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Computed NMR shielding of phosphorus-containing conjugated five-membered ring heterocycles as a measure of aromaticity

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ABSTRACT

The GIAO–HF method in Gaussian 03 was used to calculate the isotropic shielding value of the proximal hydrogen of a diatomic hydrogen probe oriented perpendicular to the plane and moved in a square grid 2.5 Å above the plane of conjugated five-membered ring heterocyclic compounds: pyrrole, furan, phosphole and thiophene and their phosphorus containing analogs. Subtraction of the calculated isotropic shielding value of diatomic hydrogen from each of these isotropic shielding values gave the shielding increment ($\Delta\sigma$) for each probe position. Plotting this value against Cartesian coordinates of the probe position allowed determination of the computed through-space shielding increment surfaces for these compounds . Substantial shielding was observed above the center of each ring, as expected for aromatic compounds. The magnitude of the shielding increment 2.5 Å above the heterocyclic ring center correlated reasonably well with the other published methods of assessing aromaticity of these systems ASE (aromatic stabilization energy), Λ (exaltation of magnetic susceptibility) and NICS(1) (nucleus-independent chemical shift) values, both of which are magnetic criteria. The magnitude of the shielding increment also correlated with the number of phosphorus atoms in the ring. Greatest shielding (5.5 ppm) was observed 2.5 Å above 2,3,4,5-tetraphosphathiophene.

1. Introduction

Although Kekulé introduced the concept of aromaticity nearly 150 years ago [1], no single method has no single method of assessing or predicting aromaticity has gained universal acceptance. This is in part because aromaticity is a multidimensional property, consisting of geometrical, energetic and magnetic components, whereas most measures focus on only one aspect [2]. As an example, the harmonic oscillator model of aromaticity, HOMA [3–6] relies on bond length similarity. Others such as aromatic stabilization energy, ASE [7–11], rely on energetics. A third category depends on magnetic properties, including the 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 [19,20]. The latter is a measure of the diatropic (for aromatic compounds) or paratropic (for antiaromatic compounds) ring current. 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 and Klod's [22,23] graphical maps of an array of NICS, named isochemical shielding surfaces (ICSS), or Stanger's partitioned distance dependent NICS [24] are newer methods to measure or predict aromaticity. Cyrañski et al. [25,26] showed that loose correlations exist among the four most widely used measures of aromaticity (ASE, Λ, HOMA and NICS) for a series of 105 five-membered ring π-electron containing compounds, including aromatic, nonaromatic and antiaromatic systems. Although some variations of NICS measurements have become the most widely used measures of aromaticity, they 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, yet it is known to be antiaromatic. The correct assignments of aromaticity and antiaromaticity are obtained if a molecular probe, such as diatomic hydrogen [27], is used to determine the through-space shielding effect [28]. A molecular probe measures not only magnetic effects, but also bond polarization effects, which are often important in predicting through-space chemical shift effects [29–31]. In contrast, the NICS method computes only the magnetic shielding at a point in space and therefore does not always reliably predict chemical shift effects, especially when the latter involve orbital interactions or perturbations, also known as steric compression effects. It should be noted that Kleinpeter et al. have shown that their spatial NICS method models well the chemical shift effect of through-space shielding in 9-arylfluorenes [32]; these structures do not exhibit steric compression effects. Kleinpeter et al. have also shown (also

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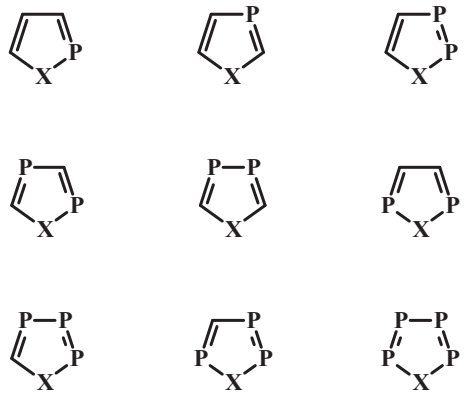

Fig. 1. Phosphorus containing structures used in the study. Y = N—H, O, P—H or S.

in systems that do not exhibit steric compression effects) that the anisotropic effect of functional groups on proton NMR spectra is the molecular response property of spatial NICS [33].

