

Arsole Aromaticity Revisited

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The aromaticity of arsoles has been debated in the literature for years. Some measures indicate arsole to be non-aromatic, others attribute at least slight aromaticity to the molecule. Here, we take a ring-current view of aromaticity, and study arsole in more detail. We make comparisons to the nitrogen analogue pyrrole, the phosphorous analogue phosphole, and the carbon analogue cyclopentadiene. While the nucleus-independent chemical shift (NICS) provides an indirect measure of the ring current induced by a magnetic field, the newly developed gauge-including magnetically induced currents (GIMIC) method provides a direct measure of the current flow in the molecule. Using GIMIC, we show arsole to be almost half as aromatic as pyrrole. Phosphole comes in between. Even cyclopentadiene is found to possess a moderately strong induced ring current, thus questioning the accepted classification of this molecule as a non-aromatic reference system.

Introduction

Many measures of aromaticity indicate arsole to be non-aromatic. It has a quite low aromatic stabilisation energy (ASE), the value depending on the definition and method used. The stabilisation energy ranges from slight destabilisation to an aromatic stabilisation of about 40 % compared to, for example, pyrrole.¹⁻⁵ Early on, certain arsoles were found to react in a way typical of non-aromatic species.⁶ But higher reactivity does not always imply lower aromaticity.⁷ The molecular structure of arsole is not planar, in contrast to many aromatic compounds, see Figure 1. Naturally, non-planarity is in itself not a direct indication of non-aromaticity.^{8,9}

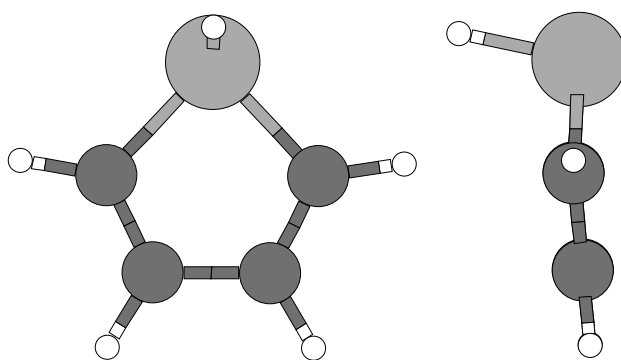


Figure 1: The molecular structure of arsole, front and side views.

Photoelectron spectroscopy studies on arsollic derivatives have indicated that arsole is non-aromatic.^{3,10} But at the same time, the ability of PE spectroscopy to identify a possible aromatic character for arsoles has been questioned.¹¹ Chesnut and Bartolotti¹² studied the aromaticity of a series of five-membered rings, and related electron localisation function (ELF)¹³ data to the ASE. They found that the

basin populations, the pair numbers, and the basin variances of the formally single C–C bond correlated quite well with the stabilisation energy. Interestingly, the C–C basin population and variance of both arsole and phosphole suggest a higher aromaticity than the stabilisation energy, which is quite small; when plotting C–C basin population or variance against the ASE, both arsole and phosphole are seen to be clear deviants in the data set. For the pair numbers, the deviance was found to be smaller.

Cyrański and co-workers have recently studied a large set of five-membered π -electron systems, including arsole and pyrrole.^{4,5} All the different energetic criteria discussed in reference [5] showed arsole to be non-aromatic. In reference [4], a number of aromaticity descriptors were considered. Of these, the stabilisation energy and the magnetic susceptibility exaltation Λ ¹⁴ showed arsole to be non-aromatic. The nucleus-independent chemical shift (NICS)¹⁵ values were also reported, both at the ring centers and 1 Ångström above the plane. The NICS results did attribute slight aromaticity to arsole; the NICS(0) and NICS(1) values for arsole were found to be 26% and 44% of the corresponding pyrrole values, respectively. The geometry-based harmonic oscillator measure of aromaticity, (HOMA),^{16–18} showed arsole to be about half as aromatic as pyrrole. In a recent paper by Pelzer *et al.*,¹⁹ another geometry based descriptor, the Julg index,²⁰ was calculated. The Julg index for arsole was found to be roughly 70% of the pyrrole value. For planar arsole, the index value was found to be of the same magnitude as for pyrrole.

