FORMATION PATHWAYS OF ETHYNYL-SUBSTITUTED AND CYCLOPENTA-FUSED POLYCYCLIC AROMATIC HYDROCARBONS

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Two novel classes of polycyclic aromatic hydrocarbons (PAH), those with ethynyl substituents (ethynyl-PAH) and those with externally fused five-membered rings (cyclopenta-fused PAH or CP-PAH), have recently been identified in the products of a variety of fuels and combustion/pyrolysis environments. However, the recently developed capacity for identifying these compounds has raised new questions about preferential reaction pathways. Specifically, across various fuels and operating conditions, experimentally observed products are (1) CP-PAH, which result from C₂H₂ addition to an aryl radical, followed by cyclization to a cyclopenta ring and (2) ethynyl-PAH, which result from C₂H₂ addition to locations on the aryl radical where cyclization is not possible. We have never observed ethynyl-PAH resulting from C₂H₂ addition to an aryl radical at a point where cyclization into a five-membered ring is possible.

To explain this behavior, we have performed AM1 semiempirical quantum chemical computations with group correction in order to examine the potential energy surfaces of the reaction pathways that lead to ethynyl-PAH and CP-PAH. We have performed computations for the parent aryl radical, possible ethynyl-PAH products, possible CP-PAH products, as well as intermediates and transition states, for C₂H₂ addition to naphthalene, anthracene, phenanthrene, acenaphthylene, fluoranthene, and pyrene. Possible CP-PAH products are acenaphthylene, aceanthrylene, acephenanthrylene, pyracylene, cyclopenta[cd]fluoranthene, and cyclopenta[cd]pyrene.

In all cases, we have found that, although energy differences between ethynyl-PAH isomers are very small (~1 kcal/mol), the experimentally observed ethynyl-PAH is almost always the lowest energy isomer. Furthermore, the observed preference for cyclization to CP-PAH over formation of an ethynyl-PAH can be explained by the significantly lower energy barrier (23 vs. 36 kcal/mol) for the cyclization reactions. Finally, we have determined that, while not prohibited, the isomerization of ethynyl-PAH to CP-PAH requires significantly higher energy than the aryl-vinyl cyclization reactions, and therefore is not expected to make a significant contribution to the product distribution. These results are sufficiently consistent that the computation of reaction pathway energy surfaces can be used to identify likely ethynyl-PAH and CP-PAH products from the addition of C₂H₂ to much larger parent PAH.

Introduction

Several investigations [1–12] of the composition of combustion and pyrolysis products from a variety of fuels and experimental conditions have led to the identification of a number of polycyclic aromatic hydrocarbons (PAH) with peripherally fused five-membered rings and/or ethynyl substituents, termed cyclopenta-PAH (CP-PAH) and ethynyl-PAH, respectively. The identifications of many of these CP-PAH and ethynyl-PAH, however, have only recently been made possible, due to the recent syntheses of authentic reference standards of such PAH [3,7,11,13–16]. Because the means of unequivocally identifying CP-PAH and ethynyl-PAH did not previously exist, these two classes of PAH, for the most part, have gone unnoticed as fuel products and thus are noticeably absent from theoretical models for PAH growth and soot formation. Despite their elusiveness, CP-PAH and ethynyl-PAH are very important, due to their biological and chemical activities. Several studies [11,17–19] suggest that CP-PAH, as a class, are generally more mutagenic than other classes of PAH. In fact, Howard et al. [20] and Durant et al. [17] have shown that the CP-PAH cyclopenta[cd]pyrene is at least as biologically active as the well-known benzenoid PAH mutagen, benzo[a]pyrene. The enhanced biological activity of CP-PAH is apparently due to the relatively facile metabolic epoxidation of the cyclopenta ring [18], which results from the more localized electronic structure in this ring [19]. The electronic structure of the cyclopenta ring may also account for why CP-PAH are more susceptible to atmospheric oxidation than benzenoid PAH [21]. CP-PAH are also of interest for their chemical behavior in combustion and pyrolysis environments. For example, an increase in temperature brings...
about an increase in both soot yield and in the CP-PAH fraction of the total PAH [22]—a behavior that suggests an interlinked chemistry between CP-PAH and soot. The chemistry of CP-PAH also appears to be linked to the formation of fullerenes, as shown by Lafleur et al. [9]: fuels and reactor configurations which produce corrulene, a possible fullerene precursor, to the exclusion of CP-PAH; however, fuels and reactor configurations in which fullerenes are not detected produce an array of CP-PAH. This behavior is evidence of competing chemical pathways that are influenced by the boundary conditions and/or the initial fuel.