We have reported the results of GIAO–HF calculations to calculate through-space NMR shielding effects on a probe molecule and to map the resulting through-space NMR shielding increments of benzene and substituted benzenes [34,35], small ring aromatic and antiaromatic hydrocarbons [28] and in aromatic ring π-stacked complexes [36]. The computed shielding effects as well as the relationship between the computed shielding effects and the extent of aromaticity of linear polycyclic aromatic hydrocarbons (PAHs) [37] have been reported. Fused aromatic/antiaromatic systems have also been investigated using the diatomic hydrogen probe method [38]. Good correlations between computed shielding increments using a diatomic hydrogen probe and several common measures of aromaticity have been demonstrated for nitrogen-substituted conjugated five-membered ring heterocyclic compounds [39] and for their benzo analogs [40]. We now report the extension of that study to include phosphorus-containing conjugated five-membered ring heterocycles. Most of these compounds have not been reported except for their computed properties, thus, this is a theoretical study of the degree of aromaticity of these heterocycles as a function of the number of phosphorus atoms in the ring.

2. Computational methods

The compounds in this study are shown in Fig. 1. They consist of pyrrole, furan, phosphole and thiophene and their mono-, di-, tri- and tetraphospha-derivatives. A model of each of these was built in Titan [41], and equilibrium geometries (confirmed by a frequency calculation) were obtained at the Hartree–Fock level of theory using the 6-31G(d,p) basis set [42]. Each of these structures is essentially planar, which allowed the Cartesian coordinate molecule description to be oriented with the ring atoms in the XY plane having the center of the molecule at the origin of Cartesian space and the varied heteroatom along the negative *Y* axis. A diatomic hydrogen (H_2) probe [27], 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 molecule. Single point NMR calculations were performed in Gaussian 03 [43] on these supramolecules using the same method and basis set, moving the H_2 in 0.5 Å increments in both the *X* and *Y* directions in 169 separate calculations covering a 6 Å by 6 Å grid.

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 hydrogens in H_2 alone (26.77 ppm) and that of the proximal hydrogen of the H_2 probe at that point relative to the heterocyclic structures. Computed isotropic shift values greater than that of isolated H_2 result in positive (shielding) $\Delta\sigma$ values; those with smaller values yield 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 SigmaPlot [44] to represent graphically the locations and magnitudes of shielding 2.5 Å over the molecules in the study. Linear correlations were determined for shielding increments computed 2.5 Å over the ring centers ($\Delta\sigma_{2.5}$) against ASE, Λ and NICS(1) values for these compounds collected by Cyrañski et al. [25]. HOMA values are not included because parameters for their computation are unavailable for PN, PO, PP and PS bonds. Good linear correlations were also observed between the shielding increment and the number of phosphorus atoms in the ring.

3. Results and discussion

Shielding increment surfaces 2.5 Å above the plane of 2-phosphafuran, 2,3-diphosphafuran, and 2,3,4,5-tetraphoshafuran are shown in Fig. 2. A mound of shielding centered over the ring midpoint characterizes each of these representative structures. Otherwise the shielding surfaces are rather featureless, unlike those of the nitrogen containing five-membered ring heterocycles [39] which showed deshielding beyond each additional ring nitrogen. The magnitude of the maximum shielding (always observed at the ring midpoint; defined as $\Delta\sigma_{2.5}$) correlates closely with the number of phosphorus atoms in the ring (r = 0.95–0.99 for the four series). The $\Delta\sigma_{2.5}$ values for all structures in this study and their parent heterocycles are collected in Table 1 along with several other published measures of aromaticity: ASE, Λ, and NICS(1) taken from Cyrañski et al. [25]. Shielding increment surfaces for all phosphorus-containing structures in the

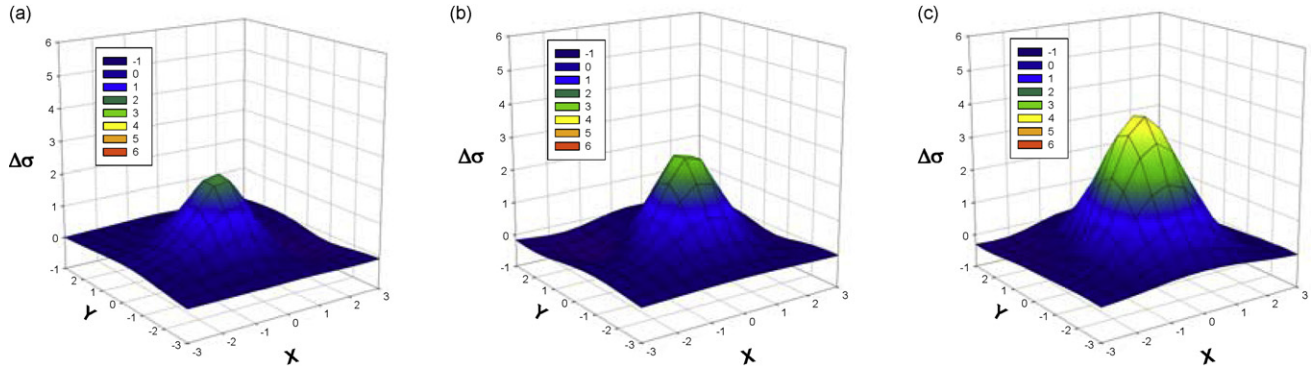

Fig. 2. NMR shielding surface 2.5 Å above the plane of (a) 2-phosphafuran, (b) 2,3-diphosphafuran and (c) 2,3,4,5-tetraphoshafuran.