No clear conclusion about the aromaticity of arsole can be drawn based upon

available data. What *is* seen, however, is that descriptors that depend on a fictitious reference system, like the magnetic exaltation and various stabilisation energy schemes show arsole to be non-aromatic. More independent measures, on the other hand, tend to favour arsole aromaticity more. In this work, we elucidate the problem by further study of the potential aromaticity of arsole, from a ring-current perspective. As mentioned above, the NICS has been studied previously, and is one of the indices attributing at least some aromaticity to arsole. Here, we employ the newly developed gauge-including magnetically induced currents (GIMIC) method to directly calculate the strengths of the induced ring currents.²¹ To get things in perspective, we also study the nitrogen analogue pyrrole, the phosphorous analogue phosphole, and the carbon analogue cyclopentadiene, as well as the planar transition states of the arsenic and phosphoric inversions of arsole and phosphole. The arch-aromatic, benzene, is included for completeness.

At this stage, we want to point out that although the concepts of ring current and aromaticity have recently been extensively reviewed,^{22–26} still, their relation has not been settled conclusively. For a review discussing the relations between different aromaticity indices, see reference [27], and in general the entire *Chemical Reviews* issue dedicated to aromaticity,²⁸ as well as a recent *Physical Chemistry Chemical Physics* issue.²⁹ Reference [30] provides a good discussion on the relation between structure and aromaticity. In the work presented here, a direct relation between the ring current strength and degree of aromaticity is assumed; the relationship is furthermore assumed to be linear.

Results and Discussion

The molecules studied here are shown in Figure 2. Figure 3 shows the magnetically induced currents in arsole, drawn as vectors. The currents both in the plane (defined by the hetero-atom and the two carbon atoms opposite) and 1 atomic unit above the plane are shown. One can see that the the inside of the ring is dominated by paramagnetic currents, while the current outside the ring is mainly diamagnetic. These opposite ring currents are predominant in the molecule as a whole. Just around the arsenic atom, they are, however, obscured by strong local currents circling the atom. From the picture, it is quite impossible to judge which type of current, diamagnetic or paramagnetic, is stronger, although the diamagnetic current covers a larger area. Indeed, the currents could well cancel almost totally, which would indicate non-aromaticity of arsole.

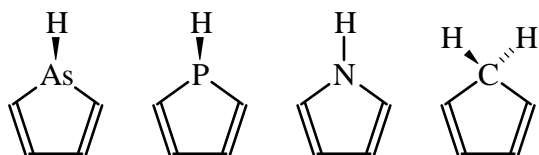


Figure 2: Formal structures of the molecules studied in this work. From left to right: arsole; phosphole; pyrrole; cyclopentadiene.

To get quantitative values, and directions, for the net current strengths in the molecules studied, the current passing a cut-plane perpendicular to the plane of the molecules was integrated numerically. The net current is in itself insensitive to

