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

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The electronic structures and properties of the fluorinated arsabenzenes series have been investigated using the basis set 6-311+G(*d*,*p*) and hybrid density functional theory. The basic measures of aromatic character derived from molecular orbitals and magnetic criteria (anisotropic susceptibilities and nucleus-independent chemical shifts) are considered. The energy criteria suggest that the F3, F36, H36, and H3 isomers are the most stable isomers in the mono-, di-, tri-, and tetrafluorinated species, respectively. Analysis of χ_{aniso} and the HOMO-LUMO gaps showed that these were not compatible with NICS data. The NICS values show that aromaticity is greater in the fluorinated derivatives.

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

INTRODUCTION

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 did not disrupt aromaticity and was chiefly responsible for the formulation of the aromaticity concept [1-3]. Phosphino- and arsabenzenes, resulting from the replacement of the CH group by P and As, respectively, also appeared to be aromatic compounds [4-8]. The relatively weak π-bonding ability of arsenic versus carbon results in interesting structural and electronic features within the benzenoid ring of arsabenzene. This substantial difference in π-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 can see that the actual experimental knowledge concerning arsaaromatic compounds is still relatively scanty because of the elusive nature of these compounds. A number of arsaaromatic compounds have been synthesized; these are 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 π orbitals. Recent studies have extended the aromaticity concepts to organometallic and all metal systems [12]. It was found that not only π-bonds but also σ-bonds show electron delocalization. For the sake of quantitative analysis, structural, energetic, magnetic, and reactivity criteria were proposed to study aromaticity. The best criterion for aromaticity is still in debate [13].

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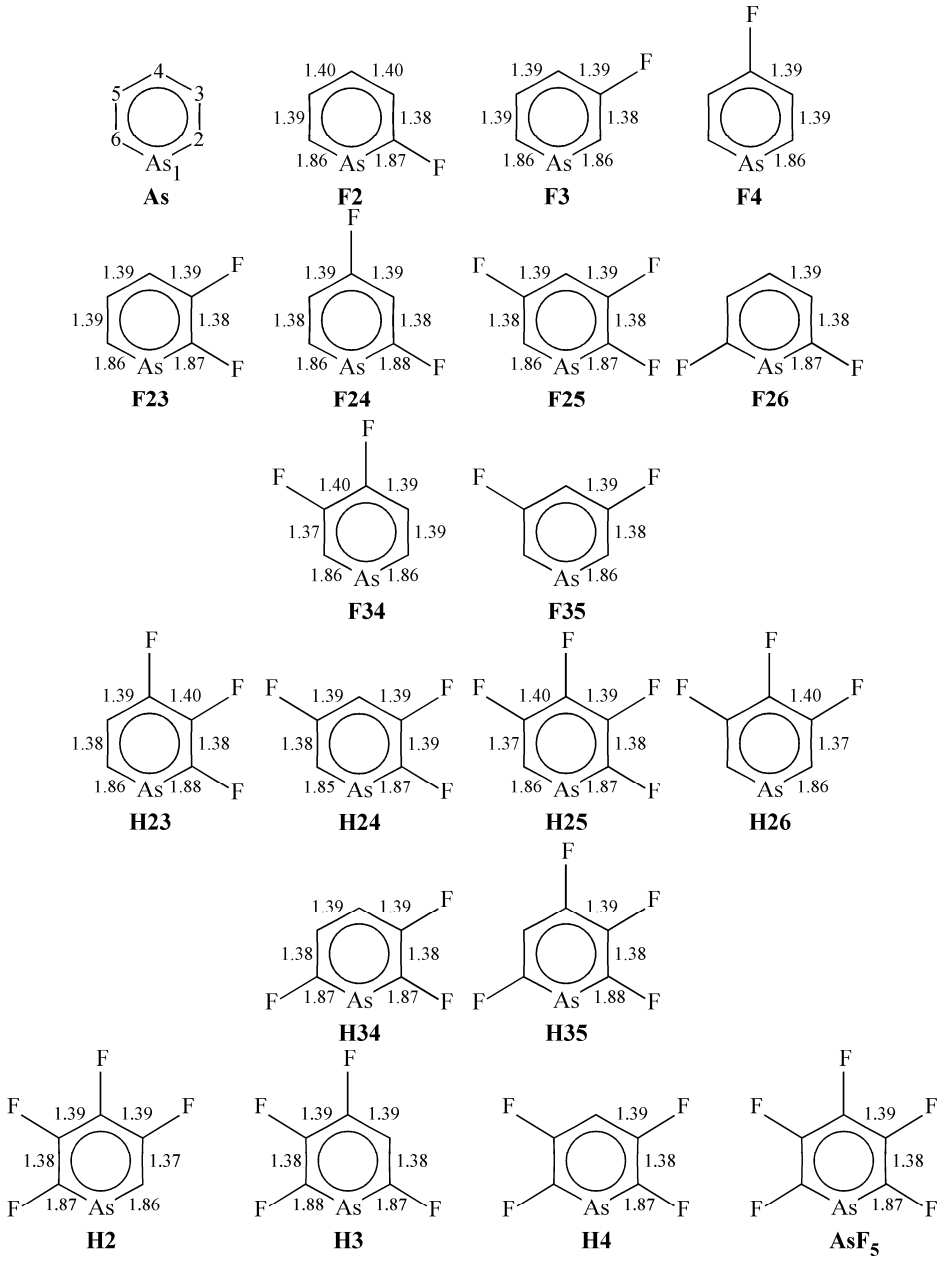

Fig. 1. Structural formulas, abbreviations, and bond lengths (Å) for arsabenzene and its fluorinated derivatives.

