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Characterization of aromatic hydrocarbons by means of average local ionization energies on their molecular surfaces[☆]

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Abstract

The average local ionization energies $\bar{I}_S(\mathbf{r})$ and the electrostatic potentials $V_S(\mathbf{r})$ have been computed on the molecular surfaces of nine aromatic hydrocarbons, at the Hartree–Fock HF/6-31G**//HF/STO-3G and Kohn–Sham B3P86/6-31G**//HF/STO-3G levels. The surface areas, the fractions covered by positive and negative potentials, and their average values are quite similar by both computational procedures. The average values of $\bar{I}_S(\mathbf{r})$ and its minima, $\bar{I}_{S,\min}$ (which indicate the most reactive electronic sites), are smaller in magnitude at the Kohn–Sham level, but the differences from the Hartree–Fock are fairly uniform and the minima occur at essentially the same positions. In nearly all instances, therefore, the same qualitative predictions result from either approach. Most of the $\bar{I}_{S,\min}$ are found in bond regions and indicate varying degrees of olefin-like behavior. Some $\bar{I}_{S,\min}$ are located near carbons, and it is proposed that these reflect some radical character. Supporting evidence is cited. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Aromatic hydrocabons; Average local ionization energies; Kohn–Sham level

1. Introduction

The ionization energy I of an atomic or molecular system has been shown to be related to both its electronegativity (or chemical potential) and its polarizability (or hardness/softness or charge capacity) [1–7]. Thus I is relevant to chemical reactivity in general, not just ionic or charge-transfer interactions. Since reactivity is site-specific rather than global, it is useful to be able to define properties such as those mentioned on a local level. This has indeed been done for the hardness and softness [3,6].

We have accordingly introduced an average local ionization energy, $\bar{I}(\mathbf{r})$, defined initially within the framework of Hartree–Fock theory by Eq. (1) [8]:

$$\bar{I}(\mathbf{r}) = \sum_i \frac{\rho_i(\mathbf{r})|\epsilon_i|}{\rho(\mathbf{r})} \tag{1}$$

$\rho_i(\mathbf{r})$ is the electronic density of the ith atomic or molecular orbital at the point $\mathbf{r}$, ϵ_i is the orbital energy, and $\rho(\mathbf{r})$ is the total electronic density function. Since Koopmans' theorem [9] provides some justification for regarding the magnitudes of Hartree–Fock orbital energies as approximations to the electronic ionization energies [10], we interpret $\bar{I}(\mathbf{r})$ as the average energy needed to remove an electron from the point $\mathbf{r}$ in the space of an atom or molecule; $\bar{I}(\mathbf{r})$ focuses upon the point in space rather than upon a particular molecular orbital. Both I and $\bar{I}(\mathbf{r})$ have been shown to be related to the polarizabilities of atoms [1,5], and we have therefore
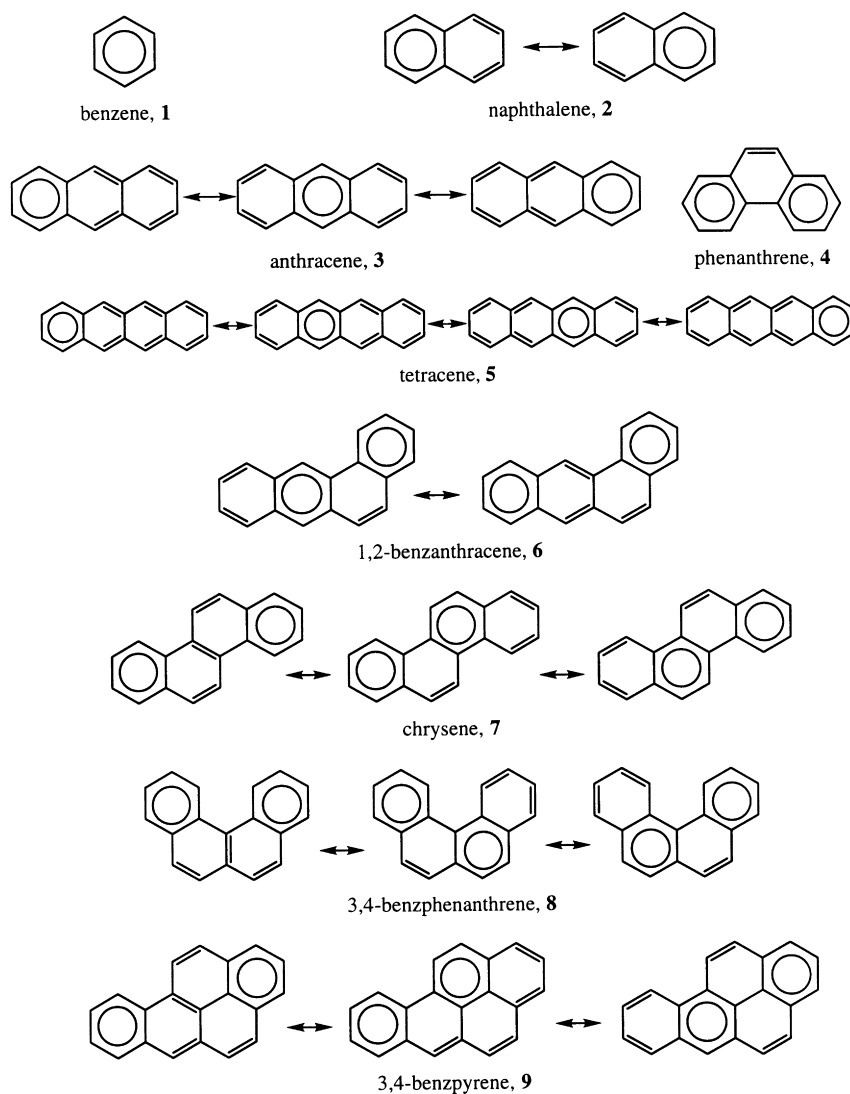

