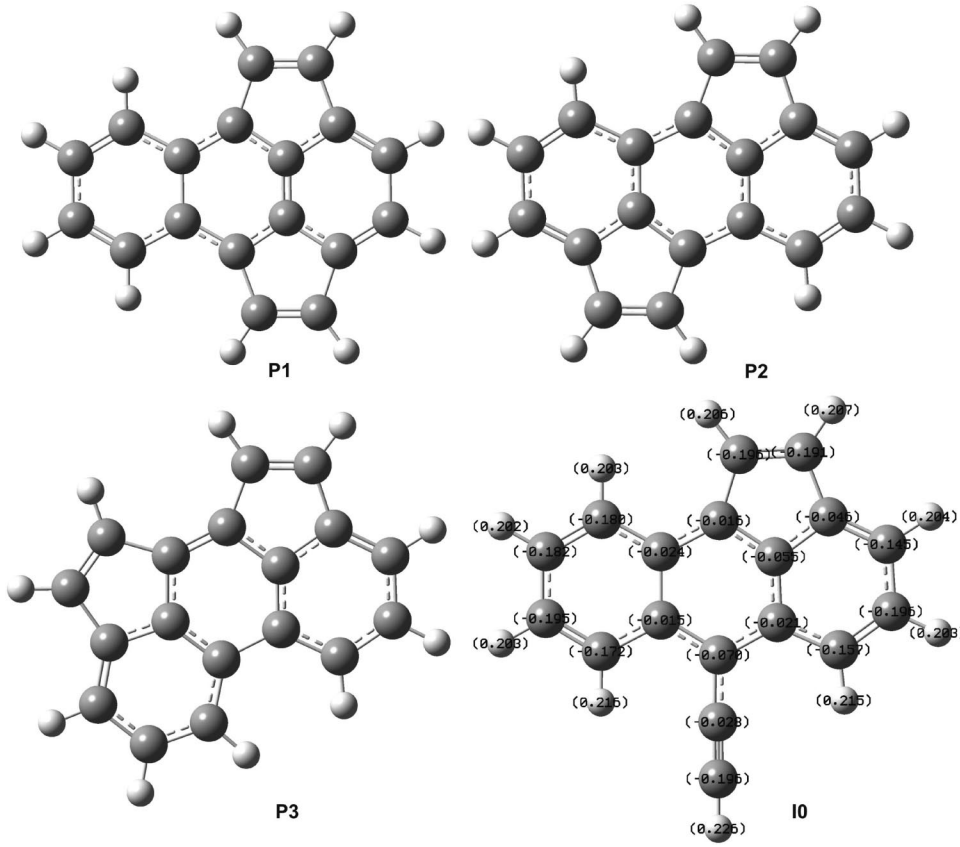
Chart 1. Optimized Geometries of Dicyclopenta[*de,mn*]anthracene (P1), Dicyclopenta[*de,kl*]anthracene (P2), Dicyclopenta[*jk,mn*]phenanthrene (P3), and Ethynylaceanthrylene (I0)[a]



[a] NBO charges of I0.

has been previously established.[18] Geometrical parameters of all investigated species were optimized in vacuum. Vibrational analysis and natural bond orbital (NBO)[27] analysis were performed for all structures. All calculated structures were verified 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. From the transition structures, the intrinsic reaction coordinates (IRCs) were obtained using the IRC routine in Gaussian.

RESULTS AND DISCUSSION

The geometries of P1, P2, and P3 were optimized (Chart 1). All molecules attain planar configuration. The NBO analysis of the molecules shows donation of density from each π bonding orbital to two adjacent π^* antibonding orbitals, in accord with the usual chemical picture of delocalized molecular systems. The free energies of P2 and P3 are by 15.34 and 22.90 kcal/mol lower than that of P1. This finding is in accord with the experimentally observed stabilities of the three isomers.[1]

Two mechanisms for the isomerization of P1 into P2 were found. The general outline of these mechanisms is presented in Scheme 1. The first mechanism occurs via ethynylaceanthrylene and is presented with pathways A and B (transformations of I0 to P2 and P1, respectively). C5 performs nucleophilic attack on H6 (pathway A) or H7 (pathway B), thus forming the intermediates aI or bI, via the transition states aTS1 or bTS1. Further transformations of aI and bI lead to the formation of products P2 and P1, via transition states aTS2 and bTS2. The second mechanism (pathway C in Scheme 1) involves a hydrogen shift from C5 to C3 of P1, forming intermediate cI via transition state cTS1. Then, H6 is transferred from C1 to C5, thus yielding P2 via transition state cTS2. Isomerization of P2 to P3 (pathway D in Scheme 1) begins with a hydrogen shift from C10 to C1, forming dI via the transition state dTS1. Further transformation includes a simultaneous ring-contraction/ring expansion process, where P3 is yielded via transition state dTS2.

