

Energetics and Site Specificity of the Homolytic C–H Bond Cleavage in Benzenoid Hydrocarbons: An ab Initio Electronic Structure Study

Jerzy Cioslowski,* Guanghua Liu, Martin Martinov, Pawel Piskorz, and David Moncrieff

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

Received January 5, 1996. Revised Manuscript Received March 27, 1996[⊗]

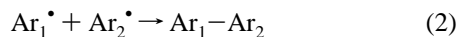
Abstract: Electronic structure calculations carried out at the BLYP/6-311G** level of theory accurately predict the dissociation energy of the C–H bond in benzene. The analogous energies of the homolytic C–H bond cleavage in the other nine polycyclic aromatic hydrocarbons (PAHs) are found to be governed almost entirely by steric factors, the hydrogens from congested regions of the PAHs being removed preferentially. The removal of hydrogens is accompanied by highly regular changes in the molecular geometries, namely a widening of the *ipso* bond angle by ca. 6.0° and a concomitant shortening of the adjacent C–C bonds by ca. 0.02 Å. These observations suggest an almost complete localization of the unpaired σ electrons on single carbon atoms and the separation of the local σ and π effects in the aryl radicals under study. This localization is confirmed by the computed charges and spin populations of atoms in the phenyl, 1-naphthalenyl, and 2-naphthalenyl radicals. In contrast with their UHF counterparts, the UBLYP electronic wave functions are only mildly spin contaminated.

Introduction

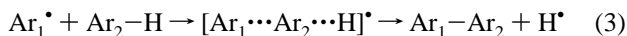
Pyrolysis of simple polycyclic aromatic hydrocarbons (PAHs) produces complex mixtures of biaryls, pericondensed PAHs, and soot.^{1,2} These products are formed in a sequence of chemical reactions² that commences with the thermally induced C–H bond cleavage,



The resulting aryl radicals furnish biaryls through either a direct recombination,



or a two-step reaction,



In turn, the biaryls undergo cyclodehydrogenation, yielding pericondensed PAHs. Iteration of this mechanism, followed if necessary by rearrangement of the carbon framework, ultimately leads to fullerenes, which have been indeed detected in fuel-rich benzene–oxygen flames³ and among the products of thermal decomposition of naphthalene,⁴ and to soot particles.

The available experimental data⁵ indicate that the above sequence of reactions is directly involved in the formation of a broad spectrum of PAHs during the combustion of solid fuels such as coal or wood.⁶ Since many of these PAHs are potent carcinogens that pose major environmental and health hazards, research on the pyrolytic reactions 1–3 is of great practical importance. Unfortunately, theoretical studies of aryl radicals that play a crucial role in these reactions have been scarce, most probably because of the very poor description of the $\text{C}_6\text{H}_5^\bullet$ species at the UHF level of theory.⁷

In this paper, we demonstrate that the use of the BLYP functional⁸ drastically reduces the spin contamination of unrestricted single-determinantal electronic wave functions of aryl radicals, opening an avenue to accurate predictions of the energetics and site specificity of the homolytic C–H bond cleavage (reaction 1). In particular, the empirical dissociation energy of the C–H bond in benzene is reproduced within a few kilocalories per mole. The site specificity of the hydrogen abstraction is found to be governed almost entirely by steric factors, the hydrogens being removed preferentially from congested regions of the parent hydrocarbons.

Details of Calculations

Geometries of all systems under study were optimized at the BLYP/6-311G** level of theory with the GAUSSIAN 92/DFT suite of programs.⁹ Unless indicated otherwise, the spin-unrestricted formalism was employed for radicals. The computed spin orbitals were checked for positive HOMO-LUMO energy gaps.

(5) Wornat, M. J.; Sarofim, A. F.; Longwell, J. P. *Energy Fuels* **1988**, *2*, 775.

(6) Sarofim, A. F.; Longwell, J. P.; Wornat, M. J.; Mukherjee, J. The Role of Biaryl Reactions in the PAH and Soot Formation. Springer Ser. Chem. Phys. **1994**, *59*, 485.

(7) Hameka, H. F. J. *Org. Chem.* **1987**, *52*, 5025. Pacansky, J.; Liu, B.; DeFrees, D. J. *Org. Chem.* **1986**, *51*, 3720.

