# Aromaticity Evaluation of $\lambda^3$-Heterobenzenes using the Magnetic Criterion and Reactivity Based Descriptors

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*The aromaticity of the heterobenzenes containing 15-group elements is investigated using the magnetic criterion (nucleus independent chemical shifts - NICS) and reactivity based descriptors (HOMO-LUMO gap) at B3LYP/6-31G(d) level, respectively B3LYP/LanL2DZ level. The results outline the difficulties that arise in quantifying a complex concept like the aromaticity.*

*Keywords: aromaticity, NICS, heterobenzenes*

The heteroanalogues of benzene where one or many CH units are replaced with isovalent atoms represent interesting research areas in experimental and theoretical chemistry [1]. Some of these compounds have been synthesized [2], and important data regarding their stability and aromatic character were obtained.

Starting from the study of the six-membered homocycles $(\lambda^3\text{-X})_6$ (X = CH, N, P, As, Sb, Bi) and six-membered alternant heterocycles $(\lambda^3\text{-X-}\lambda^3\text{-Y})_3$ (X, Y = CH, N, P, As, Sb, Bi) stability, estimated from their individual computed heat of formation [3], the aromatic character of these compounds was evaluated. The methyne groups from the benzene skeleton were replaced with dicoordinated trivalent heteroatoms, so the first condition of aromaticity - the Hückel's rule- is fulfilled.

The complexity of the concept of aromaticity and the lack of universal definition led to the emerging of different criteria for its quantification. There are often used geometric criteria [4,5] (the bond lengths and bond orders equalization), energetic criteria [6,7] (takes into account the stability of the compounds, their resonance energy) and the magnetic criteria [8,9] (based on the ring current of the aromatic compounds).

The recent development of the DFT methods led to some new criteria for quantifying the aromaticity, based on chemical reactivity. A series of properties that may be quantified with DFT methods (as, for example, the total hardness of a molecule) are used as aromaticity indexes [10].

During the last years, the magnetic criterion uses NICS (Nucleus-Independent Chemical Shift) methodology in order to evaluate the aromatic character. The method is based on the negative value of the absolute magnetic shielding, computed at the center of the ring (NICS(0)) or at point 1Å above (NICS(1)), for a better measure of the π -electron delocalization in a cyclic molecule [11].

## Experimental part

The compounds HB1-HB21 were optimized at semi-empirical level, using the PM6 method from the MOPAC 2009 [12] program and at *ab initio* level using the HF method and the basis sets 6-311G(d,p) for HB1-HB10, respectively LanL2DZ level for HB11-HB21 from the Gaussian 03 program [13]. The starting geometries used for the *ab initio* optimization are the ones obtained from the optimization at the semi-empirical level. The NICS indices were calculated at the ring centers (NICS (0)) and at 1 Å above the center of the optimized compound (NICS (1)) using the GIAO method [14] at B3LYP/6-31G level for HB1-HB10, respectively at B3LYP/LanL2DZ level for HB11-HB21. There were used both the geometries optimized at semi-empirical and *ab initio* level. The homo- and heterocycles HB1-HB21 considered for the computations are the following:

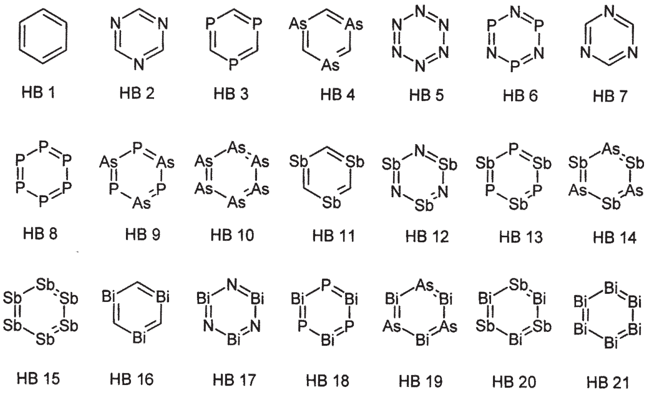

Fig. 1. Heterobenzenes series HB1-HB21

**Table 1**
HB1-HB10 SERIES; THE COMPUTATIONS WERE DONE USING THE BASIS SET 6-31G

| $(\lambda^3\text{-X-}\lambda^3\text{-Y})_3$ | CH | N | P | As |
|---|---|---|---|---|
| **CH** | HB1 | HB2 | HB3 | HB4 |
| **N** | | HB5 | HB6 | HB7 |
| **P** | | | HB8 | HB9 |
| **As** | | | | HB10 |

