

Thermal Rearrangement of Ethynylarenes to Cyclopentafused Polycyclic Aromatic Hydrocarbons: An Electronic Structure Study

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Abstract: BLYP/6-311G** electronic structure calculations are employed to elucidate the reaction mechanism of the thermal rearrangement of ethynylarenes to cyclopentafused polycyclic aromatic hydrocarbons (CP-PAHs). Out of two potentially possible unimolecular rearrangement pathways, a one-step process involving hydrogen migration immediately followed by ring closure is clearly favored thanks to a significantly lower energy barrier. Contrary to common belief, neither 2-(1-naphthyl)ethylidene carbene nor its annelated analogs are genuine chemical species. Consequently, these carbenes do not constitute intermediates pertinent to this reaction mechanism, which has the predicted activation energy of 55–62 kcal/mol depending on the extent of strain in the parent ethynylarene molecule. The present study conclusively rules out free-radical mechanisms that commence with hydrogen abstraction. However, in the case of strainless substrates and higher reaction pressures, the pathway involving initial hydrogen addition might become a viable competitor to the one-step unimolecular rearrangement.

Introduction

The presence of both five- and six-membered rings imparts unique properties, such as nonplanarity and increased reactivity, to cyclopentafused polycyclic aromatic hydrocarbons (CP-PAHs). Bowl-shaped CP-PAHs such as corannulene (**1**) constitute building blocks of fullerenes.^{1–3} Many CP-PAHs, including cyclopenta[*cd*]pyrene (**2**), are potent mutagens and carcinogens.⁴ Being abundant in combustion effluents and soot,⁵ these CP-PAHs are of great practical interest.

Thermal closure of five-membered rings is believed to constitute the major pathway from ethynylarenes (which presumably arise from PAHs through the addition of acetylenic fragments such as $\cdot\text{C}\equiv\text{C}\cdot$ or $\text{HC}\equiv\text{C}\cdot$)⁶ to the CP-PAHs produced during combustion of fossil fuels.^{7,8} Indeed, many CP-

PAHs can be obtained in high yields by flash vacuum pyrolysis (FVP) of ethynylarenes, which are often produced *in situ* from the respective (1-chloroethenyl)arene precursors. Accordingly, CP-PAHs such as **2**,⁹ acenaphthylene (**3**),^{9,10} pyracylene (**4**),^{11,12} cyclopenta[*cd*]fluoranthene (**5**),^{11,13} benz[*l*]acephenanthrylene (**6**), benz[*j*]acephenanthrylene (**7**),¹⁴ cyclopent[*hi*]aceanthrylene (**8**),¹⁵ dicyclopenta[*cd,fg*]pyrene (**9**), dicyclopenta[*cd,jk*]pyrene (**10**), dicyclopenta[*cd,mn*]pyrene (**11**),¹⁶ acephenanthrylene (**12**), and aceanthrylene (**13**)¹⁷ have been prepared recently with this versatile synthetic methodology. Analogous (multiple) closures of six-membered rings afford **1**² and other fullerene fragments.¹

In principle, the ethynylarene \rightarrow CP-PAH rearrangement may proceed through one of five distinct sequences of elementary reactions that differ in the temporal order of ring closure and hydrogen migration/transfer. The commonly assumed reaction