(8) Gill, P. M. W.; Johnson, B. G.; Pople, J. A.; Frisch, M. J. *Int. J. Quantum Chem.* **1992**, *S26*, 319.

* To whom all correspondence should be addressed.

⊗ Abstract published in *Advance ACS Abstracts*, May 15, 1996.

(1) Wornat, M. J.; Sarofim, A. F.; Lafleur, A. L. The Pyrolysis of Anthracene as a Model Coal-Derived Aromatic Compound. In *Symposium (International) on Combustion*, 24th; The Combustion Institute: Pittsburgh, 1992; p 955. Wornat, M. J.; Lafleur, A. L.; Sarofim, A. F. *Polycyclic Aromatic Compds* **1993**, *3*, 149.

(2) Badger, G. M.; Spotswood, T. M. *J. Chem. Soc.* **1960**, 4420. Badger, G. M.; Novotny, J. *J. Chem. Soc.* **1961**, 3400. Badger, G. M.; Kimber, R. W. L. *J. Chem. Soc.* **1961**, 3407. Badger, G. M.; Jolad, S. D.; Spotswood, T. M. *Aust. J. Chem.* **1964**, *17*, 771. Badger, G. M.; Kimber, R. W. L.; Novotny, J. *Aust. J. Chem.* **1964**, *17*, 778. Badger, G. M.; Donnelly, J. K.; Spotswood, T. M. *Aust. J. Chem.* **1964**, *17*, 1138, 1147.

(3) Pope, C. J.; Marr, J. A.; Howard, J. B. *J. Phys. Chem.* **1993**, *97*, 11001.

(4) Taylor, R.; Langley, G. J.; Kroto, H. W.; Walton, D. R. M. *Nature* **1993**, *366*, 728.

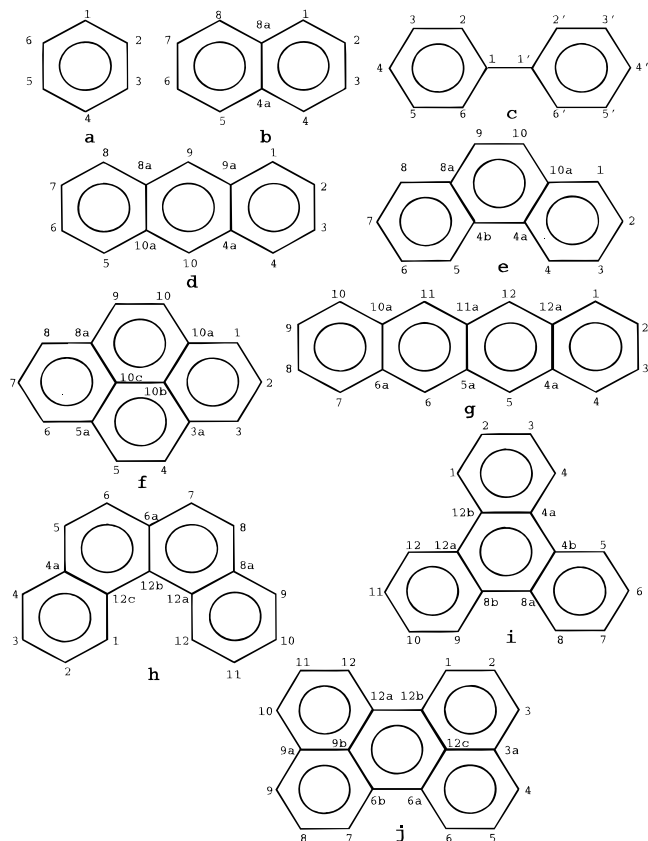


Figure 1. Numbering of carbon atoms in the systems under study: (a) benzene, (b) naphthalene, (c) biphenyl, (d) anthracene, (e) phenanthrene, (f) pyrene, (g) naphthacene, (h) benzo[*c*]phenanthrene, (i) triphenylene, and (j) perylene.

