

Nonclassical Aryl Radicals: Intermediates or Transition States for the Hydrogen Shift Reactions?

Jerzy Cioslowski,* Guanghua Liu, and David Moncrieff

Department of Chemistry and Supercomputer Computations Research Institute, Florida State University, Tallahassee, Florida 32306-3006

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Electronic properties of aryl radicals obtained by removing single hydrogen atoms from the sterically congested regions of benzo[*c*]phenanthrene, biphenyl, triphenylene, phenanthrene, and perylene are studied at the ULYP/6-311G** level of theory. Two structures are considered by each radical, the classical one involving a C–H···C arrangement of atoms and the nonclassical one possessing a three-center C–H–C linkage. The five nonclassical radicals under study are found to be transition states for degenerate 1,4- and 1,5-hydrogen shift reactions that interconvert the classical species. However, the results of the present calculations indicate that the nonclassical structures with the C–H distances in the C–H–C linkages shorter than 1.34 Å should be energy minima representing potentially observable chemical systems. The predicted energy barrier to the 1,5-hydrogen shift in the 1-benzo[*c*]phenanthrenyl radical is only 9.3 kcal/mol (6.1 kcal/mol with the zero-point energies included), making the hydrogen migration in this system facile at relatively low temperatures. Rigorous analysis of the computed electronic wave functions provides a clear-cut picture of bonding in both the classical and nonclassical aryl radicals.

Introduction

Aryl radicals are transient species involved in diverse chemical¹ and photochemical² reactions, including the formation of polycyclic aromatic hydrocarbons (PAHs) and soot during pyrolysis of simple aromatic hydrocarbons (as well as their alkyl derivatives)³ and fossil fuels such as wood and coal.⁴ Despite their obvious importance to organic chemistry, electronic properties of aryl radicals have been the subject of surprisingly few studies. The σ character of systems such as 1-naphthalenyl, 2-naphthalenyl, 1-anthracenyl, 9-anthracenyl, and 1-pyrenyl has been established by means of EPR spectroscopy⁵ and confirmed by recent semiempirical⁶ and *ab initio*^{7,8} quantum-chemical calculations. In the latter study, the inclusion of the electron correlation effects through the BLYP functional⁹ has been found to virtually eliminate

the unacceptably large spin contamination of the unrestricted Hartree–Fock (UHF) electronic wave functions that had hampered earlier theoretical work on C₆H₅.¹⁰ Consequently, the accuracy of quantum-mechanical predictions improved to the point where the experimental energy of the hydrogen abstraction from benzene, equal to 109.8 ± 0.8 kcal/mol (at 0 K),¹¹ could be reproduced to within only 3 kcal/mol.^{7,12}

Electronic structure calculations indicate that the C–H bond dissociation energies of PAHs are governed primarily by steric effects, the hydrogens being removed preferentially from congested regions of the parent hydrocarbons.⁷ In benzo[*c*]phenanthrene, the hydrogen abstraction from position 1, which is favored over the others by about 7 kcal/mol, produces a radical (Figure 1a) in which the 1,5-hydrogen shift between the atoms C₁ and C₁₂ is facilitated by their proximity. Similarly, the arrangement of atoms in the “decongested” radicals derived from PAHs such as biphenyl (Figure 1b), triphenylene (Figure 1c), phenanthrene (Figure 1d), and perylene (Figure 1e) is expected to make them prone to 1,4-hydrogen shifts.

The degenerate shifts described above proceed through nonclassical aryl radicals in which the migrating hydrogens are equidistant to two carbon atoms. In principle, these symmetrical systems could serve as either transition states (TSs) or intermediates (and thus energy minima) for the hydrogen shift reactions. Should the latter be the case, they would constitute examples of potentially observable chemical species with three-center, three-electron bonds, analogous to the *in*-carbocations¹³ in which three-center, two-electron C–H–C bonding is

* Author to whom all correspondence should be addressed.

