

# A computational study of the arsabenzenes: Structure, properties and aromaticity

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## Abstract

The electronic structure and properties of the arsabenzenes series have been investigated using hybrid density functional B3LYP theory. Basic measures of aromatic character derived from structure, molecular orbital and chemical shift. Energetic criteria suggest that 1,2,3-triarsabenzene and, to a less extent, 1,2-diarsabenzene and its complement 1,2,3,4-tetraarsabenzene enjoy conspicuous stabilization. However, by magnetic criteria, these systems are among the least aromatic of the family: population and bond order analyses reveal that they derive part of their stability from ionic contributions to the bonding. Within their isomer series, 1,3-diarsabenzene, 1,3,5-triarsabenzene, and 1,2,3,5-tetraarsabenzene are the most aromatic using magnetic criteria: overall magnetic aromaticity decreases with increasing number of As atoms.

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## 1. Introduction

The close resemblance between benzene and pyridine in terms of spectra, structure and other properties demonstrated that replacement of one methane group of benzene by an isoelectronic group does not disrupt aromaticity and is chiefly responsible for the formulation of the concept of aromaticity [1–3]. Phosphine and arsabenzene, resulting from the replacement of the methane group by P and As, respectively, were demonstrated to also be aromatic compounds [4–9]. The relatively weak  $\pi$ -bonding ability of silicon versus carbon results in interesting structural and electronic features within the benzoid framework of arsabenzene. This substantial difference in  $\pi$ -bonding for arsenic versus carbon may well be the feature that limits the successful synthesis and isolation of these potentially aromatic arsaorganic compounds and establishes them as challenges for

computational organoarsenic chemistry. From experimental and theoretical examinations one sees that the actual experimental knowledge concerning arsaaromatic compounds is still relatively scant due to the elusive nature of such compounds. The synthesis of some arsaaromatic compounds has been achieved and these form the subjects of a number of theoretical and experimental investigations [10–12].

The present study investigated the family of arsabenzene compounds in light of several of established criteria of aromaticity, using computational methodology.

## 2. Computational methods

All calculations were carried out with the GAUSSIAN 98 suite of program [13] using the 6–31g\*\* basis set for all elements (C, H, As) [14]. Geometry optimization was performed utilizing Becke's hybrid three-parameter exchange functional and the nonlocal correlation functional of Lee, Yang, and Parr (B3LYP) [15].

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A vibrational analysis was performed at each stationary point found, that confirm its identity as an energy minimum. Optimized geometries, energies of all the molecules discussed in this paper. Wiberg bond orders were calculated with the natural bond orbital (NBO) program [14] implemented in the G98 package, using B3LYP/6-31G\*\*.

Calculations of nucleus-dependent and -independent chemical shifts were carried out using the gauge-invariant atomic orbital (GIAO) approach [16,17] with the 6-31G\*\* basis sets. The magnetic susceptibility were computed using continues set gauge transformations, CSGT [18], methods also using the 6-31g\*\* basis set.

### 3. Results and discussions

#### 3.1. Relative energetics

Relative energetics at B3LYP level and 6-31g\*\* basis set considered for the all arsabenzene. See Table 1 and Fig. 1. This predict the following relative stabilities: for diarsabenzene **As12** ( $0.0 \text{ kcal mol}^{-1}$ ) > **As13** ( $11.67 \text{ kcal mol}^{-1}$ ) > **As14** ( $234.41 \text{ kcal mol}^{-1}$ ); for triarsabenzene **As123** ( $0.0 \text{ kcal mol}^{-1}$ ) > **As124** ( $24.18 \text{ kcal mol}^{-1}$ ) > **As135** ( $44.69 \text{ kcal mol}^{-1}$ ); and for tetraarsabenzene **As1234** ( $0.0 \text{ kcal mol}^{-1}$ ) > **As1235** ( $22.295 \text{ kcal mol}^{-1}$ ) > **As1245** ( $26.26 \text{ kcal mol}^{-1}$ ).

