Electronic Structure Studies of 1,2-Didehydrogenation of Arenes and Rearrangement of Arynes to Annelated Cyclopentadienylidenecarbenes

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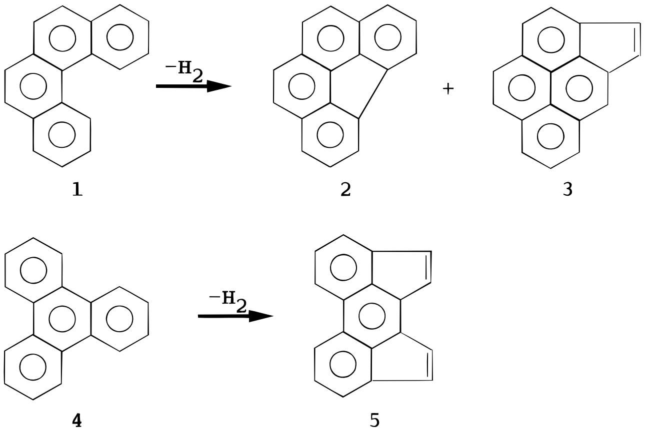
Abstract: CCSD(T)/6-311G** electronic structure calculations confirm the experimentally postulated existence of cyclopentadienylidenecarbene (CPDC) and verify the reliability of the BLYP/6-311G** predictions for thermochemistry and kinetics of the 1,2-didehydrogenation of arenes and the ring contraction of the resulting arynes. The former process is found to possess low site specificity, its energetics being influenced mostly by steric overcrowding of hydrogens. On the other hand, the energetics and barriers of rearrangements of higher arynes to annelated CPDCs are determined by the nature of bonding in the reaction products. Three distinct types of isomerizations, of which only one is observed experimentally, are readily recognizable.

Introduction

Polycyclic aromatic hydrocarbons (PAHs) undergo diverse transformations under pyrolytic conditions. Losing dihydrogen, many PAHs rearrange to nonalternant cyclopentafused species (CP-PAHs) that are known to be potent mutagens and carcinogens[1] For example, pyrolysis of benzo[*c*]phenanthrene (**1**, Scheme 1) produces not only the expected benzo[*ghi*]fluoranthene (**2**) but also cyclopenta[*cd*]pyrene (**3**).[2] Even more remarkably, flash vacuum thermolysis of triphenylene (**4**), which is commonly regarded as one of the most stable PAHs, results in its conversion to cyclopent[*h,i*]acephenanthrylene (**5**).[3] Undoubtedly, such transformations account for the presence of CP-PAHs in combustion emitants and soot.[4]

The aforementioned reactions are believed to proceed through several stages.[2,3] First, the parent arene undergoes 1,2-didehydrogenation to form the corresponding aryne. Rearrangement of the aryne yields annelated cyclopentadienylidenecarbene (CPDC), which is then trapped intramolecularly. Such a rearrangement/trapping sequence is commonly employed in syntheses of cyclopent[*a*]indene (benzopentalene)[5] and other pentalenes (including their heteroanalogs)[6] that are inaccessible via other routes. The preparative strategy of this type usually involves pyrolysis of arene-1,2-dicarboxylic acid anhydride which, losing CO and CO_2, turns into aryne that rearranges *in situ*. In fact, the 1,2-carbon scrambling observed in the products of pyrolysis of doubly ^{13}C-labeled phthalic anhydride provided the early (later disputed[7]) evidence for the thermally induced equilibration between 1,2-benzyne and CPDC.[8] The existence of this equilibration is now firmly established thanks to innovative experiments that have furnished the necessary conclusive proof.[6]

Scheme 1



Despite their obvious importance to preparative organic chemistry, combustion science, and environmental research, neither the 1,2-didehydrogenation of arenes nor the aryne → carbene rearrangement has been a subject of exhaustive theoretical investigations. Although many state of art electronic structure calculations have been carried out for the three isomers of benzyne,[9−11] only one high-level study of the CPDC has been