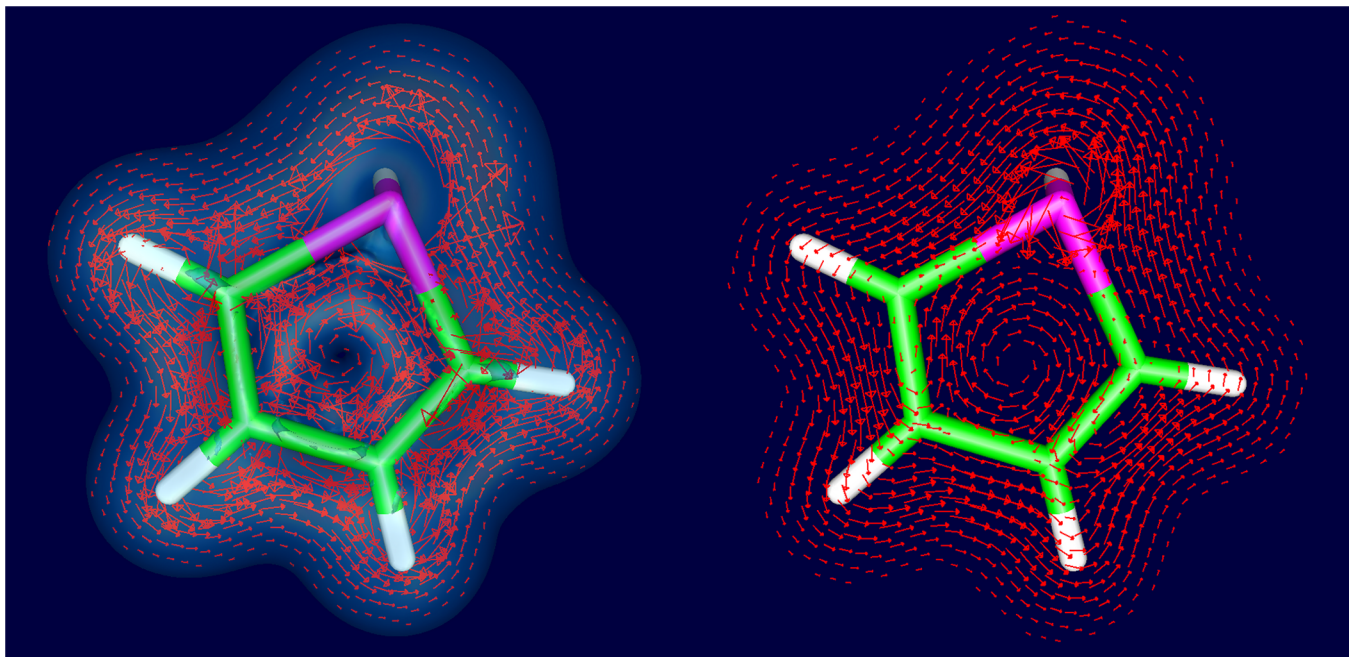


Figure 3: The induced ring current in arsole. Left: The current in the plane of the molecule, immersed in an isosurface of total current strength. Right: The current one atomic unit above the plane. The magnetic field is directed perpendicularly into the plane. Diamagnetic currents are thus seen to circle the molecule anticlockwise while paramagnetic currents are clockwise.

the choice of direction of the cut plane; a circling current has to be equally strong everywhere. The positive (diamagnetic) and negative (paramagnetic) contributions can vary however. To minimize the effect of localized currents, we chose to integrate over the bond cross section opposite to the hetero-atom, *i.e.*, for the formally single C–C bond. The induced ring-current strengths for the different molecules are tabulated in Table 1. For the BP86 calculations, also the diamagnetic and paramagnetic contributions to the net current are shown. As is seen, all molecules support at least a moderate induced ring current. The current strength

Table 1: GIMIC induced ring currents for the studied molecules, calculated at different levels of theory. The BP86 current is also separated into its diamagnetic (positive) and paramagnetic (negative) contributions, as defined by the direction of the current flow through the cut plane. The nucleus-independent chemical shift (NICS) and the aromatic ring current shielding (ARCS) values, at BP86 level, are shown for comparison.

system	induced current (nA/T)					NICS	ARCS
	HF	MP2	BP86	diam.	param.	(ppm)	(nA/T)
arsole	4.2	4.8	5.5	+10.9	−5.4	−4.2	2.6
phosphole	5.4	6.3	7.1	+12.1	−5.0	−6.1	3.6
pyrrole	12.0	12.3	11.8	+16.5	−4.7	−13.7	6.2
cyclopentadiene	4.5	4.9	5.6	+11.1	−5.4	−3.4	3.2
planar arsole	12.4	13.0	12.1	+16.4	−4.3	−15.6	6.7
planar phosphole	13.1	13.4	12.4	+16.7	−4.4	−15.9	6.6
benzene	13.0	12.9	11.8	+16.7	−4.9	−7.9	6.0

of arsole is the weakest, being 35%–47% of the current strength of pyrrole, our reference compound, which, for comparison, possesses a current as strong as in benzene. The arsole current of about 5 nA/T is, however, appreciably strong. A pure ring current definition of aromaticity thus classifies arsole as an aromatic compound.

