Ab initio calculation of through-space magnetic shielding of linear polycyclic aromatic hydrocarbons (acenes): Extent of aromaticity

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ABSTRACT

GIAO-HF within Gaussian 03 was employed to compute the NMR isotropic shielding values of a diatomic hydrogen probe above a series of acenes (linear polycyclic aromatic hydrocarbons). Subtraction of the isotropic shielding of diatomic hydrogen by itself allowed the determination of computed through-space proton NMR shielding increment surfaces for these systems. Shielding was observed above the center of each aromatic ring, but the magnitude of calculated shielding above each ring center depends on the number of fused benzenoid rings. The computed shielding increments above each ring center were correlated to other measures of extent of aromaticity, including geometric, energetic, and magnetic measurements.

1. Introduction

Since Kekulé introduced the concept of aromaticity over 140 years ago [1] numerous methods have been developed to measure or predict the extent of aromaticity of a substance. Schleyer [2] listed several of these methods in his introduction to a series of review articles on aromaticity. Some of the methods are based on geometry, such as the harmonic oscillator model of aromaticity, HOMA [3–6]. Others rely on energetics, such as aromatic stabilization energy, ASE [7–11]. A third category of methods depends on the magnetic properties associated with aromaticity. These include exaltation of magnetic susceptibility, Λ [12–14], anisotropy of the magnetic susceptibility [15], nuclear magnetic resonance shifts [16–18], and nucleus-independent chemical shifts, NICS, a measure of the diatropic (for aromatic compounds) or paratropic (for antiaromatic compounds) ring current [19,20]. NICS or one of its variations, such as aromatic ring current shieldings (ARCS) computed from NICS measurements perpendicular to the plane of aromatic rings [21], Kleinpeter's [22,23] graphical maps of NICS, named isochemical shielding surfaces (ICSS), or Stanger's partitioned NICS [24] are perhaps the more common methods in use today to measure or predict aromaticity. Cyrañski et al. [25,26] showed that for a series of 75 five-membered ring π-electron systems and 30 ring-substituted compounds (including aromatic, nonaromatic and antiaromatic systems), loose correlations exist among the four most widely used measures of aromaticity: ASE, Λ, HOMA and NICS. But NICS measurements have limitations in terms of predicting aromaticity vs. antiaromaticity. For instance, the NICS value of the antiaromatic cyclopropenyl anion is negative, indicative of an aromatic structure. Correct assignments of aromaticity and antiaromaticity are obtained if a probe molecule, such as diatomic hydrogen, is used to determine the through-space shielding effect [27]. In contrast, the NICS method involves computing the magnetic shielding at a point in space.

The results of HF-GIAO calculations to calculate through-space NMR shielding effects on a probe molecule, to map the resulting through-space NMR shielding increments, and to develop through-space NMR shielding equations for a number of common organic functional groups, including the benzene ring [28,29], the carbon–carbon double bond [30–33], the carbon–carbon triple bond, the carbon–nitrogen triple bond and the nitro group [34], and the carbonyl group [35] have been published. Computed shielding surfaces by functional groups common to peptides [36], simple aromatic and antiaromatic hydrocarbons [27], aryl–cation π-complexes [37] and aryl–aryl π-complexes [38] have been reported. We now report our computational study of the through-space NMR shielding of a diatomic hydrogen probe molecule by some linear polycyclic aromatic hydrocarbons (PAHs).

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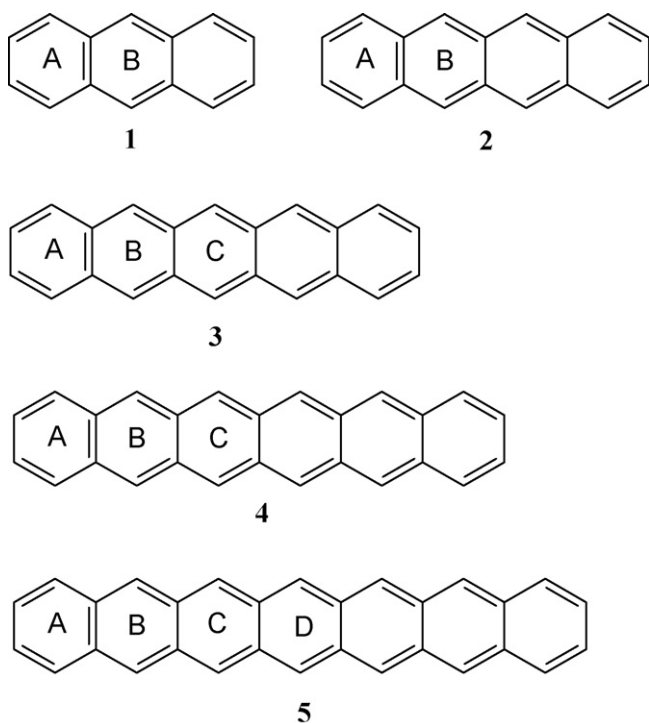E-mail address: martinn@uncw.edu (N.H. Martin).