#### 3.2. Protonation energy

Table 2 shows the proton affinity of all species. Calculations show that average protonation energy (APE) increase with  $n$  ( $C_nAs_{6-n}H_6$ ,  $n = 1-5$ ). See Fig. 2. A linear correlation has been found between APE and number of As atom ( $n = 1-5$ )

$$\text{APE} = 2.3765n + 193.11 \quad (n = 1 - 5); \quad R^2 = 0.9732.$$

The trend is compatible with charge of As (Table 3). The PE values show that more aromatic spices have higher protonation energies.

#### 3.3. Structure

A summary of structure parameters for the whole set of arsaaromatic compounds is presented in Table 4. For monoarsabenzene a AsC bond length of 1.847 Å and an average CC bond length of 1.3935 Å, both about 0.03 Å below the corresponding average of the double- and single-bond prototype systems (Table 5). This is indicative of structural aromaticity analogous to that seen in benzene.

Pentaarsabenzene exhibits significant structural delocalization, with AsC and AsAs bond lengths just below the average of the respective double- and single-bond

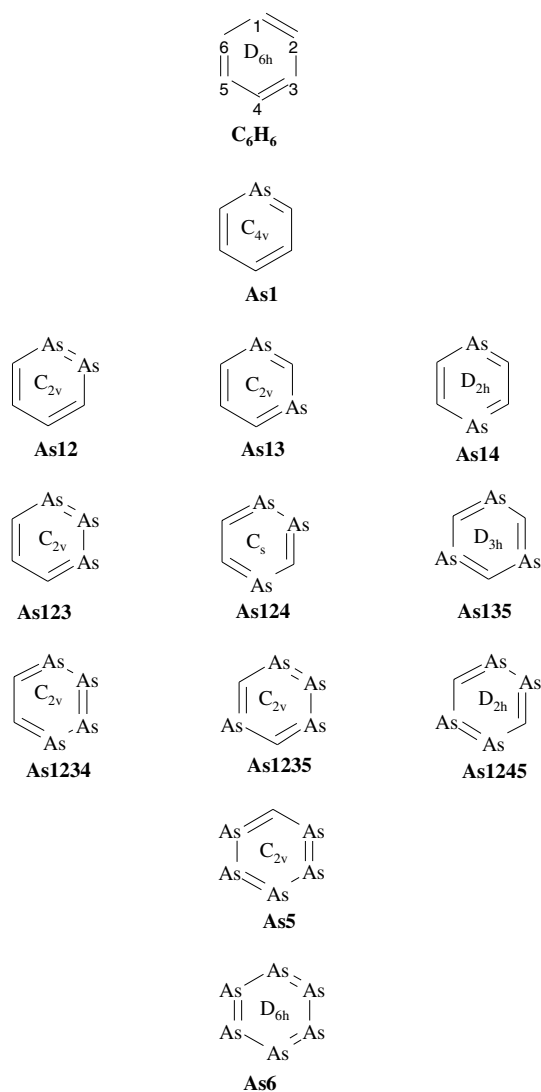


Fig. 1. Structure of all different arsabenzene isomers compounds.

Table 1  
Relative energies ( $\text{kcal mol}^{-1}$ ) for various arsabenzene at B3YP/6-31G\*\* level of theory

Structure	$E$	$\Delta E$
As1	-2427.2874463	-
As12	-4622.3516579	0
As13	-4622.3160241	11.67041
As14	-4622.3143482	23.41219
As123	-6817.4170976	0
As124	-6817.3785632	24.1807
As135	-6817.345875	44.69286
As1234	-9012.4831699	0
As1235	-9012.446585	22.95737
As1245	-9012.4413139	26.26504
As5	-11207.5507768	-
As6	-13402.6613708	-

