

UDC 539.19;547.83

## THEORETICAL STUDIES ON THE STRUCTURES, PROPERTIES, AND AROMATICITIES OF FLUORINATED ARSABENZENES

© 2008 R. Ghiasi<sup>1\*</sup>, M. Monajjemi<sup>2</sup>, E.E. Mokarram<sup>3</sup>, P. Makkipour<sup>1</sup><sup>1</sup>Department of Chemistry, East Tehran Branch (Ghiam Dasht), Islamic Azad University, Tehran, Iran<sup>2</sup>Department of Chemistry, Science and Research Branch, Islamic Azad University, Tehran, Iran<sup>3</sup>Department of Chemistry, Shahr-e-Rey Branch, Islamic Azad University, Tehran, Iran

Received 10 November, 2007

The electronic structures and properties of the fluorinated arsabenzene series have been investigated using the basis set 6-311+G(*d,p*) and hybrid density functional theory. Basic measures of aromatic character derived from molecular orbitals and magnetic criteria (anisotropic susceptibilities and nucleus-independent chemical shift) are considered. Energetic criteria suggest that F3, F36, H36 and H3 isomers are the most stable isomers in the mono-, di-, tri- and tetra-fluorinated species, respectively. Analysis of  $\chi_{\text{aniso}}$  and the HOMO-LUMO gaps are not compatible with the NICS results. The NICS values show that aromaticity is greater in the fluorinated derivatives.

**Keywords:** arsabenzene, fluorinated aromatics, aromaticity, NICS, B3LYP, GIAO, CSGT.

## INTRODUCTION

The close resemblance between benzene and pyridine in terms of spectra, structures and other properties demonstrated that replacement of one CH 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]. Phosphino- and arsabenzene, resulting from the replacement of the CH group by P and As, respectively, were demonstrated to also be aromatic compounds [4–8]. The relatively weak  $\pi$ -bonding ability of arsenic versus carbon results in interesting structural and electronic features within the benzenoid ring 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 examination 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 [9–11].

Aromaticity is an important concept in organic chemistry; it rationalizes the structural stability and chemical reactivity of molecules. The common characteristic of these molecules is their planarity with delocalized  $\pi$  orbitals. Recent studies have extended the concepts of aromaticity to organometallic and all metal systems [12]. It was found that not only the  $\pi$ -bonds but also  $\sigma$ -bonds show electron delocalization. For the sake of quantitative analysis, criteria such as structural, energetic, magnetic, and reactivity related ones were proposed to study aromaticity. The best criterion for aromaticity is still in debate [13].