Fig. 1. Hydrocarbon contributing structures.

suggested that $\bar{I}(\mathbf{r})$ may be a measure of local polarizability in molecules [5].

2. Significance of $\bar{I}(\mathbf{r})$

In applying $\bar{I}(\mathbf{r})$ to predicting and interpreting chemical behavior, we felt it most useful to look at $\bar{I}_S(\mathbf{r})$, the pattern of $\bar{I}(\mathbf{r})$ on the molecular surface, which we normally take to be defined by the 0.001 a.u. contour of $\rho(\mathbf{r})$ [11]. The minima of $\bar{I}_S(\mathbf{r})$

indicate the points on the surface at which are found, on the average, the least tightly bound, most reactive electrons. The values of these minima, $\bar{I}_{S,min}$, are invariably greater than the magnitudes of the energies of the highest occupied orbitals, because there is always some probability of finding inner, more tightly bound electrons even at these points.

In studies of benzene derivatives, we have found that the $\bar{I}_{S,min}$ correctly predict the ring-activating or -deactivating effects of substituents as well as their *ortho/para-* or *meta-* directing tendencies [8,12]; the

$\bar{I}_{S,min}$ also correlate with the Hammett and Taft substituent constants [12–14]. In addition, we have been able to relate $\bar{I}_{S,min}$ to pK_a [13–18].

While $\bar{I}(\mathbf{r})$ is clearly of practical importance with regard to chemical reactivity, it can also serve to characterize atomic and molecular systems. For example, its radial variation in ground-state atoms directly reflects their shell structures [5]. Among hydrocarbons, strained C–C bonds in three-membered rings, which show significant olefin-like properties, have $\bar{I}_{S,min}$ near their midpoints [19] (as also does ethylene), whereas those in four-membered rings do not. This feature is particularly relevant to our present objectives.

3. Aromaticity

The concept and quantification of aromaticity continue to be a focus of interest and activity [20–36]. It is important to recognize that the aromaticity may be different for the various rings in a polycyclic aromatic hydrocarbon. For example, chemical and NMR evidence indicate that phenanthrene (**4** in Fig. 1) is best depicted as having two aromatic sextets and a double bond [27,37]. Robinson [24] and Clar [27] pointed out already many years ago that it is chemically and structurally misleading (as well as mathematically impossible, given the total number of π electrons) to assign an aromatic sextet to each in a series of fused six-membered rings.

In Fig. 1, the hydrocarbons **1–9** are depicted in terms of aromatic sextets and double bonds. Only those structures having the maximum number of aromatic sextets are considered to be important contributors [27]; in the case of phenanthrene, **4**, there is only one. Our primary objective in this work has been to investigate the extent to which the average local ionization energies computed on the molecular surfaces of **1–9** can be used to help characterize these molecules. A secondary objective will be discussed in the next section.