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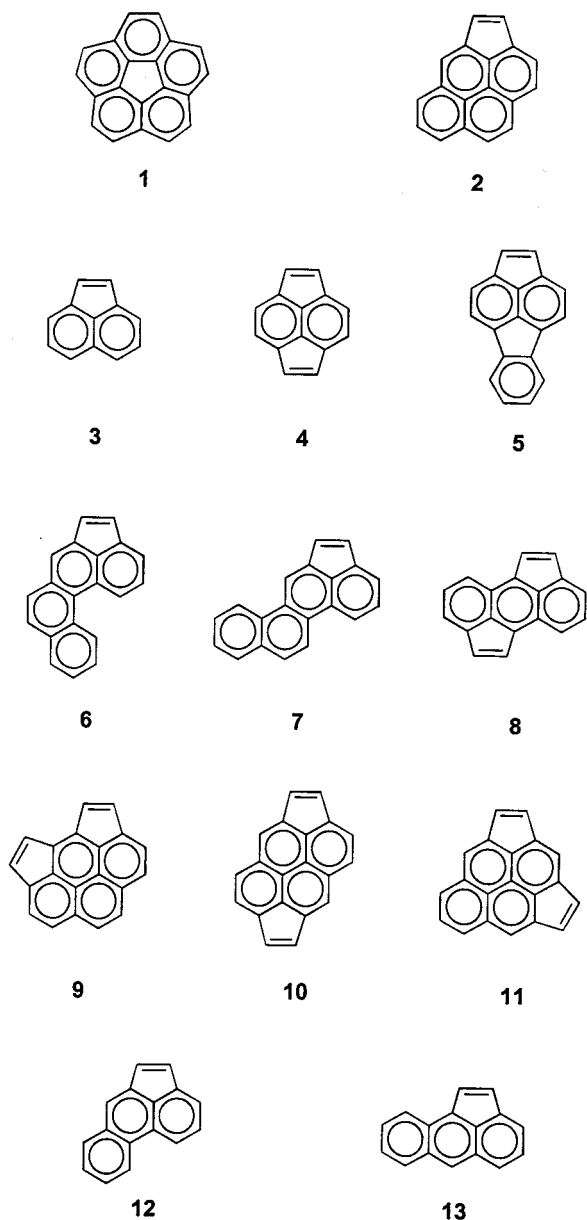


Figure 1. Examples of cyclopentafused polycyclic aromatic hydrocarbons (CP-PAHs).

mechanism^{9,12,13,17} involves intramolecular trapping of 2-arylethylidene carbene **15** generated from the corresponding ethynylarene **14** by a 1,2-hydrogen shift (mechanism I, Figure 2a). The other relevant sequence of unimolecular reactions comprises direct cyclization of **14** followed by hydrogen migration in the resulting carbene **16** (mechanism II, Figure 2b).

An alternative explanation of the thermal formation of CP-PAHs from ethynylarenes is offered by free-radical chain-reaction mechanisms. According to two of such mechanisms, the radicals **18/19**, produced by the abstraction of hydrogen from **14**, undergo ring closure to **20**. The recapture of hydrogen from **14** completes the propagation steps of these chain reactions (mechanisms III and IV, Figures 2c and 2d). The initial addition of hydrogen to **14**, followed by cyclization of **21** to **22** and subsequent hydrogen loss, constitutes another mechanistic possibility (mechanism V, Figure 2e).

Although mechanism I appears to be supported by many experimental observations (including the migration of ethynyl substituents around perimeters of PAHs¹⁸), none of the other four reaction pathways can be ruled out with certainty. For

