

## THEORETICAL CONSIDERATIONS REGARDING THE AROMATICITY OF $\Lambda^3$ -HETEROBENZENES CONTAINING 15-GROUP ELEMENTS

R. POP<sup>a\*</sup>, M. ANDONI<sup>a</sup>, J. VAN STADEN<sup>b</sup>, I. PĂUȘESCU<sup>c</sup>, M. MEDELEANU<sup>c</sup>

<sup>a</sup>University of Medicine and Pharmacy "Victor Babeș" Timisoara, Faculty of Pharmacy, Eftimie Murgu Square 2, 300041 Timișoara, Romania

<sup>b</sup>Process Analytical Technology Laboratory (PATLAB), National Institute of Research and Development for Electrochemistry and Condensed Matter (INCEMC), 202 Splaiul Independentei Str., Bucharest 060021, Romania

<sup>c</sup>University "POLITEHNICA" of Timisoara, Faculty of Industrial Chemistry and Environmental Engineering, 300006 Timisoara, Romania

The aromatic character of the 1,2,4-heterobenzenes with elements of group 15 has been investigated. Starting from the planar geometry and from the fulfilled Hückel's rule, other investigations regarding the geometric, magnetic and energetic properties of the considered heterobenzenes have been carried out. Global reactivity descriptors within the conceptual DFT (hardness, electrophilicity) have been computed and compared to the results of the other above-mentioned criteria. Fukui functions (as local reactivity descriptors) have been computed for all the six atoms of the heterobenzenoids.

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### 1. Introduction

Together with the discovery of the C<sub>60</sub> fullerene [1], the nanomaterials based on fullerenes structures have gained an increased importance in various industries. Also, investigation of the properties -like aromaticity- of the precursors of fullerenes, like polycyclic hydrocarbons or various substituted (hetero)benzenes, have offered new perspectives regarding the characteristics of their corresponding fullerenes and nanomaterials, respectively.

Aromaticity represents a key-concept in organic chemistry, having a great importance for the explanation and clarification of different aspects related on the structure, stability and reactivity of the molecules.

When dealing with the evaluation of the aromaticity, one of the major problem is the lack of an universal index [2]. The first definition of aromaticity was proposed by Hückel; based on the molecular orbital theory, he suggested that the planar cyclic hydrocarbons with  $(4n+2) \pi$  electrons posses aromatic character. Since then, for the quantitative estimation of the aromaticity, a number of criteria derived from the geometric, energetic and magnetic properties of compounds with aromatic character (like benzene) have been proposed. Development of the quantum chemical methods made possible the prediction (with sufficient accuracy) of the stability, reactivity, geometric and magnetic properties of a compound [3-7].

The predictive character of quantum chemistry is used in order to determine the possible existence and the aromaticity of a new class of compounds: 1,2,4-heterobenzenes containing dicoordinated trivalent elements of group 15, of type  $(\Lambda^3-X-\Lambda^3-Y)_3$  (X,Y=CH, N, P, As, Sb, Bi).

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\*Corresponding author: raluca<sup>pop24@gmail.com</sup>

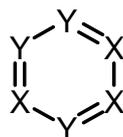


Fig. 1. General formula of the 1,2,4-heterobenzenes ( $\Lambda^3\text{-X-}\Lambda^3\text{-Y}$ )<sub>3</sub>

Table 1. Heterobenzenes series; 1-6 (optimized at HF/6-311+G(d,p) level of theory), 7-13 (optimized at HF/LanL2DZ level of theory)

X/Y	N	P	As	Sb	Bi
CH	1	2	4	7	10
N		3	5	-	-
P			6	8	11
As				9	12
Sb					13

The CH units of the benzene skeleton were replaced by dicoordinated trivalent heteroatoms from the group 15, so the Hückel's rule of aromaticity is accomplished.

There are already known 6-membered homocycles ( $\Lambda^3\text{-X}$ )<sub>6</sub> (X = N, P) or alternant 1,3,5-heterocycles ( $\Lambda^3\text{-X-}\Lambda^3\text{-Y}$ )<sub>3</sub> (X = CH, N, P) that were synthesized and characterized by various physico-chemical methods [8-11]. Other quantum-chemical studies regarding heterobenzenes with elements of the 15 group have been performed, but in almost all cases, only a CH unit was replaced by a heteroatom [12]. Also, previous studies dealt with the evaluation of the stability and the prediction of the aromaticity of the less studied 1,3,5-heterocycles ( $\Lambda^3\text{-X-}\Lambda^3\text{-Y}$ )<sub>3</sub> (where X, Y = CH, N, P, As, Sb, Bi) [13,14].

The present study aims to investigate the possible aromatic character of 1,2,4-heterobenzenes of type ( $\Lambda^3\text{-X-}\Lambda^3\text{-Y}$ )<sub>3</sub> (where X, Y = CH, N, P, As, Sb, Bi) by using the geometric, energetic and magnetic criteria of aromaticity. Also, the reactivity profile of this class of heterobenzenes has been investigated.