The default integration grids were used throughout the calculations. In order to assess the magnitude of errors due to numerical integrations employed in the evaluation of matrix elements of operators involving density functionals, calculations on the naphthalene molecule and two isomers of the naphthalenyl radical were repeated with larger integration grids. Negligible differences (<0.05 kcal/mol) between the relative energies obtained with different integration grids were found.

Vibrational frequencies were computed for all optimized geometries, confirming them to be true minima on the respective potential energy hypersurfaces. Atomic charges and spin populations in the $C_6H_5^*$, $1-C_{10}H_7^*$, and $2-C_{10}H_7^*$ radicals were calculated with the algorithms described elsewhere.¹⁰

Results and Discussion

Results obtained for the phenyl radical serve as the gauge of accuracy of the present calculations. In agreement with both the experimental evidence (the ESR spectrum)¹¹ and the previous CI study,¹² $C_6H_5^*$ is found to be a σ -type radical with the 2A_1 electronic ground state. The computed $\langle \hat{S}^2 \rangle$ expectation value equals 0.755, indicating only mild spin contamination. The predicted C–H bond dissociation energy (BDE) for benzene

(9) GAUSSIAN 92/DFT; Revision G.3; Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Wong, M. W.; Foresman, J. B.; Robb, M. A.; Head-Gordon, M.; Replogle, E. S.; Gomperts, R.; Andres, J. L.; Raghavachari, K.; Binkley, J. S.; Gonzalez, C.; Martin, R. L.; Fox, D. J.; Defrees, D. J.; Baker, J.; Stewart, J. J. P.; and Pople, J. A.; GAUSSIAN, Inc.: Pittsburgh, PA; 1993.

(10) Cioslowski, J.; Stefanov, B. B. *Mol. Phys.* **1995**, *84*, 707. Stefanov, B. B.; Cioslowski, J. *J. Comput. Chem.* **1995**, *16*, 1394. Cioslowski, J.; Nanayakkara, A.; Challacombe, M. *Chem. Phys. Lett.* **1993**, *203*, 137.

(11) Kasai, P. H.; Clark, P. A.; Whipple, E. B. *J. Am. Chem. Soc.* **1970**, *92*, 2640.

(12) Johnson, R. P. *J. Org. Chem.* **1984**, *49*, 4857.

Table 1. The Calculated Electronic Properties of Aryl Radicals

parent arene	site ^a	symmetry	$\langle \hat{S}^2 \rangle$	E_{el} (au)	E_{ZPE} (au)
benzene	1	C_{2v}	0.7548	-231.5164	0.0843
	1	C_s	0.7558	-385.1306	0.1298
naphthalene	2	C_s	0.7551	-385.1303	0.1296
	2	C_1	0.7547	-462.5267	0.1628
biphenyl	3	C_1	0.7547	-462.5259	0.1628
	4	C_2	0.7550	-462.5250	0.1628
	4	C_s	0.7557	-538.7393	0.1746
anthracene	1	C_s	0.7567	-538.7389	0.1743
	2	C_s	0.7558	-538.7389	0.1743
	9	C_{2v}	0.7584	-538.7393	0.1749
phenanthrene	1	C_s	0.7555	-538.7457	0.1751
	2	C_s	0.7550	-538.7452	0.1748
	3	C_s	0.7551	-538.7456	0.1749
	4	C_s	0.7554	-538.7487	0.1748
	9	C_s	0.7557	-538.7459	0.1750
pyrene	1	C_s	0.7565	-614.9675	0.1873
	2	C_{2v}	0.7546	-614.9681	0.1870
	4	C_s	0.7558	-614.9682	0.1873
	4	C_s	0.7576	-692.3460	0.2193
naphthacene	1	C_s	0.7566	-692.3456	0.2191
	2	C_s	0.7621	-692.3459	0.2196
	5	C_s	0.7557	-692.3601	0.2195
benzo[<i>c</i>]phenanthrene	1	C_s	0.7553	-692.3500	0.2203
	2	C_1	0.7550	-692.3493	0.2203
	3	C_1	0.7556	-692.3501	0.2206
	4	C_1	0.7558	-692.3497	0.2205
	5	C_1	0.7556	-692.3500	0.2206
	6	C_1	0.7554	-692.3611	0.2203
triphenylene	1	C_s	0.7550	-692.3567	0.2201
	2	C_s	0.7570	-768.5739	0.2321
perylene	1	C_s	0.7549	-768.5709	0.2319
	2	C_s	0.7576	-768.5703	0.2325
	3	C_s	0.7576	-768.5703	0.2325