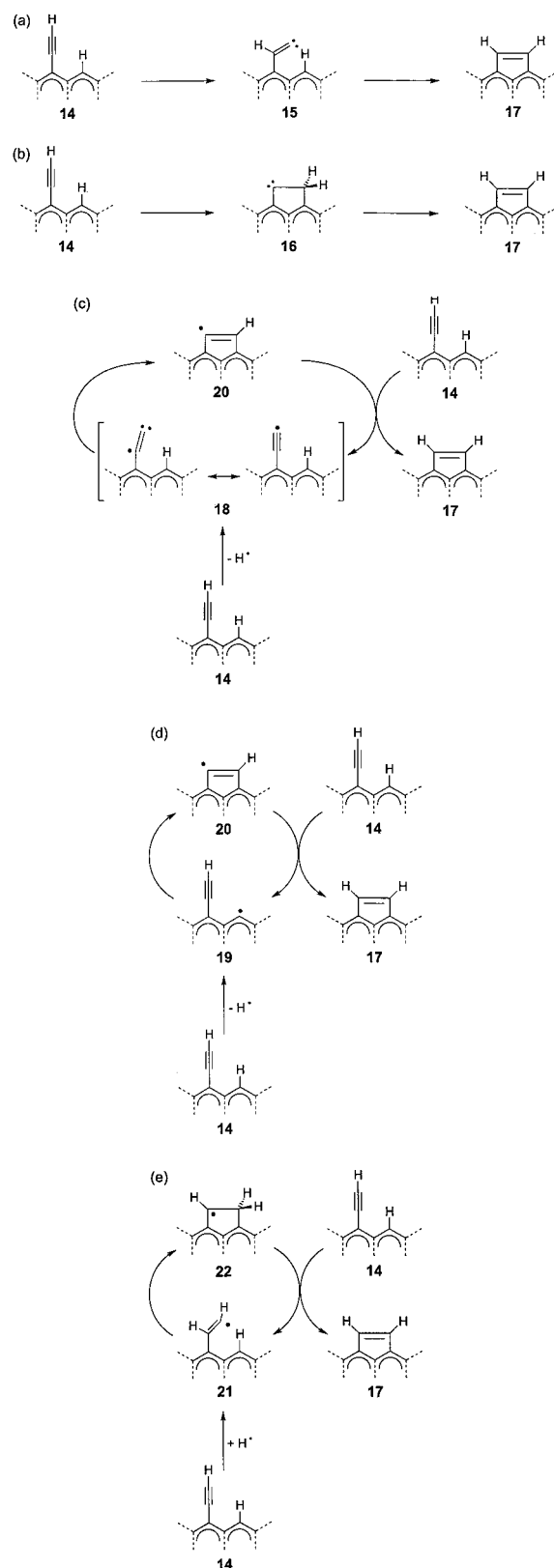


Figure 2. The five possible mechanisms of the thermal rearrangement of ethynylarenes to CP-PAHs: (a) the unimolecular mechanism I, (b) the unimolecular mechanism II, (c) the free-radical mechanism III, (d) the free-radical mechanism IV, and (e) the free-radical mechanism V.

example, since it may proceed through a symmetrical transition state involving simultaneous shifts of hydrogen and phenyl,¹⁹

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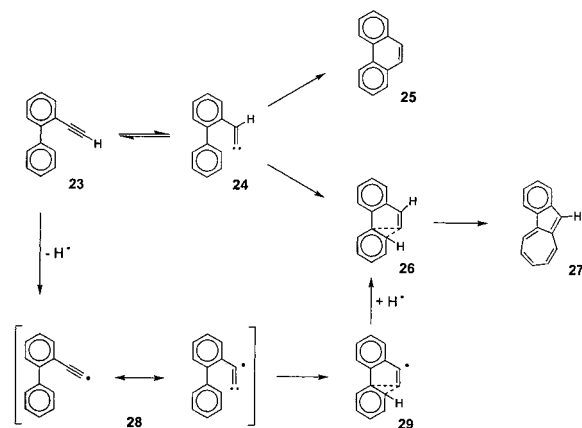


Figure 3. Two of the possible mechanisms of the thermal rearrangement of 2-ethynylbiphenyl to phenanthrene and benz[a]azulene.

the thermal scrambling of carbon atoms within the $C\equiv C$ moiety of ethynylbenzene^{20,21} does not conclusively establish the presence of high-temperature equilibria between ethynylarenes and 2-arylethylenes. Similarly, the formation of benz[a]azulene (27) as a byproduct of the thermal cyclization of 2-ethynylbiphenyl (23) to phenanthrene (25)²¹ can be explained equally well by the insertion of either the carbene (24) or the carbene-like radical (28) (Figure 3).

Some indirect empirical evidence against the free-radical mechanisms is also available. The absence of phenylethynyl among the radicals produced by pyrolysis of ethynylbenzene at 1030 °C and the formation of large quantities of $C_6H_5^{\bullet}$ under such conditions²² seem to preclude the reaction pathways initiated by hydrogen abstraction (mechanisms III and IV). Partial degradation of the starting material due to the loss of the $C\equiv C$ fragment (presumably from the arylethynyl radicals) is also evident in some FVP experiments, especially those carried out at higher temperatures.¹²

This lack of conclusive experimental data has prompted the electronic structure calculations presented in this paper. Aiming at definitive elucidation of the main sequence of reactions responsible for the thermal cyclization of ethynylarenes to CP-PAHs, these calculations have produced a wealth of theoretical predictions for the energetics and barriers of individual steps of both the unimolecular and free-radical reaction mechanisms.

Details of Calculations

All calculations of this study were carried out at the BLYP/6-311G** level of theory. The accuracy of such a theoretical treatment of reactions involving arenes, aryl radicals, arynes, and carbenes has been well documented in chemical literature. Thus, the BLYP/6-311G** C–H bond dissociation energy (BDE) of benzene equals 106.9 kcal/mol at $T = 0$ K,²³ in reasonable agreement with the recent experimental values of 109.8 ± 0.8 ²⁴ and 112.0 ± 0.6 kcal/mol.²⁵ The same density functional/basis set combination yields 82.8 kcal/mol²⁶ for the energy of 1,2-didehydrogenation of benzene (i.e., the reaction $C_6H_6 \rightarrow C_6H_4 + H_2$) at $T = 0$ K, while the experimental estimate is 86.9 ± 3.0 kcal/