## 2. Theory

Geometry optimization of the heterobenzenes that contain N, P and/or As has been performed at HF/6-311G+(d,p) level of theory. The skeletally substituted benzenes with Sb and/or Bi have been optimized using the LanL2DZ basis set. All the above-mentioned structures are found to be planar. (An exception occurred with the possible structures (N-Sb)<sub>3</sub> and (N-Bi)<sub>3</sub>, that could not be optimized, thus they are not included in the present study. The existence of two adjacent N atoms and the bond lengths N-Sb and N-Bi led to the obtaining of some open structures and the more stable N<sub>2</sub> molecule). NICS indices and the reactivity descriptors have been computed at B3LYP/6-311+G(d,p) and B3LYP/LanL2DZ level of theory. For comparison, the basis set LanL2DZ has been also employed for the computations that were previously performed with 6-311+G(d,p) basis set. All the computations have been performed with the Gaussian 09 package [24]. The electron density diagrams have been computed with the Multiwfn program [25].

## 3. Results and discussions

### Geometrical approach for estimating the aromatic character of group 15 heterobenzene series 1-13

The geometric criteria that are used for the estimation of the aromatic character of a compound are built in order to meet the requirements of the geometric characteristics of the benzene derived from the delocalization of the electrons, namely a planar structure and

equalization of bond lengths and bond angles. The optimized geometries of our benzenoid structures are all planar, so one of the first conditions of aromaticity is fulfilled.

One of the most widely used geometrical indexes, HOMA, encounters difficulties when dealing with heteroatoms, some HOMA-based indices being reformulated for structures that contain C, O and N and for bonds of type C-O, C-S, C-N, N-N [15,16]. In order to characterize the heterobenzenes series 1-13, the deviation from the mean bond length (X-Y) has been computed for each cycle. Results are presented in **Table 2**; it results that the lowest deviations have been obtained for the heterocycles where the differences between the radii of the X and Y atoms are not very large: (CH-N)<sub>3</sub>, (Sb-Bi)<sub>3</sub>, (P-Sb)<sub>3</sub>, (P-As)<sub>3</sub>.

*Table 2. Deviations of the bond length and bond angle equalization, computed for the optimized geometries at HF/6-311+G(d,p) [(CH-N)<sub>3</sub>, (CH-P)<sub>3</sub>, (CH-As)<sub>3</sub>, (N-P)<sub>3</sub>, (N-As)<sub>3</sub>, (P-As)<sub>3</sub>] and HF/LanL2DZ [(CH-Sb)<sub>3</sub>, (CH-Bi)<sub>3</sub>, (P-Sb)<sub>3</sub>, (P-Bi)<sub>3</sub>, (As-Sb)<sub>3</sub>, (As-Bi)<sub>3</sub>, (Sb-Bi)<sub>3</sub>]*

Heterobenzene	Bond Length Equalization Deviation (%)	Bond Angle Equalization Deviation (%)
(CH-N) <sub>3</sub>	1.90	2.06
(CH-P) <sub>3</sub>	7.32	10.55
(CH-As) <sub>3</sub>	9.43	11.33
(CH-Sb) <sub>3</sub>	12.00	13.15
(CH-Bi) <sub>3</sub>	12.73	13.42
(N-P) <sub>3</sub>	10.44	10.60
(N-As) <sub>3</sub>	13.35	10.07
(P-As) <sub>3</sub>	2.00	1.19
(P-Sb) <sub>3</sub>	5.19	3.71
(P-Bi) <sub>3</sub>	0.80	2.04
(As-Sb) <sub>3</sub>	2.94	2.18
(As-Bi) <sub>3</sub>	3.87	2.70
(Sb-Bi) <sub>3</sub>	0.69	0.74

These are also the compounds with the lowest deviations from the mean bond angle of 120° (**Table 2**). The results appear to obey the rule that states that the aromatic character increases as well as the electronegativity differences between two neighbor atoms decreases [17].

### **Magnetic approach for predicting the aromatic character of group 15 heterobenzene series 1-13**

During the last years, NICS index has become one of the most widely used indicators of the aromatic character [6]. The magnetic shielding computed at a distance of 1Å above the center of the cycle (NICS(1) or also NICS(1)zz indices) are considered to give better results in quantifying the aromaticity of the heterocycles, due to the neglect of the  $\sigma$  contributions, thus giving a more accurate evaluation of the chemical shifts caused by the  $\pi$  electrons system [18,19].

Table 3. NICS values computed at \*HF/6-311+G(d,p) and HF/LanL2DZ level of theory, respectively

Heterobenzene	NICS(0) (ppm)	NICS(1) ppm	NICS(1)zz (ppm)
*(CH-N) <sub>3</sub>	-4.68	-11.32	-30.11
*(CH-P) <sub>3</sub>	-6.46	-9.76	-24.58
*(CH-As) <sub>3</sub>	-5.73	-8.50	-20.32
(CH-Sb) <sub>3</sub>	-2.30	-5.66	-13.03
(CH-Bi) <sub>3</sub>	-1.20	-4.55	-11.45
*(N-P) <sub>3</sub>	0.56	-6.90	-13.60
*(N-As) <sub>3</sub>	1.02	-4.32	-4.69
*(P-As) <sub>3</sub>	-7.96	-10.24	-23.70
(P-Sb) <sub>3</sub>	-1.66	-4.42	-16.46
(P-Bi) <sub>3</sub>	-2.55	-4.99	-18.84
(As-Sb) <sub>3</sub>	-3.48	-5.70	-19.57
(As-Bi) <sub>3</sub>	-4.50	-6.44	-22.33
(Sb-Bi) <sub>3</sub>	-5.85	-7.22	-23.77

It appears that the values of NICS index for the considered heterobenzenes series are highly influenced by the geometry of the cycle: comparing the results presented in **Table 3** with these ones, it results that the “more negative” values of the chemical shifts have been obtained for the heterobenzenes that present a higher degree of bond length and bond angle equalization. Lowest (or positive) values of the various NICS indices, an indicator of a low or non-aromatic character) have been obtained for (CH-Sb)<sub>3</sub>, (CH-Bi)<sub>3</sub>, (N-P)<sub>3</sub> and (N-As)<sub>3</sub>, the heterobenzenes with the strongest deviation from the geometric principle of bonds and angles equalization of the benzenoid compounds.

