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EVALUATION OF THE AROMATIC CHARACTER OF λ^3-HETEROBENZENES USING THE MAGNETIC CRITERION

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ABSTRACT. The aromaticity of the heterobenzenes containing 15-group elements, namely the six-membered homocycles $(\lambda^3\text{-X})_6$ (X = CH, N, P, As) and the six-membered alternant heterocycles $(\lambda^3\text{-X-}\lambda^3\text{-Y})_3$ (X, Y = CH, N, P, As) is investigated using magnetic and geometric criteria at B3LYP/6-31G (d,p) level.

The NMR isotropic shielding values of a molecule of H_2 placed at a distance of 2.5Å above the center of the heterobenzenes were computed using the GIAO method at 6-31G(d,p) level. The results are compared with the negative values of the absolute magnetic shielding, computed at the center of ring (NICS index), at B3LYP/6-31G (d,p) level. An angle-based index is used as geometric criterion for the evaluation of the aromatic character.

Keywords: *heterobenzenes, aromaticity, shielding increments, angle-based index*

INTRODUCTION

The benzene ring, with its delocalized 6 π-electrons, planar geometry, bond lengths equalization and ability of sustaining a diatropic ring current remains the key-molecule for the evaluation of the aromatic character [1]. There are also known hetero-analogues of benzene, compounds obtained by replacing one or many CH groups with isovalent atoms that show similar properties with the above-mentioned ones (an example is the pyridine). Hetero-analogues of benzene with dicoordinated trivalent atoms of 15 group (N, P, As) of type $(\lambda^3\text{-X-}\lambda^3\text{-Y})_3$ (where X, Y = CH, N, P, As - Figure 1) have been investigated in order to evaluate their possible aromatic character. Our previous papers [2, 3] reported studies regarding the stability of homo- and heterobenzenes containing 15 group atoms, estimated by their heat of formation computations [2] and also an evaluation of the aromatic character of the heterobenzenes series by means of geometric, magnetic and chemical reactivity criteria [3].

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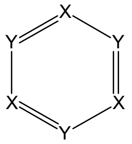
Concerning the use of the magnetic criteria to evaluate the aromaticity, one of the most used indices is NICS (Nucleus Independent Chemical Shift) [4], computed at the center of the molecule (NICS(0)) or at 1Å distance above the molecule's geometric center. Recent work of Martin et al. [5, 6] report the use of computed NMR shielding effects on a molecular probe (a diatomic hydrogen molecule, placed at a 2-2.5 Å above the geometric center of the ring) in order to evaluate the aromatic character of fused hydrocarbons. The same methodology was applied to the heterobenzenes of series $(\lambda^3\text{-X-}\lambda^3\text{-Y})_3$ (where X, Y = CH, N, P, As) and the shielding values of different heterobenzenes on the diatomic hydrogen probe (placed at 2.5 Å above the center of molecule) were compared with NICS(2.5) values. Moving the H_2 probe along x and y coordinates of the geometric center of the rings (step size 0.5 Å, three steps in each direction) leads to a complete evaluation of the shielding/deshielding effects.



X, Y: CH, N, P, As

Figure 1. General formula of the heterobenzenes $(\lambda^3\text{-X-}\lambda^3\text{-Y})_3$

RESULTS AND DISCUSSION

In a previous paper [3] we reported the evaluation of the aromatic character of the same heterobenzenes series using bond length- and bond order-based indices. No concluding results were obtained, mostly due to the D_{3h} and D_{6h} symmetry of the compounds that strongly influences the values of bond length- and bond order-based indices. A possible method for avoiding such situation is the use of geometric angle-based indices.

Doerksen et al. [7, 8] mentioned two indices based on alternance of the angles, namely AVGNEXT and ADIFFPC and they assigned the maximum value (100) to benzene ring and the minimum value (0) to a six-membered cycle with alternant angles of 110° and 130°, respectively. For the heterobenzene series of this study, the minimum value will correspond to a six-membered cycle with alternant angles of 100° and 135°, respectively.

$$AVGNEXT = 100\left[1 - \frac{1}{35n}\sum_{i}^{n}\left|\theta_i - \theta_{i+1}\right|\right] \tag{1}$$

$$ADIFFPC = 100\left[1 - \frac{1}{1837.5}\sum_{i}^{n}\left(\theta_{med} - \theta_i\right)^2\right] \tag{2}$$

Table 1. Angle-based geometric indices, using geometries optimized at *ab initio* level (HF/6-31G)