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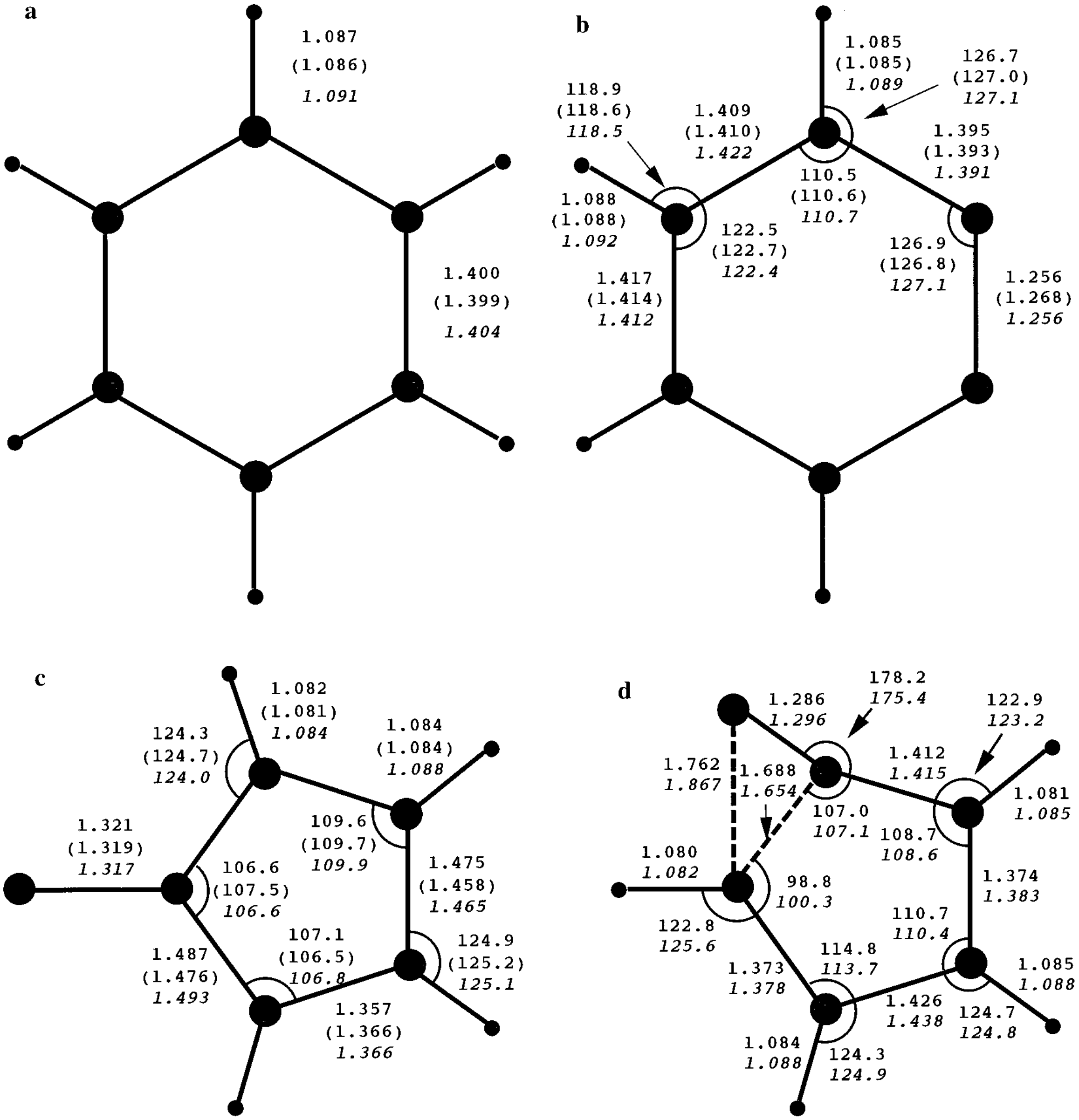

Figure 1. The QCISD/6-311G** optimized geometries of (a) benzene, (b) 1,2-benzyne, (c) cyclopentadienylidenecarbene (CPDC), and (d) the transition state of the 1,2-benzyne → CPDC rearrangement. The corresponding MP2/6-311G** and BLYP/6-311G** data are listed in parentheses and in italics, respectively.

published thus far.[11] Theoretical predictions of electronic properties and thermochemistry of annelated analogs of these species are not available at present.