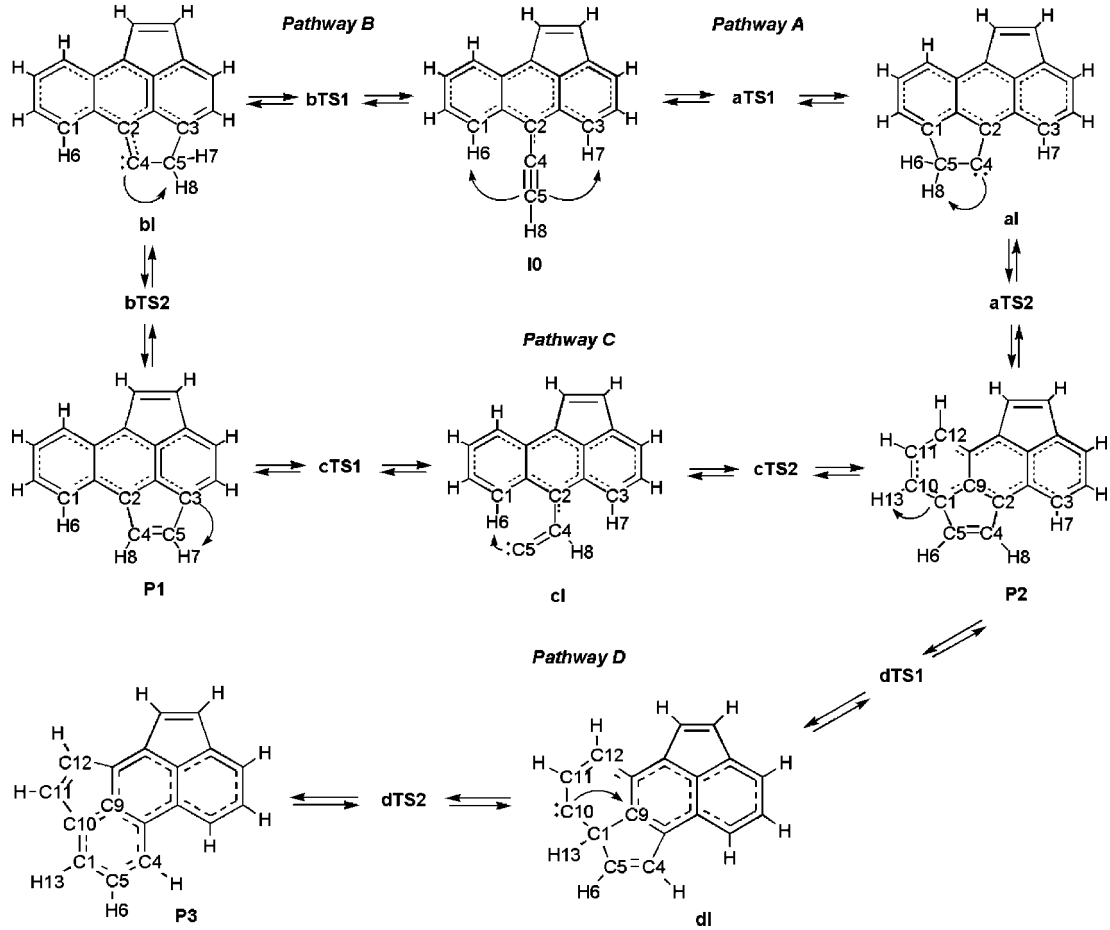
The optimized geometries of all transition states are presented in Chart 2. Selected bond distances of transition states and intermediates are given in Tables 1 and 2. The energetic diagram of the transformations is depicted in Figure 1, whereas total energies, enthalpies, and free energies of all relevant species are provided as Supporting Information.