Heterobenzene	AVGNEXT	ADIFFPC
C_6H_6	100	100
$(CH\text{-}\lambda^3\text{-}N)_3$	71.4	90.1
$(CH\text{-}\lambda^3\text{-}P)_3$	22.1	38.7
$(CH\text{-}\lambda^3\text{-}As)_3$	17.1	31.3
$(\lambda^3\text{-}N)_6$	100	100
$(\lambda^3\text{-}N\text{-}\lambda^3\text{-}P)_3$	38.0	61.6
$(\lambda^3\text{-}N\text{-}\lambda^3\text{-}As)_3$	41.1	65.3
$(\lambda^3\text{-}P)_6$	100	100
$(\lambda^3\text{-}P\text{-}\lambda^3\text{-}As)_3$	97.1	99.9
$(\lambda^3\text{-}As)_6$	100	100

As it can be seen, the maximum value of both indices is obtained for the homocycles $(\lambda^3\text{-}X)_6$ but, even in this case, the angle-based geometric index is influenced by the symmetry of molecules.

NICS(2.5) values and shielding increments $\Delta\sigma$ were computed for the heterobenzenes series $(\lambda^3\text{-}X\text{-}\lambda^3\text{-}Y)_3$ (where X, Y = CH, N, P, As) at B3LYP/6-31G level (Table 2).

Table 2. NICS (2.5) (ppm) and shielding increments $\Delta\sigma$ (ppm) computed at *ab initio* level (B3LYP/6-31G)

Heterobenzene	NICS 2.5 (ppm)	$\Delta\sigma$ (ppm)
C_6H_6	-0.2935	0.974
$(CH\text{-}\lambda^3\text{-}N)_3$	-2.7228	3.707
$(CH\text{-}\lambda^3\text{-}P)_3$	-3.6526	4.439
$(CH\text{-}\lambda^3\text{-}As)_3$	-3.8539	4.478
$(\lambda^3\text{-}N)_6$	-2.9665	4.353
$(\lambda^3\text{-}N\text{-}\lambda^3\text{-}P)_3$	-1.6690	2.647
$(\lambda^3\text{-}N\text{-}\lambda^3\text{-}As)_3$	-2.0210	2.362
$(\lambda^3\text{-}P)_6$	-5.7005	6.151
$(\lambda^3\text{-}P\text{-}\lambda^3\text{-}As)_3$	-6.7035	6.447
$(\lambda^3\text{-}As)_6$	-18.6155	7.203

A qualitative comparison of NICS(2.5) index and shielding increments $\Delta\sigma$ values shows a very similar trend. Higher values (even greater than for the benzene ring) are recorded for the heterobenzenes $(\lambda^3\text{-}P)_6$, $(\lambda^3\text{-}P\text{-}\lambda^3\text{-}As)_3$, $(\lambda^3\text{-}As)_6$ and predict a pronounced aromatic character. Our previous study [3] regarding the estimation of aromaticity of the heterobenzenes series using the magnetic (NICS(0) and NICS(1)) and reactivity-based criteria showed similar results; the highest NICS values belong to the heterobenzenes having the closest geometry to the benzene ring (equalization of bond lengths and bond angles), namely: $(\lambda^3\text{-}N)_6$, $(\lambda^3\text{-}P)_6$, $(\lambda^3\text{-}P\text{-}\lambda^3\text{-}As)_3$ and $(\lambda^3\text{-}As)_6$.

The same explanation seems to be appropriate for the values obtained for the shielding increments. The results presented in Table 1 show that all the heteroanalogues of benzene have positive shielding increments, revealing a possible aromatic character in all of the cases. The largest values of both NICS(2.5) index and Δσ are obtained in case of heterobenzenes $(\lambda^3\text{-P})_6$, $(\lambda^3\text{-P-}\lambda^3\text{-As})_3$ and $(\lambda^3\text{-As})_6$.

Shielding increments have also been computed at three different steps in x and y directions (0.5 Å, 1.0 Å, 1.5 Å); the results are presented in Table 3 and Table 4.