mol (at $T = 298$ K).²⁷ The BLYP/6-311G** energy of the benzyne \rightarrow cyclopentadienyldiene carbene isomerization, which equals 32.2 kcal/mol, is close to the CCSD(T)/6-311G** value of 29.2 kcal/mol.²⁶ Similarly impressive agreement is observed between the BLYP/cc-pVTZ predictions for the energy and barrier of the $H_2C=C: \rightarrow HC\equiv CH$ rearrangement (-41.82 and 1.44 kcal/mol, respectively²⁸) and their experimental counterparts (-43 ± 2 and 1.3 kcal/mol²⁹), proving that the inexpensive BLYP calculations can rival the best theoretical approaches³⁰ in accuracy.

Geometries of all the species under study were fully optimized and checked for the number of imaginary vibrational frequencies. In some cases, reaction paths were also determined. All calculations were carried out with the GAUSSIAN 94 suite of programs.³¹ The reaction energies and barriers quoted in this paper pertain to $T = 0$ K and include zero-point energies.

The Unimolecular Reaction Pathways

At 1000 °C/0.01 Torr, FVP of either 1-ethynyl-naphthalene or its 1-(1-chloroethenyl)naphthalene precursor produces acenaphthylene (3) in yields as high as 80%.^{9,10} This prototype ethynylarene \rightarrow CP-PAH rearrangement is commonly believed to involve 2-(1-naphthyl)ethylidene carbene (15, Figure 2a) as an intermediate. The present calculations find the carbene molecule to be a minimum on the potential energy hypersurface and place it 46.0 kcal/mol above the respective ethyne (Table 1). However, upon the inclusion of zero-point energies, the pertinent transition state, which is very late (Figure 4), is predicted to lie *below* the carbene. Consequently, as there is no barrier to prevent it from collapsing to 1-ethynyl-naphthalene, 2-(1-naphthyl)ethylidene carbene is not even a transient species.³² Thus, the unimolecular reaction mechanism I (Figure 2a) comprises a *one-step process* in which the migration of hydrogen is immediately followed by ring closure in absence of any intermediate. The transition state for this process, which is again quite late (Figure 5a), corresponds to the overall reaction barrier of 55.2 kcal/mol.

With the predicted reaction barrier of 69.8 kcal/mol, the direct cyclization of 1-ethynyl-naphthalene, which constitutes the first step of the unimolecular reaction mechanism II (Figure 2b), does not appear energetically competitive. In contrast to its ethylidene counterpart, the carbene intermediate (16, Figure 6a) is a genuine chemical species that readily rearranges (the reaction barrier of only 8.5 kcal/mol) through 1,2-hydrogen shift to 17. The transition state for this shift is nonplanar (Figure 6b).

The relative energies of 2-arylethylidene carbenes derived from other PAHs span the narrow range of 45.8–46.7 kcal/mol (Table 1). As none of these carbenes is protected from