---

\* E-mail: rezaghiasi1353@yahoo.com

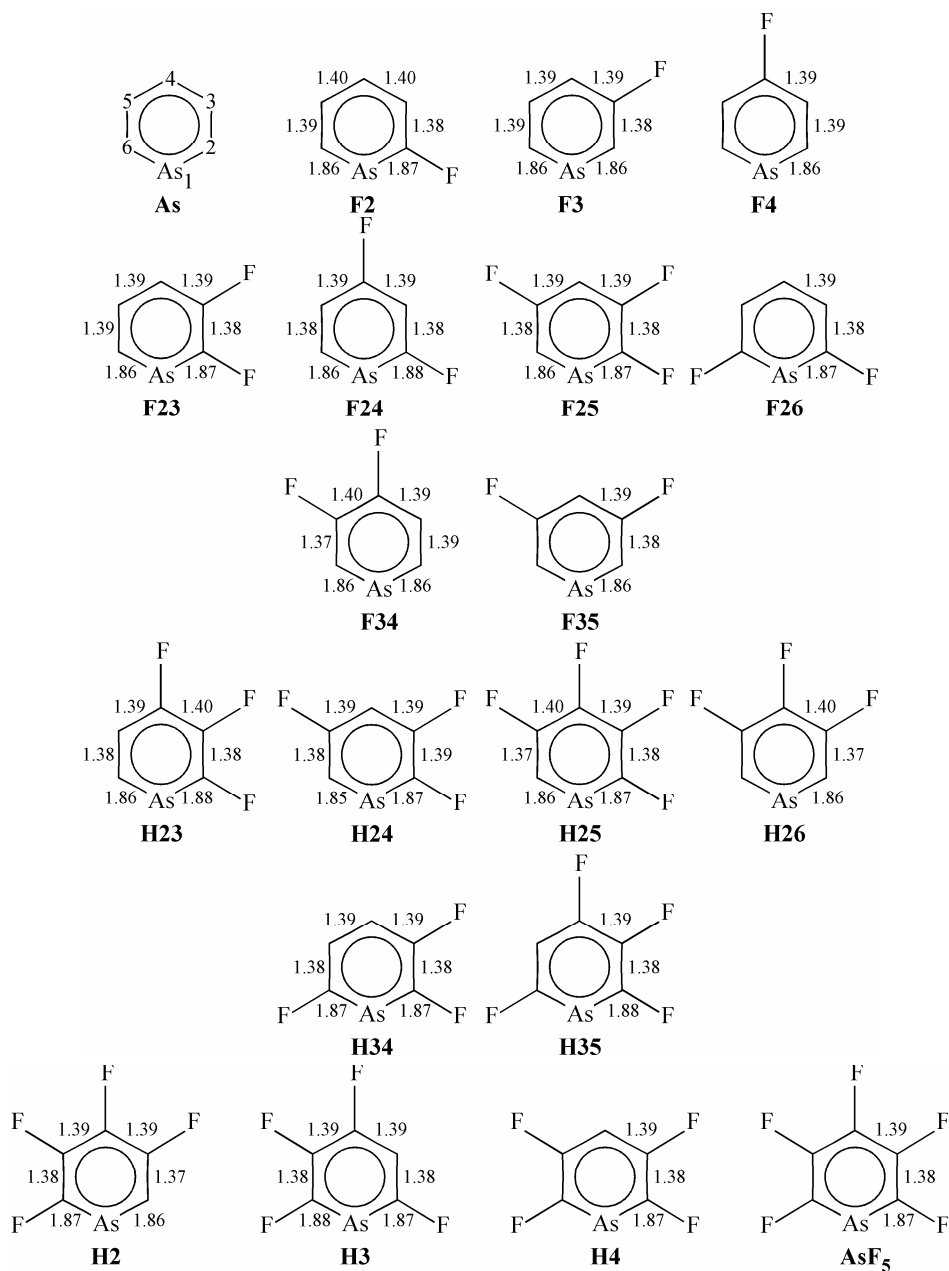


Fig. 1. Structural formulas, abbreviations and bond lengths (Å) for arsabenzene and its fluorinated derivatives

Among the widely used magnetic criteria for aromaticity and antiaromaticity, the nuclear independent chemical shift (NICS) is a simple, efficient probe [14]. Calculations of NICS in all the compounds studied herein confirm that these structures are aromatic.

The lack of experimental information on the structure and bonding of fluorinated arsabenzene necessitates theoretical studies on these compounds. This paper focuses on the structure and aromaticity of fluorinated arsabenzene (Fig. 1).

#### COMPUTATIONAL METHODS

All calculations were carried out with the Gaussian-98 suite of programs [15] using the 6-311+G(*d,p*) basis set for all elements (C, H, As, F) [16]. Geometry optimization was performed using Becke's hybrid three-parameter exchange functional and the nonlocal correlation functional of Lee, Yang and Parr (B3LYP) [17].

A vibrational analysis was performed at each stationary point found which confirms its identity as an energy minimum.

Atomic charges were calculated with the natural bond orbital (NBO) program [ 21 ] implemented in the G98 package, using the same 6-311+G(*d,p*) basis set.

Calculations of nucleus-dependent and -independent chemical shifts were carried out using the gauge-invariant atomic orbital (GIAO) approach with the 6-311+G(*d,p*) basis sets [ 18 ]. The magnetic susceptibility were computed using continuous set gauge transformation (CSGT) methods also using the 6-311+G(*d,p*) basis set [ 19 ].

The nucleus independent chemical shift (NICS) was used as a descriptor of aromaticity from the magnetic point of view. The index is defined as the negative value of the absolute magnetic shielding computed at ring centers [ 20 ] or another point of interest of the system [ 21 ]. Rings with highly negative values of NICS are quantified as aromatic by definition, whereas those with positive values are anti-aromatic. NICS values have been calculated with the GIAO method at B3LYP level of theory.

## RESULTS AND DISCUSSION

**Relative energetics.** The relative energies and the bond lengths at B3LYP/6-311G+(*d,p*) level of theory are reported in Table and Fig. 2. These values show that **F3**, **F36**, **H36** and **H3** isomers (cf. Fig. 1) are the most stable isomers in the mono-, di-, tri- and tetra-fluorinated species, respectively.

**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. Using Koopman's approximation, hardness ( $\eta$ ) is defined as half of the magnitude of the energy difference between the HOMO and LUMO [ 22 ].