Table 3. Shielding increments Δσ (ppm) computed in three different points along the x axis (B3LYP/6-31G level)

Heterobenzene	**Δσ $_{(x=0.5)}$ (ppm)**	**Δσ $_{(x=1.0)}$ (ppm)**	**Δσ $_{(x=1.5)}$ (ppm)**
C_6H_6	0.974	0.938	0.896
$(\text{CH-}\lambda^3\text{-N})_3$	3.444	2.789	2.056
$(\text{CH-}\lambda^3\text{-P})_3$	4.147	3.385	2.463
$(\text{CH-}\lambda^3\text{-As})_3$	4.173	3.381	2.446
$(\lambda^3\text{-N})_6$	4.076	3.373	2.520
$(\lambda^3\text{-N-}\lambda^3\text{-P})_3$	2.513	2.162	1.678
$(\lambda^3\text{-N-}\lambda^3\text{-As})_3$	2.232	1.902	1.467
$(\lambda^3\text{-P})_6$	5.925	5.325	4.509
$(\lambda^3\text{-P-}\lambda^3\text{-As})_3$	6.215	5.600	4.778
$(\lambda^3\text{-As})_6$	6.690	6.315	5.453

Table 4. Shielding increments Δσ (ppm) computed at three different points along the y axis (B3LYP/6-31G level)

Heterobenzene	**Δσ $_{(y=0.5)}$ (ppm)**	**Δσ $_{(y=1.0)}$ (ppm)**	**Δσ $_{(y=1.5)}$ (ppm)**
C_6H_6	1.009	0.936	0.898
$(\text{CH-}\lambda^3\text{-N})_3$	3.445	2.804	2.065
$(\text{CH-}\lambda^3\text{-P})_3$	4.158	3.456	2.573
$(\text{CH-}\lambda^3\text{-As})_3$	4.188	3.472	2.601
$(\lambda^3\text{-N})_6$	4.076	3.375	2.521
$(\lambda^3\text{-N-}\lambda^3\text{-P})_3$	2.505	2.119	1.579
$(\lambda^3\text{-N-}\lambda^3\text{-As})_3$	2.224	1.867	1.391
$(\lambda^3\text{-P})_6$	5.925	5.308	4.395
$(\lambda^3\text{-P-}\lambda^3\text{-As})_3$	6.219	5.591	4.670
$(\lambda^3\text{-As})_6$	6.961	6.300	5.323

The results presented in Table 2 and Table 3 show insignificant differences between the values of the shielding increments computed along x and y axes and this a possible consequence of the symmetry of the studied heterobenzenes.

CONCLUSIONS

Computations of AVGNEXT and ADIFFPC indices lead to maximum values for the benzene ring, as well as for the homocycles $(\lambda^3\text{-X})_6$. The results prove the difficulties that appear in quantifying the aromatic character of the heterobenzene series $(\lambda^3\text{-X-}\lambda^3\text{-Y})_3$ by using the geometric criterion. In the absence of any experimental data, it is difficult to make statements regarding the identical values obtained for the geometric indices in case of benzene, hexazine (known as unstable compound) and hexaphosphabenzene and hexaarsabenzene.

Using the magnetic criterion for evaluating the aromaticity, the results of NICS(2.5) index presented in Table 2 show negative values in case of all the heterobenzenes, thus predicting an aromatic character for all these compounds. As in the case of the angle-based geometric index, higher negative values of NICS index were obtained for the heteroanalogs of benzene $(\lambda^3\text{-P})_6$, $(\lambda^3\text{-P-}\lambda^3\text{-As})_3$, $(\lambda^3\text{-As})_6$. A similar situation is the one of the shielding increments Δσ, that also predict a strong aromatic character of the heterobenzenes $(\lambda^3\text{-P})_6$, $(\lambda^3\text{-P-}\lambda^3\text{-As})_3$, $(\lambda^3\text{-As})_6$ (Table 2). The very close values of the shielding increments computed in three different points along x and y axes also prove that the results may be a consequence of the geometry of the heterobenzenes series, especially of their symmetry.

COMPUTATIONAL SECTION

The heterobenzenes series have been first optimized at semi-empirical level (PM3 method) using MOPAC2009 program [9], then optimization at *ab initio* level (HF/6-31G) using Gaussian 03 package [10], has been performed. The geometries of all heteroanalogues of benzene are planar. NICS(2.5) indices have been computed at a 2.5 Å distance above the geometric center of each ring, using the GIAO method [g] at B3LYP/6-31G level. Computations of the shielding effects on the molecular probe of H_2 have also been performed at B3LYP/6-31G level, first at 2.5 Å above the geometric center of each ring and then at three different points along the x and y axis of the center of the molecule (0.5 Å, 1.0 Å and 1.5 Å in each direction). The shielding increments (Δσ) were obtained by subtracting the shielding value corresponding to one of the H atoms of the H_2 probe alone (26.77 ppm) [5] from the shielding value of the closest H atom of the H_2 molecule relative to the heterobenzene plane.

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