4. Kohn–Sham calculations

Recent years have seen rapidly increasing use of Kohn–Sham density functional methods in computational chemistry [38–40], reflecting their feasibility for much larger systems than ab initio techniques of a comparable level of accuracy. The Kohn–Sham procedure, like the Hartree–Fock, involves the iterative solution of a set of one-particle equations, and produces a set of electronic orbitals $\{\varphi_i\}$ and corresponding orbital energies $\{\epsilon_i\}$. In Hartree–Fock theory, there is some justification for viewing the magnitudes of the latter as approximations to the ionization energies of the respective electrons [9,10], i.e.

$$|\epsilon_{HF,i}| \approx I_i \qquad (2)$$

Such justification is not available in Kohn–Sham theory, except for the highest-occupied orbital, φ_{HOO}; it has been proven [41–44] (but subsequently challenged [45,46]) that the magnitude of its energy, in an exact Kohn–Sham treatment, is rigorously equal to the first ionization energy of the system:

$$|\epsilon_{KS,HOO}| = I_{min} \qquad (3)$$

Thus, while $\bar{I}(\mathbf{r})$ can be defined and evaluated by means of Eq. (1) in Kohn–Sham theory just as in Hartree–Fock, it is not immediately clear that it can be used in the same manner.

Comparisons of Hartree–Fock and Kohn–Sham orbital energies with experimental ionization energies have shown [47,48], for a series of molecules, that in general,

$$|\epsilon_{KS,i}| < I_i < |\epsilon_{HF,i}| \qquad (4)$$

For these approximate Kohn–Sham treatments, the magnitudes of the orbital energies (including $\epsilon_{KS,HOO}$) may differ by several electron-volts from the experimental values, depending upon which functional combination is used; however the deviations tend to be roughly the same for all of the valence orbitals, for a given molecule and functional combination. This suggests that at least the pattern and trends of the Kohn–Sham $\bar{I}_S(\mathbf{r})$ may be physically meaningful.

An initial test was carried out for a group of benzene derivatives [49]. We found that the Kohn–Sham $\bar{I}_{S,min}$ did correctly predict both the activating or deactivating effects and the directing tendencies of the substituents, and correlated well with the Hammett constants of the latter. One of our objectives in the present work is to further investigate the significance of Kohn–Sham $\bar{I}_{S,min}$; we shall compare them to their Hartree–Fock counterparts for the aromatic hydrocarbons **1–9**, and

Table 1

Calculated HF/STO-3G bond lengths, with experimental values in parentheses. Sources of experimental bond lengths: **1** [78]; **2**, **3** [79]; **4** [80]; **7** [81]; **8** [82]; **9** [83]. The values for **4** and **8** are averages over the two sides of the symmetry planes

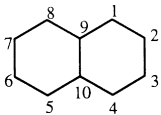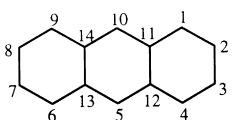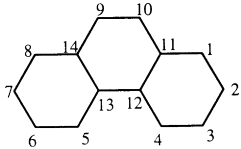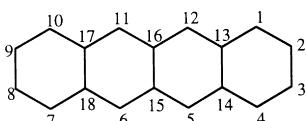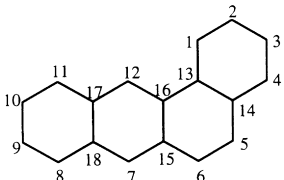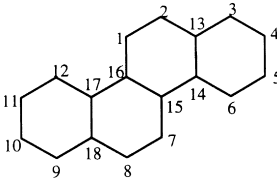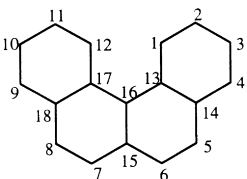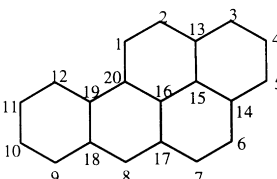| Molecule	Bond lengths (Å)
benzene, **1**	C–C: 1.387 (1.396)
naphthalene, **2**	C_1–C_2: 1.353 (1.364) C_2–C_3: 1.426 (1.406) C_1–C_9: 1.431 (1.420) C_9–C_{10}: 1.405 (1.422)
anthracene, **3**	C_1–C_2: 1.341 (1.356) C_2–C_3: 1.444 (1.410) C_1–C_{11}: 1.451 (1.430) C_{11}–C_{12}: 1.425 (1.435) C_{10}–C_{11}: 1.393 (1.400)
phenanthrene, **4**	C_1–C_2: 1.363 (1.374) C_2–C_3: 1.408 (1.386) C_3–C_4: 1.365 (1.399) C_4–C_{12}: 1.418 (1.412) C_{12}–C_{13}: 1.473 (1.464) C_1–C_{11}: 1.416 (1.428) C_{10}–C_{11}: 1.455 (1.450) C_9–C_{10}: 1.334 (1.341) C_{11}–C_{12}: 1.402 (1.416)
tetracene, **5**	C_1–C_2: 1.335 C_2–C_3: 1.454 C_1–C_{13}: 1.461 C_{13}–C_{14}: 1.442 C_{12}–C_{13}: 1.373 C_{12}–C_{16}: 1.417 C_{15}–C_{16}: 1.427
1,2-benzanthracene, **6**	C_1–C_2: 1.371 C_1–C_{13}: 1.410 C_2–C_3: 1.401 C_3–C_4: 1.370 C_4–C_{14}: 1.408 C_5–C_{14}: 1.466 C_5–C_6: 1.328 C_6–C_{15}: 1.466 C_{15}–C_{16}: 1.434 C_7–C_{15}: 1.377 C_7–C_{18}: 1.407 C_8–C_{18}: 1.442 C_8–C_9: 1.346 C_9–C_{10}: 1.436 C_{10}–C_{11}: 1.346

