Comparisons Between the Aromatic Character of 1,2,4-(λ^3-CH-λ^3-X)$_3$ and 1,3,5-(λ^3-CH-λ^3-X)$_3$ Heterobenzenes

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The aromatic character of the heterobenzenes of type 1,2,4-(λ^3-CH-λ^3-X)$_3$ and 1,3,5-(λ^3-CH-λ^3-X)$_3$ where X is an element from group 15: N, P, As, Sb or Bi, has been investigated. Ab initio and DFT methods have been used in order to compute properties like bond orders based indices, anisotropy of the magnetic susceptibility, electron density and Laplacian of the electron density at the ring critical points of the heterocycles, natural charges for each C and X atoms of the heterobenzenes.

Keywords: aromatic character, heterobenzenes, ab initio

The concept of aromaticity, used within the computational chemistry area, deals with a number of indices derived from the geometric, magnetic and energetic properties of benzene [1-4].

The investigations of the aromatic character of various classes of compounds – polycyclic aromatic hydrocarbons, heterocycles, substituted benzenes – have also thrown light in aspects regarding their structure, stability and reactivity [5,6].

Substitution of a CH unit of benzene with an isoelectronic atom of group 15 fulfills the Hückel's rule of aromaticity, the existence of (4n +2) π electrons. This way, all the 1,2,4- and 1,3,5-substituted heterobenzenes of type (CH-λ_3-X)$_3$, where X = N, P, As, Sb, Bi, have a potential aromatic character. The predictive character of the computational chemistry has been used for determining the stability and the possibility of synthesis of the heterobenzenes [7,8].

Previous studies [9-11] dealt with the estimation of the heats of formation (using semiempirical methods) of the alternant heterobenzenes and also with the investigation of the magnetic (NICS index) and geometric (HOMA and angle-based indices) properties of the alternant 1,3,5-heterobenzenes and 1,2,4-heterobenzenes. In both cases [9,10], the results concluded that the geometry of molecules has a large influence on the magnetic properties of these compounds (namely, bond length equalization leads to high values of NICS index).

It has been showed [7] that topological characteristics like the electron density, the Laplacian of the electron density, the Hamiltonian kinetic energy and the Lagrangian kinetic energy are proper indicators of aromaticity for the monosubstituted heterobenzenes with elements from the groups 13-16. Also, other authors [12] have showed that the largest (absolute) negative value of the anisotropy of magnetic susceptibility is correlated to an enhanced degree of aromaticity of the molecules [13]. The enthalpies of formation, computed at *ab initio* level by means of an isolobal reaction scheme for a number of azines, have found to correlate well with the existing experimental data [14].

The study presents the characteristics of each of the two types of substitution (1,2,4- and 1,3,5-) in terms of two topological characteristics computed at the ring critical points of the heterobenzenes, heats of formation, natural charges of C and X atoms, anisotropy of the magnetic susceptibility. The compounds that are investigated during this study are presented in figure 1.

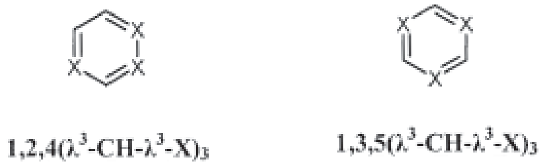

Fig. 1. Heterobenzenes with elements of group 15 (X = N, P, As, Sb, Bi)

Experimental part

All the computations that involved the heterobenzenes containing N, P and As have been performed using the 6-311+G(d,p) basis set. For the compounds with Sb and Bi, LanL2DZ basis set has been used. All the optimized structures are found to be minima and show planar geometry. NBO analysis and the magnetic susceptibilities have been computed at B3LYP/6-311+G(d,p) and B3LYP/LanL2DZ, respectively. Computations of the enthalpies of formation have been performed using the isolobal reaction scheme proposed by Williams and Whitehead [14] for azines. The heats of formation for the monosubstituted heterobenzenes of type C_5H_5X (X = N, P, As, Sb, Bi) were considered the ones determined by Shobe [15]. The computations have been performed with the Gaussian 09 package [16]. Topological analysis and graphical representations of the distribution of the electron density have been performed with the Multiwfn program [17].