Fig. 1. Structures of the acenes in this study: **1**, anthracene; **2**, tetracene; **3**, pentacene; **4**, hexacene; **5**, heptacene.

2. Computational methods

Structures of the hydrocarbons in this study are shown in Fig. 1. A model of each of these was built in Titan [39], then a geometry optimization calculation was performed at the Hartree-Fock level of theory using the 6-31G(d,p) basis set [40]. These structures are all planar, which allowed the Cartesian coordinate molecule description to be oriented in the XY plane. A diatomic hydrogen (H_2) probe [41], previously geometry optimized at HF/6-31G(d,p), was placed along the Z axis with the proximal hydrogen at a distance of 2.5 Å from the plane of each planar molecule. A series of single point NMR calculations[1] using the GIAO subroutine in Gaussian 03 [43] was performed on these supramolecules using the same method and basis set, moving the H_2 in 1.0 Å increments in both the X and Y directions in separate calculations. Calculations were also performed with the diatomic hydrogen probe above the geometric midpoint of each unique ring (indicated by letter in Fig. 1). The process was repeated with the H_2 probe at proximate hydrogen distances of 3.0 Å and 4.0 Å from the plane of the molecule being studied. These calculations covered a grid that extended in the X and Y directions beyond the positions of the carbon atoms. The symmetry of the structures allowed only one-fourth of the grid to be calculated and the data to be replicated by a reflection across the X and Y axis. Each of the structures was oriented with the carbon atoms in the XY plane with the center of the molecule at the origin of Cartesian space. The shielding increment ($\Delta\sigma$) at a given point in Cartesian space was determined by taking the difference between the calculated isotropic shielding value of one of the hydrogen in the H_2 probe alone (26.77 ppm) and

that of the proximal hydrogen of the H_2 probe at that point relative to the modeled structures. Isotropic shift values greater than the calculated isolated H_2 isotropic shielding value (26.77 ppm) give positive (shielding) $\Delta\sigma$ values, and those with smaller values give negative (deshielding) $\Delta\sigma$ values. The shielding increments ($\Delta\sigma$) are therefore equal in magnitude but opposite in sign to differences in ^{1}H NMR chemical shifts ($\Delta\delta$). Three-dimensional NMR shielding increment surfaces ($\Delta\sigma$ vs. X and Y at a fixed value of Z) were prepared using TableCurve 3D [44] to represent graphically the locations and magnitudes of shielding over the molecules in the study.

