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Thermally Induced Cyclodehydrogenation of Biaryls: A Simple Radical Reaction or a Sequence of Rearrangements?

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Comprehensive BLYP/6-311G** calculations identify three distinct reaction pathways relevant to the thermally induced cyclodehydrogenation of 1-phenylnaphthalene (and, by analogy, other aromatic hydrocarbons). The first pathway, which is expected to predominate at lower temperatures, involves the formation of biarylyls, followed by their rapid cyclization to transient radical intermediates that ultimately lose hydrogen to yield fluoranthene. The second reaction channel commences with the dehydrogenation of biarylyls to arylarynes, which then either directly cyclize to fluoranthene or rearrange to cyclopentadienylidenecarbenes. Rapid intramolecular trapping ultimately converts the latter species to cyclopentafused isomers of fluoranthene. Direct equilibration of these isomers and fluoranthene itself, which constitutes the third reaction pathway, is associated with very high activation energies. For this reason, such equilibration is not expected to be operative under normal pyrolytic conditions.

Introduction

The formation of polycyclic aromatic hydrocarbons (PAHs) that accompanies incomplete combustion of fossil fuels involves a complicated sequence of reactions. According to Badger's free radical mechanism, which is supported by extensive experimental evidence,[1−6] simple aromatic hydrocarbons that are either present in the starting material or thermally generated from smaller molecules first lose hydrogen through a C−H bond cleavage, producing aryl radicals. Recombination of these radicals yields biaryls, which in turn are subject to further dehydrogenation.

Recent electronic structure studies have shown that the energetics of the initial C−H bond cleavage in simple PAHs is determined mostly by steric effects.[7] Consequently, the loss of hydrogen is expected to occur preferentially at sterically congested sites, implying the propensity of biaryls to undergo, whenever possible, cyclodehydrogenation rather than dehydrogenative polymerization. Being a fast intramolecular process with a low energy barrier, cyclodehydrogenation is favored over the diffusion-controlled bimolecular radical recombination at low reactant concentrations that are prevalent upon pyrolytic conditions. Indeed, pyrolysis of benzene produces a mixture of biphenyl, *p*-terphenyl, triphenylene, and *m*-terphenyl,[2] whereas only binaphthyls, benzofluoranthenes, and perylene are obtained from naphthalene.[3] Similarly, dehydrogenative trimerization does not appear to be a viable reaction pathway in the pyrolysis of anthracene.[4,6] This preference for relief of steric overcrowding through cyclodehydrogenation has been exploited in the recently published innovative synthesis of a fullerene subunit.[8]

The simplest reaction mechanism that can be conceived for the cyclodehydrogenation of biaryls commences with the formation of biarylyl radicals. The biarylyls then yield pericondensed PAHs via ring closures followed by C−H bond scissions in the radical intermediates. Although seemingly obvious, such a mechanism does not account for the presence of cyclopentafused aromatic hydrocarbons (CP-PAHs) among the products of pyrolysis of simple PAHs. For example, thermal dehydrogenation of benzo[*c*]phenanthrene produces not only the expected benzo[*ghi*]fluoranthene but also cyclopenta[*cd*]pyrene.[9] Both the latter species and other CP-PAHs, such as dicyclopentapyrenes[10] are present in combustion effluents.[11] Being potent mutagens and carcinogens,[12] these CP-PAHs are of great interest to environmental science and biochemistry.

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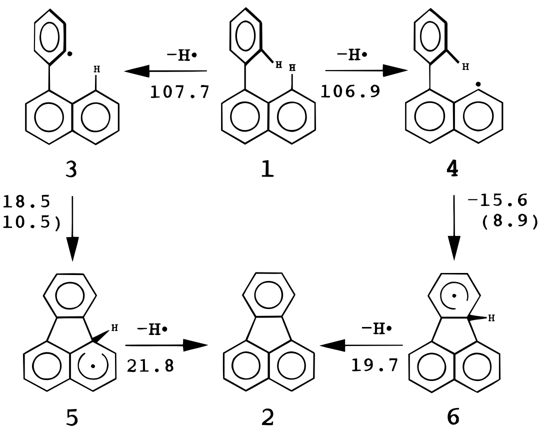

Figure 1. The direct radical mechanism of the cyclodehydrogenation of **1** with the reaction and activation enthalpies (in parentheses) (kcal/mol) listed.