#### Evaluation of the stability of the heterobenzene series 1-13

Indices of the molecular kinetic stability have been mentioned as good evaluators of the aromatic character of some skeletally substituted benzenes [20].

There were considered two indicators of the stability of molecules, namely the HOMO-LUMO and the singlet-triplet gaps, for characterizing the heterobenzenes. When possible, the basis set 6-311+G(d,p) was used ((CH-N)<sub>3</sub>, (CH-P)<sub>3</sub>, (CH-As)<sub>3</sub>, (N-P)<sub>3</sub>, (N-As)<sub>3</sub>,

(P-As)<sub>3</sub>); in the case of the heterobenzenes that contain Sb or Bi, computations were performed with the basis set LanL2DZ.

Table 4. HOMO-LUMO gap ( $\Delta$ ) and singlet-triplet gap ( $\Delta E_{ST}$ ) computed at HF/6-311+G(d,p)\* and HF/LanL2DZ, respectively

Heterobenzene	$\Delta E_{ST}$ (eV)	$\Delta$ (eV)
(CH-N) <sub>3</sub>	3.15*	4.40*
(CH-P) <sub>3</sub>	3.02*	4.25*
(CH-As) <sub>3</sub>	1.49*	3.62*
(CH-Sb) <sub>3</sub>	0.73	2.83
(CH-Bi) <sub>3</sub>	0.63	2.63
(N-P) <sub>3</sub>	0.64*	1.89*
(N-As) <sub>3</sub>	0.73*	1.60*
(P-As) <sub>3</sub>	2.36*	2.87*
(P-Sb) <sub>3</sub>	1.41	2.37
(P-Bi) <sub>3</sub>	1.37	2.30
(As-Sb) <sub>3</sub>	0.93	2.62
(As-Bi) <sub>3</sub>	0.83	2.53
(Sb-Bi) <sub>3</sub>	0.55	2.47

Lower stabilities have been obtained for the heterobenzenes (N-P)<sub>3</sub> and (N-As)<sub>3</sub>, results that are in good agreement with the evaluation of the aromaticity by means of the geometrical and magnetic approach. An explanation for the low stability of the heterobenzenes when one of the heteroatoms is N could consist in the repulsions between the lone pairs of the two adjacent nitrogen atoms; in the case of phosphorus and other elements of the group 15, the atomic radius is larger, so the repulsions are no longer very strong. A similar situation has been encountered in a study of some mono- and disubstituted benzenoids [20]. Computations of the singlet-triplet gap show that all the single states of the heterobenzenes are more stable than the corresponding triplet ones. The lowest values of the  $\Delta E_{ST}$  are also found for the heterobenzenes (N-P)<sub>3</sub> and (N-As)<sub>3</sub>, but also for the compounds containing heteroatoms like As, Sb, Bi. In a study regarding the singlet-triplet energy gaps of five-membered cycles containing N, P and As, there is also mentioned that the smaller singlet-triplet gap have been recorded for the compounds that had two As atoms, followed by the one with two P atoms [21].

### Reactivity descriptors of aromaticity

Reactivity descriptors within the frame of conceptual DFT theory –hardness ( $\eta$ ), chemical potential ( $\mu$ ), electrophilicity ( $\omega$ ) and Fukui functions ( $f^+$ ,  $f^-$ )– have been used for predicting the aromatic character of the heterobenzenes. The descriptors  $\eta$  and  $\omega$  act as indices of the stability and global reactivity of a compound: an increased hardness means also an increased stability, while lower electrophilicity index predict a possible aromatic character [22].

Table 5. Reactivity descriptors  $\eta$ ,  $\mu$  and  $\omega$  (B3LYP/LanL2DZ)

Heterobenzene	Hardness ( $\eta=(E_L - E_H)/2$ ) (eV)	Chemical potential ( $\mu=(E_H + E_L)/2$ ) (eV)	Electrophilicity ( $\omega=\mu^2/2\eta$ ) (eV)
(CH-N) <sub>3</sub>	2.20	-4.61	2.41
(CH-P) <sub>3</sub>	2.12	-5.06	3.01
(CH-As) <sub>3</sub>	1.80	-4.80	3.19
(CH-Sb) <sub>3</sub>	1.42	-4.40	3.41
(CH-Bi) <sub>3</sub>	1.32	-5.36	3.10
(N-P) <sub>3</sub>	0.95	-4.87	6.25
(N-As) <sub>3</sub>	0.80	-4.66	6.82
(P-As) <sub>3</sub>	1.43	-5.49	5.26
(P-Sb) <sub>3</sub>	1.18	-5.29	5.91
(P-Bi) <sub>3</sub>	1.15	-4.95	5.33
(As-Sb) <sub>3</sub>	1.30	-5.35	5.45
(As-Bi) <sub>3</sub>	1.26	-5.02	4.98
(Sb-Bi) <sub>3</sub>	1.23	-4.95	4.95

The values of the electrophilicity index place the (N-P)<sub>3</sub> and (N-As)<sub>3</sub> heterobenzenes as the most “non-aromatic” ones, in good agreement with the other criteria that were employed during the study. On the other hand, the most pronounced aromaticity is predicted for the heterocycles of type (CH-X)<sub>3</sub>, where X = N, P, As, Sb and Bi. There is the first index that ranks the (CH-Sb)<sub>3</sub> and (CH-Bi)<sub>3</sub> as possible more aromatic than (P-As)<sub>3</sub>, (P-Sb)<sub>3</sub>, (P-Bi)<sub>3</sub>.