Table 1 (*continued*)

Molecule	Bond lengths (Å)
	C_{11}–C_{17}: 1.442 C_{17}–C_{18}: 1.413 C_{12}–C_{17}: 1.409 C_{12}–C_{16}: 1.378 C_{13}–C_{16}: 1.486 C_{13}–C_{14}: 1.402
chrysene, **7**	C_1–C_2: 1.340 (1.365) C_1–C_{16}: 1.447 (1.423) C_2–C_{13}: 1.442 (1.418) C_3–C_{13}: 1.442 (1.427) C_3–C_4: 1.358 (1.361) C_4–C_5: 1.414 (1.392) C_5–C_6: 1.360 (1.379) C_6–C_{14}: 1.425 (1.405) C_{13}–C_{14}: 1.464 (1.465) C_{15}–C_{16}: 1.389 (1.397)
3,4-benzphenanthrene, **8**	C_1–C_2: 1.361 (1.378) C_1–C_{13}: 1.426 (1.433) C_2–C_3: 1.412 (1.409) C_3–C_4: 1.358 (1.374) C_4–C_{14}: 1.421 (1.391) C_{13}–C_{14}: 1.407 (1.431) C_5–C_{14}: 1.444 (1.443) C_5–C_6: 1.338 (1.342) C_6–C_{15}: 1.445 (1.430) C_{15}–C_{15}: 1.338 (1.412) C_{13}–C_{16}: 1.470 (1.446)
3,4-benzpyrene, **9**	C_1–C_2: 1.340 (1.352) C_1–C_{20}: 1.451 (1.423) C_2–C_{13}: 1.447 (1.441) C_3–C_{13}: 1.409 (1.412) C_{13}–C_{15}: 1.406 (1.417) C_3–C_4: 1.371 (1.375) C_4–C_5: 1.399 (1.378) C_5–C_{14}: 1.381 (1.402) C_{14}–C_{15}: 1.423 (1.415) C_6–C_{14}: 1.470 (1.433) C_6–C_7: 1.327 (1.342) C_7–C_{17}: 1.471 (1.446) C_{15}–C_{16}: 1.446 (1.419) C_{16}–C_{17}: 1.444 (1.444) C_{16}–C_{20}: 1.393 (1.393) C_8–C_{17}: 1.360 (1.361) C_8–C_{18}: 1.427 (1.418) C_{18}–C_{19}: 1.408 (1.410) C_9–C_{18}: 1.431 (1.425) C_9–C_{10}: 1.35. (1.374) C_{10}–C_{11}: 1.422 (1.397) C_{11}–C_{12}: 1.355 (1.364) C_{12}–C_{19}: 1.431 (1.418) C_{19}–C_{20}: 1.449 (1.436)

shall extend the comparison to include as well some other properties of the molecular surfaces.

5. Methods

The geometries of **1**–**9** were optimized at the HF/STO-3G level, using the GAUSSIAN 94 code [50]. As shall be seen in the next section, this minimum basis set was found to produce satisfactory structures for these hydrocarbons. The electronic densities $\rho(\mathbf{r})$, the average local ionization energies on the molecular surfaces $\bar{I}_S(\mathbf{r})$, and the electrostatic potentials on the molecular surfaces $V_S(\mathbf{r})$ were then computed by the Hartree–Fock HF/6-31G** and the Kohn–Sham B3P86/6-31G** procedures; the latter involves the Becke three-parameter hybrid functional [51], with the Perdew-86 treatment of correlation [52]. The molecular surfaces were taken to be the 0.001 a.u. contours of the electronic densities $\rho(\mathbf{r})$ [11].