Table 1 also reports the NICS values of the compounds, calculated at BP86 level. Some correlation between the ring current strength and NICS can be noted. The biggest deviation is actually seen for benzene, the NICS value of which is only

58% of the pyrrole value. Although being quite useful as a first approximation to the ring currents present in a molecule, NICS cannot be considered a quantitative measure of current strength.

The NICS related aromatic ring current shielding (ARCS) method³¹ was also employed, and the results are shown in the last column of Table 1. The ARCS values correlate better than NICS with the explicitly calculated ring current strength; they are, however, consistently about 50% too low. Figure 4 shows the ARCS functions for arsole, pyrrole and benzene. The pronounced long range shielding well outside the region of appreciable electron density (ca 2.5 Å), a typical feature of aromatic systems, is clearly seen for all species.

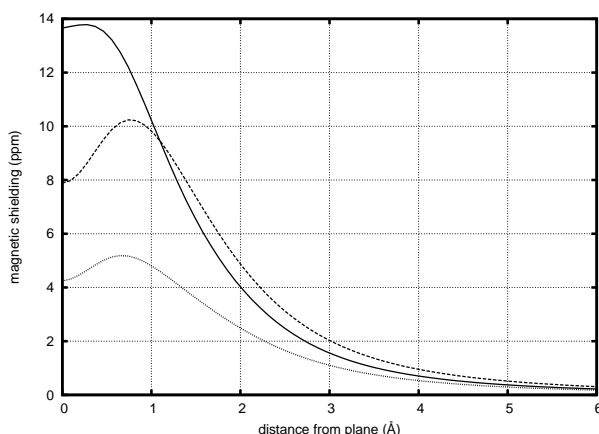


Figure 4: The aromatic ring current shielding (ARCS) curve for pyrrole (whole line), benzene (dashed line) and arsole (dotted line).

A small surprise, at least for us, was that the ring current in cyclopentadiene actually is slightly stronger than in arsole. Thus, the use of cyclopentadiene as a non-aromatic reference compound, for example when calculating aromatic stabilisation energies, seems less than optimal. The ambiguity of the aromatic stabilisation energy definition has been discussed in recent work.^{4,5,32} The idea

of cyclopentadiene aromaticity was raised already in the early nineteenseventies, based on magnetic susceptibility anisotropies.^{33–35} A recent paper by Nyulászai and Schleyer³⁶ also discussed the topic, and ways of aromatic enhancement of the molecule. The idea of a ring current in C_5H_6 has been contemplated also earlier by Fleischer *et al.*,³⁷ but the authors found no direct evidence for a current. Now, this direct, although computational, evidence is available.

The existing induced ring current in cyclopentadiene might seem contradictory, at least in light of its use as a classic example of a non-aromatic system. The view of its non-aromaticity arises, we think, largely from the fact that its deprotonated anion has a much higher aromaticity. This is also the case for arsole and phosphole. At the BP86 level, the induced ring current strengths were found to be 12.7, 12.9, and 12.7 nA/T for the arsolide, phospholide, and cyclopentadienyl anions, respectively. This fact also affects the reactive behavior of these compounds. The existence of a strongly aromatic, deprotonated derivative does not, of course, exclude the possibility of parent compound aromaticity; the aromaticity of the latter might be dwarfed in comparison, but still present. For completeness, we also calculated the ring current of cyclopentene. It was found to be small, but not vanishingly so; HF, BP86, and MP2 all give a ring-current strength of about 1.7 nA/T. The ring currents of partly and fully saturated cyclic hydrocarbons will be discussed more extensively in future work.