The literature [23,24] suggests that CP-PAH form from the addition of C\textsubscript{2}H\textsubscript{2} to aryl radicals abundantly present in combustion and pyrolysis environments. However, as these works [23,24] show, C\textsubscript{2}H\textsubscript{2} addition does not necessarily result in cyclopenta fusion; it can also yield ethynyl-substituted PAH. Fig. 1 illustrates the possible results [24] of C\textsubscript{2}H\textsubscript{2} addition to the two aryl radicals that come from H abstraction of naphtalene, the 1-naphthyl and 2-naphthyl radicals. In row (i) of Fig. 1, C\textsubscript{2}H\textsubscript{2} addition to the 1-naphthyl radical is followed by loss of H, resulting in 1-ethynylnaphthalene. Alternatively, as shown in row (ii) of Fig. 1, the same sequence of C\textsubscript{2}H\textsubscript{2} addition and H loss can lead to cyclization across a “valley” to produceacenaphthylene. In contrast, as shown in row (iii) of Fig. 1, C\textsubscript{2}H\textsubscript{2} addition to the 2-naphthyl radical can only yield 2-ethynylnaphthalene, as there is no valley-adjacent carbon available for cyclization. Fig. 1 thus demonstrates that C\textsubscript{2}H\textsubscript{2} addition to aryl radicals has the potential of producing a mixture of CP-PAH and isomeric ethynyl-PAH—the complexity of this mixture depending on the number of possible aryl radicals to which the C\textsubscript{2}H\textsubscript{2} can add.

The multiplicity of isomeric ethynyl-PAH and CP-PAH structures, of course, poses serious challenges to the separation and identification of constituents of fuel product mixtures, since most analytical techniques rely on chromatographic and spectrometric methods that may not be capable of distinguishing between isomers. Nevertheless, we have shown that reverse-phase high-pressure liquid chromatography (HPLC) coupled with ultraviolet-visible absorption spectroscopy is capable of distinguishing isomers, both CP-PAH from ethynyl-PAH, and ethynyl-PAH from each other [3,25–27]. As we have recently observed [1–5], the application of this analytical technique to fuel products yields results that expose a whole new set of questions as to why certain products are common to a variety of fuels and systems, while others prove never to be observed.

Figure 2 presents the portion of an HPLC chromatogram depicting the two- to five-ring PAH produced from the pyrolysis of a brown coal at 1000 °C [1,5,28–30]. Although over 50 PAH product species have been unequivocally identified [5,28–31] in this product sample, the only product structures drawn in Fig. 2 are those of the CP-PAH and ethynyl-PAH discussed in this paper. Fig. 2 shows that—of the three possible products of C\textsubscript{2}H\textsubscript{2} addition to naphtalene's aryl radicals (shown in Fig. 1)—only acenaphthylene and 2-ethynylnaphthalene are present among the brown coal pyrolysis products; 1-ethynylnaphthalene is not [5]. This observation suggests that the reactions depicted in rows (ii) and (iii) of Fig. 1 are active; the one in row (i) is not. Similarly, Fig. 2 reveals that for C\textsubscript{2}H\textsubscript{2} addition to anthracene's
aryl radicals, aceanthrylene and 2-ethynylanthracene are present; 1-ethynylanthracene is not. For phenanthrene’s aryl radicals, acephenanthrylene and 2-ethynylphenanthrene are present; 9-ethynylphenanthrene is not [5].