Table 2

The energy values of protonated isomers, proton affinity, relative energies (kcal mol<sup>-1</sup>) for various arsabenzene at B3YP/6-31G\*\* level of theory

Structure	<i>E</i>	PA
Asp1	-2427.5981435	194.9654
As12p1	-4622.671247	200.5452
As13p1	-4622.6303639	197.2512
As14p1	-4622.6264266	195.8322
As123p1	-6817.7387812	201.8595
As123p2	-6817.7426641	204.2961
As124p1(124)	-6817.6916006	196.4339
As124p3(124)	-6817.7009032	202.2714
As1345p1	-9012.7605783	197.0338
As1235p3	-9012.7706001	203.3226
As1235p4	-9012.7751986	206.2082
As1245p1	-9012.764062	202.5275
As1234p1	-9012.8056481	202.3581
As1234p2	-9012.8096353	204.8601
As12345p1	-11207.8725842	201.9372
As12345p2	-11207.8786082	205.7173
As12345p3	-11207.878463	205.6262
As6p	-13402.9099924	156.01241

lengths. There is perhaps less delocalization in the AsC bond than in the AsAs bonds, the former being about 0.04 Å below average and the latter being some 0.02 Å

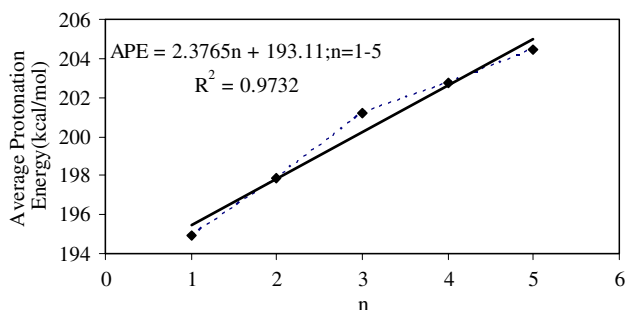


Fig. 2. Variation of average protonation energy with number of As ( $n = 1-5$ ) for arsabenzene.

Table 3

NPA charges for various arsabenzene at B3YP/6-31G\*\* level of theory

Structure	1	2	3	4	5	6
C <sub>6</sub> H <sub>6</sub>	-0.23898	-0.23898	-0.23898	-0.23898	-0.23898	-0.23898
As1	0.69474	-0.61217	-0.24134	-0.21760	-0.24134	-0.61217
As12	0.32191	0.32191	-0.59429	-0.22561	-0.22561	-0.59429
As13	0.76201	-1.08327	0.76201	-0.60792	-0.24352	-0.60792
As14	0.71935	-0.61378	-0.61378	0.71935	-0.61378	-0.61378
As123	0.38213	-0.09118	0.38213	-0.59690	-0.23880	-0.59690
As124	0.32846	0.38076	-1.07885	0.78645	-0.60691	-0.59049
As135	0.82094	-1.08856	0.82094	-1.08856	0.82094	-1.08856
As1234	0.38138	-0.04822	-0.04822	0.38138	-0.59230	-0.59230
As1235	0.44099	-0.10158	0.44099	-1.08265	0.84319	-1.08265
As1245	-1.05932	-1.05932	0.39377	-1.05932	-1.05932	0.39377
As5	-1.09168	0.44949	-0.06192	0.03918	-0.06192	0.44949
As6	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000

below average. Additionally, the AsC bond lengths are almost identical to those in monoarsabenzene.