3. Results and discussion

The shielding surfaces of the acenes in this study (Fig. 1: anthracene **1**, tetracene **2**, pentacene **3**, hexacene **4**, heptacene **5**) are smooth variously elongated mounds that generally represent the shape and size of the molecule causing the shielding (Fig. 2). The maximum shielding is located over the middle of each structure. No perturbations associated with individual benzenoid rings are evident in the shielding surfaces. As the probe distance was increased to 3.0 Å and 4.0 Å, each shielding surface became flatter and the maximum shielding increments decreased. Only the shielding increment surfaces determined with the proximal hydrogen of the probe molecule at a distance of 2.5 Å are shown. The shielding surfaces show a smooth variation as the number of fused rings in the structure increases.
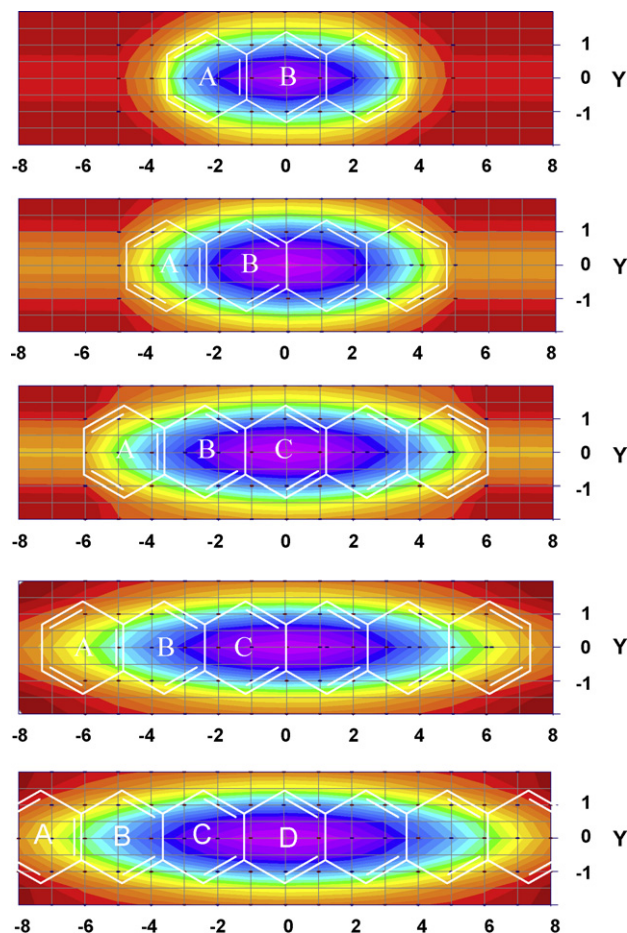

Fig. 2. Shielding increment surfaces (top view) of the acenes computed at 2.5 Å above the plane of the structures. X (not labeled) and Y values are Angstroms. The approximate location of the carbon skeleton is indicated in white.

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[1] Previous calculations [31,34,35] have shown that basis set superposition error, as measured by the counterpoise method of Boys and Bernardi [42], has a negligible effect on shielding values. BSSE is typically no greater than 0.05 ppm. Furthermore, the difference between the shielding values obtained using single point calculations and constrained geometry-optimized calculations is also negligible [41].
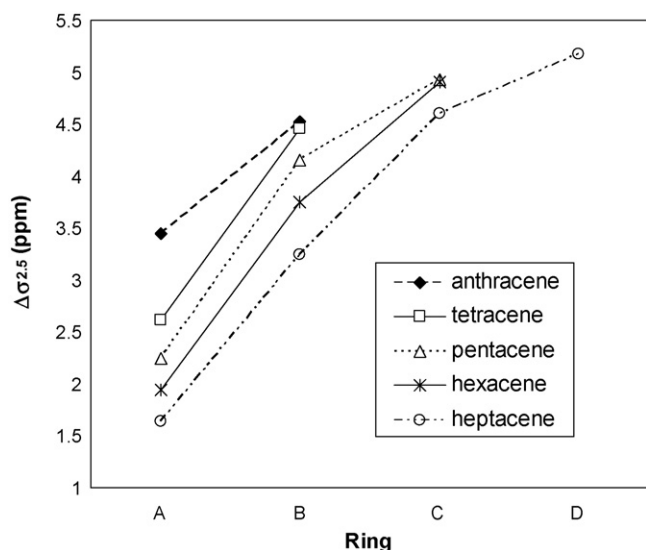
Fig. 3. Graph of the shielding increment 2.5 Å above the ring midpoint ($\Delta\sigma_{2.5}$) in the acenes vs. the letter label of the ring in Figs. 1 and 2.

The benzenoid rings become progressively more shielding from the outer ring inward, with the maximum shielding observed above the central ring or rings (Fig. 3). The shielding maximum above the middle of the molecule increase as the number of linear-fused benzenoid rings increases. The difference in the shielding values from outermost to innermost ring increases dramatically as the number of fused rings increases (Table 1). The mean difference in shielding over the ring centers of adjacent rings is 1.34 ppm, with the greatest mean difference (1.64 ppm) found between the outermost A ring and the B ring. Acenes with an odd number of rings have slightly larger maximum shielding values than the next longer acene with an even number of fused rings.