*Calculated E(Hartree), relative energy  $\Delta E$  (kcal/mol),  $\epsilon$ (HOMO) (eV),  $\epsilon$ (LUMO) (eV), HOMO-LUMO gap  $\Delta\epsilon$  (eV), magnetic susceptibility anisotropies  $\chi_{\text{aniso}}$  (ppm), NICS(0), NICS(0.5), NICS(1.0) of benzene, arsabenzene and fluorinated derivatives at the B3LYP/6-311+G(*d,p*) level of theory*

	<i>E</i> (Hartree)	$\Delta E$	$\epsilon$ (HOMO)	$\epsilon$ (LUMO)	$\Delta\epsilon$	$\chi_{\text{aniso}}$	NICS(0.0)	NICS(0.5)	NICS(1.0)
Benzene	-232.31125	-	-7.07	-0.49	6.60	-67.48	-11.11	-9.77	-7.19
As	-2429.45120	-	-6.61	-1.90	4.71	-77.04	-7.90	-9.47	-9.49
F2	-2528.71682	3.24	-6.72	-2.15	4.58	-70.61	-9.48	-10.46	-12.42
F3	-2528.72197	0.00	-6.88	-2.20	4.68	-71.95	-9.74	-10.64	-11.83
F4	-2528.72063	0.84	-6.64	-1.99	4.65	-72.55	-9.39	-10.46	-11.31
F23	-2627.97906	7.69	-7.02	-2.39	4.62	-65.91	-11.21	-11.66	-10.08
F24	-2627.98498	3.98	-6.80	-2.23	4.56	-64.71	-11.47	-11.79	-10.00
F25	-2627.98525	3.81	-6.94	-2.48	4.47	-62.99	-10.93	-11.35	-9.84
F26	-2627.98121	6.34	-6.91	-2.37	4.54	-62.91	-11.53	-11.74	-9.86
F34	-2627.98377	4.74	-6.88	-2.29	4.62	-67.37	-11.01	-11.55	-10.16
F36	-2627.99132	0.00	-7.21	-2.50	4.70	-66.14	-11.40	-11.70	-10.08
H23	-2727.23981	5.09	-7.05	-2.48	4.58	-61.24	-12.58	-12.53	-10.31
H24	-2727.24650	0.89	-7.24	-2.69	4.53	-59.26	-12.81	-12.59	-10.21
H25	-2727.24621	1.08	-6.99	-2.53	4.47	-59.07	-12.65	-12.51	-10.20
H26	-2727.24592	1.26	-7.16	-2.56	4.60	-63.47	-12.69	-12.61	-10.45
H34	-2727.24161	3.96	-7.16	-2.64	4.51	-58.23	-12.72	-12.54	-10.16
H36	-2727.24792	0.00	-6.97	-2.45	4.53	-55.91	-12.81	-12.49	-9.87
H2	-2826.50047	0.44	-7.27	-2.75	4.51	-58.15	-14.47	-13.77	-10.75
H3	-2826.50116	0.00	-7.18	-2.69	4.49	-53.21	-13.92	-13.27	-10.24
H4	-2826.50109	0.04	-7.43	-2.91	4.53	-54.47	-14.48	-13.71	-10.53
F5	-2925.75378	-	-7.43	-2.94	4.49	-52.88	-15.84	-14.65	-10.90

Fig. 2. Dependence of NICS (0.5) on the number of F substituents

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

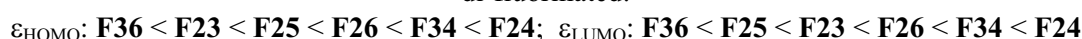
The frontier orbital energies and the hardness of arsabenzene computed at the B3LYP/6-311+G(*d,p*) level are given in Table.

For the fluorinated species the  $\varepsilon_{\text{HOMO}}$  and  $\varepsilon_{\text{LUMO}}$  values increase with the following trends:

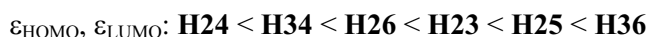
mono-fluorinated:



di-fluorinated:



tri-fluorinated:



tetra-fluorinated:



The increase in  $\varepsilon_{\text{LUMO}}$  indicates a decrease in the electron accepting nature. On the other hand, an increase in the HOMO energy level indicates better donors as their nucleophilicity increases.

From Table it can be seen that the HOMO-LUMO band gaps is larger for the more aromatic systems [ 23 ]. Therefore, aromaticity decreases in fluorinated arsabenzene.