All of these cases—and the other products illustrated in Fig. 2—adhere to the following two rules: (1) the only ethynyl-PAH observed are those resulting from C₂H₂ addition at a position that does not allow for cyclization to a five-membered ring; and (2) in any case where C₂H₂ is added at a position that does allow for cyclization, the cyclization product is observed, and the ethynyl-PAH is not. Not only are these two rules exhibited by the products of brown coal pyrolysis in Fig. 2, but they are also consistent with the CP-PAH and ethynyl-PAH product distributions obtained from the other fuels we have examined—a high-rank coal [4,5], anthracene [2], and benzene [3]—all of which have been pyrolyzed or combusted in different reactor systems, spanning a wide range of reaction conditions. This uniformity of behavior suggests that there is some chemical preference for the formation of the cyclopenta ring over that of the ethynyl group. Sarobe et al. [32–35] have investigated various isomerizations between ethynyl-PAH and CP-PAH. However, with the exception of acenaphthylene [36], the potential energies of the formation paths of cyclopenta-PAH and ethynyl-PAH via C₂H₂ addition have never, until now, been examined.

In the following, we perform semiempirical quantum chemical computations of the heats of formation of intermediates, products, and transition states, in order to examine the competing pathways for the formation of several CP-PAH—acenaphthylene, aceanthrylene, acephenanthrylene, pyracylene, cyclopenta[cd]fluoranthene, and cyclopenta[cd]-pyrene—and the corresponding ethynyl-PAH. Identification of the theoretically preferred pathways may permit explanation of the qualitatively uniform CP-PAH and ethynyl-PAH product distribution patterns we observe experimentally for a wide range of fuels and combustion/pyrolysis conditions.

### Theoretical Approach

Because of the large number and sizes of species examined here, we have chosen to compute properties using semiempirical quantum methods. Heats of formation are determined for all species and transition states using the AM1 Hamiltonian [37] of the MOPAC 97 [38] program. Species are first optimized for lowest-energy geometries using the keyword GNORM = 0.1. More stringent criteria including keywords GNORM = 0.01 and PRECISE were examined but did not produce significant improvements in the calculated energies. Transition states of unimolecular reactions are determined using the SADDLE keyword and refined with the TS keyword. Dissociation and recombination reactions are optimized to transition state (keyword TS) by defining the bond to be broken as the reaction coordinate.

Wang and Frenklach [39] showed that semiempirical computations introduce increasingly large errors as aromatic rings are added, resulting from approximations of the interatomic potential profile. This error is particularly problematic in the case of peripheral five-membered rings, exactly the compounds we examine here. For acenaphthylenes, the simplest CP-PAH, the ΔHₚ₀ is overpredicted by 25%. Fortunately, Wang and Frenklach [39] also show that these errors are systematic and can be corrected to within a few kilocalories for the species they study. Their methodology is used here.

The method is based on the group additivity method of Benson [40] but makes the improvement of using group characteristics for corrections to the computed ΔHₚ₀, rather than simply summing group contributions to achieve the final value. In the method of Wang and Frenklach [36], each benzenoid C atom is classified as either A, peripheral and bonded to H; B, peripheral but bonded to two type As and one non-A; C, peripheral but bonded to one type A and two non-As; or D, internal and not bonded to any type As. Wang and Frenklach developed correction parameters for these atom types, as well as for numerous substituent groups and radicals, so that

\[ ΔH_{p0}^{corr} = ΔH_{p0}^{corr}(AM1) + \sum GC_i \]  

where GCᵢ is the correction parameter for that group. We have devised an additional group correction of 14.1 kcal/mol to account for internal five-membered rings like that in fluoranthene, based on the measured ΔHₚ₀ of fluoranthene of 69.2 kcal/mol [41]. The remaining group correction parameters used in this study, along with additional parameters for other groups, can be found in Ref. [39]. Discussion of the uncertainties in this method can be found in Refs. [36] and [39].