Thus far, the sequence of reactions responsible for the formation of CP-PAHs has not been characterized experimentally. One possible pathway entails a further hydrogen loss from the biarylyl radical. Rearrangement of the resulting arylaryne affords a substituted cyclopentadienylidenecarbene, which in turn is trapped intramolecularly to form a CP-PAH. This mechanism is supported by the recently observed unexpected conversion of triphenylene to cyclopent[*hi*]acephenanthrylene upon flash vacuum thermolysis.[13] Moreover, the benzyne → cyclopentadienylidenecarbene rearrangement[14] is a well-established reaction that is widely employed in organic synthesis.[14−16] However, it should be emphasized that direct equilibration between the pericondensed PAHs and the CP-PAHs has not been ruled out.[9,17]

The importance of the aforedescribed interconversions of PAHs to both pure and applied chemical research combined with the lack of definite experimental evidence for either mechanism has prompted us to carry out a comprehensive state-of-art electronic structure study of cyclodehydrogenation of 1-phenylnaphthalene **1** (Figure 1), which is the simplest biaryl capable of such a reaction (one should also note that benzo[*c*]phenanthrene may be regarded as a rigid analog of **1**). The results of this study are reported in this paper.

Details of Calculations

All calculations reported in this paper were carried out with the GAUSSIAN 94 suite of programs.[18] Geometries of all species under study were fully optimized, and their vibrational frequencies were calculated. All the predictions of reaction energetics and barriers cited in the following text and figures pertain to standard enthalpies of formation computed at the BLYP/6-311G** level of theory. The suitability of this level of theory for studies of reactions involving aryl radicals, arynes, and carbenes has been previously established.[7,19] For instance, the BLYP/6-311G** estimate for the energy of the 1,2-didehydrogenation of benzene (i.e. the reaction $C_6H_6 \rightarrow C_6H_4 + H_2$) equals 82.8 kcal/mol, in good agreement with both the experimental value of 86.6 ± 3.0 kcal/mol,[20] and the CCSD(T)/6-311G** prediction of 86.8 kcal/mol.[19] A similar agreement has been found for the BLYP/6-311G** and CCSD(T)/6-311G** energies of the benzyne → cyclopentadienylidenecarbene isomerization (32.2 vs 29.2 kcal/mol) and the corresponding reaction barriers (33.2 vs 31.2 kcal/mol).[19]

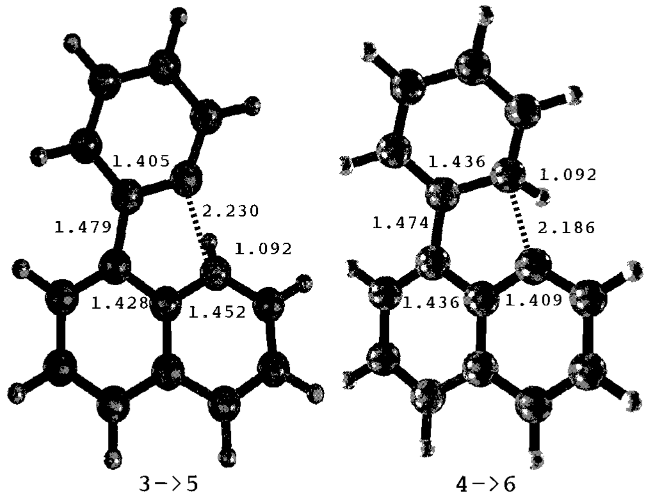

Figure 2. Selected C−C and C−H bond lengths (Å) in the transition states of the intramolecular ring closures **3** → **5** and **4** → **6**.

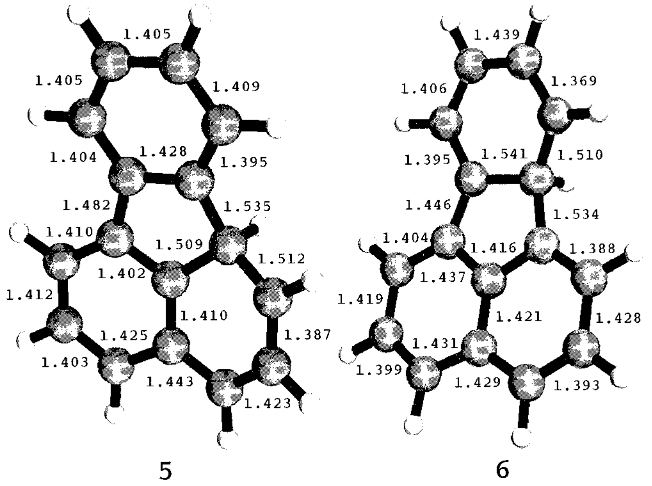

Figure 3. The C−C bond lengths (Å) in the radical intermediates **5** and **6**.