ISOMERIZATION OF DICYCLOPENTA[*de*,*mn*]ANTHRACENE TO DICYCLOPENTA[*de*,*kl*]ANTHRACENE

Isomerization via Ethynylaceanthrylene. The NBO charge distribution of I0 (Chart 1) shows that C5 belongs to a group of few carbon atoms that bear partial negative charges. Our investigation reveals that C5 performs a nucleophilic attack on partially positively charged H6 or H7.

In pathway A this attack leads to the formation of aTS1, requiring an activation energy (E_a) of 72.51 kcal/mol. In aTS1 the C1, C5, and H6 form a three-membered ring where H6 is placed above the plane of the molecule (Chart 2). As H6 is transferred from C1 to C5, simultaneous formation of the C1−C5 bond occurs, and carbene aI is built. The NBO

Scheme 1. Mechanisms of Thermal Isomerizations of Dicyclopenta[*de,mn*]anthracene (P1) to Dicyclopenta[*de,kl*]anthracene (P2) and of P2 to Dicyclopenta[*jk,mn*]phenanthrene (P3)[a]



[a] I0 and I1 denote intermediates, whereas TS1 and TS2 stand for transition states in the transformation reactions. Prefixes a, b, c, and d refer to the pathways A, B, C, and D, respectively.

analysis of this intermediate shows that hybridization on C4 is close to sp^2, with a lone pair in a pure p orbital. In addition, the HOMO of aI is delocalized over several atoms, but the greatest contribution to the HOMO comes from C4 (Figure 2). These facts indicate the reactive site in aI.

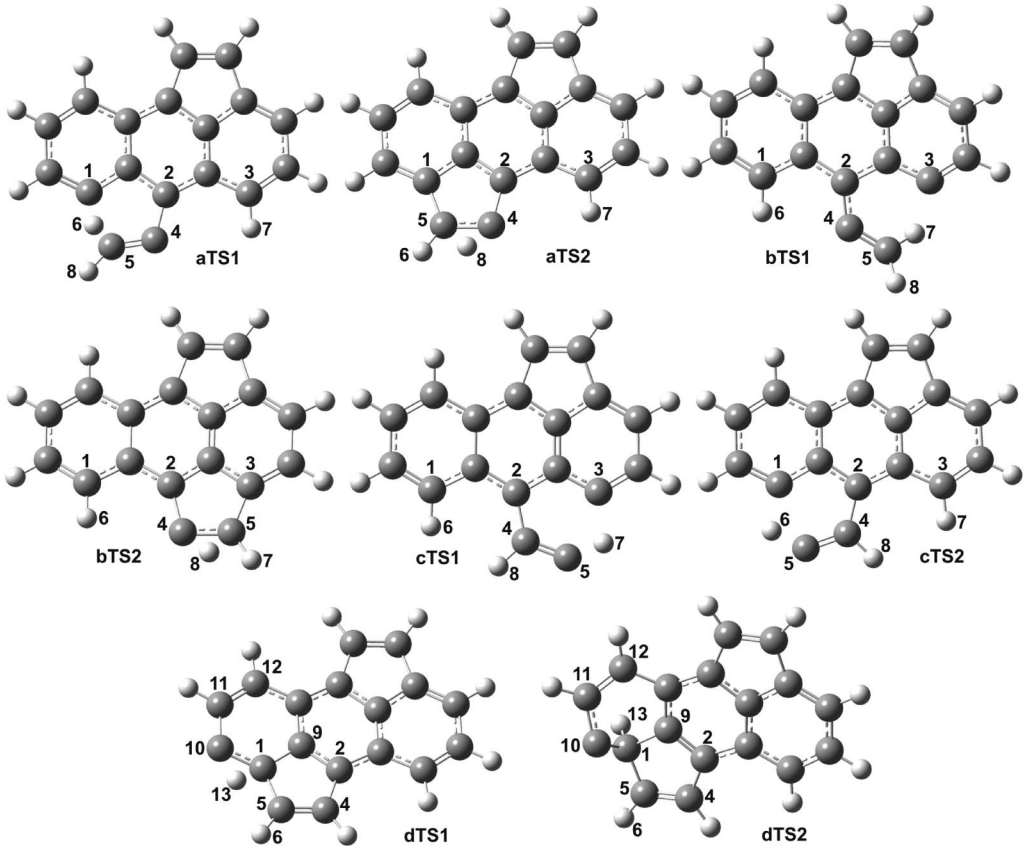
In the further course of the reaction C4 performs a nucleophilic attack on H8, requiring E_a of 11.59 kcal/mol. The transition state aTS2 is formed, where the C5−H8 bond is being broken, and the C4−H8 bond is being formed (Chart 2). An interesting feature of aTS2 is that C4, H8, and C5 form a three-membered cycle, where H8 lies over the molecular plane. As aTS2 is further transformed, P2 is yielded.