^a The site of the hydrogen abstraction (carbon atoms numbered according to the Chemical Abstracts convention, see Figure 1).

amounts to 106.9 kcal/mol at $T = 0$ K. This figure compares well with the recently published experimental BDE values of 109.8 ± 0.8 ¹³ and 112.0 ± 0.6 kcal/mol.¹⁴

The satisfactory performance of the UBLYP/6-311G** level of theory is in sharp contrast with the totally unacceptable results obtained from conventional UHF calculations carried out with the same basis set. Such calculations yield the $\langle \hat{S}^2 \rangle$ expectation value of 1.403, reflecting a very substantial spin contamination of the UHF electronic wave function. Not surprisingly, this spin contamination gives rise to a spurious overstabilization of $C_6H_5^*$ relative to C_6H_6 , producing a theoretical value of BDE equal to 78.5 kcal/mol (ZPEs included). The ROHF/6-311G** calculations fare only slightly better, predicting a BDE value of 88.3 kcal/mol, which is still too low by over 20 kcal/mol. Only the inclusion of electron correlation effects through the BLYP functional brings the calculated BDE into agreement with its experimental counterpart. One should mention that, because of the poor UHF zeroth-order reference, the traditional perturbation treatment (such as MP2) is expected to encounter convergence difficulties in this case.

The total energies of ZPEs of the 10 parent hydrocarbons (benzene, naphthalene, biphenyl, anthracene, phenanthrene, pyrene, naphthacene, benzo[*c*]phenanthrene, triphenylene, and perylene; Figure 1), from which the aryl radicals under the present study are derived, yielding the corresponding relative stabilities that match closely the respective differences of the experimentally determined standard enthalpies of formation. For example, phenanthrene is predicted to be more stable than anthracene by 4.5 kcal/mol, which compares well with the

(13) Berkowitz, J.; Ellison, G. B.; Gutman, D. *J. Phys. Chem.* **1994**, *98*, 2744.

(14) Davico, G. E.; Bierbaum, V. M.; DePuy, C. H.; Ellison, G. B.; Squires, R. R. *J. Am. Chem. Soc.* **1995**, *117*, 2590.