The Direct Radical Mechanism

The cyclodehydrogenation of 1-phenylnaphthalene **1** may proceed through the initial loss of hydrogen at either

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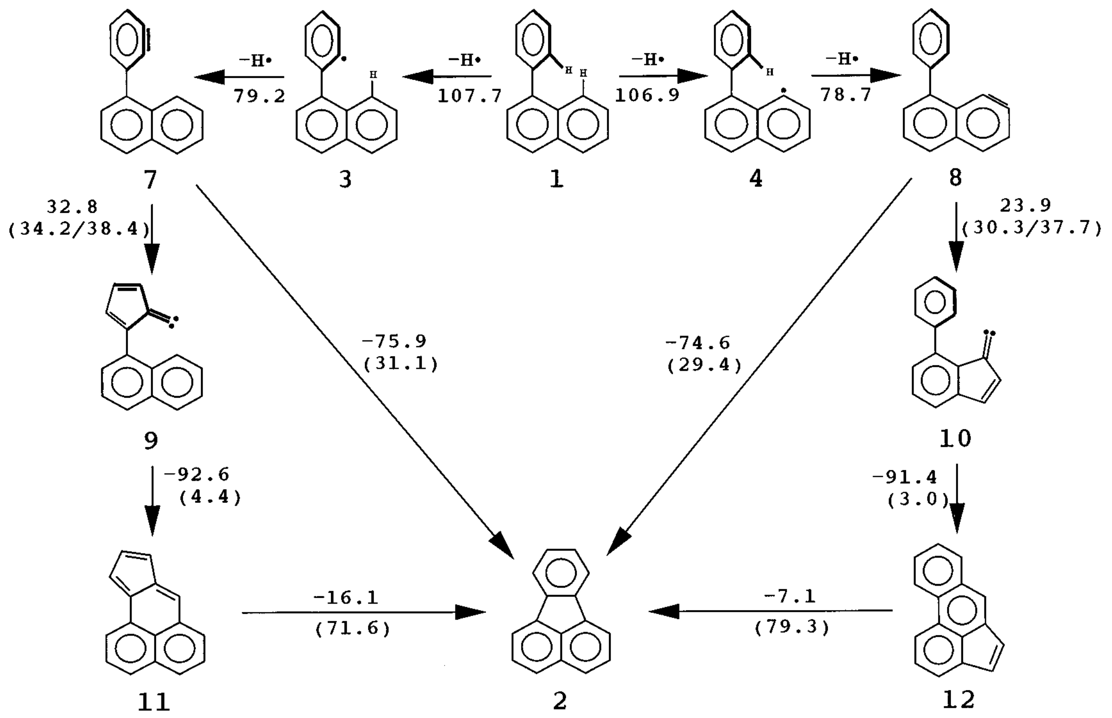

Figure 4. The arylaryne/annelated cyclopentadienylidenecarbene mechanism of the cyclodehydrogenation of **1** with the reaction and activation enthalpies (in parentheses) (kcal/mol) listed.

the benzene or naphthalene moiety.[21] Because of the small difference in the respective C–H bond dissociation energies (Figure 1) and the facile interconversion of the resulting radicals **3** and **4** via a 1,5-hydrogen shift,[22,23] the two reaction channels are expected to contribute equally to the formation of fluoranthene **2**. The average interring dihedral angles in **3** or **4** are smaller (43.6° and 44.4°, respectively) than that in **1** (59.1°),[24] as the removal of hydrogen lessens the steric congestion present in the parent biaryl.

Both **3** or **4** are predicted to readily undergo intramolecular ring closures to intermediates **5** and **6**. The transition states of these reactions are found to be quite early, with the lengths of the C–C bonds under formation amounting to ca. 2.2 Å (Figure 2). Unpaired electrons in the nonplanar intermediates **5** and **6** are well delocalized, as indicated by the patterns in the computed C–C bond lengths (Figure 3). Nevertheless, the partial losses of aromaticity that accompany the ring closures largely offset the energy gains due to formation of C–C bonds, resulting in the predicted reaction exothermicities of less than 20 kcal/mol.