Results and discussions

Geometric criterion applied for evaluating the aromatic character

Most of the geometric indices of aromaticity are based on the bond lengths, but in the case of the heterocycles, the bond length is highly influenced by the size of the heteroatom. In order to avoid the difficulties that can arise when dealing with the bonds that contain one or two atoms from group 15, bond order based indices have been proposed. In this regard, the Bird index I_6 [3], which uses the variation of the bond orders, has been employed. The results are presented in table 1, and, for the case of the

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Table 1
BIRD INDEX OF THE CORRESPONDING HETEROBENZENES, COMPUTED AT HF/6-311+G(d,p) AND HF/LanL2DZ* LEVEL OF THEORY, RESPECTIVELY

Heterobenzenes	1,2,4(λ^3-CH-λ^3-X)$_3$	1,3,5(λ^3-CH-λ^3-X)$_3$
(CH-N)$_3$	82.60	100
(CH-P)$_3$	69.94	100
(CH-As)$_3$	59.14	100
*(CH-Sb)$_3$	24.54	100
*(CH-Bi)$_3$	15.85	100

1,3,5-substituted heterobenzenes, appears impossible to establish a hierarchy of the aromatic character based on this geometric criterion.

The values that were obtained for the 1,3,5-substituted heterobenzenes are most likely due to the symmetry rather than to the aromaticity, so other criteria must be used. As regards the 1,2,4-substituted heterobenzenes, it seems that the aromatic character decreases along with the increase of the atomic number of the elements from group 15.

Magnetic criterion applied for evaluating the aromatic character

Our previous studies showed that NICS(0) and NICS(1) indices computed for this class of compounds [9,10] are also highly influenced by the symmetry of the molecules. In this regard, computations of the anisotropy of the magnetic susceptibility, considered a good indicator of the ring delocalization [12,13] and, as a consequence of aromaticity, have been performed. Results are presented in the table below:

Table 2
ANISOTROPY OF THE MAGNETIC SUSCEPTIBILITY (B3LYP/6-311+G(d,p) AND B3LYP/LanL2DZ*)

Heterobenzenes	1,2,4(λ^3-CH-λ^3-X)$_3$ $\Delta\chi^m$ (cgs ppm)	1,3,5(λ^3-CH-λ^3-X)$_3$ $\Delta\chi^m$ (cgs ppm)
(CH-N)$_3$	-63.369	-52.419
(CH-P)$_3$	-88.842	-85.386
(CH-As)$_3$	-107.817	-104.110
*(CH-Sb)$_3$	-143.031	-133.433
*(CH-Bi)$_3$	-159.925	-172.980

Larger (absolute) negative values of $\Delta\chi^m$ are associated to molecules with higher aromatic character. According to this rule, it results that the most aromatic heterobenzenes are the ones containing Sb and Bi. Our previous studies that dealt with the computations of NICS index do not show large differences among the NICS values for the heterobenzenes of type (λ^3-CH-λ^3-X)$_3$ (also, negative values meaning a possible aromatic character have been obtained for all the heterocycles that were mentioned above). An interesting situation occurs in the case of 1,3,5-triazine and 1,2,4-triazine, when the latter is showed to possess a higher aromatic character.

Stability of the 1,2,4- and 1,3,5-substituted heterobenzenes

In order to accurately determine the stability of the above-mentioned heterobenzenes, their enthalpies of formation –by means of a hypothetical reaction– have been determined. In this regard, the isolobal reaction scheme proposed by Williams and Whitehead [12] for the ab initio computation of the heats of formation of various azines has been employed (fig. 2).