Another criterion of aromaticity may be considered the reactivity toward electrophiles. In order to estimate the local reactivity of the 6 possible reaction centers of the heterobenzenes, the respective Fukui functions were computed. A large value of the Fukui function corresponds to an enhanced reactivity of a specific site.

The equation that defines the Fukui function is [23]:

$$f_k^\alpha = \sum_{\mu \in k} |c_{\mu}^\alpha|^2,$$

where  $\alpha$  – HOMO orbital (for an electrophilic attack) ( $f$ ) or LUMO orbital (for a nucleophilic attack) ( $f^+$ ), with neglect of the overlap integrals.

At first, the Fukui functions ( $f$ ) for an electrophilic attack were calculated and, as expected, the results were the following: the more electronegative the atom, the most probable is the electrophilic substitution reaction to occur. The results clearly show that an eventual substitution is oriented at the most electronegative atom.

For the same heterobenzenes series, computations of the Fukui functions for a nucleophilic attack ( $f^+$ ) were performed. A larger value of  $f^+$  or  $f$  computed for the same atom serve as a reliable index in order to predict the site reactivity toward a nucleophile or an electrophile, respectively. The results divided the heterobenzenes into three categories:

- the ones where the atoms with largest  $f$  have lower  $f^+$  (and viceversa, lower  $f^-$  of the less electronegative atoms correspond to higher  $f^+$  values), predicting a greater availability toward an electrophilic attack at the most electronegative atom (**3, 5, 6, 8, 9, 11, 12**);
- the ones where the results of  $f^+$  for all the six atoms exceed the values of  $f$ , predicting thus an enhanced reactivity toward nucleophiles (instead toward electrophiles, as expected for an aromatic compound) (**4, 7, 10, 13**);
- heterobenzenes **1** and **2**, where the atom with largest  $f$  value is only the 5-N (and 5-P, respectively) atom of the benzenoid structure.

In order to have a better insight of the electronic interactions that occur in the heterobenzenes series, NBO analysis has been performed. Results are presented in **Table 6** (LanL2DZ values are presented; 6-311+G(d,p) was also used when possible -for six heterobenzenes- but the differences don't change the general trend).

This way, second order perturbation theory analysis gives the measure of the stabilization due to the electron transfer from a filled orbital (the donor) to an empty orbital (acceptor).

Only the first three donor-acceptor interactions (in terms of energy value) are presented for each investigated heterobenzene. The general trend is to present low energy stabilization values along with the increase of the heteroatoms size (smaller values were obtained for the heterobenzenes that contain Sb and Bi). (N-P)<sub>3</sub> and (N-As)<sub>3</sub> are the heterocycles that were estimated, by all the criteria of aromaticity that were applied, to be the less aromatic ones. Highest stabilization energies from the donor-acceptor interactions have been obtained for these two compounds and they are also the only ones where the interactions between the lone pair of electrons of one of the nitrogen atoms rank in the first three stabilization energies.

Table 6. Selected NBO analysis of the heterobenzenes 1-13 (B3LYP/LanL2DZ)