This lack of information has prompted the research described in this paper. Large-scale calculations on the prototype systems have been performed to verify the appropriateness of using the BLYP density functional in studies of the formation and rearrangements of 1,2-didehydroarenes (referred to as arynes in the following text) derived from naphthalene, anthracene, and phenanthrene. The present study not only confirms the usefulness and reliability of this approach in such investigations[12] but also affords a comprehensive description of these important reactions.

The 1,2-Didehydrogenation of Benzene and the 1,2-Benzyne → CPDC Rearrangement. Since neither of the two reactions under study is isodesmic, accurate inclusion of electron correlation effects is prerequisite for obtaining quantitative thermochemical predictions. Although the prototype reactions that involve benzene as the parent arene can be treated at reasonably high levels of theory, the size of molecules derived from higher PAHs effectively limits the available pool of feasible quantum-chemical methods to those based on density functional theory.

The BLYP/6-311G** approximation has been successfully employed in several recent studies of the homolytic C−C, C−H, and C−Cl bond cleavages in aliphatic and aromatic systems.[13−15] In general, satisfactory agreement with the experimental data

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has been observed, the bond dissociation energies (BDEs) being usually underestimated by less than 5 kcal/mol. However, spectacular failures of both the BLYP and B3LYP functionals have been encountered in polychlorinated systems, in which the improper description of the Cl···Cl dispersion interactions results in errors in BDEs that are as large as 20 kcal/mol.[15]

To assess the reliability of the BLYP/6-311G** predictions for the two reactions under study, benchmark MP2/6-311G**, QCISD/6-311G**, and CCSD(T)/6-311G** calculations have been carried out.[16] For the energy of the 1,2-didehydrogenation of benzene (i.e., the reaction $C_6H_6 \rightarrow C_6H_4 + H_2$) at $T = 0$ K, these methods produce the values of 86.1, 91.2, and 86.8 kcal/mol, respectively, whereas the BLYP/6-311G** calculations yield 82.8 kcal/mol. All of these figures agree quite well with the recent experimental estimate of 86.6 ± 3.0 kcal/mol (at $T = 298$ K),[17] and the previously CCSD(T)/6-31G* reaction energy of 91.0 kcal/mol.[9] The agreement among the predictions of the three theoretical methods carries over to the optimized geometries of benzene, 1,2-benzyne, and CPDC (Figure 1).

Examination of the computed vibrational frequencies of the CPDC molecule reveals the poor performance of the MP2 approximation. Whereas the BLYP/6-311G** and QCISD(T)/6-311G** structures correspond to local minima on the corresponding potential energy hypersurfaces, their MP2/6-311G** counterpart is a transition state. Thus, in contradiction with the experimental evidence, MP2/6-311G** calculations predict the carbene to be a transition state rather than a transient intermediate on the reaction path describing 1,2-carbon scrambling in 1,2-benzyne (Figure 2). On the other hand, the BLYP/6-311G** prediction of the carbene being a shallow minimum parallels both the data produced by the two more sophisticated approaches employed in this study and the previously published results of CISD calculations.[11] Interestingly, the BLYP/6-311G** occupancies of the Kohn−Sham orbitals in the CPDC molecule follow those of their Hartree−Fock counterparts.

The BLYP/6-311G** energy of the benzyne → carbene isomerization equals 32.2 kcal/mol, being in close agreement with the CCSD(T)/6-311G** value of 29.2 kcal/mol. The corresponding QCISD/6-311G** value is 24.7 kcal/mol. The respective reaction barriers amount to 33.2, 31.2, and 29.3 kcal/mol (all data inclusive of ZPEs). The MP2/6-311G** prediction of 39.7 kcal/mol for the relative energy of CPDC is obviously too high. In both the BLYP/6-311G** and QCISD/6-311G** optimized geometries of the transition state (TS) of the isomerization, the pivoting C=C bond is almost collinear with one of the intraring carbon atoms (Figure 1d). This geometrical arrangement of three carbon atoms recurs as a prominent feature in TSs of many other aryne → carbene rearrangements (see below).