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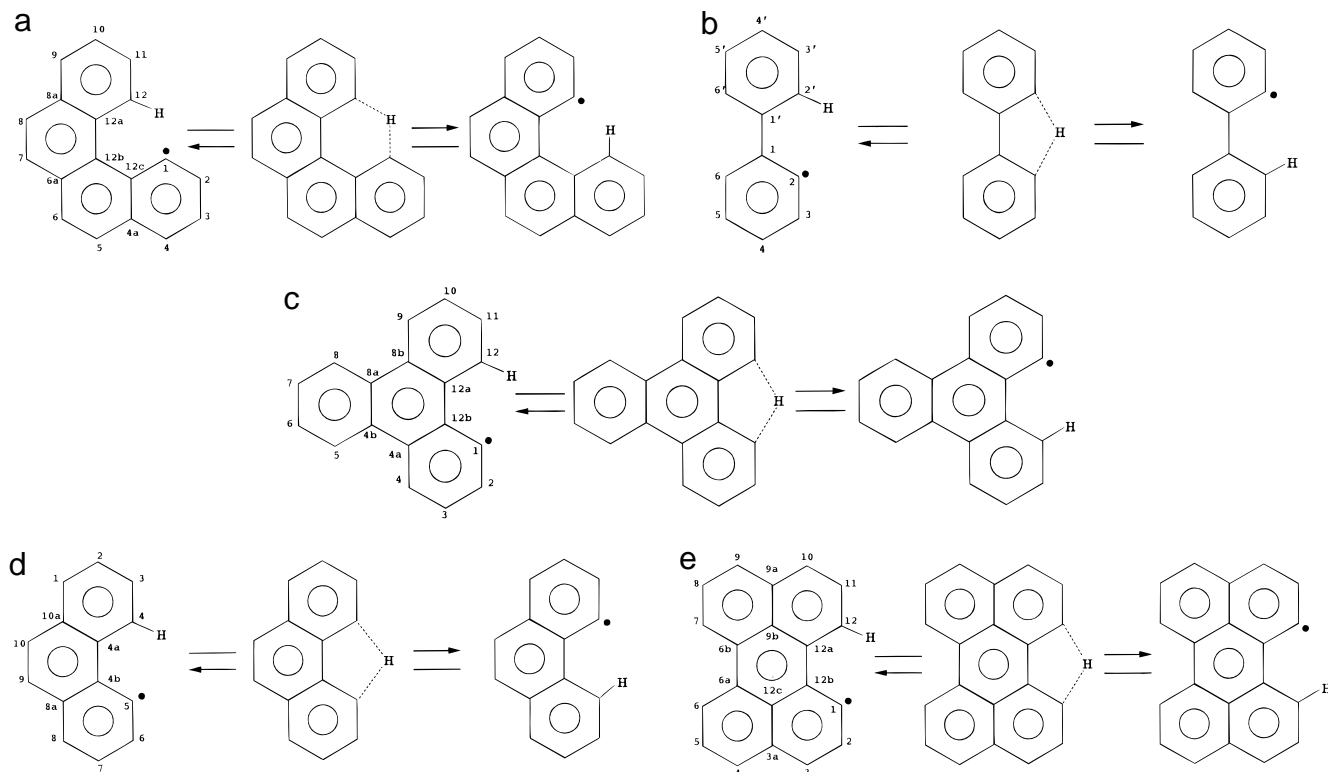


Figure 1. Hydrogen shifts in the "decongested" radicals derived from (a) benzo[*c*]phenanthrene, (b) biphenyl, (c) triphenylene, (d) phenanthrene, and (e) perylene.

Table 1. Calculated Properties of the Energy Minima and Transition States of the Degenerate Hydrogen Shift in Aryl Radicals

parent arene	position ^a	energy minimum ^b		transition state ^c			
		R_{C-H} [Å]	$R_{C...H}$ [Å]	ΔE^d [kcal/mol]	ν_{TS} [cm ⁻¹]	R_{C-H} [Å]	α_{C-H-C} [deg]
benzo[<i>c</i>]phenanthrene	1	1.094	2.096	9.25	1551.4 _i	1.354	143.8
biphenyl	2	1.091	2.695	23.63	1808.6 _i	1.391	124.8
triphenylene	1	1.091	2.563	29.14	1954.1 _i	1.435	124.6
phenanthrene	4	1.091	2.669	32.49	1981.1 _i	1.446	124.6
perylene	1	1.091	2.623	33.86	2028.8 _i	1.464	124.2

^a The site of the hydrogen abstraction (carbon atoms numbered according to the *Chemical Abstracts* convention, see Figure 1). ^b The classical radical. ^c The nonclassical radical. ^d ZPEs not included.

present.¹⁴ In this paper, electronic properties of several classical aryl radicals and their nonclassical counterparts are investigated, and the nature of the latter systems is elucidated.