6. Results

6.1. Structures

Our optimized HF/STO-3G bond lengths for **1**–**9** are given in Table 1. They are in generally good agreement with the available experimental values; the average absolute deviation is 0.014 Å and the standard deviation is 0.017 Å.

6.2. Molecular surface areas and electrostatic potentials

The electrostatic potential $V(\mathbf{r})$ created at any point **r** by the electrons and nuclei of a molecule is given by Eq. (5),

$$V(\mathbf{r}) = \sum_A \frac{Z_A}{|\mathbf{R}_A - \mathbf{r}|} - \int \frac{\rho(\mathbf{r}')\,\mathrm{d}\mathbf{r}'}{|\mathbf{r}' - \mathbf{r}|} \tag{5}$$

in which Z_A is the charge on nucleus A, located at $\mathbf{R}_A$. The electrostatic potential has been used extensively to interpret and predict various aspects of molecular interactive behavior [53–56]. We have shown that a number of liquid, solid and solution phase properties (including critical constants, enthalpies of phase transitions, solubilities and solvation energies, partition coefficients, diffusion constants, viscosities,

etc.) can be expressed analytically in terms of specific features of $V(\mathbf{r})$ on the molecular surfaces [57–59]. Very recently, Suresh and Gadre [36] have proposed that local and global aromaticity can be related to $V(\mathbf{r})$.

In Table 2 are listed the computed surface areas, the ratios of the portions of the surfaces that have positive and negative electrostatic potentials A_S^+ and A_S^-, and the average values of these potentials, $\bar{V}_S^+$ and $\bar{V}_S^-$. These data are given for both B3P86/6-31G** and HF/6-31G** calculations. For comparison purposes, Table 2 also includes these results for benzene, **1**, when the 6-31+G** basis set is used to optimize the geometry and compute the properties.

The Kohn–Sham and Hartree–Fock surface areas are essentially the same for all of these molecules. The ratio of positive to negative surface, A_S^+/A_S^-, is also quite similar by the two procedures, although the Kohn–Sham predicts a slightly larger fraction to be positive. The magnitudes of the Hartree–Fock average potentials, $\bar{V}_S^+$ and $\bar{V}_S^-$, are consistently larger than the Kohn–Sham, but by less than 1.0 kcal/mol. These statements all apply as well to the 6-31+G** results for benzene, **1**; there are only small changes in the values, compared to the 6-31G**.

For molecules in general, of various chemical types, the surface area with positive electrostatic potential is usually greater than that with negative, but the latter is stronger in magnitude [60]. Thus, typically $A_S^+ > A_S^-$ but $|\bar{V}_S^-| > \bar{V}_S^+$. Exceptions to this are observed for molecules having several strongly electron-attracting components, such as polynitro systems [60]; then $\bar{V}_S^+ > |\bar{V}_S^-|$. Table 2 shows that the polycyclic aromatic hydrocarbons **3**–**9** are also exceptions to the customary pattern, but of a different sort; $|\bar{V}_S^-| > \bar{V}_S^+$, as usual, but now $A_S^- > A_S^+$, and this becomes more so in going to the larger systems. The key point is presumably the number of π electrons relative to the total surface area. In going from benzene, **1** (which shows the normal relationship of positive to negative surface) to anthracene, **3**, to 3,4-benzpyrene, **9**, the number of π electrons per Å^2 increases from 0.049 to 0.065 to 0.074. Thus there is an increasing surface density of delocalized π electrons.

Table 2
Comparison of Hartree–Fock and density functional molecular surface properties (areas in are A^2, $\bar{V}_S^+$ and $\bar{V}_S^-$ in kcal/mol, and $\bar{I}_S$(ave.) in eV)