In summary, the CCSD(T)/6-311G** energetics of the species involved in both the 1,2-didehydrogenation of benzene and the 1,2-benzyne → CPDC rearrangement are accurately reproduced by the BLYP/6-311G** method, warranting its use in studies of analogous reactions of higher PAHs. On the other hand, despite its high computational cost, the MP2/6-311G** approach yields predictions for the rearrangement that are qualitatively incorrect.

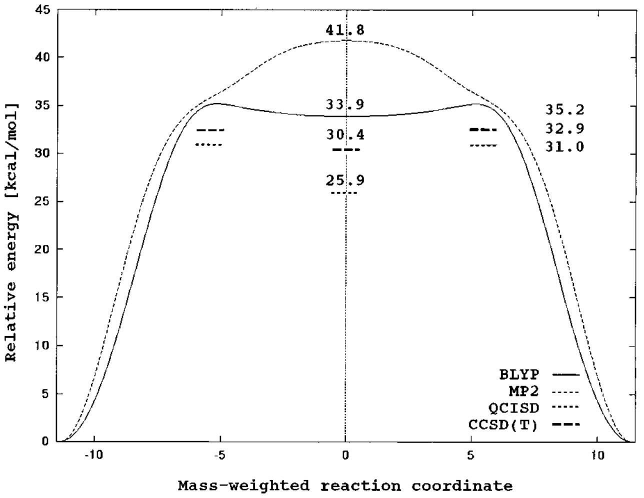

Figure 2. The BLYP/6-311G** and MP2/6-311G** energy profiles of the 1,2-carbon scrambling in 1,2-benzyne that proceeds through the 1,2-benzyne → CPDC rearrangement. The QCISD/6-311G** and CCSD(T)/6-311G** single-point energies of CPDC and the transition state are also shown. All values are given in kcal/mol relative to that of 1,2-benzyne (exclusive of ZPEs).

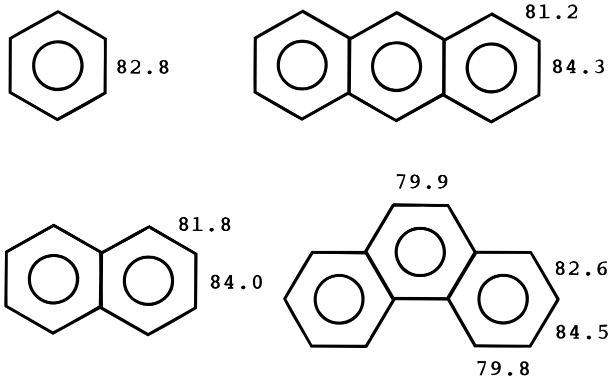

Figure 3. The BLYP/6-311G** 1,2-didehydrogenation energies at different sites in benzene, naphthalene, anthracene, and phenanthrene. All values are given in kcal/mol (inclusive of ZPEs).

1,2-Didehydrogenations of Naphthalene, Anthracene, and Phenanthrene. The energetics of the homolytic C−H bond cleavage in PAHs is governed by steric rather than electronic effects.[13] Accordingly, the C−H BDEs of arenes are almost constant, except for sites at which the removal of hydrogen relieves steric overcrowding. The energies of 1,2-didehydrogenations of PAHs also vary little from one site/molecule combination to another, although some subtle regularities are clearly discernible in the BLYP/6-311G** data (Figure 3). In general, the double removal of hydrogens attached to the 1,2-carbon atoms is somewhat preferred to that involving the 2,3-carbons. Lacking steric repulsions between the 4,5-hydrogens, 3,4-phenanthryne is more stable than the corresponding 1,2 and 2,3 isomers. One of the possible reasons for the lower energy of 9,10-phenanthryne is the presence of a particular pattern of conjugation in the parent arene that, extending over its two benzene rings but barely affecting the −CH=CH− bridge

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(16) All the calculations reported in this paper were carried out with the Gaussian 94 suite of programs: *Gaussian 94*; Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T. A.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A.; Gaussian, Inc.: Pittsburgh, PA, 1995. Molecular geometries were fully optimized and vibrational frequencies were computed at all levels of theory, except for CCSD(T)/6-311G** for which the QCISD/6-311G** geometries and ZPEs were used. Total energies, ZPEs, vibrational frequencies, and structural parameters of all the species mentioned in this work are available from the corresponding author upon request by e-mail.