Similar changes occur in the pathway B. E_a of 77.92 kcal/mol is required for the formation of the late transition state bTS1, where the C3−H7 bond is broken, the weak C5−H7 bond is formed, and the C3−C5 bond is being formed (Chart 2). The results of the IRC calculation for bTS1 are available in the Supporting Information. In carbene bI (Scheme 1) the breaking and formation of the respective bonds is accomplished. The shape of the HOMO of bI and a lone pair in the pure p orbital of the C4 atom indicate that C4 performs a nucleophilic attack on H8, yielding P1 via transition state bTS2, with E_a of 14.60 kcal/mol.

Such high calculated energies of activation are in accord with the temperature regime of the FVP experiments. Table 1 in the Supporting Information and Figure 1 show that I0 is a very stable intermediate. Its stability is probably due to the fact that its aceanthrylene-type aromatic structure is preserved to the similar extent as those of P1 and P2 (Chart 1). We assume that I0 does form in the FVP experiments, but, faced to extremely high temperatures, it rapidly rearranges. The rate determining steps (RDS) in pathways A and B are the formations of aTS1 and bTS1, respectively, where E_a for the formation of bTS1 is by 5.41 kcal/mol higher. It turns out that it is more probable that I0 takes pathway A than pathway B. We suppose that high temperature provides conditions for the formation of bTS1 and thus P1. Once formed, P1 can undergo reverse reactions building I0, where the RDS is the formation of bTS2 (E_a = 69.22 kcal/mol). This E_a is lower by 8.70 kcal/mol than that required for the RDS in pathway B, indicating that, at increased temperature, the equilibrium of the reaction will be shifted to the right, i.e., P1 will isomerize to P2.

Isomerization Involving Hydrogen Shifts. It is known that electron rich cyclic conjugated systems are suitable for migration of hydrogen along the perimeter of the system.[6−12,14−16,21,28] This fact motivated us to examine transfer of H7 from C5 to C3 as the first step of isomerization of P1 to P2 (Scheme 1). The transition state cTS1 is obtained, where the H7 atom lies in the plane of the molecule, between C3 and C5 (Chart 2). E_a of 79.37 kcal/mol is required for the formation of cTS1. Further breakage and formation of the C5−H7 and C3−H7 bonds lead to the formation of

Chart 2. Optimized Geometries of Transition States in the Transformations of I0 to P2 (Pathway A) and P1 (Pathway B) and in the Isomerizations of P1 to P2 (Pathway C) and P2 to P3 (Pathway D)[a]



[a] See Scheme 1 for definition of symbols.

Table 1. Bond Distances That Undergo Significant Changes during the Isomerization Processes of Dicyclopenta[*de,mn*]anthracene to Dicyclopenta[*de,kl*]anthracene

	pathway A					pathway B				pathway C		
distance (Å)	I0	aTS1	aI	aTS2	P2	bTS1	bI	bTS2	P1	cTS1	cI	cTS2
C2−C4	1.422	1.450	1.438	1.485	1.466	1.392	1.446	1.502	1.491	1.477	1.458	1.462
C4−C5	1.206	1.344	1.521	1.439	1.363	1.317	1.542	1.441	1.364	1.328	1.304	1.332
C1−C5	3.664	1.814	1.523	1.490	1.468	–	–	–	4.585	4.480	2.885	2.107
C3−C5	3.752	–	–	–	4.627	2.553	1.539	1.512	1.488	2.160	4.329	4.561
C1−H6	1.083	1.295	2.198	2.280	2.271	1.084	1.084	1.084	1.084	1.084	1.092	1.439
C3−H7	1.083	1.083	1.083	1.083	1.084	2.148	2.214	2.381	2.293	1.536	1.084	1.084
C5−H6	3.659	1.275	1.098	1.086	1.081	–	–	–	4.377	4.144	2.059	1.156
C5−H7	3.148	–	–	–	4.515	1.115	1.097	1.086	1.081	1.148	3.940	4.325
C4−H6	2.511	2.206	2.146	1.371	2.226	–	–	–	–	–	–	–
C4−H7	2.718	–	–	–	3.160	2.070	2.160	2.219	2.176	–	–	–
C4−H8	2.268	2.253	2.146	1.371	1.081	2.152	2.160	1.367	1.081	1.086	1.103	1.086
C5−H8	1.062	1.078	1.098	1.260	2.178	1.083	1.097	1.269	2.171	2.057	1.881	2.061