### Results and Discussion

Figures 3–8 show the computed potential energy paths for the addition of C₂H₂ to naphthalene, anthracene, phenanthrene, acenaphthylenes, fluoranthene, and pyrene, respectively. As shown in the figures for each of these parent PAH, the initial step of the reaction is the addition of C₂H₂ to a terminal aryl radical of the parent PAH, forming PAH with terminal vinyl radicals. Once formed, these vinyl radicals can then follow any one of the following three routes: Pathway A, H removal from the vinyl radical to form the ethynyl-PAH; Pathway B, cyclization [36] of the vinyl radical (where a “valley”-adjacent carbon is available) to form an aryl radical with...
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Fig. 3. Potential energy surface of the formation of ethynylphenanthrenes and acephenanthrylene from phenanthryl radicals. Solid line, 1-phenanthryl parent; dotted line, 2-phenanthryl parent; dotted-dashed line, 9-phenanthryl parent. Species in bold (2-ethynylphenanthrene and acephenanthrylene) have been identified in fuel products. Pathways A, B, and C (defined in text) are indicated.

Fig. 4. Potential energy surface of the formation of ethynlanthracenes and aceanthrylene from anthryl radicals. Solid line, 1-anthryl parent; dotted line, 2-anthryl parent; dotted-dashed line, 9-anthryl parent. Species in bold (2-ethynlanthracene and aceanthrylene) have been identified in fuel products. Pathways A, B, and C (defined in text) are indicated.

Fig. 5. Potential energy surface of the formation of ethynylacenaphthenes and pyracylene from acenaphthyl radicals. Solid line, 5-acenaphthyl parent; dotted line, 1-acenaphthyl parent; dotted-dashed line, 4-acenaphthyl parent. Species in bold (1-ethynylacenaphthylene) have been identified in fuel products. Pathways A, B, and C (defined in text) are indicated.

Fig. 6. Potential energy surface of the formation of ethynylacenaphthenes and pyracylene from acenaphthyl radicals. Solid line, 5-acenaphthyl parent; dotted line, 1-acenaphthyl parent; dotted-dashed line, 4-acenaphthyl parent. Species in bold (1-ethynylacenaphthylene) have been identified in fuel products. Pathways A, B, and C (defined in text) are indicated.

an ethylene bridge, followed by H loss from the base of the ethylene bridge to form the cyclopenta-PAH; or Pathway C, hydrogen migration to the vinyl group, followed by cyclization to the just-vacated radical site, and then H loss from the saturated corner of the five-membered ring. Ethynyl-PAH result from Pathway A; CP-PAH result from Pathways B and C. We now examine each of these steps in turn for their significance in the formation of ethynyl-substituted and cyclopenta-fused PAH.

As suggested by their starting points, the first step in all of the reaction schemes of Figs. 3–8 is actually the formation of the PAH aryl radicals. We have chosen to begin our analyses with the radicals already in place, however, because the radicals can be formed in a variety of ways: abstraction by H atoms in a pyrolysis environment, OH attack in a combustion environment, or even the artifact of a previous cyclization-type step, for example, the formation of naphthalene from the cyclization of 1-ethynyl-2-vinylbenzene. Of primary interest are the energies of the radicals themselves, particularly any differences resulting from radical location. In fact, radical location has very little effect on the energy of the radical PAH. The 1-, 2-, and 9-phenanthryl radicals (Fig. 5) are virtually indistinguishable, while in the cases of
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Fig. 7. Potential energy surface of the formation of ethynylfluoranthenes and cyclopenta[cd]fluoranthene from fluoranthyl radicals. Solid line, 3-fluoranthyl parent; dotted line, 2-fluoranthyl parent. Species in bold (cyclopenta[cd]fluoranthene) have been identified in fuel products. Pathways A, B, and C (defined in text) are indicated.

Fig. 8. Potential energy surface of the formation of ethynylpyrenes and cyclopenta[cd]pyrene from pyrenyl radicals. Solid line, 1-pyrenyl parent; dotted line, 2-pyrenyl parent; dotted-dashed line, 4-pyrenyl parent. Species in bold (cyclopenta[cd]pyrene) have been identified in fuel products. Pathways A, B, and C (defined in text) are indicated.

the naphthyl (Fig. 3) and fluoranthyl (Fig. 7) radicals, the 2-isomer, which can only lead to the ethynyl-substituted isomer, has a negligibly lower energy. The 9-anthryl radical (Fig. 4) has a marginally higher energy, likely the result of “crowding” by the adjacent H atoms on the zigzag edge. Only aceenaphthyl (Fig. 6) exhibits a significant energy difference, with 1-aceenaphthyl lying 8 kcal/mol above the other aceenaphthyl radicals. This is most likely a result of the more localized electronic structure of the ethylene bridge [19,25], resulting in a slightly higher bond dissociation energy at this site.