The C–H bond cleavage in either **5** or **6** completes the pathway from **1** to **2**.[21] The restoration of aromaticity upon the removal of hydrogen makes the reactions **3** → **2** + $H^{\bullet}$ and **4** → **2** + $H^{\bullet}$ almost thermoneutral. Thus, once formed, biarylyls are rapidly converted to pericondensed PAHs and $H^{\bullet}$ in a two-step process with low energy barriers. This prediction is confirmed by the mild reaction conditions required by the Pschorr synthesis of **2** from a diazonium salt derived from **1**.[25]

The Arylaryne/Annelated Cyclopentadienylidenecarbene Mechanism

Their high propensity to cyclization notwithstanding, the biarylyl radicals **3** and **4** may undergo further dehydrogenation when exposed to pyrolytic conditions. Each of the resulting highly reactive arylarynes **7** and **8** is expended through two competing reaction pathways (Figure 4). The first pathway leads directly to fluoranthene **2** via a highly exothermic one-step cyclization concomitant with a 1,3-hydrogen shift. In the case of the phenylnaphthalyne **8**, the predicted activation enthalpy of this cyclization (29.4 kcal/mol) is comparable to that of the respective aryne → carbene rearrangement (30.3 kcal/mol). On the other hand, the cyclization of the naphthylbenzyne **7** has a somewhat lower reaction barrier than its conversion to the carbene **9**.

The properties of the carbenes **9** and **10** follow closely those of their unsubstituted prototypes.[26] Thus, the enthalpy of the reaction **7** → **9** is almost the same as that of the benzyne → cyclopentadienylidenecarbene rearrangement.[19] The computed lengths of the analogous C–C bonds in **9** (Figure 5) and cyclopentadienylidenecarbene are also quite similar, indicating the lack of significant conjugation between the naphthalene and cyclopentadiene moieties. In the highly nonplanar carbene **10**, the bond lengths and angles within the phenyl ring (Figure 5) are practically the same as those in the benzene molecule.

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[21] The hydrogens in **1**, **5**, and **6** are most probably abstracted by the hydrogen radical. In the naphthalene molecule, such a process involves a barrier of ca. 37 kcal/mol and is endothermic by only ca. 16 kcal/mol; see: Takano, K.; Mihashi, M.; Hirano, T. *Fullerene Sci. Tech.* **1998**, *6*, 283.

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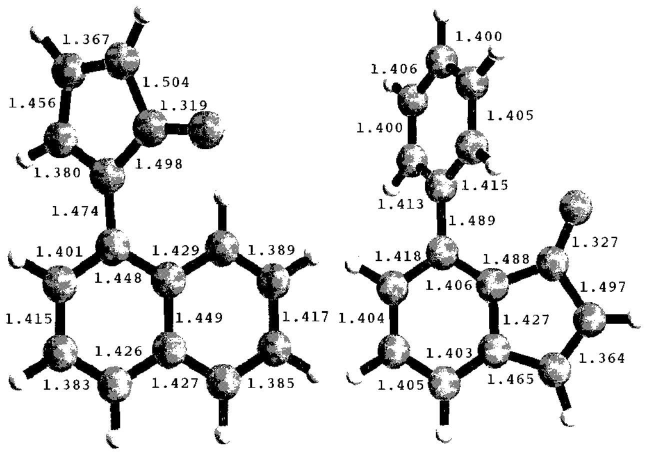
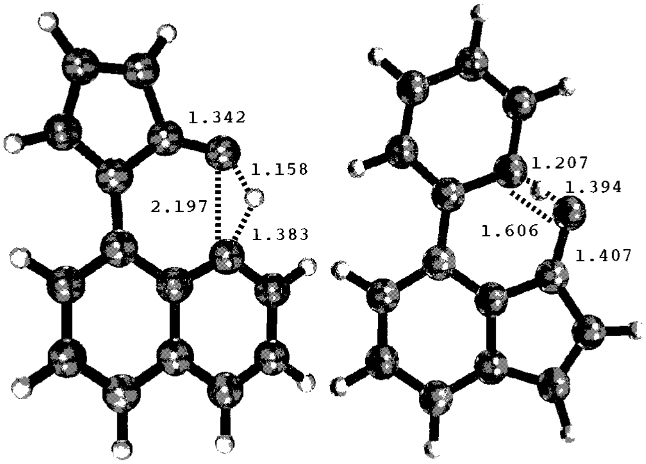


9 **10**

Figure 5. The C−C bond lengths (Å) in the annelated cyclopentadienylidenecarbenes **9** and **10**.