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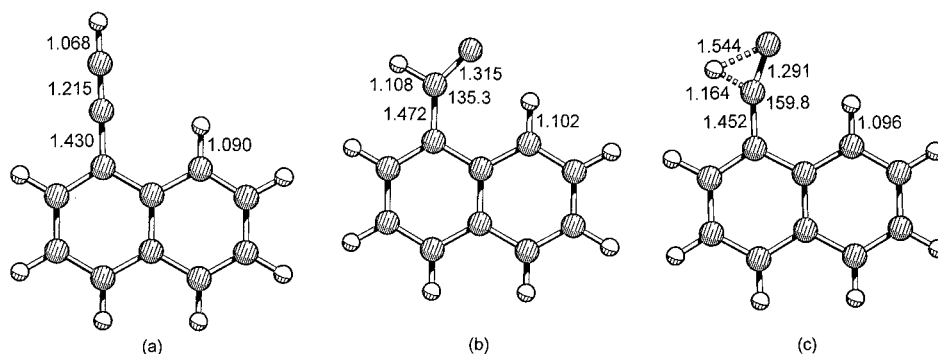
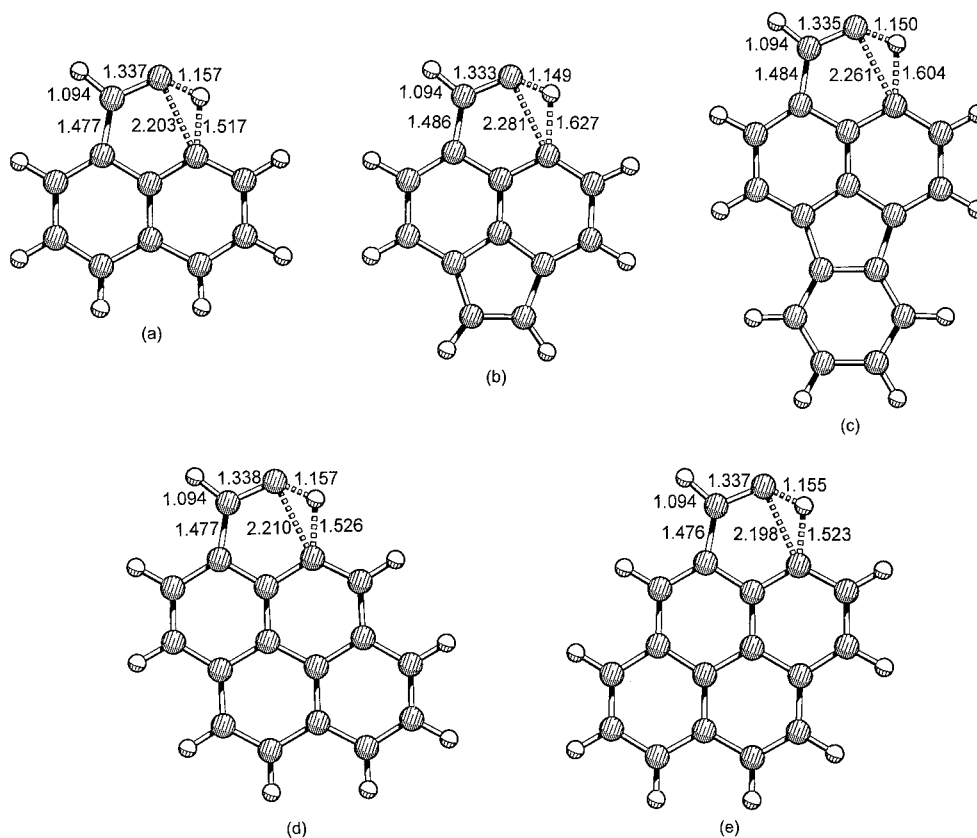
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Table 1. The Predicted Relative Energies of Products, Intermediates, and Transition States of the Unimolecular Reaction Mechanisms I and II^a

substrate (14)	relative energy, kcal/mol						
	14 → 15	15	15 → 17	14 → 16	16	16 → 17	17
1-ethynynaphthalene	45.9	46.0	55.2	69.8	39.0	47.5	-23.5
5-ethynylacenaphthylene	46.2	46.7	62.2	73.6	49.6	60.9	-9.4
3-ethynylfluoranthene	46.1	46.6	61.1	72.8	48.0	58.4	-12.1
1-ethynylpyrene	46.2	46.4	56.1	68.5	38.1	48.7	-22.4
4-ethynylpyrene	45.8	45.8	55.3	70.2	40.6	48.3	-23.0

^a All energies relative to the substrate. See Figures 2a and 2b for the numbering of individual species.

**Figure 4.** The BLYP/6-311G** optimized geometries (Å and deg) of (a) 1-ethynynaphthalene, (b) 2-(1-naphthyl)ethylidene carbene, and (c) the respective transition state.**Figure 5.** The BLYP/6-311G** optimized geometries (Å and deg) of the transition states for the one-step rearrangements (mechanism I) of (a) 1-ethynynaphthalene to acenaphthylene, (b) 5-ethynylacenaphthylene to pyracylene, (c) 3-ethynylfluoranthene to cyclopenta[cd]fluoranthene, (d) 1-ethynylpyrene to cyclopenta[cd]pyrene, and (e) 4-ethynylpyrene to cyclopenta[cd]pyrene.

collapsing to the respective ethynylarene, the formation of the corresponding CP-PAHs is again predicted to entail a one-step process with an energy barrier dependent on the strain present in the substrate. In the cases of 1-ethynylpyrene and 4-ethynylpyrene that derive from strainless PAHs, the predicted reaction barriers are very similar to that computed for 1-ethynynaphthalene. On the other hand, ring closures in the strained