Table 2. The Calculated Changes in Geometry upon the Hydrogen Abstraction

parent arene	site ^a	bond lengths ^b						bond angles ^c		
		Ar*	ArH	diff	Ar*	ArH	diff	Ar*	ArH	diff
benzene	1	1.382	1.404	−0.022	1.382	1.404	−0.022	125.9	120.0	5.9
naphthalene	1	1.364	1.385	−0.021	1.406	1.428	−0.022	126.8	120.9	5.9
	2	1.363	1.385	−0.022	1.401	1.423	−0.022	126.4	120.3	6.1
biphenyl	2	1.378	1.401	−0.023	1.393	1.414	−0.021	127.2	121.0	6.2
	3	1.379	1.401	−0.022	1.382	1.403	−0.021	126.2	120.3	5.9
	4	1.382	1.403	−0.021	1.382	1.403	−0.021	125.3	119.4	5.9
anthracene	1	1.358	1.379	−0.021	1.413	1.436	−0.023	126.9	121.0	5.9
	2	1.357	1.379	−0.022	1.409	1.431	−0.022	126.5	120.4	6.1
	9	1.387	1.408	−0.021	1.387	1.408	−0.021	127.8	121.9	5.9
phenanthrene	1	1.367	1.388	−0.021	1.400	1.422	−0.022	127.1	121.1	6.0
	2	1.367	1.388	−0.021	1.393	1.414	−0.021	125.5	119.6	5.9
	3	1.369	1.391	−0.022	1.393	1.414	−0.021	126.4	120.4	6.0
	4	1.369	1.391	−0.022	1.399	1.422	−0.023	127.2	121.5	5.7
	9	1.348	1.368	−0.020	1.418	1.440	−0.022	127.3	121.3	6.0
pyrene	1	1.380	1.401	−0.021	1.392	1.413	−0.021	126.7	120.8	5.9
	2	1.379	1.401	−0.022	1.379	1.401	−0.022	126.7	120.7	6.0
	4	1.350	1.371	−0.021	1.420	1.442	−0.022	127.4	121.4	6.0
naphthacene	1	1.355	1.376	−0.021	1.416	1.439	−0.023	127.0	121.1	5.9
	2	1.355	1.376	−0.021	1.412	1.435	−0.023	126.7	120.5	6.2
	5	1.380	1.402	−0.022	1.395	1.417	−0.022	127.9	122.0	5.9
benzo[<i>c</i>]phenanthrene	1	1.368	1.390	−0.022	1.402	1.428	−0.026	128.0	122.0	6.0
	2	1.367	1.390	−0.023	1.393	1.414	−0.021	126.7	120.7	6.0
	3	1.365	1.386	−0.021	1.393	1.414	−0.021	125.2	119.2	6.0
	4	1.365	1.386	−0.021	1.401	1.424	−0.023	127.2	121.3	5.9
	5	1.349	1.370	−0.021	1.411	1.433	−0.022	126.4	120.4	6.0
	6	1.349	1.370	−0.021	1.413	1.436	−0.023	127.4	121.3	6.1
triphenylene	1	1.369	1.390	−0.021	1.397	1.421	−0.024	127.5	122.0	5.5
	2	1.368	1.390	−0.022	1.387	1.408	−0.021	125.5	119.6	5.9
perylene	1	1.379	1.402	−0.023	1.390	1.411	−0.021	127.6	122.0	5.6
	2	1.363	1.384	−0.021	1.388	1.411	−0.023	126.4	120.4	6.0
	3	1.364	1.384	−0.020	1.403	1.425	−0.022	126.2	120.3	5.9
average:				−0.021			−0.022			5.9

^a The site of the hydrogen abstraction (carbon atoms numbered according to the Chemical Abstracts convention, see Figure 1). ^b Lengths (Å) of the two C–C bonds adjacent to the hydrogen abstraction site. ^c The C–C–C bond angle (deg) at the hydrogen abstraction site.

measured relative enthalpy of 5.5 kcal/mol¹⁵ and surpasses in accuracy the HF/6-31G*¹⁶ and HF/6-31G**¹⁷ estimates of 6.9 kcal/mol. Similarly, triphenylene is found to be 4.4 kcal/mol lower in energy than benzo[*c*]phenanthrene, in much better agreement with the experimental enthalpy difference of 3.1 kcal/mol¹⁵ than the HF/6-31G* prediction of 7.1 kcal/mol.¹⁶

Steric congestion in biphenyl and benzo[*c*]phenanthrene brings about distortions from planarity in their equilibrium geometries. These distortions are faithfully reproduced by the present calculations. In the biphenyl molecule, the C₂–C₁–C_{1'}–C_{2'} (Figure 1) dihedral angle is predicted at 40.3°, which is somewhat smaller than the experimental value of 44.4 ± 1.2°¹⁸ and the previous theoretical estimates of 45.5° (HF/6-31G**) and 46.2° (HF/6-311G**).¹⁹ On the other hand, the calculated C₁–C_{12c}–C_{12b}–C_{6a} (Figure 1) dihedral angle in benzo[*c*]phenanthrene, which amounts to 161.6°, is virtually identical with the published experimental (161.4°) and theoretical (the HF/6-31G* value: 161.2°) data.¹⁶

The hydrogen abstraction from the aforescribed PAHs gives rise to 31 distinct aryl monoradicals, properties of which are summarized in Table 1 and 2. All of these radicals are found to be of the σ type, confirming the previous empirical interpretations of the ESR spectra of the 1-naphthalenyl,

2-naphthalenyl, 1-anthracenyl, 9-anthracenyl, and 1-pyrenyl species.¹¹ Being in agreement with the recent MNDO calculations,²⁰ this finding contradicts the arguments according to which a switch from the σ to the π ground state should be expected to occur in larger aryl radicals.¹¹ The computed $\langle \hat{S}^2 \rangle$ expectation values remain very close to 0.75 for all the systems under study (Table 1). In contrast, the magnitudes of $\langle \hat{S}^2 \rangle$ produced by test UHF/STO-3G calculations appear to be size-extensive, reaching values close to 20. (!) for the largest radicals under study.