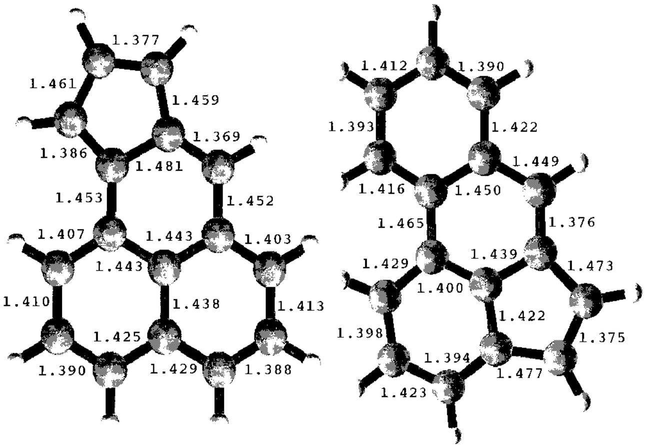


9->11 10->12

Figure 6. Selected C−C and C−H bond lengths (Å) in the transition states of the cyclizations **9** → **11** and **10** → **12**.

In agreement with the conclusions afforded by the previously published study of the stabilities of annelated cyclopentadienylidenecarbenes,[19] the carbene **9** is found to be thermodynamically and kinetically less stable than its isomer **10**. Whereas the two transition states for the reverse **10** → **8** rearrangement lie 6.4 and 13.8 kcal/mol above **10**, **9** is barely protected by the energy barrier of 1.4 kcal/mol. Consequently, once formed, **10** is expected to rapidly cyclize to the CP-PAH **12**. The highly exothermic cyclization, which involves formation of a C−C bond concurrent with a 1,2-hydrogen shift, is predicted to possess activation enthalpy of only 3.0 kcal/mol and a very late transition state (Figure 6). On the other hand, the analogous reaction leading to the CP-PAH **11** is expected to be hardly competitive with the reverse rearrangement of **9** to **7**.

The C−C bond fixation is much more pronounced in **11** than in **12** (Figure 7). In particular, **12** can be viewed as phenanthrene with an annelated five-membered ring, whereas in **11** only a naphthalene framework is aromatic. The different extents of aromaticity are reflected in the relative stabilities of the PAHs **2**, **11**, and **12**. However, being separated from **2** by energy barriers in excess of 70 kcal/mol (Figure 4), **11** and **12** are predicted to be kinetically stable.



11 **12**

Figure 7. The C−C bond lengths (Å) in the CP-PAHs **11** and **12**.

Conclusions

The present study identifies three distinct pyrolytic pathways connecting 1-phenylnaphthalene **1** with fluoranthene **2** and the CP-PAHs **11** and **12**. The first pathway involves the formation of the radicals **3** and **4**, followed by their rapid cyclization to the intermediates **5** and **6**, which ultimately lose hydrogen to yield **2**. Among these three steps, only the initial dehydrogenation of **1** requires substantial amounts of energy. Consequently, this pathway is expected to predominate at lower temperatures.

The second reaction channel commences with the dehydrogenation of **3** and **4** to the corresponding arylarynes **7** and **8**. In order to represent a viable mechanistic alternative to the direct radical pathway, this dehydrogenation has to be fast enough to kinetically compete with the low-barrier cyclizations **3** → **5** and **4** → **6**. The subsequent transformations of **7** and **8** proceed through substantial energy barriers. A one-step cyclization to **2** appears to be the energetically favorable reaction channel for **7**, whereas **8** is predicted to be also capable of rearranging to the carbene **10**. The initial expenditure of energy necessary to remove the hydrogen atom from **4** is then recovered in the rapid cyclization of **10** to **12**. Because of the instability of the carbene **9** with respect to the reverse rearrangement to **7**, the formation of **11** is not likely.

Direct equilibration of the PAHs **2**, **11**, and **12**, which constitutes the third reaction pathway, is associated with very high activation energies. For this reason, it is expected to be operative under normal pyrolytic conditions.

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