Heterobenzene	Donor-acceptor interaction	E (kcal/mol)
(CH-N) <sub>3</sub> 1	$\pi^*C_2-N_3 \leftrightarrow \pi^*C_4-N_5$	30.33
	$\pi C_4-N_5 \leftrightarrow \pi^*C_1-N_6$	27.49
	$\pi C_1-N_6 \leftrightarrow \pi^*C_2-N_3$	21.44
(CH-P) <sub>3</sub> 2	$\pi^*P_5-P_6 \leftrightarrow \pi^*P_3-C_4$	38.35
	$\pi^*P_3-C_4 \leftrightarrow \pi^*C_1-C_2$	27.49
	$\pi P_3-C_4 \leftrightarrow \pi^*P_5-P_6$	16.63
(CH-As) <sub>3</sub> 4	$\pi^*As_5-As_6 \leftrightarrow \pi^*As_3-C_4$	24.88
	$\pi As_3-C_4 \leftrightarrow \pi^*As_5-As_6$	13.58
	$\pi^*As_3-C_4 \leftrightarrow \pi^*C_1-C_2$	13.40
(CH-Sb) <sub>3</sub> 7	$\pi^*Sb_5-Sb_6 \leftrightarrow \pi^*Sb_3-C_4$	15.07
	$\pi Sb_3-C_4 \leftrightarrow \pi^*Sb_5-Sb_6$	11.15
	$\pi Sb_5-Sb_6 \leftrightarrow \pi^*Sb_3-C_4$	9.88
(CH-Bi) <sub>3</sub> 10	$\pi^*Bi_5-Bi_6 \leftrightarrow \pi^*Bi_3-C_4$	12.97
	$\pi Bi_3-C_4 \leftrightarrow \pi^*Bi_5-Bi_6$	10.01
	$\pi Bi_5-Bi_6 \leftrightarrow \pi^*Bi_3-C_4$	9.07
(N-P) <sub>3</sub> 3	$\pi^*P_3-N_4 \leftrightarrow \pi^*N_1-N_2$	51.44
	$\pi^*P_5-P_6 \leftrightarrow \pi^*P_3-N_4$	34.20
	$LP N_2 \leftrightarrow \pi^*N_1-P_6$	19.08
(N-As) <sub>3</sub> 5	$\sigma^*N_1-As_6 \leftrightarrow \sigma^*N_2-As_3$	35.85
	$LP N_2 \leftrightarrow \sigma^*N_1-As_6$	20.45
	$LP N_1 \leftrightarrow \sigma^*N_2-As_3$	16.05
(P-As) <sub>3</sub> 6	$\sigma P_2-As_3 \leftrightarrow \sigma^*P_4-As_5$	22.79
	$\pi As_5-As_6 \leftrightarrow \pi^*P_1-P_2$	10.84
	$\pi As_3-P_4 \leftrightarrow \pi^*As_5-As_6$	10.74
(P-Sb) <sub>3</sub> 8	$\sigma^*P_1-Sb_6 \leftrightarrow \sigma^*P_4-Sb_5$	12.09
	$\sigma^*P_2-Sb_3 \leftrightarrow \sigma^*P_4-Sb_5$	8.81
	$\pi Sb_5-Sb_6 \leftrightarrow \pi^*P_1-P_2$	8.12
(P-Bi) <sub>3</sub> 11	$\sigma^*P_1-Bi_6 \leftrightarrow \sigma^*P_4-Bi_5$	9.84
	$\pi Bi_3-P_4 \leftrightarrow \pi^*Bi_5-Bi_6$	7.57
	$\pi Bi_5-Bi_6 \leftrightarrow \pi^*P_1-P_2$	7.55
(As-Sb) <sub>3</sub> 9	$\pi Sb_5-Sb_6 \leftrightarrow \pi^*As_1-As_2$	8.85
	$\pi Sb_3-As_4 \leftrightarrow \pi^*Sb_5-Sb_6$	8.66
	$\pi Sb_5-Sb_6 \leftrightarrow \pi^*Sb_3-As_4$	7.87
(As-Bi) <sub>3</sub> 12	$\pi Bi_5-Bi_6 \leftrightarrow \pi^*As_1-As_2$	8.29
	$\pi Bi_3-As_4 \leftrightarrow \pi^*Bi_5-Bi_6$	7.93
	$\pi Bi_5-Bi_6 \leftrightarrow \pi^*Bi_3-As_4$	7.28
(Sb-Bi) <sub>3</sub> 13	$\pi Bi_5-Bi_6 \leftrightarrow \pi^*Sb_1-Sb_2$	7.83
	$\pi Bi_5-Bi_6 \leftrightarrow \pi^*Bi_3-Sb_4$	7.67
	$\pi Bi_3-Sb_4 \leftrightarrow \pi^*Bi_5-Bi_6$	7.56

The following figure presents the electron density distribution of heterobenzenes:

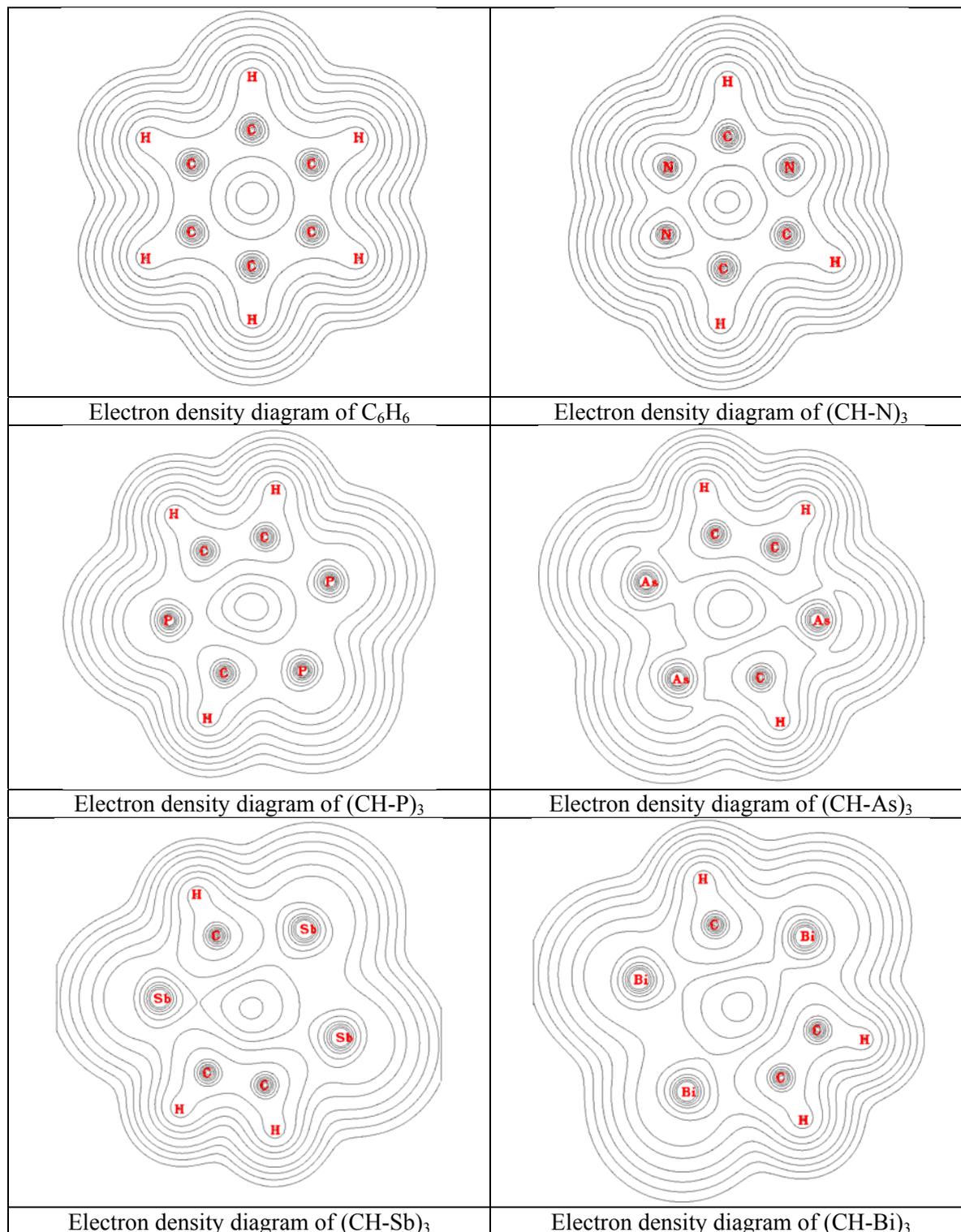


Fig. 2a. The electron density diagram of heterobenzenes 1-5

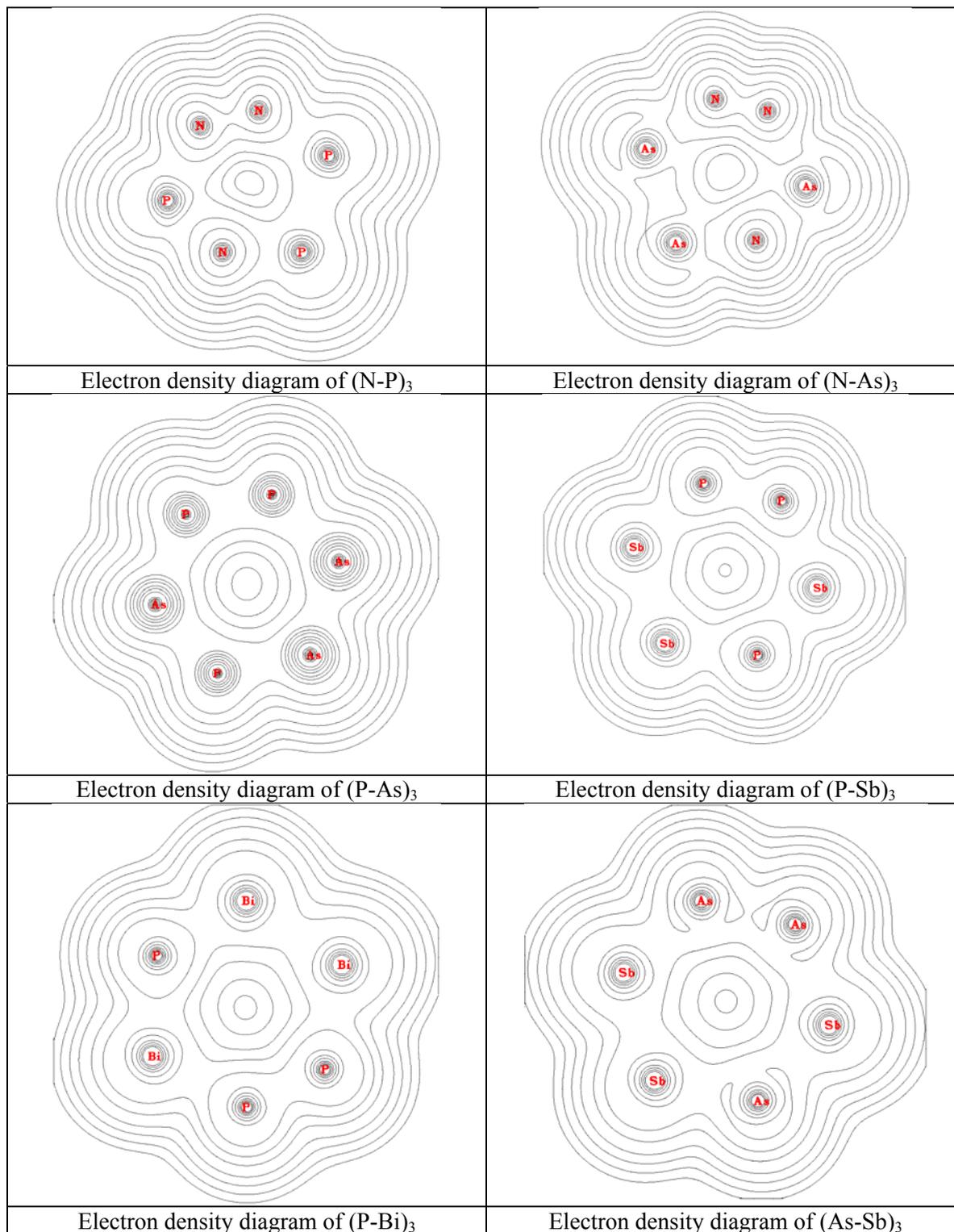


Fig. 2b. The electron density diagram of heterobenzenes 6-11

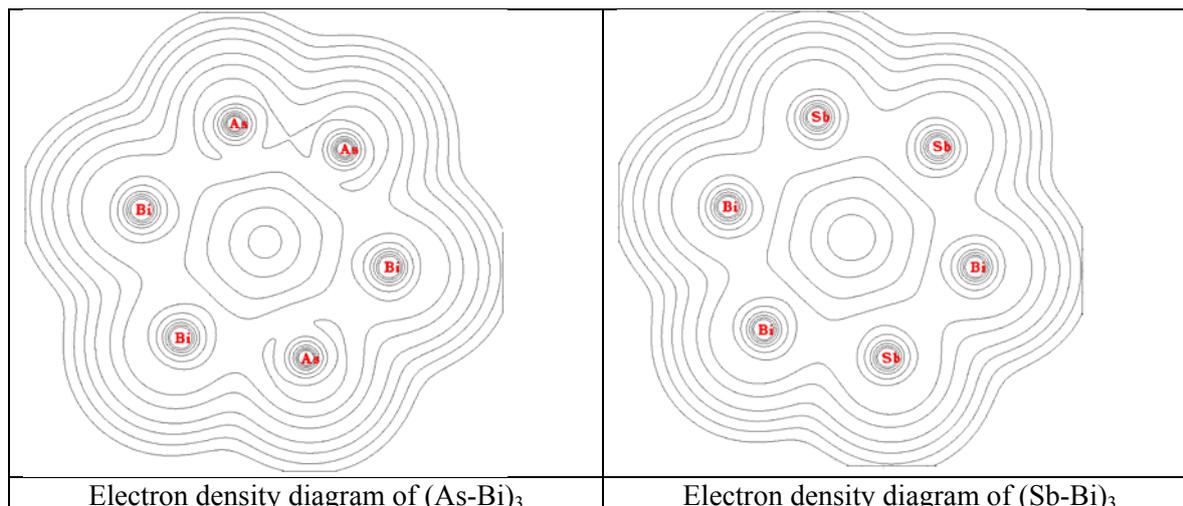


Fig. 2c. The electron density diagram of heterobenzenes 12-13

The electron density diagrams of heterobenzenes can be relevant for estimating the delocalization degree of the electrons. For a delocalized molecule like benzene, the electron density will cover the entire region (see Figure 2a); similar distribution have been obtained for  $(\text{CH-N})_3$ ,  $(\text{P-As})_3$  and  $(\text{Sb-Bi})_3$ . The largest differences from the key-molecule  $\text{C}_6\text{H}_6$  have been