Details of Calculations

Full geometry optimizations, followed by calculations of vibrational energies, were carried out at the BLYP/6-311G** level of theory with the GAUSSIAN 92/DFT suite of programs.¹⁵ Standard integration grids were used and found to yield sufficiently accurate results. The calculated electronic wave functions are only slightly spin-contaminated, the $\langle \hat{S}^2 \rangle$ expectation values of less than 0.76 being observed in all cases. Atomic charges and spin population were computed with the methods described elsewhere.¹⁶

Results and Discussion

In contrast to its parent arene, the classical 1-benzo[*c*]phenanthrenyl radical is planar,⁷ the formally trivalent C₁ carbon atom (Figure 1a) being located only ca. 2.1 Å apart from the nearest hydrogen. The analogous distances ($R_{C...H}$, Table 1) are longer in the classical radicals derived from biphenyl, triphenylene, phenanthrene, and perylene, in which the carbon frameworks are compatible with direct 1,4-hydrogen shifts rather than the 1,5 ones. The 1-triphenylenyl, 4-phenanthrenyl, and 1-perylenyl molecules are predicted to be planar, whereas the optimized geometry of the 2-biphenylenyl radical is characterized by the C₂-C₁-C_{1'}-C_{2'} dihedral angle of 27.6°, which is much smaller than the respective angle of 40.3° computed for biphenyl.

The nonclassical aryl radicals, including the species derived from biphenyl, possess planar geometries with hydrogens located symmetrically between carbon atoms. In all five cases under study, they are found to be transition states with the computed imaginary vibrational frequencies (ν_{TS}) and energy barriers to the hydrogen shift (ΔE) that correlate well with the C-H distances (R_{C-H}) in their C-H-C linkages. In particular,

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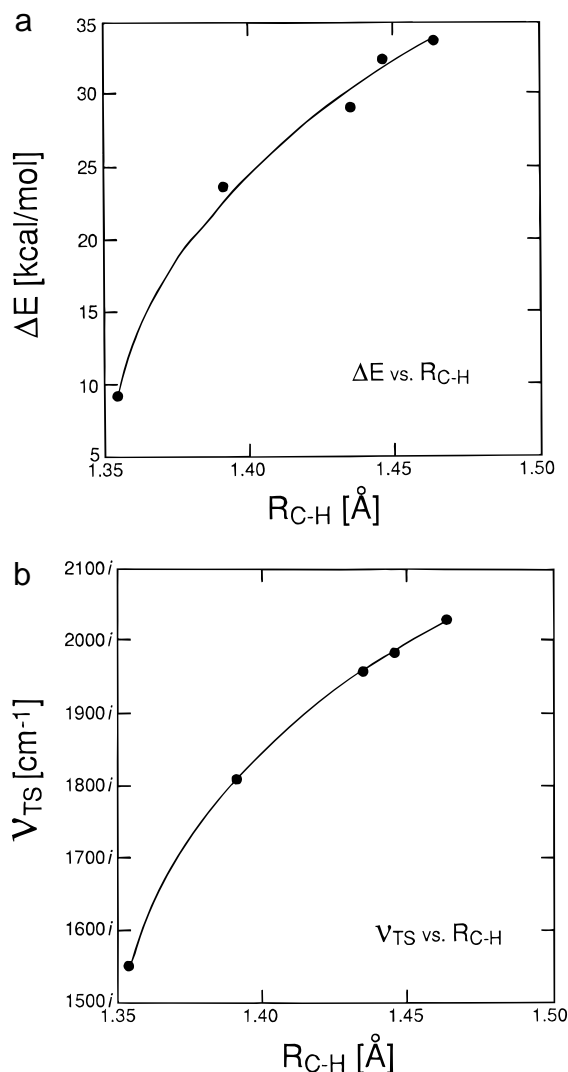


Figure 2. Plots of (a) ΔE vs R_{C-H} and (b) ν_{TS} vs R_{C-H} . The solid lines depict the predictions of eqs 1 and 2, respectively.

the empirical relationships of eqs 1 and 2 accurately

$$\Delta E \approx 80.32 (R_{C-H} - 1.348)^{2/5} \quad (1)$$

$$\nu_{TS} \approx 2667i (R_{C-H} - 1.337)^{2/15} \quad (2)$$

reproduce the values of ΔE (Figure 2a) and ν_{TS} (Figure 2b) in spite of the fact that both 1,4- and 1,5-hydrogen shifts are included in the correlations. Interestingly, neither ΔE nor ν_{TS} correlates with the $R_{C\cdots H}$ distances in the classical radicals.