The UBLYP/6-311G** optimized geometries of aryl radicals exhibit remarkable regularities (Table 2). The relatively broad range of bond lengths (1.368–1.442 Å) and bond angles (119.2–122.0°) present in the carbon frameworks of the parent hydrocarbons notwithstanding, the hydrogen abstraction is invariably accompanied by a widening of the *ipso* bond angle by ca. 6.0° and a concomitant shortening of the adjacent C–C bonds by ca. 0.02 Å. This constancy of the geometry change upon the hydrogen removal provides strong evidence for an almost complete localization of the unpaired electrons and the separation between the local σ and π interactions in the aryl radicals under study.

The calculated atomic charges and spin populations in the phenyl, 1-naphthalenyl, and 2-naphthalenyl radicals (Figure 2) testify to the localization of unpaired electrons in these species. In C₆H₅•, the spin population of the hydrogen-abstracted carbon atom is 0.851, the two carbon atoms in the *meta* positions bearing most of the remaining spin. The patterns of atomic spin populations are very similar in the naphthalenyl radicals. In all three species, charges on all atoms are close to zero, the

(15) For a compilation of experimental enthalpies of formation of various hydrocarbons see: Herndon, W. C. *Chem. Phys. Lett.* **1995**, *234*, 82.

(16) Peck, R. C.; Schulman, J. M.; Disch, R. L. *J. Phys. Chem.* **1990**, *94*, 6637.

(17) Cioslowski, J.; O'Connor, P. B.; Fleischmann, E. D. *J. Am. Chem. Soc.* **1991**, *113*, 1086.

(18) Almennigen, A.; Bastiansen, O.; Fernholt, L.; Cyvin, B. N.; Cyvin, S. J.; Samdal, S. J. *Mol. Struct.* **1985**, *128*, 59.

(19) Cioslowski, J.; Mixon, S. T. *J. Am. Chem. Soc.* **1992**, *114*, 4382.

(20) Chen, R. H.; Kafafi, S. A.; Stein, S. E. *J. Am. Chem. Soc.* **1989**, *111*, 1418.

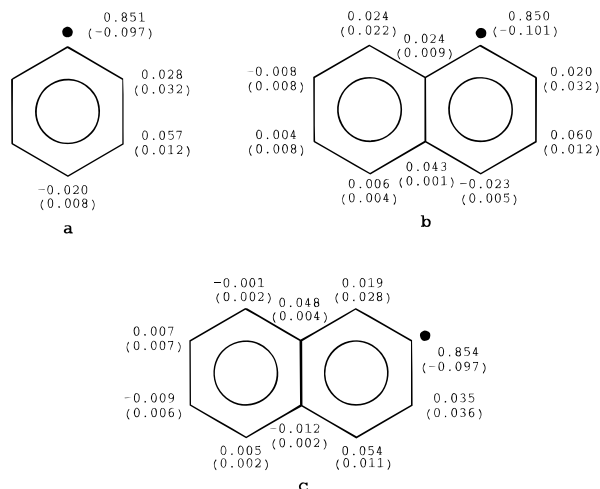


Figure 2. Atomic spin populations and charges (in parentheses) in (a) phenyl radical, (b) 1-naphthalenyl radical, and (c) 2-naphthalenyl radical.