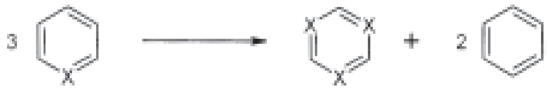


Fig. 2. The hypothetical reaction scheme for the determining of the enthalpies of formation of the 1,2,4- and 1,3,5-heterobenzenes of type (λ^3-CH--λ^3-X)$_{3,}$)$_3$; (X = N, P, As, Sb, Bi)

The results are presented in table 3.

The enthalpies of formation are lower in the case of the 1,3,5-isomers only when the heteroatom is nitrogen. 1,2,4- and 1,3,5-triphosphabenzenes show similar values, while for the others (X = As, Sb, Bi) the 1,2,4-isomers appear to be more stable.

Structural aspects regarding the 1,2,4- and 1,3,5-substituted heterobenzenes

The natural charges of the three carbon atoms and the three heteroatoms of each cycle have been computed. The results show a symmetric distribution of the charges in the case of the 1,3,5-isomers, while as regards the 1,2,4-substituted heterocycles, the following observations are made: the mean value of both positive and negative charges is lower than the corresponding one of the 1,3,5-heterobenzenes; also, highest positive natural charge was found at the X atom (X = P, As, Sb, Bi) that lies between two C atoms, while the highest negative natural charge appears at the C atoms between two X heteroatoms (X = P, As, Sb, Bi). The results are summarized in table 4 and (graphical) in figure 3.

Topological analysis

The topological characteristics of (3,+1) ring critical points are also considered potential indicators of aromaticity [7]. In this regard, the electron density (ρ) and the Laplacian of electron density ($\nabla^2\rho$) have been computed for each of the considered heterobenzenes.

Highest values are obtained for the two isomers of triazine, followed by the triphosphabenzene. Larger differeneces between the 1,2,4- and the 1,3,5-isomers have been found for triarsabenzenes, the 1,3,5-isomer showing properties that suggest an enhanced aromatic character. There have been obtained values that suggest very similar properties of 1,2,4(CH-λ^3-As)$_3$ 1,2,4(CH-λ^3-Sb)$_{3,}$ and 1,3,5(CH-λ^3-Sb)$_{3,}$ 1,2,4(CH-λ^3-Bi)$_3$ and 1,3,5(CH-λ^3-Bi)$_3$.

Table 3
ENTHALPIES OF FORMATION OF THE 1,2,4- AND 1,3,5-HETEROBENZENES OF TYPE (λ^3-CH--λ^3-X)$_{3,}$ COMPUTED AT HF/6-311+G(D,P) AND HF/LANL2DZ* LEVEL OF THEORY, RESPECTIVELY

Heterobenzenes	ΔH_f(1,2,4(λ^3-CH-λ^3-X)$_3$) (kcal/mol)	ΔH_f(1,3,5(λ^3-CH-λ^3-X)$_3$) (kcal/mol)
(CH-N)$_3$	95.9	62.6
(CH-P)$_3$	103.1	104.6
(CH-As)$_3$	120.1	139.3
*(CH-Sb)$_3$	82.6	105.8
*(CH-Bi)$_3$	168.6	209.5

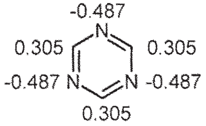
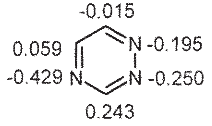
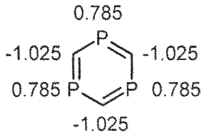
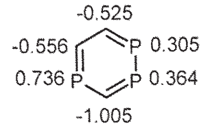
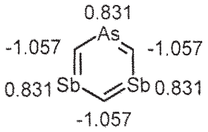
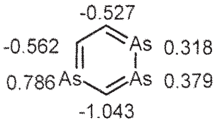
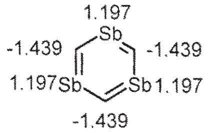
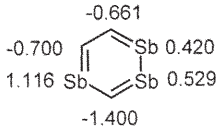
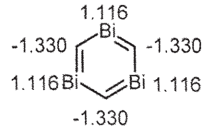
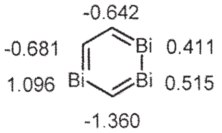
Heterobenzenes	1,2,4(λ^3-CH-λ^3-X)$_3$	1,3,5(λ^3-CH-λ^3-X)$_3$
(CH-N)$_3$		
(CH-P)$_3$		
(CH-As)$_3$		
*(CH-Sb)$_3$		
*(CH-Bi)$_3$		