The existence of the relationships given by eqs 1 and 2 is significant, as it allows one to predict the critical value of R_{C-H} below which the nonclassical aryl radicals are expected to become local minima. According to eqs 1 and 2, this critical R_{C-H} lies somewhere between 1.34 and 1.35 Å, i.e., not too far from the C–H distance computed for the C–H–C linkage in the nonclassical benzo[*c*]phenanthrenyl radical. It is therefore not surprising at all that the 1,5-hydrogen shift in the corresponding classical species is predicted to proceed through an energy barrier of only 9.3 kcal/mol (Table 1), which should make it facile at relatively low temperatures. In contrast, the 1,4-hydrogen shifts in the other four classical radicals require activation energies that vary between 23.6 and 33.9 kcal/mol. The predicted barriers are

Table 2. Calculated Properties of the Critical Points Pertaining to the C–H Bonds of the C–H–C Linkages Present in the Nonclassical Aryl Radicals^a

parent arene	ρ	ρ^s	$\nabla^2\rho$
benzo[<i>c</i>]phenanthrene	0.1436	0.0221	−0.1930
biphenyl	0.1331	0.0184	−0.1600
triphenylene	0.1210	0.0158	−0.1318
phenanthrene	0.1181	0.0150	−0.1250
perylene	0.1135	0.0145	−0.1135

^a All quantities in au.

Table 3. Calculated Charges and Spin Populations of the Atoms Involved in the C–H–C Linkages of the Nonclassical Aryl Radicals^a

parent arene	structure	atom(s) ^b	spin pop.	charge
benzo[<i>c</i>]phenanthrene	en. min.	C ₁	0.7834	−0.1056
		C ₁₂	0.0527	−0.0264
		H	0.0167	0.0486
benzo[<i>c</i>]phenanthrene	TS	C ₁ , C ₁₂	0.4303	−0.1139
		H	0.0017	0.1502
biphenyl	TS	C ₂ , C _{2'}	0.4379	−0.1136
		H	−0.0027	0.1282
triphenylene	TS	C ₁ , C ₁₂	0.4375	−0.1141
		H	−0.0088	0.1291
phenanthrene	TS	C ₄ , C ₅	0.4368	−0.1152
		H	−0.0105	0.1297
perylene	TS	C ₁ , C ₁₂	0.4403	−0.1187
		H	−0.0133	0.1263

^a Properties of the atoms encompassed by the C–H \cdots C fragment of the classical 1-benzo[*c*]phenanthrenyl radical are also listed for the sake of comparison. ^b See Figure 1 for atom numbering.

consistently lowered by 3.0–3.5 kcal/mol upon the inclusion of zero-point energies.

Valuable insights into the dominant interactions in molecules can be gathered through the analysis of the topological properties of their electron densities.^{17,18} In particular, the electron density at the bond critical point (ρ) is known to correlate with the bond strength. For the C–H bonds of the symmetrical C–H–C linkages present in the nonclassical radicals under study, the calculated values of ρ decrease steadily with increasing R_{C-H} , the corresponding spin densities (ρ^s) following the same trend (Table 2). The values of the electron density Laplacian at the bond point ($\nabla^2\rho$) are negative in all cases, indicating the shared (covalent) nature of the bonds.¹⁷ The C–H \cdots C fragments of the classical radicals possess pairs of attractor interaction lines, each pair consisting of a C–H bond path and a line describing a strong steric interaction¹⁸ between the hydrogen and the formally trivalent carbon. In the 1-benzo[*c*]phenanthrenyl radical, the bond critical point that belongs to the former line (C₁₂–H, Figure 1a) is characterized by ρ of 0.2750 au, ρ^s of 0.0096 au, and $\nabla^2\rho$ of −0.9086 au, whereas the corresponding values for the bond point on the latter line (C₁ \cdots H, Figure 1a) read 0.0255, 0.0080, and 0.0657 au. The relative magnitudes of ρ underscore the fact that the ordinary C–H bonds are stronger than those involved in the symmetrical C–H–C linkages, whereas the opposite signs of $\nabla^2\rho$ signify the repulsive character of the C \cdots H steric interactions.