#### MAGNETIC PROPERTIES

**Magnetic susceptibilities.** The aromaticity of arsabenzene and its fluorinated derivatives was also assessed with global magnetic aromaticity indicators, such as anisotropy [ 24 ]. This is defined as the difference between the out-of-plane and the average in-plane diamagnetic susceptibilities ( $\Delta\chi$ ) for a ring lying in the (*xy*) plane, using the following equation:

$$\Delta\chi = \chi_{zz} - (1/2)[\chi_{xx} + \chi_{yy}].$$

An advantage of this index is its independence from a reference system.

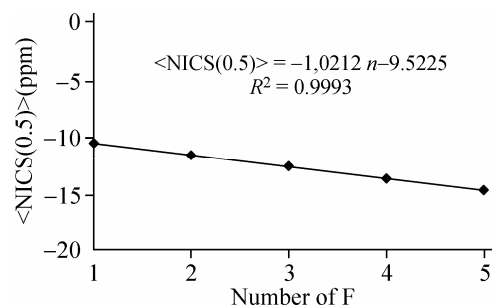
Magnetic properties including magnetic shielding, magnetic susceptibilities,  $\chi_{\text{iso}}$ , and magnetic susceptibility anisotropies,  $\chi_{\text{aniso}}$ , have been computed for all structures and are summarized in Table.

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.

Anisotropic values predict decreasing aromaticity in the fluorinated species. For the mono-fluorinated isomers the anisotropic values predict aromaticity in the order: **F4** > **F3** > **F2**. For the di-fluorinated isomers  $\chi_{\text{aniso}}$  values predict a trend in aromaticity of **F34** > **F36** > **F23** > **F24** > **F25** > **F26**. For the tri-fluorinated isomers the anisotropic values predict the trend in aromaticity of **H26** > **H23** > **H24** > **H25** > **H34** > **H36**. For the tetra-fluorinated isomers the anisotropic values predict the aromaticities as **H2** > **H3** > **H4**. A good linear correlation has been found between the average of the magnetic susceptibility and the number of F atoms:

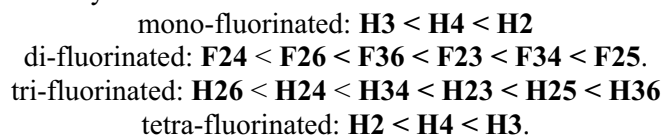
$$\langle \chi_{\text{Anisotropic}} \rangle = -21.896n - 35.15; \quad R^2 = 0.9921.$$

**Nucleus-Independent Chemical Shift (NICS).** NICS is a simple magnetic criterion for aromaticity. Negative NICS indicates aromaticity and positive NICS indicates antiaromaticity. A very small NICS value means nonaromaticity. For points located at the arsabenzene ring center and at points located above these ring centers, by 0.5 and 1.0 Å, the data in Table confirm that aromaticity increases in fluorinated derivatives. This result is not compatible with the HOMO-LUMO gaps and  $\chi_{\text{Anisotropic}}$  values.



According to the calculated NICS(1.0) values, all fluorinated arsabenzene are aromatic. To further analyze the aromaticity, NICS(0.5) values have been calculated. The results also are listed in Table. These values show that NICS(0.5) values are more negative than NICS(0.0), NICS(1.0) in mono- and di-fluorinated derivatives. But, NICS(0.5) values are more negative than NICS(0.0), NICS(1.0) in tri-, tetra- and penta-fluorinated derivatives.

The NICS(0.5) values vary as:



### CONCLUSION

In this paper it has been shown that **F3**, **F36**, **H36** and **H3** isomers of fluorinated arsabenzene are the most stable isomers in the mono-, di-, tri- and tetra-fluorinated species, respectively. The NICS values show that the aromaticity of fluorinated arsabenzene is greater in fluorinated derivatives. These results are not compatible with the results for  $\chi_{\text{aniso}}$  or HOMO-LUMO gaps.