5-ethynylacenaphthylene and 3-ethynylfluoranthene are expected to require activation energies that are 6–7 kcal/mol higher (compare the **15** → **17** entries in Table 1). These barrier height increases are caused by the unfavorable orientation of the C≡C moiety with respect to the C–H bond at which the insertion takes place (compare the geometries of the pertinent transition states, Figure 5) and the necessity to overcome

Table 2. The Predicted Relative Energies of Intermediates and Transition States of the Free-Radical Reaction Mechanisms III, IV, and V^a

substrate (14)	relative energy, kcal/mol							
	18	18 → 20	19	19 → 20	20	21	21 → 22	22
1-ethynyl-naphthalene	117.4	150.3	107.4	121.7	88.0	-30.7	-21.8	-67.0
5-ethynyl-acenaphthylene	116.7	155.0	108.2	128.2	102.0	-31.0	-16.7	-60.4

^a All energies relative to the substrate with a hydrogen atom added or subtracted as appropriate. See Figures 2c, 2d, and 2e for the numbering of individual species.

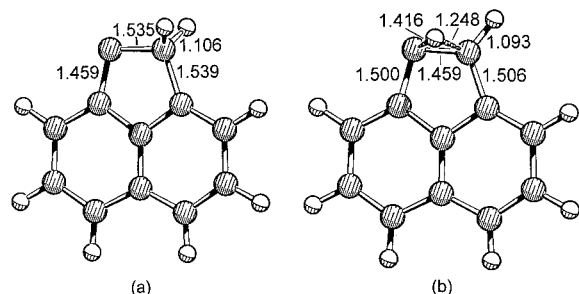


Figure 6. The BLYP/6-311G** optimized geometries (Å and deg) of (a) the carbene intermediate of the two-step rearrangement (mechanism II) of 1-ethynyl-naphthalene to acenaphthylene and (b) the corresponding transition state for 1,2-hydrogen shift.

additional strain brought upon the formation of a new five-membered ring. The latter effect also influences the overall reaction energetics.

The experimentally observed variations in yields of FVP syntheses of CP-PAHs are in full agreement with these predictions. Thus, whereas the (1-chloroethenyl)arene precursor of 1-ethynylpyrene produces up to 90% of cyclopenta[*cd*]pyrene at 1000 °C/0.01 Torr, cyclopenta[*cd*]fluoranthene is formed in less than 40% yield.^{11,13} Similarly, FVP of 5-ethynylacenaphthylene produces pyracylene (through a concomitant hydrogen loss from the dihydro derivative) under much milder conditions and with much better yields than that of the more strained 5-ethynylacenaphthylene.^{11,12}

The Free-Radical Chain-Reaction Pathways

Inspection of Table 1 reveals that, thanks to a substantially lower activation energy, the unimolecular one-step mechanism I is preferable to its two-step counterpart in all instances. The free-radical chain-reaction mechanisms III, IV, and V that involve bimolecular processes are less likely to be of relevance at the low-pressure conditions characteristic of typical FVP experiments. Moreover, as shown by the present calculations, the reaction pathways III and IV can be conclusively ruled out for other reasons.

In the case of the prototype 1-ethynyl-naphthalene → acenaphthylene rearrangement, the initiation step of mechanism III calls for 117.4 kcal/mol spent on the removal of hydrogen from the C≡CH moiety of the substrate (Table 2).³³ The resulting radical (**18**, Figure 2c) possesses a carbene-like structure conspicuously reflected in the pattern of the C–C bond lengths and the out-of-plane bending of the [–C≡C ↔ –C*=C:] pair of carbons (Figure 7). Ring closure in this radical involves a reaction barrier of 32.9 kcal/mol. The subsequent abstraction of hydrogen from 1-ethynyl-naphthalene by the product of this ring closure (**20**,

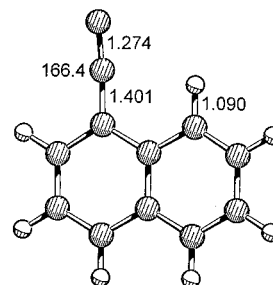


Figure 7. The BLYP/6-311G** optimized geometry (Å and deg) of the (1-naphthyl)ethynyl radical.

Figure 2c) yields acenaphthylene and recovers the (1-naphthyl)-ethynyl radical, thus completing the chain propagation step.