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 arsabenzenes necessitates theoretical studies on these compounds. This paper focuses on the structure and aromaticity of fluorinated arsabenzenes (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].

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 viewpoint. 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 antiaromatic. NICS values were calculated by 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 the **F3**, **F36**, **H36**, and **H3** isomers (cf. Fig. 1) are the most stable isomers in the mono-, di-, tri-, and tetrafluorinated species, respectively.

TABLE 1. Calculated Energies *E*(Hartree), Relative Energies Δ*E* (kcal/mol), ε(HOMO) (eV), ε(LUMO) (eV), HOMO-LUMO Gaps Δε (eV), Magnetic Susceptibility Anisotropies χ_{aniso} (ppm), NICS(0), NICS(0.5), and NICS(1.0) of Benzene, Arsabenzene, and Fluorinated Derivatives at the B3LYP/6-311+G(*d*,*p*) Level of Theory

	E(Hartree)	Δ*E*	ε(HOMO)	ε(HOMO)	Δε	χ_{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

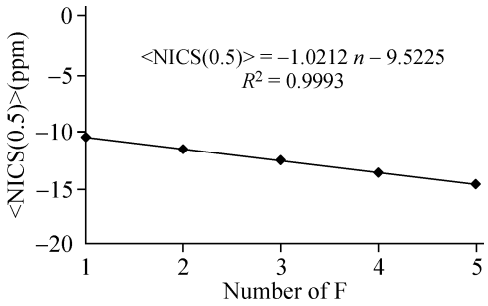

Fig. 2. Dependence of NICS (0.5) on the number of F substituents.

Frontier orbital energies and chemical hardness. Absolute chemical hardness (η) was used as a measure of kinetic stability or the reactivity of organic compounds. Using Koopman's approximation, hardness (η) is defined as half of the magnitude of the energy difference between the HOMO and LUMO [22].

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

The frontier orbital energies and the hardness of arsabenzenes computed at the B3LYP/6-311+G(*d*,*p*) level are given in Table 1.

For the fluorinated species, the ε_{HOMO} and ε_{LUMO} values increase in the following series,

monofluorinated

ε_{HOMO}, ε_{LUMO} **F3 < F2 < F4**

difluorinated

ε_{HOMO}: **F36 < F23 < F25 < F26 < F34 < F24**; ε_{LUMO}: **F36 < F25 < F23 < F26 < F34 < F24**

trifluorinated

ε_{HOMO}, ε_{LUMO}: **H24 < H34 < H26 < H23 < H25 < H36**

tetrafluorinated

ε_{HOMO}, ε_{LUMO}: **H3 < H2 < H4**.

The increase in ε_{LUMO} indicates that the electron accepting nature decreases. On the other hand, the increased HOMO energy level indicates that the species are better donors as their nucleophilicity increases.

From Table 1 it can be seen that the HOMO-LUMO band gaps are larger for more aromatic systems [23]. Therefore, aromaticity decreases in fluorinated arsabenzenes.

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 (Δχ) 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 of the reference system.

Magnetic properties including magnetic shielding, magnetic susceptibilities, χ_{iso}, and magnetic susceptibility anisotropies, χ_{aniso}, were computed for all structures and are summarized in Table 1.

The magnetic susceptibility tensor describes the quadratic response of a molecule to the external magnetic field, and its isotropic and anisotropic components as such are relevant quantities to consider the types of molecule 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, the χ_{aniso} values predict that aromaticity changes in the series **F34** > **F36** > **F23 > F24 > F25 > F26**. For the trifluorinated isomers, the anisotropic values predict the sequence **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 magnetic susceptibility and the number of F atoms,

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

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 center of the arsabenzene ring and at points located 0.5 Å and 1.0 Å above the center, the data of Table 1 confirm that aromaticity increases in fluorinated derivatives. This result is not compatible with the HOMO-LUMO gaps and χ_{aniso} values.

According to the calculated NICS(1.0) values, all fluorinated arsabenzenes are aromatic. To further analyze aromaticity, NICS(0.5) values were calculated. The results also are listed in Table 1. These values show that the NICS(0.5) values are higher negative values than NICS(0.0), NICS(1.0) in mono- and di-fluorinated derivatives. The values of NICS(0.5), however, are more negative than NICS(0.0), NICS(1.0) in tri-, tetra-, and pentafluorinated derivatives.

The NICS(0.5) values vary as

monofluorinated: **H3 < H4 < H2**

difluorinated: **F24** < **F26 < F36 < F23 < F34 < F25**.

trifluorinated: **H26** < **H24** < **H34 < H23 < H25 < H36**

tetrafluorinated: **H2 < H4 < H3**.

CONCLUSIONS

It has been shown that the **F3**, **F36**, **H36**, and **H3** isomers of fluorinated arsabenzenes are the most stable isomers in the mono-, di-, tri-, and tetrafluorinated species, respectively. The NICS values show that the aromaticity of fluorinated arsabenzens is greater in fluorinated derivatives. These results are not compatible with the results for χ_{aniso} or HOMO-LUMO gaps.

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