The aromaticities of planar arsole and phosphole were found to be much enhanced compared to the relaxed structures, in line with earlier studies;^{19,38–42} the ring currents are even slightly stronger than in the naturally planar pyrrole. The aromatic stabilisation is, therefore, smaller than the relaxation stabilisation resulting from bending the ring. Aromaticity does lower the inversion barrier quite

significantly, though.¹⁹

Conclusions

We have shown arsole to be mildly aromatic according to the magnetic criterion. The induced ring current strength is about 40% of that of pyrrole. The ring current in phosphole is a bit stronger. The planar transition states of both arsole and phosphole possess strong ring currents. The magnetic criterion for arsole aromaticity is thus in contrast with the most sophisticated energetic criterions, which indicate arsole to be non-aromatic.^{4,5} As the energetic and magnetic criterions are, arguably, the two most convincing indicators of aromaticity, the contradiction is interesting. The elusiveness of a conclusive definition of aromaticity makes the decisive assessment of arsole aromaticity difficult. Here, the magnetic criterion seems better motivated than the energetic one, however. For example, the aromaticity of planar arsole seems quite clear. But as it is a transition state between two ground state conformations, the energetic criterion would, of course, indicate an even *smaller* degree of aromaticity, in fact, anti-aromaticity. Some of the energetic criterions for arsole aromaticity also depend on the classification of cyclopentadiene as non-aromatic. We have shown this classification to be questionable; the induced ring current in cyclopentadiene is actually slightly higher than in arsole.

Are arsole, phosphole, and cyclopentadiene aromatic, then? The direct, quantitative measure of the physically real induced currents strongly supports this view. But, pending a universally accepted definition of aromaticity, we are content in concluding that the molecules surely possess reasonably strong ring currents, thus fulfilling at least the *magnetic* aromaticity criterion.

Methods

The molecular structures have been optimised at Hartree–Fock (HF),^{43,44} second order Møller–Plesset perturbation theory (MP2),⁴⁵ and density functional theory (DFT) level.^{46,47} The semi-local gradient-corrected density functional BP86^{48,49} has been used throughout this work. The resolution of the identity (RI) density-fitting approximation of the Coulomb interaction was used in the DFT^{50,51} and MP2^{52,53} geometry optimisations.

For arsole and phosphole, the calculations exploited the C_s symmetry of the molecules. For the transition states, planarity was imposed by a C_{2v} symmetry restriction. C_{2v} symmetry was also used for the naturally planar pyrrole and cyclopentadiene. The HF, MP2, and DFT calculations were performed with the TURBOMOLE program suite, v5.6,⁵⁴ modified to provide the perturbed densities necessary for the ring current calculations. TURBOMOLE’s standard, doubly polarised basis sets of triple-zeta quality, TZVPP,^{53,55,56} was used on all atoms.

With the newly developed gauge-including magnetically induced currents (GIMIC) method by Jusélius, Sundholm, and Gauss,²¹ a quantitative measure of the induced ring current can be obtained. In GIMIC, the magnetically induced current is calculated explicitly, and from first principles, in points in space. By defining suitable cut planes, the net current in the ring can be obtained by numerical quadrature. We believe this to be the most direct way of explicitly extracting the induced ring current strength currently available.

The aromatic ring current shielding (ARCS) method³¹ which builds on the NICS idea, can provide a quantitative estimate for the strength of the ring-current (or lack thereof). In the ARCS method one calculates a set of NICS values on

a line perpendicular to the ring plane. By analyzing the long range decay of the magnetic shielding using Biot–Savart’s law for a thin, circular current loop, one can obtain values for both the ring size and the current strength. The ARCS data was fitted starting from a distance of 3 au from the ring center in order to avoid problems of non-Biot–Savart behaviour inside the electron density.

Figures were produced using XMakemol⁵⁷ and gOpenMol.^{58–60}

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Figure for Graphical Abstract.