(17) Wenthold, P. G.; Squires, R. R. *J. Am. Chem. Soc.* **1994**, *116*, 6401 and the references cited therein.

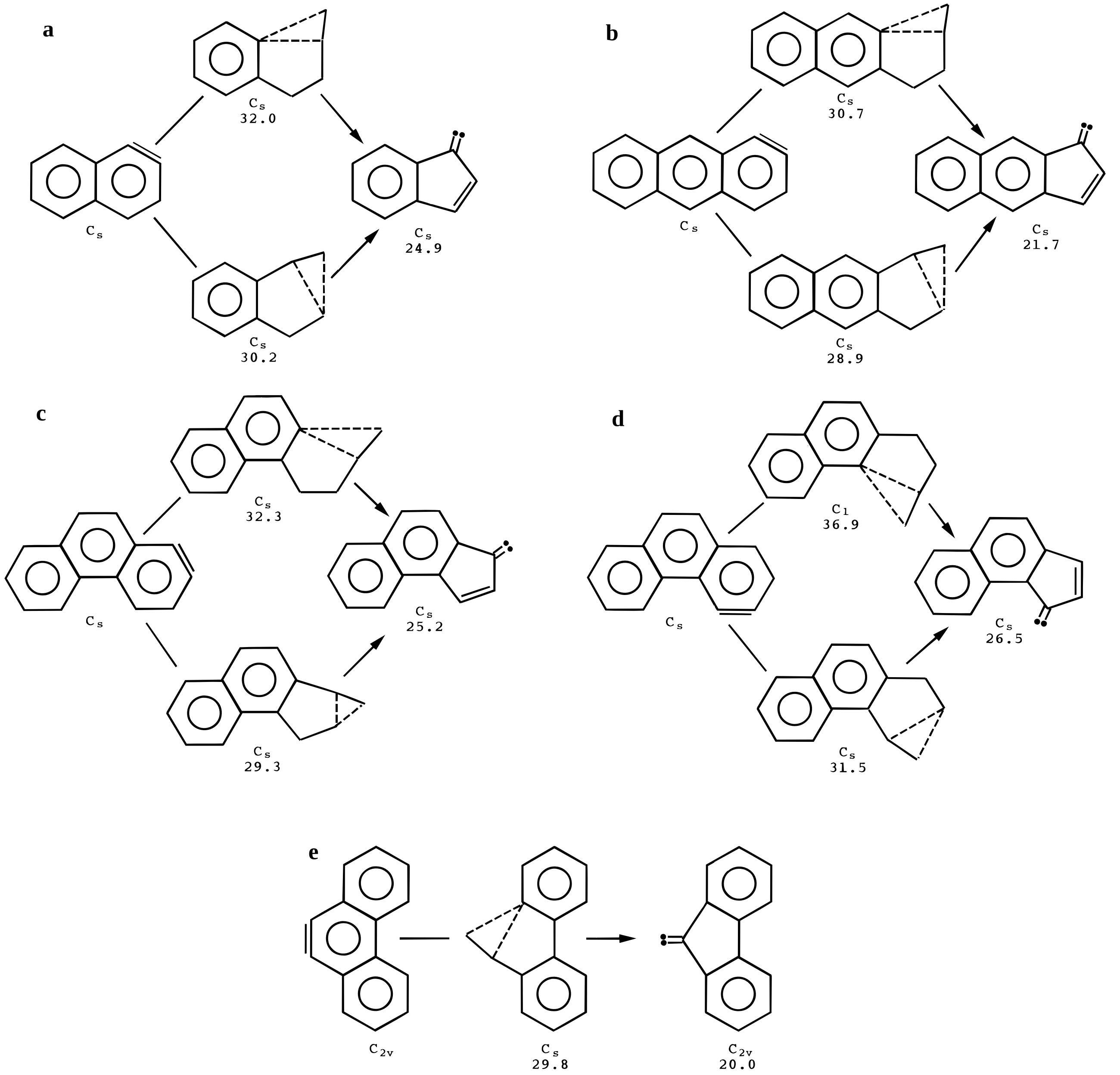

Figure 4. The type I aryne → carbene rearrangements of (a) 1,2-naphthalyne, (b) 1,2-anthracyne, (c) 1,2-phenanthryne, (d) 3,4-phenanthryne, and (e) 9,10-phenanthryne. All energies are given in kcal/mol computed at the BLYP/6-311G** level of theory (inclusive of ZPEs), relative to those of the respective arynes.

between them, is only marginally disrupted by the removal of the 9,10-hydrogens.

The energy of removing hydrogens linked to two carbons generally increases with the length of the respective C−C bond in the arene, but the correlation between these two quantities is not good enough to be of any predictive value. On the other hand, the lengths of the analogous C−C bonds in arenes and arynes (including those in the benzene/1,2-benzyne pair) are related by a surprisingly accurate (errors less than 0.001 [Å]) formula

$$R_{\mathrm{CC}}(\text{aryne}) = 0.468R_{\mathrm{CC}}(\text{arene}) + 0.599\ \text{Å} \tag{1}$$

The previously found regularities[13] in the C−C−C bond angles of aryl radicals are not observed in arynes.

Rearrangements of Arynes Derived from Naphthalene, Anthracene, and Phenanthrene to Annelated Cyclopentadienylidenecarbenes. The present BLYP/6-311G** calculations reveal the existence of three distinct types of the aryne → carbene rearrangement (ring contraction). The type I isomerizations produce CPDCs annelated at one of the intraring double bonds of the cyclopentadienylidene moiety. The resulting stabilization of the rearrangement products is reflected in the lower relative