Density functional calculations using 6-31g\*\* basis set predict some of delocalization for the three isomers of diarsabenzene, i.e., *ortho*, *meta*, *para* arrangement of arsenic atoms within the ring. All ring bond lengths being between the corresponding isolated single- and double-bond lengths. However, the *ortho* isomer exhibits a distinct an alternating long-short character (Table 4), suggesting a geometry learning toward a Kékulé structure in which the As-As and two C-C bonds are localized. More careful analysis, however, reveals that

Table 4

Comparison of computed structural parameters (Å) for various arsaaromatic compounds at B3LYP/6-31G\*\* level of theory

Structure	<i>r</i> (CC)	<i>r</i> (CAs)	<i>r</i> (AsAs)
As1	1.388 1.399	1.847	-
As12	1.382 1.411	- 1.857	- 2.317
As13	1.392 -	1.836 1.848	- -
As14	1.378	1.853	-
As123	1.393	1.847	2.325
As124	1.373	1.829 1.844 1.865	- - 2.325
As135	-	1.839	-
As1234	1.373	-	2.335
As1235	-	1.836 1.841	- 2.332
As1245	-	1.839	2.346
As5	-	-	2.325
As6	-	1.840	2.339
As6	-	-	2.330



Table 7

Frontier orbital energies ( $\epsilon_{\text{HOMO}}$  and  $\epsilon_{\text{LUMO}}$ ) absolute chemical hardness ( $\eta$ ) for different isomers of arsabenzenes obtained at B3LYP/6-31G\*\*

Structure	$\epsilon_{\text{HOMO}}$	$\epsilon_{\text{LUMO}}$	$\Delta E$	$\eta = (\epsilon_{\text{HOMO}} - \epsilon_{\text{LUMO}})/2$
As1	-0.23439	-0.05435	112.9768	56.4884
As12	-0.23753	-0.08383	96.44821	48.22411
As13	-0.23884	-0.07267	104.2733	52.13665
As14	-0.22720	-0.08834	87.13597	43.56799
As123	-0.24359	-0.09683	92.09329	46.04665
As124	-0.23501	-0.10281	82.95676	41.47838
As135	-0.25135	-0.08498	104.3988	52.1994
As1234	-0.23992	-0.11580	77.88648	38.94324
As1235	-0.24275	-0.11333	81.21228	40.60614
As1245	-0.23738	-0.11701	75.53332	37.76666
As5	-0.24268	-0.12819	71.84356	35.92178
As6	-0.25211	-0.13772	71.78081	9.414733

### 3.5. Frontier orbital energies and chemical hardness

Absolute chemical hardness ( $\eta$ ) has been used as a measure of kinetic stability or the reactivity of organic compounds. Within Koopman's approximation, hardness ( $\eta$ ) is defined as half of the magnitude of the energy difference between the HOMO and LUMO [19,20].

$$\eta = \frac{(\epsilon_{\text{LUMO}} - \epsilon_{\text{HOMO}})}{2}$$

The frontier orbital energies and the hardness of arsabenzenes computed at the B3LYP/6-31G\*\* level are given in the Table 7. For diarsabenzene the  $\epsilon_{\text{HOMO}}$  values increases with the following trend: **As13** < **As12** < **As14**. The  $\epsilon_{\text{LUMO}}$  values increases with the following trend: **As14** < **As12** < **As13**. This indicates the decrease in electron accepting nature. For triarsabenzene the  $\epsilon_{\text{HOMO}}$  values increases with the following trend: **As124** < **As123** < **As135**. The  $\epsilon_{\text{LUMO}}$  values increases with the following trend: **As135** < **As123** < **As124**. This indicates the decrease in electron accepting nature. For tetraarsabenzene the  $\epsilon_{\text{HOMO}}$  values increases with the following trend: **As1245** < **As1234** < **As1235**. The  $\epsilon_{\text{LUMO}}$  values increases with the following trend: **As1235** < **As1234** < **As1245**. This indicates the decrease in electron accepting nature.

On the other hand, an increase in the HOMO energy level shows better donors and their nucleophilicity increases. The hardness values indicate that the overall reactivity of monoarsabenzene is less compared to the others arsabenzenes. The decrease in the  $\eta$  values of di-, tri-, tetra-, penta- and hexa-arsabenzene indicates the lowering of kinetic stability of these species.