Molecule	Method	Area	A_S^+/A_S^-	$\bar{V}_S^+$	$\bar{V}_S^-$	$\bar{i}_S$(ave.)
1	B3P86/6-31G**//HF/STO-3G	122.3	1.22	7.42	−9.25	11.76
	HF/6-31G**//HF/STO-3G	123.1	1.17	8.04	−9.95	15.12
2	B3P86/6-31G**//HF/STO-3G	170.0	1.07	8.05	−9.67	11.69
	HF/6-31G**//HF/STO-3G	170.0	1.03	8.84	−10.47	14.96
3	B3P86/6-31G**//HF/STO-3G	215.8	0.987	8.50	−9.70	11.64
	HF/6-31G**//HF/STO-3G	217.9	0.959	9.32	−10.60	14.87
4	B3P86/6-31G**//HF/STO-3G	213.6	0.968	8.56	−9.85	11.67
	HF/6-31G**//HF/STO-3G	213.7	0.945	9.38	−10.71	14.88
5	B3P86/6-31G**//HF/STO-3G	262.0	0.935	8.79	−9.72	11.61
	HF/6-31G**//HF/STO-3G	262.1	0.915	9.66	−10.61	14.80
6	B3P86/6-31G**//HF/STO-3G	259.6	0.930	8.84	−9.77	11.64
	HF/6-31G**//HF/STO-3G	260.1	0.907	9.74	−10.69	14.82
7	B3P86/6-31G**//HF/STO-3G	256.4	0.918	8.87	−9.88	11.66
	HF/6-31G**//HF/STO-3G	257.0	0.893	9.75	−10.78	14.84
8	B3P86/6-31G**//HF/STO-3G	255.8	0.920	8.37	−9.75	11.64
	HF/6-31G**//HF/STO-3G	256.3	0.902	9.17	−10.57	14.83
9	B3P86/6-31G**//HF/STO-3G	269.7	0.880	8.97	−9.95	11.63
	HF/6-31G**//HF/STO-3G	270.4	0.855	9.89	−10.81	14.77
1	B3P86/6-31 + G**	123.9	1.24	8.37	−9.03	11.64
	HF/6-31 + G**	123.7	1.19	9.05	−9.61	14.87

6.3. Average local ionization energies on molecular surfaces

For the molecules **1**–**9**, the Kohn–Sham $\bar{I}_S(\mathbf{r})$ range from 9.42 to 14.50 eV, while the Hartree–Fock are between 11.45 and 19.04 eV. Table 2 gives the average over each molecular surface, $\bar{I}_S$(ave.). These are quite uniform for this series of molecules. The Kohn–Sham values vary between 11.61 and 11.76 eV, the Hartree–Fock between 14.77 and 15.12 eV. The Kohn–Sham $\bar{I}_S$(ave.) are consistently about 3.2 eV lower than the Hartree–Fock.

In Table 3 are presented for each molecule the magnitudes and approximate locations of the lowest (and therefore most important) $\bar{I}(\mathbf{r})$ minima on its surface, the $\bar{I}_{S,min}$. (The dots do not indicate the exact positions of the $\bar{I}_{S,min}$, but only whether they are near a carbon or in a bond region.) These are the sites, on the average, of the most reactive, least tightly bound electrons. Again, the difference between the Kohn–Sham and the Hartree–Fock values is quite consistent, about 2.0 eV. What is particularly significant is that, for each molecule taken separately, the $\bar{I}_{S,min}$ obtained by the two procedures are always in approximately the same locations and nearly always show the same trend in magnitudes. Their linear

correlation coefficient, for all nine molecules taken together, is 0.960.

For the four acenes, **1**–**3** and **5**, chemical reactivity is known to increase with the number of rings [27]. This is fully in agreement with both $\bar{I}_S$(ave.) and the lowest $\bar{I}_{S,min}$ decreasing in the same order.

7. Discussion

The variability in the locations and values of the $\bar{I}_{S,min}$ in Table 3 reveals the heterogeneity that can be associated with the rings in polycyclic aromatic hydrocarbons. This emphasizes the importance of recognizing different degrees of local aromaticity, such as are indicated graphically in Fig. 1. Accordingly, several procedures for quantifying local aromaticity have been proposed [61–63], which sometimes yield contradictory results; for example, some predict the aromaticities of the rings in acenes, such as **3** and **5**, to increase from the ends toward the center [35,61] while others predict the reverse [34,36,62].

Benzene, **1**, is generally viewed as having the highest degree of local aromaticity. Table 3 shows that its $\bar{I}_{S,min}$ are located near the carbons rather than in internuclear regions, indicating the absence of any