energies of the annelated CPDCs (Figure 4). Thus, although CPDC itself lies 32.2 kcal/mol above 1,2-benzyne, the benzannelated CPDC produced from 1,2-naphthalyne is only 24.9 kcal/mol less stable than the parent aryne (Figure 4a), whereas double benzannelation produces the energy difference of only 20.0 kcal/mol (Figure 4e). Depending on the orientation of the naphthalene unit, naphthannelation can be either more or less stabilizing than benzannelation (Figure 4, b−d). In general, annelation negligibly affects the equilibrium geometries of the CPDCs, except for the ring fusion sites, which adopt the bond lengths of the annelating arene units. All of the CPDCs under study that arise from the type I rearrangements are planar.

The rearrangements of 1,2-naphthalyne, 1,2-anthracyne, 1,2-

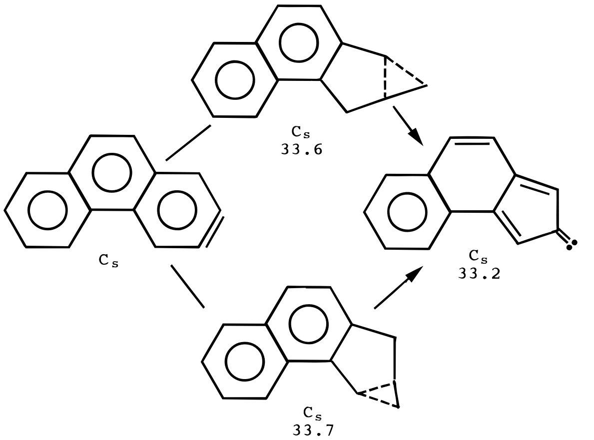

Figure 5. The type II aryne → carbene rearrangement of 2,3-phenanthryne. See the caption of Figure 4 for details.

phenanthryne, and 3,4-phenanthryne can each proceed through two distinct transition states. In all four cases, bond making/breaking away from the ring fusion site produces lower reaction barriers than that involving migration of the carbon atom originally linked to the annelating unit (Figure 4, a−d). In the former transition states, the pivoting C=C bonds are almost collinear with the neighboring carbon atoms but slightly bent toward the emerging five-membered rings, whereas in the latter TSs the bending is directed outward. With the exception of one of the species derived from 3,4-anthracyne (Figure 4d, note the much higher energy of this TS due to steric overcrowding), all of these TSs possess planar geometries.