While the thermodynamic stabilities of the compounds under study are controlled by the skeleton of their structure, the kinetic stability seems to be dictated by the number of the As atom. Compounds containing less number of As are found to be more reactive.

### 3.6. Magnetic properties

Magnetic properties including magnetic shielding, magnetic susceptibilities,  $\chi_{\text{iso}}$ , and magnetic susceptibility anisotropies,  $\chi_{\text{aniso}}$ , have been computed for the set of arsaaromatic compounds and are summarized in Table 8. The magnetic susceptibility tensor describes the quadratic response of a molecule to an external magnetic field, and as such its isotropic and anisotropic components are relevant quantities to consider for the types of molecules studied here.

Now consider the diarsabenzene. Isotropic and anisotropic values predict the aromaticity ordering **As13** > **As14** > **As12**. For the triarsabenzene isomers isotropic values predict **As135** > **As124** > **As123**. Again minor variations from this theme are seen in the anisotropic (**As135** > **As123** > **As124**) trends. For the tetraarsabenzene isomers  $\chi_{\text{iso}}$  values predict **As1235** > **As1245** > **As1234** trend. In this case, while  $\chi_{\text{aniso}}$  instead suggests **As1235** > **As1234** > **As1245**. A good linear

Table 8  
B3LYP/6-31G\*\* computed magnetic properties (ppm) related to aromaticity for arsaaromatic compounds, using CSGT method

Structure	Isotropic	Anisotropic
C <sub>6</sub> H <sub>6</sub>	-48.1332	34.6660
As1	-61.5643	40.2110
As12	-74.1214	53.4435
As13	-76.1230	47.3080
As14	-76.0916	48.2922
As123	-88.1739	61.1951
As124	-89.0868	64.2335
As135	-91.3463	48.8831
As1234	-103.8926	82.1845
As1235	-105.6729	76.1729
As1245	-104.5118	85.5895
As5	-127.5020	110.8363
As6	-167.9164	156.7438

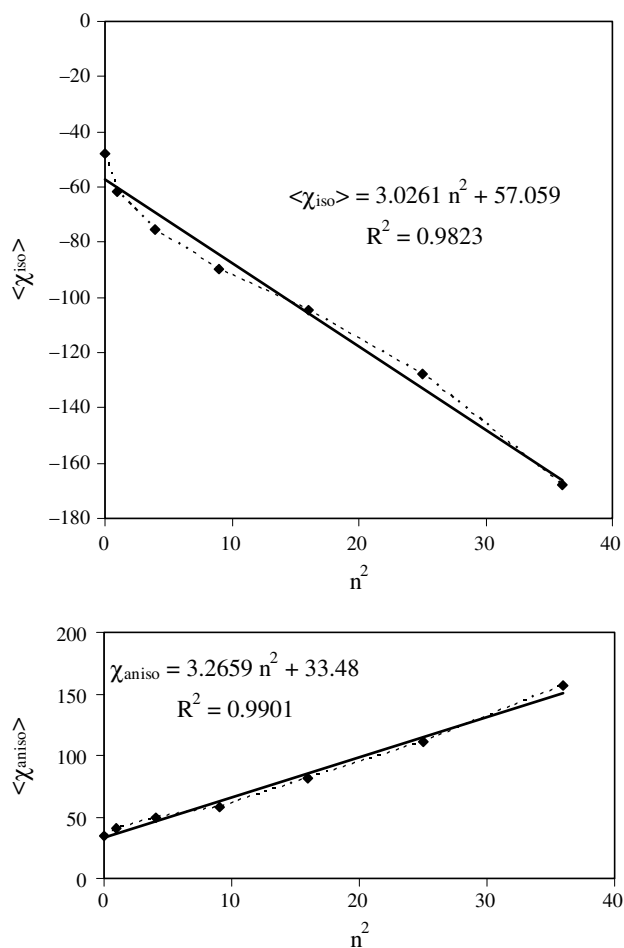


Fig. 3. Dependencies of average magnetic,  $\langle \chi_{iso} \rangle$ , susceptibility and anisotropic susceptibility,  $\langle \chi_{aniso} \rangle$ , of arsabenzene on  $n^2$  ( $n$  = number of arsenic number).