The fact that the energies of the various isomers of the aryl radicals are nearly indistinguishable means that the preferential formation of certain ethynyl-PAH isomers does not result from a preferential formation of particular aryl radicals. In fact, examination of the rest of Pathway A, the addition of C2H2 to form aryl-vinyl radicals followed by loss of H from the vinyl radical to produce the ethynyl-PAH, shows that the entire path is energetically similar for different substituent locations, as can be seen in Figs. 3–8. However, despite the small differences in energy, a common trend arises: the aryl-vinyl radicals that have the opportunity to cyclize into a CP-PAH have slightly higher energies than those that lack a cyclization route (likely a result of the more proximate H atom at the valley-adjacent site). For example, in Fig. 3, 1-vinylnaphthyl lies 2 kcal/mol higher than 2-vinylnaphthyl; in Fig. 4, 1- and 9-vinylanthryl lie 2 and 3 kcal/mol higher than 2-vinylanthryl. This trend is repeated for the ethynyl-PAH themselves; for example, 1-ethynylanthralhene has a slightly higher energy than 2-ethynylnaphthalene (Fig. 3), and 1- and 9-ethynylanthracene have slightly higher energies than 2-ethynylanthracene (Fig. 4). Furthermore, all of the ethynyl-PAH that have been experimentally identified in fuel products are those with the marginally lower energy; 2-ethynylnaphthalene [1,3,4,12,28], 2-ethynylanthracene [2,5], 2-ethynylphenanthrene [5], and 1-ethynylacenaphthylene [1–4,28]. However, the small energy difference is not sufficient to explain the complete lack of slightly higher-energy ethynyl-PAH isomers.

The energies of the cyclization routes provide a more convincing explanation. We have examined two possible paths for this process. The first, Pathway B [36], is a two-step process where the vinyl radical displaces the adjacent H atom and closes the ring, resulting in a relatively low-energy aryl radical, followed by a loss of the displaced H atom to form the CP-PAH. The second path, Pathway C [42], involves a shift of the adjacent H atom to the terminal end of the vinyl radical, resulting in a radical at the ring-closure site. The terminal vinyl group then closes on the new radical site, resulting in a partially hydrogenated ethylene bridge. Loss of the extra H atom again results in the CP-PAH.

In all the cases examined here, the largest energy barrier to the formation of the Pathway B intermediate is little more than half that of the barrier to form the ethynyl-PAH, by Pathway A. As shown by Frenklach et al. [42], the barrier for the H migration, Pathway C, is significantly smaller than that of the two-step process, nearly half again as much. Furthermore, the barrier for the ring closure step of Pathway C is nearly identical to that of the ring-closure step in Pathway B. Geometry optimizations of Pathway B show that the displaced H atom is ultimately located perpendicular to the plane of the PAH, often with a significant amount of twisting to the entire molecule. Despite this strained configuration, however, the Pathway B intermediate has a relatively low energy. Finally, we observe that the
predicted cyclization product of C2H2 addition to PAH. It should be noted here that pyracylene, the lower than the highest barriers in the paths to CP-ring. For the other CP-PAH, Figs. 3–5 and Fig. 8, the of pyracylene has been measured exper-
pose [34], so its absence as a product might be ex-
other hand, pyracylene is known to readily decom-
might indicate the difficulty of this step. On the other hand, pyracylene is known to readily decompose [34], so its absence as a product might be explained by destruction routes not examined here. The acenaphthylene and fluoranthene cases are also the exceptions in the final step, H loss resulting in the CP-PAH, which have barriers that are 6 and 4 kcal/mol higher, respectively, than any other step in Pathway B or C, the formation of the cyclopenta ring. For the other CP-PAH, Figs. 3–5 and Fig. 8, the barriers for the final H loss are 6–10 kcal/mol lower than the highest barriers in the paths to CP-PAH. It should be noted here that pyracylene, the predicted cyclization product of C2H2 addition to acenaphthylene, has not been observed as a fuel product in any work that has been able to distinguish it from the ethynylacenaphthylene isomers. The high barriers to the formation of pyracylene, about the same as the barriers to form ethynylacenaphthylene, might indicate the difficulty of this step. On the other hand, pyracylene is known to readily decompose [34], so its absence as a product might be explained by destruction routes not examined here. The ΔH^f298 of pyracylene has been measured experimentally as 98 kcal/mol [43], which agrees within a few kcal/mol with ab initio results [44] and the value used here (103 kcal/mol).