Since the effect of annelation on the barriers to the forward reactions is much less pronounced than that on the reaction energies, CPDCs produced from higher arynes by the type I rearrangements enjoy much greater barriers to the reverse reactions than the prototype carbene does. In particular, the doubly benzannelated CPDC lies in a minimum that is ca. 10.0 kcal/mol deep (Figure 4e). These predictions are in agreement with the experimental observation of facile isomerizations of 1,2-naphthalyne and 3,4-phenanthryne.[6]

Ring contraction of 2,3-phenanthryne constitutes an example of the type II rearrangement. It produces a planar CPDC in which annelation partially disrupts conjugation within the naphthalene unit (Figure 5). The optimized geometry of this CPDC exhibits a clearly discernible pattern of C−C bond fixation in one of the six-membered rings and bond equalization in the other. The C−C bonds of the cyclopentadienylidene moiety at and around the ring fusion site are somewhat longer than those in the unannelated carbene.

The partial loss of aromaticity in the reaction product has a readily recognizable effect on the isomerization energetics. The reaction energy becomes comparable to that of the unannelated species and the barrier to the reverse reaction drops to only 0.4 kcal/mol (Figure 5), putting the actual existence of 3,4-(1,2-naphtho)CPDC in doubt. The observation that 2,3-phenanthryne does not undergo ring contraction under experimental conditions known to induce the type I aryne → carbene rearrangements[6] appears to confirm this prediction.

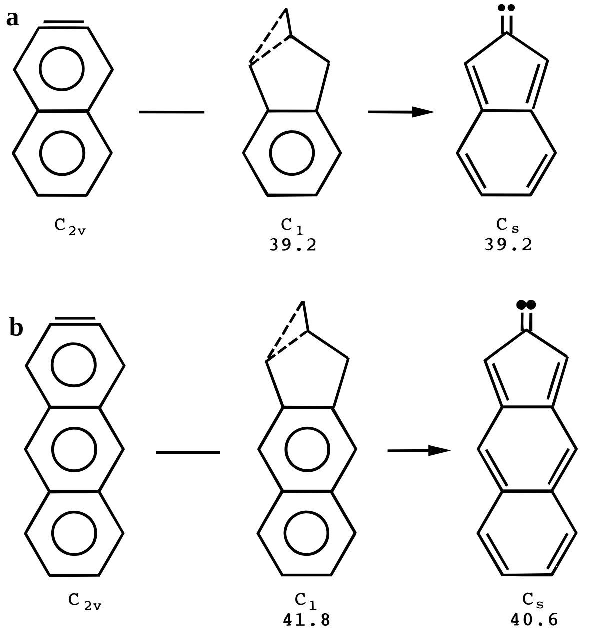

Figure 6. The type III aryne → carbene rearrangements of (a) 2,3-naphthalyne and (b) 2,3-anthracyne. See the caption of Figure 4 for details.

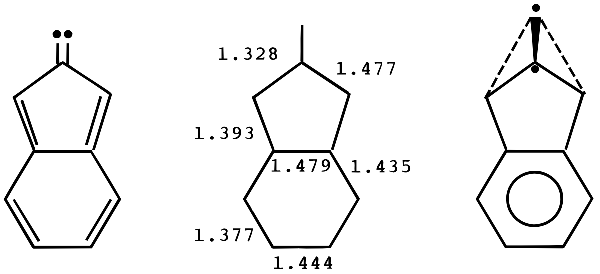

Figure 7. The 3,4-benzocyclopentadienylidenecarbene molecule. Left: the quinoid structure. Middle: the BLYP/6-311G** bond lengths. Right: the nonclassical 1,2-biradicaloid structure.