recorded for  $(\text{CH-Sb})_3$ ,  $(\text{CH-Bi})_3$  and  $(\text{N-As})_3$ ; these are also the heterobenzenes with the smallest negative values of the NICS index.

#### 4. Conclusions

The possible aromatic character of a new heterobenzenes series has been investigated. The absence of an “universal” aromaticity index leads to the obtaining of different results from the different criteria (geometric, magnetic, energetic) that have been employed. This way, the geometric characteristics like bond length and bond angle equalization can be correlated with the NICS results (higher degree of equalization means a higher “negative” NICS value).

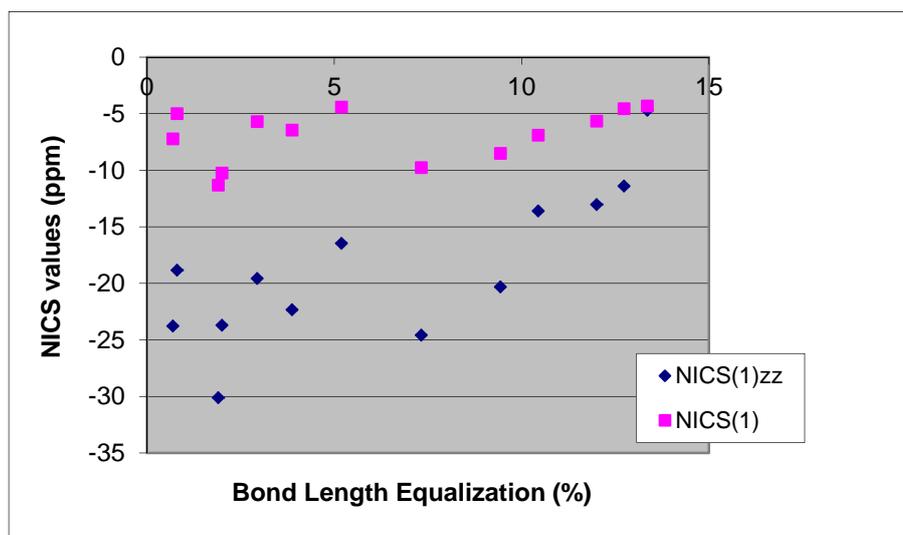
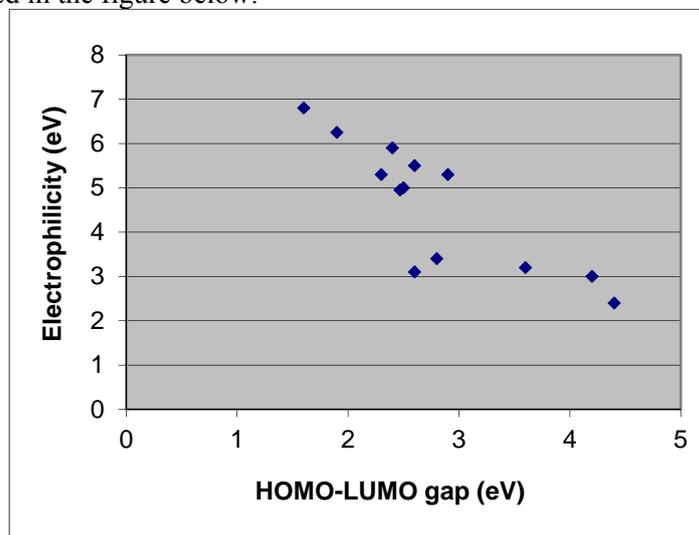