Table 1
Computed shielding increment ($\Delta\sigma_{2.5}$) along with other published methods of aromaticity taken from Cyrañski et al. [25].

Compound	ASE	Λ	NICS(1)	$\Delta\sigma_{2.5}$
Pyrrole	20.57	−6.48	−10.60	2.04
2-Phosphapyrrole	20.31	−6.12	−10.77	2.58
3-Phosphapyrrole	19.91	−6.85	−11.33	2.26
2,3-Diphosphapyrrole	19.17	−6.70	−11.61	2.75
2,4-Diphosphapyrrole	18.85	−6.16	−11.39	3.09
2,5-Diphosphapyrrole	19.24	−6.41	−10.85	3.37
3,4-Diphosphapyrrole	19.47	−6.96	−11.97	3.02
2,3,4-Triphosphapyrrole	18.38	−6.82	−12.35	3.69
2,3,5-Triphosphapyrrole	17.96	−6.11	−11.63	3.64
2,3,4,5-Tetraphosphapyrrole	17.12	−5.98	−12.98	4.44
Furan	14.77	−2.90	−9.36	1.79
2-Phosphafuran	13.19	−1.60	−9.34	2.26
3-Phosphafuran	13.50	−2.99	−10.26	1.92
2,3-Diphosphafuran	12.23	−2.01	−10.36	2.33
3,4-Diphosphafuran	12.18	−3.33	−11.12	2.58
2,4-Diphosphafuran	12.14	−1.65	−10.14	2.66
2,5-Diphosphafuran	12.69	−1.11	−9.28	2.96
2,3,4-Triphosphafuran	11.84	−2.93	−11.37	3.20
2,3,5-Triphosphafuran	12.72	−1.19	−10.34	3.12
2,3,4,5-Tetraphosphafuran	12.30	−2.45	−11.97	3.87
Phosphole	3.20	−1.68	−5.97	1.54
2-Phosphaphosphole	4.97	−4.91	−7.73	1.94
3-Phosphaphosphole	3.03	−2.74	−6.90	1.97
2,3-Diphosphaphosphole	4.25	−5.52	−9.17	2.74
2,4-Diphosphaphosphole	6.18	−7.08	−9.34	2.76
2,5-Diphosphaphosphole	7.97	−9.75	−10.85	3.04
3,4-Diphosphaphosphole	4.11	−4.90	−8.48	2.79
2,3,5-Triphophaphosphole	8.93	−12.38	−11.88	3.76
2,3,4-Triphosphaphosphole	7.22	−11.47	−11.75	3.25
2,3,4,5-Tetraphosphaphosphole	11.24	−20.82	−14.93	4.79
Thiophene	18.57	−7.00	−10.79	2.35
2-Phosphathiophene	17.45	−7.21	−11.40	3.05
3-Phosphathiophene	17.01	−8.40	−11.59	2.94
2,3-Diphosphathiophene	15.14	−8.79	−12.24	3.52
2,4-Diphosphathiophene	16.14	−8.37	−12.16	3.75
2,5-Diphosphathiophene	16.02	−7.91	−11.99	3.92
3,4-Diphosphathiophene	16.75	−9.64	−12.37	3.89
2,3,4-Triphosphathiophene	15.23	−10.25	−13.21	4.63
2,3,5-Triphosphathiophene	14.53	−8.77	−12.91	4.48
2,3,4,5-Tetraphosphathiophene	12.79	−10.57	−14.38	5.52

study are found in Supplemental material. Those for the parent heterocycles have been published [39].