### REFERENCES

1. *Minkin V.I., Glukhotsev M.N., Simkin B.Y.* // Aromaticity, Antiaromaticity. Electronic, Structural Aspects, Wiley, New York, 1994. (b) *Garratt P.J.* Aromaticity, Wiley, New York, 1986. (c) *Badger G.M.* // Aromatic Character, Aromaticity, University Press, Cambridge, 1969.
2. *Katritzky R., Karelson M., Malhotra N.* // Heterocycles. – 1991. – **32**. – P. 127 – 161.
3. *Krygowski T.M., Cyranski M.K., Czarnocki Z. et al.* // Tetrahedron. – 2000. – **56**. – P. 1783 – 1796.
4. *Ashe J.* // Acc. Chem. Res. – 1978. – **11**. – P. 153 – 157.
5. *Frison G., Sevin A., Avarvari N. et al.* // J. Org. Chem. – 1999. – **64**. – P. 5524 – 5529.
6. *Baldrige K.K., Gordon M.S.* // J. Amer. Chem. Soc. – 1988. – **110**. – P. 4204 – 4208.
7. *Dewar M.J.S., Holder A.J.* // Heterocycles. – 1989. – **28**. – P. 1135 – 1156.
8. *Bird C.W.* // Tetrahedron. – 1990. – **46**. – P. 5697 – 5702. (b) *Herndon W.C.* // Tetrahedron Lett. – 1979. – **35**. – P. 3283 – 3286.
9. *Cheung Y.S., Wong C.K., Li W.K.* // J. Mol. Struct. (THEOCHEM). – 1998. – **454**. – P. 17 – 24. (b) *Li Z.R., Rogers D.W., McLafferty F.J. et al.* // J. Phys. Chem. – 1999. – **A103**. – P. 426 – 430.
10. *Schulman J.M., Disch R.L.* // J. Amer. Chem. Soc. – 1985. – **107**. – P. 5059 – 5061. (b) *Newton M.D., Schulman J.M., Manus M.M.* // Ibid. – 1974. – **96**. – P. 17 – 23.
11. *Johnson R.P., Daoust K.J.* // Ibid. – 1996. – **118**. – P. 7381 – 7385.
12. *Ghiasi R.* // J. Mol. Struct. (THEOCHEM). – 2005. – **718**. – P. 225 – 233. (b) *Ghiasi R.* // J. Organomet. Chem. – 2005. – **690**. – P. 4761 – 4767. (c) *Ghiasi R.* // Main Group Chemistry. – 2006. – **5**. – P. 153 – 161. (d) *Ghiasi R.* // Ibid. – 2006. – **5**. – P. 203 – 214. (e) *Ghiasi R.* // Ibid. – 2007. – **6**. – P. 43 – 51. (f) *Ghiasi R.* // J. Mol. Struct. (THEOCHEM). – In press.
13. *Li W.Q., Tian W.Q., Feng J.K. et al.* // J. Phys. Chem. – 2005. – **A109**. – P. 8391 – 8397.
14. *Chen Z.F., Wannere C.S., Corminboeuf C. et al.* // Chem. Rev. – 2005. – **105**. – P. 3842 – 3888.
15. *Frisch M.J., Trucks G.W., Schlegel H.B. et al.* Gaussian-98, Revision A.7, Gaussian, Inc., Pittsburgh PA, 1998.
16. *Carpenter J.E., Weinhold F.* // J. Mol. Struct. (THEOCHEM). – 1988. – **169**. – P. 41 – 62.
17. *Becke D.* // J. Chem. Phys. – 1993. – **98**. – P. 5648 – 5652.
18. *Wolinski K., Hinton J.F., Pulay P.* // J. Amer. Chem. Soc. – 1990. – **112**. – P. 8251 – 8260. (b) *Ditchfield R.* // Mol. Phys. – 1974. – **27**. – P. 789 – 807.
19. *Cheeseman J.R., Trucks G.W., Keith T.A., Frisch M.J.* // J. Chem. Phys. – 1996. – **104**. – P. 5497 – 5509. (b) *Keith T.A., Bader R.F.W.* // Chem. Phys. Lett. – 1993. – **210**. – P. 223 – 231. (c) *Keith T.A., Bader R.F.W.* // Ibid. – 1992. – **194**. – P. 1 – 8.
20. *Schleyer P.V., Maerker C., Dransfield A. et al.* // J. Amer. Chem. Soc. – 1996. – **118**. – P. 6317 – 6318.
21. *Cyranski M.K., Krygowski T.M., Wisiorowski M. et al.* // Angew. Chem., Int. Ed. – 1998. – **37**. – P. 177 – 180.
22. *Pearson R.G.* // J. Org. Chem. – 1989. – **54**. – P. 1423 – 1430. (b) *Zhou Z.X., Parr R.G.* // J. Amer. Chem. Soc. – 1989. – **111**. – P. 7371 – 7379. (c) *Minsky A., Meyer A.Y., Rabinovitz M.* // Tetrahedron. – 1985. – **41**. – P. 785 – 791. (d) *Pearson R.G.* // J. Amer. Chem. Soc. – 1988. – **110**. – P. 2092 – 2097.
23. *Jalbout F., Fernandez S.* // J. Mol. Struct. (THEOCHEM). – 2002. – **584**. – P. 169 – 182.
24. *De Proft F., Geerlings P.* // Chem. Rev. – 2001. – **101**. – P. 1451 – 1464.