The hypothetical type III isomerizations lead to CPDCs in which the annelation occurs at the single bond of the cyclopentadienylidene moiety (Figure 6). In principle, such annelation should result in C−C bond fixation within the entire annelating unit, bringing about a complete loss of aromaticity. Indeed, the CPDCs derived from 2,3-naphthalyne (Figure 6a) and 2,3-anthracyne (Figure 6b) are substantially less stable than their type I counterparts. Even more importantly, the barriers to reverse rearrangements are very small for these species. These data are in accordance with the results of isotope labeling experiments that provide ample evidence for the inability of 2,3-naphthalyne to isomerize.[6]

Interestingly, the optimized geometries of the type III CPDCs do not support the notion of quinoid structures of these species. In particular, such structures do not explain the strong bending of the C=C: bonds out of the planes of the five-membered rings, which are otherwise almost planar.[18] Amounting to 27.9 and 45.0° in 3,4-benzoCPDC and 3,4-(2,3-naphtho)CPDC, respectively, this bending appears to increase with the extent of conjugation in the annelating unit. A concomitant reduction in C−C bond alternation is also observed. In fact, although the bond alternation is relatively well pronounced in the 3,4-benzo species (Figure 7), the pattern of the C−C bond lengths in the naphthalene portion of 3,4-(2,3-naphtho)CPDC is only distantly reminiscent of that depicted in Figure 6b. Therefore, one may conclude that bonding in the type III CPDCs is best represented by the resonance between quinoid and nonclassical structures, the latter having a 1,2-biradicaloid character (Figure 7). The relative importance of these two structures is determined by the balance between the loss of aromaticity on one hand

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(18) The planar C_{2v} geometries of both the 3,4-benzoCPDC and 3,4-(2,3-naphtho)CPDC molecules correspond to saddle points (one imaginary frequency in each case) on the respective potential energy hypersurfaces.

and the high energy of the 1,2-biradicaloid arrangement of unpaired electrons on the other. This balance convincingly accounts for the aforementioned trends in the computed geometries.

Since the 2,3-naphthalyne and 2,3-anthracyne molecules are planar, their isomerizations to nonplanar CPDCs must proceed along bifurcated reaction paths. Being very late, the respective transition states also lack planarity, although the bending of their C═C: bonds is appreciably less than that in the reaction products. Thus, the type III rearrangements are predicted to involve pairs of enantiomeric transition states.

Conclusions

The electronic structure studies presented in this paper provide a wealth of information on two reactions of great importance to pyrolytic processes, namely the 1,2-didehydrogenation of PAHs and the ring contraction of the resulting arynes. Benchmark CCSD(T)/6-311G** calculations confirm the experimentally postulated existence of cyclopentadienylidenecarbene (CPDC) and verify the reliability of the BLYP/6-311G** predictions. Although capable of reproducing the experimental energy of the 1,2-didehydrogenation of benzene, the MP2/6-311G** method yields qualitatively incorrect results for the benzyne → CPDC rearrangement.

The present investigation reveals the low site specificity of the 1,2-didehydrogenation of PAHs. The energetics of this reaction is affected mostly by steric overcrowding of hydrogens. The lengths of the formally triple C−C bonds in arynes correlate well with those of the corresponding C−C bonds in the parent arenes.

The nature of bonding in the reaction products determines the energetics and barriers of rearrangements of higher arynes to annelated CPDCs. Three distinct types of isomerizations are readily recognizable. The type I rearrangements produce relatively stable, planar CPDCs with aromatic conjugation unaffected by the cyclopentadienylidene moiety. In general, annelation lowers both energies and barriers of these rearrangements, while raising the barriers to the reverse reactions. In most cases, two alternative reaction paths are possible, one of them being usually favored by a few kilocalories per mole. The type II rearrangements yield planar CPDCs with partially fixed C−C bonds. These CPDCs are barely protected from the reverse reactions by vanishingly low energy barriers. The type III isomerizations furnish nonplanar, highly unstable carbenes. Rather unexpectedly, these carbenes are found to possess complex bonding patterns that are best described as arising from the resonance between the conventional quinoid and nonclassical 1,2-biradicaloid structures. Only the type I rearrangements are observed experimentally.

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