Shielding increment surfaces 2.5 Å above the plane of 2-phosphathiophene, 2,3-diphosphathiophene, and 2,3,4,5-tetraphoshathiophene are shown in Fig. 3. Each of the shielding increment surfaces shows a dominant mound of shielding near the center of the ring and a region of slight deshielding beyond the sulfur heteroatom. Again, the maximum shielding values ($\Delta\sigma_{2.5}$) correlate well with the number of phosphorus atoms in the ring ($r = 0.99$ for the thiophenes). It is not at all clear what factors determine the exact order of aromaticity (i.e., of shielding effects) other than the increasing number of phosphorus atoms in the ring. Any other factors are very subtle and have relatively little effect on shielding. Generally the differences in shielding increment are much smaller among compounds with similar number of phosphorus atoms than between compounds having different numbers of phosphorus atoms. The parent heterocycles were the least shielding (=least aromatic). In all except the phosphole series, the 3-phospha-derivative was less shielding than the 2-phospha-derivative. The order of increasing shielding was identical after the monophosphorus containing rings for all of the series: 2,3-diphospha-, followed by 2,4-diphospha-, then 3,4-diphospha- and 2,5-diphospha-.

Next most shielding were the triphosphorus derivatives in the following order of increasing shielding: 2,3,5-triphospha-, then 2,3,4-triphospha-. Last, the most shielding (most aromatic) was the 2,3,4,5-tetraphospha-substituted heterocycle.

Similar shielding surfaces were obtained for phosphorus-containing pyrroles and phospholes. The most notable observation is that greatest maximum shielding was computed 2.5 Å above the ring center of 2,3,4,5-tetraphosphathiophene (5.5 ppm). The ring displaying the next most shielding was 2,3,4,5-tetraphosphaphosphole (4.8 ppm). Several of the phosphorus containing phospholes display a region of deshielding in the vicinity of the lone pair of electrons of the phosphole, as has been reported previously [39]. The greater shielding over the compounds containing more phosphorus atoms correlates quite well with greater aromaticity as measured by other accepted methods (Table 2), with the exception of the computed exaltation of magnetic susceptibility of phosphorus containing furans and pyrroles, where correlation was poor. Cyrañski et al. [25] also found weaker correlation between other measures and exaltation of magnetic susceptibility.

Table 2
Correlation coefficients for correlation of our $\Delta\sigma_{2.5}$ values in four different series of heterocycles to accepted measures of aromaticity taken from Cyrañski et al. [25].

	Pyrroles	Furans	Phospholes	Thiophenes
ASE	0.94	0.67	0.92	0.93
Λ	0.40	0.23	0.96	0.85
NICS (1)	0.78	0.66	0.98	0.98

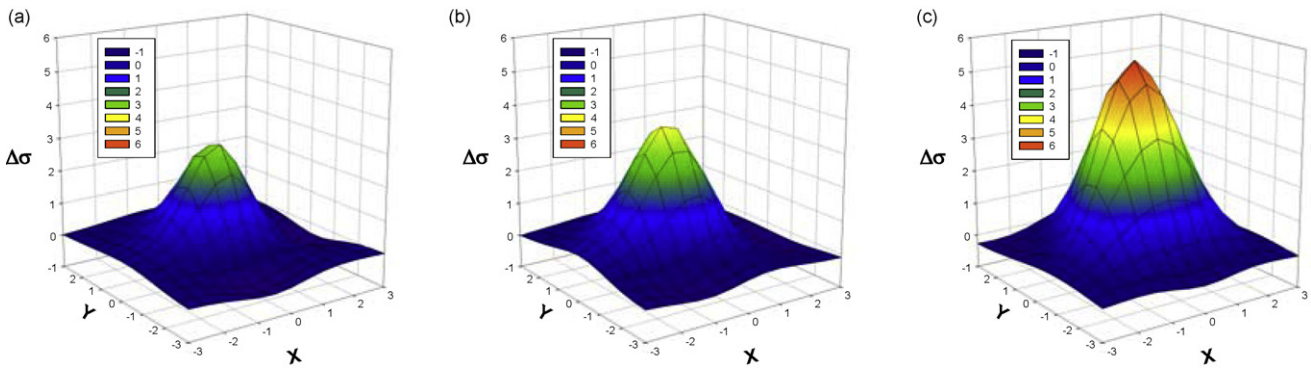

Fig. 3. NMR shielding surface 2.5 Å above the plane of (a) 2-phosphathiophene, (b) 2,3-diphosphathiophene and (c) 2,3,4,5-tetraphoshathiophene.

4. Conclusions

Diatomic hydrogen was used as a computational probe to compute through-space NMR shielding over phosphorus-containing five-membered ring heterocycles. Shielding increment surfaces 2.5 Å above the plane of these structures showed a mound of shielding centered over the structure. The maximum shielding value (over the structure midpoint) correlated well with other accepted measures of aromaticity for this series of forty structures and with increasing number of phosphorus atoms in the ring. The shielding increment method that we use has been shown to have the advantage of predicting chemical shifts, which many of the other measures of aromaticity do not predict reliably, especially when bond polarization (steric compression) effects occur.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jmgm.2012.07.008.

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