Table 3

Values and approximate locations of $\bar{I}_{S,min}$ for **1**–**9**. The dots indicate only whether the minima are near carbons or in bond regions. The positions are not necessarily exactly the same for the Kohn–Sham and the Hartree–Fock procedures
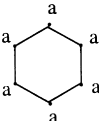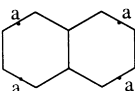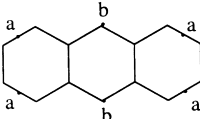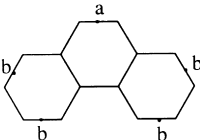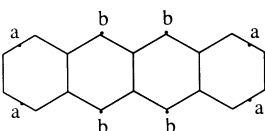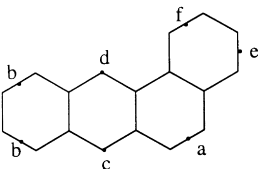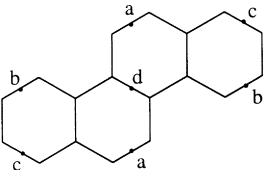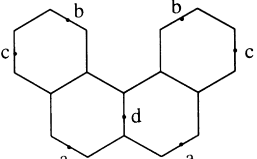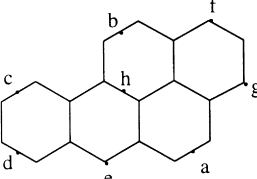
Molecule	$\bar{I}_{S,min}$ (eV)	
	B3P86/6-31G**// HF/STO-3G	HF/6-31G**// HF/STO-3G
benzene, **1**	a: 9.76	a: 11.92
naphthalene, **2**	a: 9.54	a: 11.60
anthracene, **3**	a: 9.47	a: 11.50
	b: 9.66	b: 11.66
phenanthrene, **4**	a: 9.45	a: 11.50
	b: 9.65	b: 11.73
tetracene, **5**	a: 9.44	a: 11.45
	b: 9.65	b: 11.59
1,2-benzanthracene, **6**	a: 9.42	a: 11.47
	b: 9.53	b: 11.56
	c: 9.69	c: 11.69
	d: 9.71	d: 11.72
	e: 9.71	e: 11.81
	f: 9.72	f: 11.81

Table 3 (*continued*)

Molecule	$\bar{I}_{S,min}$ (eV)	
	B3P86/6-31G**// HF/STO-3G	HF/6-31G**// HF/STO-3G
chrysene, **7**	a: 9.51	a: 11.56
	b: 9.63	b: 11.69
	c: 9.65	c: 11.71
	d: 10.15	d: 12.03
3,4-benzphenanthrene, **8**	a: 9.51	a: 11.56
	b: 9.61	b: 11.65
	c: 9.62	c: 11.68
	d: 10.13	d: 12.04
3,4-benzpyrene, **9**	a: 9.44	a: 11.49
	b: 9.54	b: 11.58
	c: 9.60	c: 11.64
	d: 9.60	d: 11.65
	e: 9.63	e: 11.56
	f: 9.68	f: 11.72
	g: 9.72	g: 11.73
	h: 10.28	h: 12.19

significant double-bond character. In naphthalene, **2**, on the other hand, the primary $\bar{I}_{S,min}$ are in the C_1–C_2 and C_3–C_4 bond regions, and indeed these bonds are shorter than those in benzene while the others are longer (Table 1). In all of the remaining molecules, **3**–**9**, at least some of the $\bar{I}_{S,min}$ are associated with bonds, and these are invariably the shorter ones in the molecule.

Anthracene, **3**, begins a pattern that is repeated in tetracene, **5**, and 1,2-benzanthracene, **6**. In their linear chains of three or four rings, the two terminal ones have $\bar{I}_{S,min}$ in bond regions while the inner ring or rings have them near the *para* carbons. Some time ago, in a study of propellane, **10**,

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we found $\bar{I}_{S,min}$ to the outsides of the central carbons

anthracene, **3A**

tetracene, **5A**

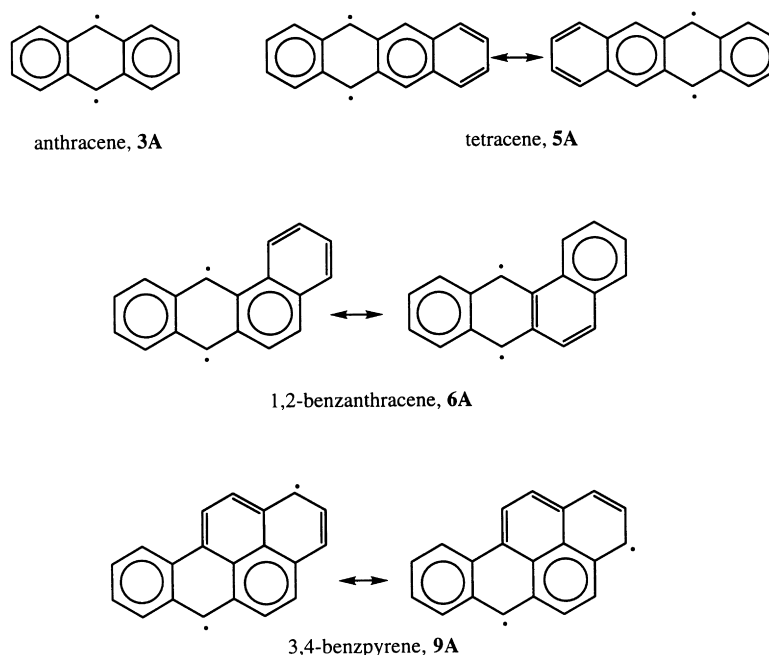1,2-benzanthracene, **6A**

3,4-benzpyrene, **9A**

Fig. 2. Proposed biradical contributing structures.