Table 2. Bond Distances That Undergo Significant Changes during the Isomerization Process of Dicyclopenta[*de,kl*]anthracene to Dicyclopenta[*jk,mn*]phenanthrene

	pathway D				
distance (Å)	P2	dTS1	dI	dTS2	P3
C1−C5	1.468	1.501	1.513	1.504	1.388
C1−C9	1.424	1.460	1.482	1.561	2.405
C1−C10	1.373	1.442	1.485	1.453	1.383
C9−C10	2.404	2.555	2.574	2.158	1.410
C10−C11	1.430	1.473	1.453	1.430	1.471
C1−H13	2.152	1.209	1.125	1.104	1.085
C10−H13	1.085	1.445	1.884	2.183	2.160

carbene cI. In this intermediate C5 is approximately $sp^{1.5}$ hybridized and contains a lone pair in the NBO of predominant s character with 35% p mixing. This lone pair performs a nucleophilic attack on H6 which is partially positively charged (0.208). In this way cTS2 is built, with E_a of 13.22 kcal/mol. The structure of cTS2 is similar to that of cTS1: H6 lies between C1 and C5 in the molecular plane. As the C1−H6 distance increases, C5 approaches C1. In the further course of the reaction the C1−C5 and C5−H6 bonds are built, and P2 is yielded.

The RDS of this reaction is the formation of cTS1 (Table 1 in the Supporting Information and Figure 1). In a possible reverse reaction the RDS would be the formation of cTS2 from P2 (E_a = 86.59 kcal/mol). A much higher activation energy for the reverse reaction indicates that the equilibrium between P1 and P2 is shifted to the right side of the reaction.

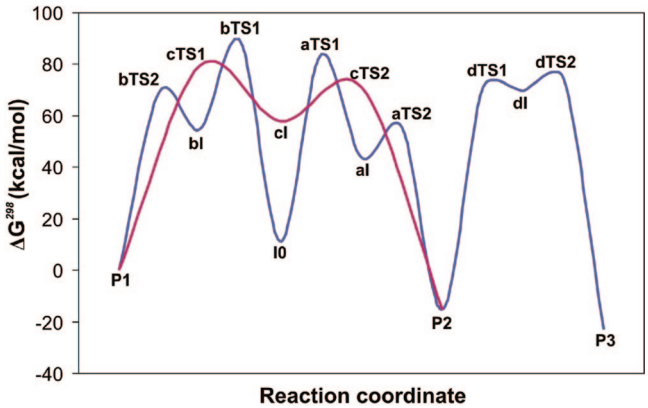


Figure 1. Energy profile for intraconversions of P1 to P2 and P2 to P3. See Scheme 1 for definition of symbols.

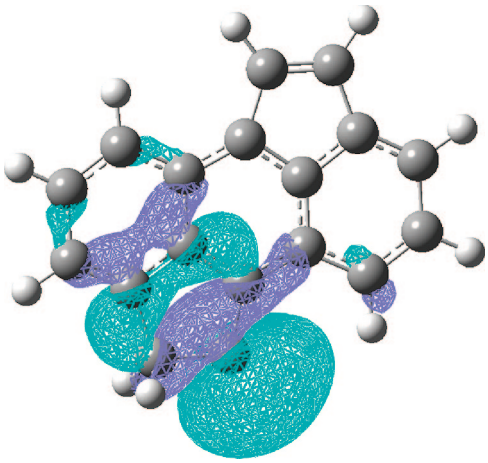


Figure 2. HOMO of aI. See Scheme 1 for definition of the symbol.

In other words, both investigated isomerization processes favor the formation of P2. When these two isomerization reactions are compared it is noticeable that E_a for the formation of cTS1 is even higher than those for the formations of aTS1 from I0 and bTS2 from P1. On the other hand, the ΔG^{298} values of bTS1 and aTS1 are higher than ΔG^{298} of cTS1 by 9.74 and 4.33 kcal/mol. These facts indicate that both ways of isomerization of P1 into P2 are possible under the high temperature conditions.