Fig. 3. Relationship between the NICS index values and the geometric index of bond length equalization

Instead, the values of singlet-triplet gap show that less stable are the heterobenzenes that contain Sb and Bi and their combinations with As, namely (CH-Sb)<sub>3</sub>, (CH-Bi)<sub>3</sub>, (As-Sb)<sub>3</sub>, (As-Bi)<sub>3</sub>, (Sb-Bi)<sub>3</sub> and also the heterobenzenes (N-P)<sub>3</sub> and (N-As)<sub>3</sub>. Among all, (N-P)<sub>3</sub> and (N-As)<sub>3</sub> have been classified as the most “non-aromatic” ones. It can be also noticed a correlation between the HOMO-LUMO gap and the global electrophilicity index (lower HL gap, higher electrophilicity values), as presented in the figure below:



Also, reactivity descriptors within the conceptual DFT frame have been computed. As expected, a possible electrophilic substitution reaction is thought occurring at the most electronegative heteroatom of the cycle. NBO analysis shows that, together with an increase in the size of heteroatoms, the stabilization energy due to the donor-acceptor interactions decreases.

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### References

- [1] H. W. Kroto, J. R. Heath, S. C. O'Brien, R. F. Curl, R. E. Smalley, *Nature* **318**, 162 (1985).
- [2] A. R. Katritzky, K. Jug, C. D. Oniciu, *Chem. Rev.* **101**, 1421 (2001).
- [3] T. M. Krygowski, M. K. Cyranski, *Tetrahedron* **52**, 10255 (1996).
- [4] P. v. R. Schleyer, H. Jiao, *Pure Appl. Chem.* **68**, 209 (1996).
- [5] C. W. Bird, *Tetrahedron* **41**, 1409 (1985).
- [6] P. v. R. Schleyer, C. Maerker, A. Dransfeld, H. Jiao, N. J. R. Hommes, *J. Am. Chem. Soc.* **118**, 6317 (1996).
- [7] T. M. Krygowski, M. K. Cyranski, *Chem. Rev.* **101**, 1385 (2001).
- [8] P. Binger, S. Leininger, J. Stannek, B. Gabor, R. Mynott, J. Bruckmann, C. Kruger, *Angew. Chem., Int. Ed. Engl.* **34**, 2227 (1995).
- [9] S. M. Bachrach, P. Magdalinos, *J. Mol. Struct. (Theochem)* **368**, 1 (1996).
- [10] R. Gleiter, H. Lange, P. Binger, J. Stannek, C. Krüger, J. Bruckmann, U. Zenneck, S. Kummer, *Eur. J. Inorg. Chem.* 1619 (1998).
- [11] M. Hofmann, P. v. R. Schleyer, M. Regitz, *Eur. J. Org. Chem.* 3291 (1999).
- [12] M. Z. Kassaei, N. Jalalimanesh, S. M. Musavi, *J. Molec. Structure (THEOCHEM)*, **816**, 153 (2007).
- [13] R. Pop, M. Medeleanu, C. Csunderlik, M. Mracec, *Revista de Chimie* **61**(5), 483 (2010).
- [14] R. Pop, M. Medeleanu, M. Mracec, *Studia UBB Chemia* **4**, 147 (2010).
- [15] E. D. Raczynska, M. Hallman, K. Kolczynska, T. M. Stepniewski, *Symmetry* **2**, 1485 (2010).
- [16] C. P. Frizzo, M. A. P. Martins, *Struct. Chem.* **23**(2), 375 (2012).

- [17] P. Bao, Z. H. Yu, *J. Phys. Chem. A* **111**, 5304 (2007).
- [18] M. Solà, F. Feixas, J. Oscar, C. Jiménez-Halla, E. Matito, J. Poater, *Symmetry* **2**, 1156 (2010).
- [19] J. Oscar, C. Jimenez-Halla, C. Matito, J. Robles, M. Sola, *Journal of Organometallic Chemistry* **691**, 4359 (2006).
- [20] U. D. Priyakumar, G. N. Sastry, *Proc. Indian Acad. Sci. (Chem. Sci.)* **115**(1), 49 (2003).
- [21] E. Vessally, *Phosphorus, Sulfur, and Silicon and the Related Elements* **184**(7), 1805 (2009).
- [22] R. Parthasarathi, J. Padmanabhan, M. Elango, V. Subramanian, P. K. Chatarraj, *Chem. Phys. Lett.* **394**, 225 (2004).
- [23] R. Contreras, P. Fuentealba, M. Galvan, P. Perez, *Chem. Phys. Lett.* **304**, 405 (1999).
- [24] Gaussian 09, Revision B.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2010.
- [25] Tian Lu, "Multiwfn: A multifunctional wavefunction analyzer", Version 2.61, <http://Multiwfn.codeplex.com>