Linear correlations between the computed shielding increment at 2.5 Å ($\Delta\sigma_{2.5}$) above a ring midpoint of the linear acenes and various other reported measures of aromaticity were determined. The resulting r^2 values are presented in Table 2. Geometric data (HOMA), energetic data derived from bond lengths (REC/n), and magnetic data (NICS) collected by Cyrañski et al. [45] were used to determine correlations with our $\Delta\sigma_{2.5}$ values. These three sets of data were selected for comparison with $\Delta\sigma_{2.5}$ values because they represent a variety of approaches to measuring aromaticity, and because they provided Cyrañski with the best correlations. Correlation was very good between $\Delta\sigma_{2.5}$ and HOMA, REC/n, and NICS for ring A (r^2 = 0.92, 0.87 and 0.99, respectively). The r^2 values between $\Delta\sigma_{2.5}$ and those same measures for ring B were 0.79, 0.59 and 0.99, respectively. Similar correlations for ring C gave r^2 values of 0.57, 0.70, and 1.0. The high correlation between

Table 1
Computed shielding increments ($\Delta\sigma_{2.5}$) of a diatomic hydrogen probe molecule 2.5 Å above the center of each ring.

	Maximum shielding increment ($\Delta\sigma$) 2.5 Å above the ring center (ppm)			
	Ring A	Ring B	Ring C	Ring D
Anthracene (**1**)	3.45	**4.52**	–	–
Tetracene (**2**)	2.62	**4.46**	–	–
Pentacene (**3**)	2.25	4.15	**4.93**	–
Hexacene (**4**)	1.94	3.75	**4.91**	–
Heptacene (**5**)	1.64	3.25	4.60	**5.17**

The maximum shielding increment for each structure is shown in bold.

Table 2
r^2 Values for linear correlation between computed shielding increments ($\Delta\sigma_{2.5}$) of a diatomic hydrogen probe molecule 2.5 Å above the center of each ring of the acenes and various measures of aromaticity.

	r^2 Values for correlation of $\Delta\sigma_{2.5}$ with			
	HOMA	REC/n	NICS	EC
Ring A	0.92	0.87	0.99	0.99
Ring B	0.79	0.59	0.99	0.80
Ring C	0.57	0.70	1.00	0.67

Ring D of heptacene was omitted from the correlation because there is only one ring D value.

Table 3
r^2 Values for linear correlation between maximum computed shielding increments ($\Delta\sigma_{2.5max}$) of a diatomic hydrogen probe molecule 2.5 Å above the plane of the acenes and various estimates of whole-molecule aromaticity.

r^2 Values for correlation of $\Delta\sigma_{2.5max}$ with:		
HOMA	ASE/n	MEC/n
0.71	0.81	0.70

NICS and $\Delta\sigma_{2.5}$ is expected; they arise from a similar calculation, the difference being that NICS measures shielding at a point in space, whereas $\Delta\sigma_{2.5}$ uses a diatomic hydrogen probe molecule.

Also collected in Table 2 are correlations between $\Delta\sigma_{2.5}$ and the π electron content (EC) values of Balaban and Randić [46]. The EC values are derived by mathematically partitioning the π electrons in polycyclic systems according to whether the π bond is shared with another ring or not in a given Kekulé structure, and averaging over all Kekulé structures assuming equal weights. Over ring A these values correlate very well (r^2 = 0.99); ring B gives good correlation (r^2 = 0.80), and ring C shows fair correlation (r^2 = 0.67).

Whole-molecule measures of aromaticity compiled by Cyrañski et al. [45] were also correlated with the maximum shielding values obtained over each structure ($\Delta\sigma_{2.5max}$). The latter is essentially identical to the $\Delta\sigma_{2.5}$ over the middle ring. The r^2 values for these correlations are shown in Table 3. Correlation was good between $\Delta\sigma_{2.5}$ and HOMA, ASE/n (E) and MEC/n, giving r^2 values of 0.71, 0.81, and 0.70 respectively.

4. Conclusions

Acenes, the linear polycyclic aromatic hydrocarbons, exert substantial through-space magnetic shielding effects above the plane of the multi-ring structure. The maximum shielding at a given distance above the molecular plane depends on the number of fused benzenoid rings, reaching as high as 5.2 ppm above the middle ring of heptacene, the largest structure in this study. The outermost ring generally causes the least shielding, the magnitude of which diminishes as the number of fused rings increases. The maximum shielding occurs over the middle of the polycyclic ring system. The computed shielding increment at 2.5 Å above the center of each ring ($\Delta\sigma_{2.5}$) correlates reasonably well with other established methods of assessing aromaticity of individual rings. The maximum shielding increment computed over each structure ($\Delta\sigma_{2.5max}$) correlates moderately well with established methods of estimating whole-molecule aromaticity.

Acknowledgment

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