ISOMERIZATION OF DICYCLOPENTA[*de*,*kl*]ANTHRACENE TO DICYCLOPENTA[*jk*,*mn*]PHENANTHRENE

Transfer of H13 from C10 to C1 is examined as the first step of the isomerization of P2 to P3 (Scheme 1). The transition state dTS1, whose formation requires E_a of 86.31 kcal/mol, is found. In this transition state H13 lies above the molecular plane (Chart 2). As the C10−H13 bond is broken, the C1−H13 bond is built, and dI is formed. In this carbene the C1 atom, that is approximately sp^3 hybridized, is bonded to the sp^2 hybridized carbons. This structural feature of dI induces significant strain in the intermediate, since the bond angles deviate from the usual dihedral bond angle. This occurrence can be attributed to the particular instability of dI (Table 1 in the Supporting Information and Figure 1). C10 has a lone pair in the orbital with predominant p character with 40% s mixing. The map of the HOMO in dI is presented in Figure 3. The HOMO map delineates the

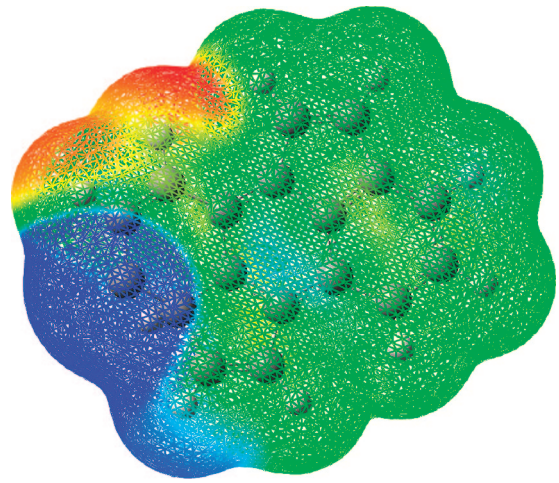


Figure 3. HOMO map of bI. The regions where the values of the HOMO are greatest are indicated in blue, whereas the regions where they are least are indicated in red.

area that is most electron-sufficient (C10). This carbon performs a nucleophilic attack on C9, with E_a of 4.92 kcal/mol. As the C9−C10 distance is shortened and C1−C9 is elongated, simultaneous ring contraction/ring extension (i.e., the formation of P3) is realized.

A very high activation barrier of the RDS indicates that the reaction of intraconversion of P2 to P3 requires extreme temperature conditions. If a reverse reaction is considered, i.e. the isomerization of P3 to P2, E_a for the RDS (formation of dTS2 from P3) is even higher and equals 97.39 kcal/mol. We suppose that the experimental conditions of the reaction (1100 °C) enable some molecules to undergo mutual isomerization, thus forming a mixture of P2 and P3.

CONCLUDING REMARKS

Our investigation shows that P1, P2, and P3 can undergo different intraconversion patterns for mutual isomerizations. All investigated mechanisms involve the formation of carbenes. The suggestion of Scott et al., i.e., that I0 is formed from 9,10-diethynylanthracene during the FVP experiments, is confirmed. Due to the high temperature conditions (900 °C), I0 can transform to either P1 or P2. P2 is more stable than P1, and the RDS for the isomerization of I0 to P2 requires lower activation energy than that for the isomerization to P1. It turns out that I0 will isomerize to P2 but not to P1. Even if formed, at the high temperature of the FVP experiments, P1 can surmount activation barriers to return to I0 and further to P2. In addition, another reaction path for the intraconversion of P1 to P2 is found, based on hydrogen shift. Under the conditions of extreme temperature (1100 °C), P2 and P3 can undergo mutual isomerization, overcoming the high energy barrier and forming the isomeric mixture. In this way, the formation of P2 as the only product of the FVP experiments under the high-temperature regime and the formation of the mixture consisting of P2 and P3 under extremely high temperature are explained.

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Supporting Information Available: Table 1, Figure 1, and Cartesian coordinates for all computed species (P1, bTS2, bI, bTS1, I0, aTS2, aI, aTS2, P2, cTS1, cI, cTS2, dTS1, dI, dTS2, and P3). This material is available free of charge via the Internet at http://pubs.acs.org.

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