Although all the radicals considered in this paper are predicted to be of the σ type, the classical systems differ from their nonclassical counterparts in the extent of spin localization. Whereas the unpaired electrons are well localized on the formally trivalent carbon atoms of the

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Table 4. Selected Localized Spin Orbitals of the 1-Benzo[c]phenanthrenyl Radical and Its Nonclassical Counterpart

structure	spin	LSO	loc. no.	atomic occupancy ^a	description
en. min.	α	40	1.246	89.5% C ₁	loc. unpaired electron
		41	2.119	54.8% C ₁₂ , 41.4% H	C–H bond (13.9% ionic)
	β	58	2.267	50.3% C ₁₂ , 43.2% H	C–H bond (7.6% ionic)
TS	α	40	1.677	74.8% C ₁ , 18.9% H	C–H bond (59.6% ionic)
		41	1.677	74.8% C ₁₂ , 18.9% H	C–H bond (59.6% ionic)
	β	59	3.212	28.0% C ₁ , 28.0% C ₁₂ , 39.3% H	

^a See Figure 1a for atom numbering.

classical radicals,⁷ in the nonclassical structures they are shared by the carbons of C–H–C linkages, the hydrogens possessing negligible spin populations (Table 3). Interestingly, despite a relatively wide range of C–H distances, both the spin populations and the charges of the atoms involved in these linkages are found to vary little among the nonclassical radicals.

The localized spin orbitals (LSOs) produced by the AOM-based scheme¹⁹ furnish a clear-cut description of bonding in the systems under study. In the classical 1-benzo[c]phenanthrenyl radical, LSO number 40 (Table 4) unambiguously assigns the unpaired electron to the formally trivalent C₁ carbon atom. The C₁₂–H bond is described by a pair of well-localized (as reflected by their localization numbers that are close to 2.0, see Table 4) LSOs representing electrons with opposite spins. The conventional character of this bond, implied by such a description, is confirmed by the calculated covalent bond order²⁰ that equals 0.929. In contrast, the covalent bond order of the C₁···H fragment amounts to only 0.108.

A much more interesting pattern of bonding is encountered in the corresponding nonclassical radical, in which two α electrons occupy a pair of symmetry-related LSOs (numbers 40 and 41) that describe highly ionic C₁–H and C₁₂–H bonds. At the same time, a single β electron is employed in a tricentric C₁–H–C₁₂ bond. Thus, the overall description of the C₁–H–C₁₂ linkage is that of a three-center, three-electron bond with a C–H covalent bond order of 0.537. As the α and β electrons contribute comparably (0.308 vs 0.229) to this bond order, the strength of the C–H–C linkage is a function of two factors, namely, the C–H distance and the deviation of the C–H–C angle (α_{C-H-C}) from the optimal value of 180°. Inspection of Table 1 reveals that, owing to a favorable alignment of carbon atoms, this deviation is much smaller in the nonclassical radical derived from benzo[c]phenanthrene than in the other four species.

Conclusions

The steric congestion present in certain PAHs can be partially relieved by removing one atom from a pair of closely positioned hydrogens. Two distinct structures are

possible for the resulting “decongested” aryl radicals. In the classical structure a normal C–H bond and a C···H steric interaction are present, whereas in the nonclassical one a more or less symmetrical C–H–C linkage is formed by two carbon atoms and a hydrogen located between them. Although the present calculations have found the nonclassical radicals to constitute transition states (TSs) for the 1,4- and 1,5-hydrogen shifts that interconvert the respective classical species, the existence of energy minima corresponding to nonclassical structures cannot be ruled out in general. In fact, the trends observed in the calculated energy barriers to the hydrogen shift and the imaginary vibrational frequencies of the TSs strongly suggest that these structures should become local minima (and thus observable species) once the C–H distance between the atoms of the C–H–C linkage falls below 1.34 Å. It is entirely possible that this goal can be achieved by a judiciously chosen replacement of the C–H units in the 1-benzo[c]phenanthrene molecule by heteroatoms.

Rigorous analysis of the computed electronic wave functions furnishes a clear-cut picture of bonding in the nonclassical aryl radicals. The atoms of the C–H–C linkage are held together by a three-center, three-electron bond, which consists of two C–H half-bonds involving two α electrons and a tricentric C–H–C half-bond with one β electron. Such a bonding pattern implies the nonclassical structures being favored by carbon frameworks compatible with a linear C–H–C arrangement.

We believe that this study will partially fill the gaps in the current knowledge of electronic properties of aryl radicals. We expect the predictions of the present calculations to stimulate further experimental and theoretical research on the subject of chemical systems with tricentric bonds.

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Supporting Information Available: Total and zero-point energies of classical and nonclassical aryl radicals under study (1 page). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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