[19]. This was consistent with our earlier conclusion [64], based on electrostatic potential calculations, that the molecule has biradical character, and indeed there is chemical evidence, cited elsewhere [7,64], that this is the case. We now suggest that the patterns of $\bar{I}_{S,min}$ for **3**, **5** and **6** also indicate some degrees of radical character, and that the contributing structures for those molecules include not only those in Fig. 1 but also the additional ones shown in Fig. 2. For anthracene and tetracene, the possibly destabilizing effect of the radical sites in **3A** and **5A** may be partially offset by the presence of two aromatic sextets, compared to one in **3** and **5**. It should be noted that Polansky and Derflinger [65] proposed **3A** for anthracene already some time ago. 3,4-Benzpyrene, **9**, also has $\bar{I}_{S,min}$ near carbons, at three positions (Table 3). Accordingly, we suggest that the contributing structures **9A** (Fig. 2) should be included in its description.

The relative ease with which molecules such as **3**, **5** and **6** undergo addition across the *para* positions [66,67] is consistent with these having some radical character. Additional evidence in the case of anthracene is its formation of a dimer through C_9–$C_{9'}$ and C_{10}–$C_{10'}$ bonds [66]. Newman has described C_7 in

1,2-benzanthracene as the "position of maximum chemical reactivity" [68,69]. (C_{12} is presumably somewhat sterically hindered by the nearby ring.) In **9**, NMR analyses [70,71] have shown the most reactive carbon to be C_8, which is a radical site in both **9A** structures, followed by C_3 and C_5, which are the other two radical sites in **9A**. It is notable that this molecule forms two quinones, and the oxygens in these are at C_3,C_8 in one and at C_5,C_8 in the other [66].

Further indication of some radical character in **3**, **5**, **6** and **9** is provided by the patterns of their π delocalization energies. This quantity has long been used as a guide to site reactivity in conjugated and aromatic systems [67,72]; its magnitude reflects the densities of the most energetic π electrons at a given position [73]. The calculated delocalization energies for the carbons in **3**, **5**, **6** and **9** are largest at exactly those positions that are shown as radical sites in the contributing structures in Fig. 2 [73].

The reactivities of the *para* positions in molecules such as **3**, **5** and **6** was recognized in a prominent early effort to rationalize the carcinogenic activities of polycyclic aromatic hydrocarbons [74–77]. Reactions at these positions, labeled the L region, were viewed as

competing with the tumorigenic processes, which were believed to involve a relatively electron-rich and reactive K region. The prototype for the latter is the $C_9–C_{10}$ bond in phenanthrene, **4**, which is known to be quite olefin-like [27,37,66]; for example, it readily adds Cl_2 and Br_2. Each of the molecules **6**–**9** has at least one bond that can be viewed as structurally analogous to the $C_9–C_{10}$ of **4**, and hence is a K region; these are $C_5–C_6$ in **6**, $C_1–C_2$ and $C_7–C_8$ in **7**, $C_5–C_6$ and $C_7–C_8$ in **8**, and $C_1–C_2$ and $C_6–C_7$ in **9**. Table 3 does indeed show that the lowest $\bar{I}_{S,min}$ in **6**–**9** are associated with these bonds.

8. Summary

The average local ionization energies $\bar{I}_S(\mathbf{r})$ on the molecular surfaces of a group of aromatic hydrocarbons, as computed by both Kohn–Sham and Hartree–Fock procedures, show minima (indicating the most reactive electronic sites) in certain bond regions and near specific carbons. The former characterizes bonds with olefin-like properties; the latter, for the polycyclic systems, are proposed to reflect some degree of radical character.

The key features of the Kohn–Sham and the Hartree–Fock $\bar{I}_S(\mathbf{r})$ show parallel trends and thus lead to similar predictions, although the former are smaller in magnitude. The surface electrostatic potentials of the polycyclic aromatic hydrocarbons differ from what is normally observed in that the negative regions are larger in area than the positive.

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