Table 3. The Calculated Energies of the Homolytic C–H Bond Cleavage (eq 1)^a

parent arene	site ^b	ΔE_{el}	ΔE_{ZPE}	ΔE
benzene	1	115.1	-8.1	106.9
	naphthalene	1	115.0	-8.0
biphenyl	2	115.2	-8.1	107.1
	2	114.4	-8.1	106.3
	3	114.9	-8.1	106.8
	4	115.5	-8.1	107.4
anthracene	1	115.0	-8.0	107.0
	2	115.2	-8.2	107.1
	9	115.0	-7.8	107.2
	1	115.1	-8.0	107.1
phenanthrene	2	115.4	-8.1	107.3
	3	115.1	-8.1	107.1
	4	113.2	-8.1	105.1
	9	115.0	-8.0	107.0
pyrene	1	115.4	-7.9	107.5
	2	115.1	-8.1	107.0
	4	115.0	-8.0	107.0
	naphthacene	1	115.0	-8.0
benzo[<i>c</i>]phenanthrene	2	115.2	-8.1	107.1
	5	115.0	-7.8	107.2
	1	108.6	-8.6	100.0
	2	115.0	-8.1	106.9
	3	115.4	-8.1	107.3
triphenylene	4	114.9	-8.0	106.9
	5	115.1	-8.0	107.1
	6	115.0	-8.0	107.0
	1	112.5	-8.0	104.5
perylene	2	115.3	-8.1	107.2
	1	113.2	-8.2	105.0
	2	115.1	-8.3	106.7
perylene	3	115.5	-8.0	107.6

^a All energies in kcal/mol. ^b The site of the hydrogen abstraction (carbon atoms numbered according to the Chemical Abstracts convention, see Figure 1).

most negative ones appearing at the carbons from which the hydrogen atoms have been removed.

Consistent with these observations are the calculated energies of the homolytic C–H bond cleavage (reaction 1) (Table 3). The computed BDEs vary very little (from 106.7 to 107.6 kcal/mol), except for the cases where the hydrogen removal eases

steric congestion. In such instances, the computed BDEs are depressed by the amounts of energy lowering due to the reduction of steric repulsions. This energy lowering can be substantial, amounting to as much as ca. 7 kcal/mol for the hydrogen abstraction from position 1 of benzo[*c*]phenanthrene. The relief of steric overcrowding is accompanied by a flattening of molecular geometries in the aryl radicals. For example, the C₂–C₁–C_{1'}–C_{2'} dihedral angle in the 2-biphenyl radical is only 27.6°, which is much less than the analogous angles of 40.3, 40.0, and 41.4° predicted for the parent hydrocarbon and the products of the hydrogen abstraction from its 3- and 4-positions, respectively. Similarly, the 2-, 3-, 4-, 5-, and 6-isomers of the benzo[*c*]phenanthrenyl radical are twisted, whereas the 1-isomer is found to be planar.

Finally, it should be mentioned that the present BDE data are in disagreement with the previously published results of MNDO calculations on selected aryl radicals.²⁰ In those calculations, the BDEs have been found to vary by as much as 2.6 kcal/mol for the uncongested PAHs. In particular, a considerable preference for the hydrogen abstraction from the 9-position in anthracene has been predicted. In light of the difficulties with the description of electronic structures of aryl radicals (see above) that are encountered by conventional Hartree–Fock calculations, the MNDO data appear to be less reliable than the present ones.

Conclusions

The BLYP/6-311G** level of theory provides a tool for accurate predictions of the energetics of both benzoid hydrocarbons and the aryl radicals derived from them by the hydrogen abstraction. In contrast with conventional UHF calculations, which yield electronic wave functions that are grossly spin-contaminated, the UBLYP method correctly describes electronic structures of diverse aryl radicals. The stability of these radicals is predominantly determined by steric factors.

All of the radicals under the present study are of the σ type, with the unpaired electrons almost completely localized on single carbon atoms. Consequently, the perturbations to molecular geometries brought about by the removal of hydrogens are both localized and highly predictable. These perturbations involve a widening of the bond angle at the *ipso* carbon by about 6.0° and the accompanying shortening of the adjacent C–C bonds by ca. 0.02 Å.

The reliability of UBLYP calculations on aryl radicals opens an avenue to theoretical studies of many important reactions of organic chemistry. In particular, further research on pyrolytic reactions holds the promise of providing the means for a substantial reduction of the amounts of harmful PAHs that are produced during the combustion of solid fuels. Such a reduction would confer major benefits to both the environment and the health of the general population.

Acknowledgment. The research described in this publication has been supported by the U.S. Department of Energy under Grant No. DE-FG05-95ER-14523.

Supporting Information Available: Table of calculated energies of arenes (1 page). Ordering information is given on any current masthead page.

JA9600439