correlation has been found between average magnetic susceptibility and square number of As atom

$$\langle \chi_{iso} \rangle = 3.0261n^2 + 57.059; \quad R^2 = 0.9823.$$

This shows that aromaticity increasing with the increasing number of arsenic atom. See Fig. 3. Also, magnetic susceptibility anisotropies,  $\chi_{aniso}$ , depend on number of As atom. See Fig. 3. This shows that  $\chi_{aniso}$  quite well with the square number of As atom:

$$\langle \chi_{aniso} \rangle = 3.2659n^2 + 33.48; \quad R^2 = 0.9901.$$

Fig. 3 predicts that aromaticity decreasing with the increasing number of arsenic atom.

We obtained the B3LYP/6-31G\*\* -computed  $^1\text{H}$  NMR chemical shifts for the set of arsaromatic species. Consideration of the  $^1\text{H}$  shifts for H (-C) atoms in monoarsabenzene suggests a strong *ortho*, a moderate *meta*, and weak *para* upfield effect. From considering the shift on H2, in 1,3-diarsabenzene, it appears that a “double-*ortho*” As substitution results in a strong upfield effect. The trends in the  $^1\text{H}$  shifts on H (-C) atoms in Table 9 can largely be rationalized in terms of these effects. The strongest upfield has been showed for pentaarsabenzene (14.19 ppm).

#### 4. Conclusion

1. In the present article, stability of arsabenzene increases with the number of As atoms. **As12**, **As123** and **As1234** isomers are most stable isomers.
2. A linear correlation has been found between APE and number of As atom ( $n = 1-5$ ).
3. Comparing structural, energetic, and magnetic effects in benzene with those in arsaromatic compounds, several points are noted. First, energetics, structural parameters, and orbital structures (including partial charges and computed bond orders) effectively provide insight in  $\pi$  electron delocalization tendencies.
4. Absolute chemical hardness ( $\eta$ ) has been used as a measure of kinetic stability or the reactivity of arsabenzene.

Table 9

Computed B3LYP/6-31G\*\* isotropic chemical shifts for  $^1\text{H}$  in arsabenzene compounds<sup>a</sup>

Structure	Sym	1H-1	1H-2	1H-3	1H-4	1H-5	1H-6
C <sub>6</sub> H <sub>6</sub>	D <sub>6h</sub>	7.1524	7.1524	7.1524	7.1524	7.1524	7.1524
As1	C <sub>2v</sub>	–	9.558	7.8275	7.3326	7.8275	9.558
As12	C <sub>2v</sub>	–	–	10.2829	7.9191	7.9191	10.2829
As13	C <sub>2v</sub>	–	12.5009	–	9.6833	8.2448	9.6833
As14	D <sub>2h</sub>	–	10.1807	10.1807	–	10.1807	10.1807
As123	C <sub>2v</sub>	–	–	–	10.4627	8.2936	10.4627
As124	C <sub>s</sub>	–	–	13.2889	–	10.1631	10.7029
As135	D <sub>3h</sub>	–	12.44781	–	12.4479	–	12.4479
As1234	C <sub>2v</sub>	–	–	–	–	10.783	10.783
As1235	C <sub>2v</sub>	–	–	13.2747	–	–	13.2747
As1245	D <sub>2h</sub>	–	–	14.0806	–	–	14.0806
As5	C <sub>2v</sub>	–	–	–	–	–	14.1922
As6	D <sub>6h</sub>	–	–	–	–	–	–

<sup>a</sup> Values respect to TMS (31.5018 ppm).

5.  $^1\text{H}$  NMR calculations have been used for comparison the chemical shifts.

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