Table 4

COMPUTATIONS OF THE NATURAL CHARGES (WITHIN NBO ANALYSIS), COMPUTED AT B3LYP/6-311+G(d,p) AND B3LYP/LanL2DZ* LEVEL OF THEORY, RESPECTIVELY

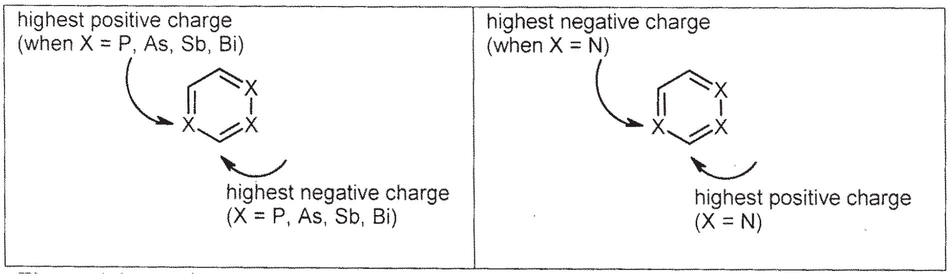


Fig. 3. Natural charge distribution within the heterobenzenes

Heterobenzenes	electron density (ρ)		Laplacian of the electron density ($\nabla^2\rho$)	
	1,2,4(CH-λ^3-X)$_3$	1,3,5(CH-λ^3-X)$_3$	1,2,4(CH-λ^3-X)$_3$	1,3,5(CH-λ^3-X)$_3$
(CH-N)$_3$	0.0280	0.0300	0.2250	0.2391
(CH-P)$_3$	0.0122	0.0124	0.0658	0.0672
(CH-As)$_3$	0.0051	0.0096	0.0199	0.0521
*(CH-Sb)$_3$	0.0061	0.0065	0.0272	0.0306
*(CH-Bi)$_3$	0.0053	0.0046	0.0227	0.0188

Table 5

ELECTRON DENSITY (ρ) AND THE LAPLACIAN OF ELECTRON DENSITY ($\nabla^2\rho$) COMPUTED AT THE RING CRITICAL POINTS OF THE HETEROBENZENES

Conclusions

Several indicators of aromaticity, as Bird index, anisotropy of the magnetic susceptibility, heats of formation and topological properties of ring critical points of the heterobenzenes of type 1,2,4(CH-λ^3-X)$_3$ and 1,3,5(CH-λ^3-X)$_3$ (X = N, P, As, Sb, Bi) have been computed.

The results clearly show that the most stable and the more „aromatic" one is 1,3,5(CH-λ^3-N)$_3$ followed by its isomer 1,2,4(CH-λ^3-N)$_3$. As concerns the heterobenzenes containing P, As, Sb or Bi, it can be said that only slight differences between the two isomers appear (differeneces that seem to favour the 1,2,4-isomers). There are also outlined the difficulties that appear when the geometric criteria of aromaticity are used on highly symmetric molecules like the 1,3,5(CH-λ^3-X)$_3$ heterobenzenes. The topological properties computed at the ring critical point of each heterocycle give another perspective regarding the aromatic properties. The differences that appear in the 1,2,4-isomers due to the interrupting of the C-X bond alternation are emphasized by the results of the natural charge distribution within the two types of heterobenzenes.

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