Finally, we examine an alternate and frequently invoked path for the formation of cyclopenta rings [13.32–34,45,46], shown (for the formation of acenaphthylene only) in Fig. 9. The pathways depicted in Fig. 2 are repeated here for comparison. The additional path allows for conversion of ethynyl-
then inserts into the adjacent C–H bond, forming a five-membered cyclopenta ring. This reaction path is invoked most often for the unimolecular isomerization of ethynyl-PAH into CP-PAH in synthetic preparatory schemes [13,32–34,45,46], for example, flash vacuum thermolysis. As can be seen in Fig. 9, the ΔH^f298 of the biradical intermediate is significantly larger than the barriers for the paths examined previously. However, all points on this path include an additional 52.1 kcal/mol to account for the free H atom, to remain consistent with the energies given for the other paths. In other words, in systems where free H is not significant (for example, synthetic preparation via unimolecular isomerization), formation of the biradical is not unreasonable. Even in combustion environments, the unimolecular reaction should not be prohibited, but the energy is sufficiently high that it should not be significant when compared with the other routes examined here.

Summary and Conclusions

To better understand the mechanisms of formation of ethynyl-PAH and CP-PAH, we have performed AM1 semiempirical quantum chemical computations with group correction on paths of the potential energy surfaces of these compounds. We have focused on groups of isomers that have previously identified in real combustion and pyrolysis products, and have included related species that were not evident in those products, in order to understand why certain compounds appear preferential over others. For each potential energy surface, we have examined the precursor aryl radicals, the ethynyl-PAH and CP-PAH isomers, and the vinyl radical species and intermediates, as well as the transition states for each step. We have employed the group correction method particularly to avoid the large errors in the AM1 computation of cyclopenta rings; this method is sufficiently robust that the ΔH^f298 found for the single dicyclopenta species, pyracylene, agrees exactly with ab initio calculations and is within a few kcal/mol of the experimental value.

We have found that the location of the initial radical site makes little difference in the energy of the reaction path, suggesting that the formation of the initial radical site does not control the nature of the product of the reaction. Rather, the energy barrier for the formation of the ethynyl-substituted isomers is always much larger than that for the formation of intermediates to the CP-PAH—strong evidence that the CP-PAH should be preferentially formed when that path is available. In only two cases, pyracylene and cyclopenta(e/d) fluoranthene, is the barrier for the formation of the CP-PAH anywhere close to the barrier for the formation of the ethynyl-PAH, and of
these two, only the one with the lower barrier, cyclopenta[cd]fluoranthene, is ever found in any products. Finally, we have found that the isomerization of ethynyl-PAH to CP-PAH is a relatively high-energy process, suggesting that it is not the primary source of CP-PAH when lower-energy routes are available.

In our examination of C2H2 addition to six different parent PAH, we have found that the potential energy surfaces developed by AM1 computation with group correction accurately predict the preferred isomers experimentally observed in the products of a variety of fuels and configurations. Because we have evidence that ethynyl-PAH and CP-PAH are not limited to the small parent PAH examined here [47], these kinds of calculations will provide a useful tool for determining which larger ethynyl-PAH and CP-PAH isomers are most likely to occur. In conjunction with analytical methods such as spectroscopy [25, 26] and chromatography [27], the identification of previously unknown compounds of these classes can be greatly facilitated. Furthermore, the elucidation of the participation of ethynyl substitution and cyclopenta fusion in PAH growth will improve detailed kinetic models which attempt to accurately reflect real PAH yields and distributions, by adding appropriate product species which would otherwise go unnoticed.

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