The obvious problem with this mechanistic scenario stems from the competing abstraction of hydrogen from the ring perimeter of the naphthalene moiety, which is favored by as much as 10.0 kcal/mol (Table 2). Although ring closure of the resulting 1-ethynyl-naphthalen-8-yl radical (**19**, Figure 2d) involves a reaction barrier of only 14.3 kcal/mol, its formation does not appear likely in light of the steric hindrance experienced by the abstracting species (which is not a factor for hydrogen abstractions at the other perimeter sites that are predicted to be almost isoenergetic³⁴). Consequently, reaction pathway IV does not emerge as a viable alternative to the conventional mechanism I.

The third free-radical reaction mechanism commences with an exothermic addition of hydrogen from a suitable donor.³⁵ The resulting species (**21**, Figure 2e) readily closes (the reaction barrier of 8.9 kcal/mol) to form the 1-acenaphthylenyl radical (**22**, Figure 2e), which then donates hydrogen to the reaction substrate in a somewhat endothermic (12.8 kcal/mol) process that completes chain propagation. Thus, since none of these steps proceeds through a large barrier, mechanism V might become a competitor to the unimolecular rearrangement at normal-pressure conditions, especially in the presence of hydrogen donors.

Similar conclusions can be drawn about the free-radical pathways for the formation of pyracylene from the strained 5-ethynylacenaphthylene. However, in this case the last step of mechanism V turns out to be endothermic by 19.9 kcal/mol and thus less facile.

Conclusions

Five distinct mechanisms are potentially possible for the thermal rearrangement of ethynylarenes to cyclopentafused polycyclic aromatic hydrocarbons (CP-PAHs). Out of two unimolecular rearrangement pathways, a one-step process involving hydrogen migration immediately followed by ring closure is clearly favored thanks to a significantly lower energy

(33) Although this initial step is likely to involve an abstracting species (such as a radical absorbed on the reactor wall) and thus require considerably less energy than direct C–H bond cleavage, the equilibrium for the propagation step $20 + 14 \rightarrow 18 + 17$ is very unfavorable as indicated by the predicted $\Delta G = 8.3$ kcal/mol at $T = 1200$ K (Table 3). The corresponding values for the reactions $20 + 14 \rightarrow 19 + 17$ and $22 + 14 \rightarrow 21 + 17$ are -2.7 and 15.5 kcal/mol, respectively.

(34) The corresponding BDEs range from 107.1 to 108.1 kcal/mol according to the present BLYP/6-311G** calculations; see also ref 23.

(35) The exothermicities of all other hydrogen additions to carbons at the naphthalene perimeter do not exceed that of the addition relevant to mechanism V by more than 2 kcal/mol.

Table 3. The Predicted Thermochemical Data for the Species Involved in the 1-Ethynyl-naphthalene \rightarrow Acenaphthylene Rearrangement^a

species	ΔE (0 K), kcal/mol	ΔH (1200 K), kcal/mol	ΔG (1200 K), kcal/mol
14 \rightarrow 15	45.9	44.5	47.6
15	46.0	46.3	45.7
15 \rightarrow 17	55.2	53.7	60.4
14 \rightarrow 16	69.8	68.3	73.7
16	39.0	37.9	44.1
16 \rightarrow 17	47.5	44.8	56.2
17	-23.5	-25.4	-13.5
18	117.4	120.3	82.6
18 \rightarrow 20	150.3	152.8	118.7
19	107.4	111.1	71.6
19 \rightarrow 20	121.7	123.1	92.4
20	88.0	89.6	60.8
21	-30.7	-33.6	0.2
21 \rightarrow 22	-21.8	-27.1	15.3
22	-67.0	-71.4	-28.8

^a All values relative to 1-ethynyl-naphthalene.

barrier. Contrary to common belief, neither 2-(1-naphthyl)-ethylidene carbene nor its annelated analogs are genuine chemical species.³² Consequently, these carbenes do not constitute intermediates pertinent to this reaction mechanism, which

has the predicted activation energy of 55–62 kcal/mol depending on the extent of strain in the parent ethynylarene molecule.

The present study conclusively rules out free-radical mechanisms that commence with hydrogen abstraction. However, in the case of strainless substrates and higher reaction pressures, the pathway involving an initial hydrogen addition might become a viable competitor to the unimolecular rearrangement.

The inferences about the relevance of individual reaction mechanisms, which are based upon the predicted relative energies at $T = 0$ K, are upheld upon inspection of the relative enthalpies and free enthalpies computed at $T = 1200$ K, i.e., the temperature of a typical FVP experiment (Table 3).

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