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**Table 2**
HB11-HB21 SERIES; THE COMPUTATIONS WERE DONE USING THE BASIS SET LANL2DZ

| $(\lambda^3\text{-X-}\lambda^3\text{-Y})_3$ | CH | N | P | As | Sb | Bi |
|---|---|---|---|---|---|---|
| **Sb** | HB11 | HB12 | HB13 | HB14 | HB15 | |
| **Bi** | HB16 | HB17 | HB18 | HB19 | HB20 | HB21 |

## Results and discussion

The NICS index values were computed for the heterobenzenes HB1-HB21 series using the geometries optimized both at semi-empirical and *ab initio* level. The NICS values were calculated both at the ring center (NICS(0)) and at 1Å above it (NICS(1)).

**Table 3**
NICS VALUES (PPM) AND THE HOMO-LUMO ENERGY GAP (eV) CALCULATED AT B3LYP/6-31G(D) LEVEL FOR THE HB1-HB10 COMPOUNDS OPTIMIZED AT *AB INITIO* LEVEL

| HB | NICS(0) (ppm) | NICS(1) (ppm) | $\Delta\varepsilon$ (LUMO-HOMO) (eV) |
|---|---|---|---|
| **HB1** | -9.5923 | -11.2577 | 6.89 |
| **HB2** | -4.4902 | -5.2236 | 6.08 |
| **HB3** | -5.2236 | -8.6337 | 4.65 |
| **HB4** | -4.3302 | -8.1043 | 4.48 |
| **HB5** | 4.5410 | -10.5602 | 3.93 |
| **HB6** | 3.8290 | -3.3177 | 3.77 |
| **HB7** | 4.5304 | -2.8934 | 3.55 |
| **HB8** | -8.0236 | -10.5729 | 3.11 |
| **HB9** | -10.7168 | -12.2594 | 3.10 |
| **HB10** | -12.9378 | -13.7870 | 3.09 |

**Table 4**
NICS VALUES (ppm) CALCULATED AT B3LYP/6-31G(d) LEVEL, FOR THE HB1-HB10 COMPOUNDS OPTIMIZED AT SEMI-EMPIRICAL LEVEL

| HB | NICS(0) (ppm) | NICS(1) (ppm) |
|---|---|---|
| **HB1** | -9.6782 | -11.1190 |
| **HB2** | -4.7621 | -10.1757 |
| **HB3** | -5.8329 | -8.7654 |
| **HB4** | -4.1433 | -8.1117 |
| **HB5** | 1.3859 | -9.7370 |
| **HB6** | 2.1119 | -4.1893 |
| **HB7** | 6.9466 | -1.0770 |
| **HB8** | -8.0236 | -10.5729 |
| **HB9** | -12.9293 | -16.4260 |
| **HB10** | -11.0581 | -12.7517 |

**Table 5**
NICS VALUES (PPM) AND THE HOMO-LUMO ENERGY GAP (eV) CALCULATED AT B3LYP/6-31G(d) LEVEL FOR THE HB11-HB21 COMPOUNDS OPTIMIZED AT *AB INITIO* LEVEL

| HB | NICS(0) (ppm) | NICS(1) (ppm) | $\Delta\varepsilon$ (LUMO-HOMO) (eV) |
|---|---|---|---|
| **HB11** | -1.7483 | -5.5245 | 8.27 |
| **HB12** | 7.7391 | 0.6382 | 2.79 |
| **HB13** | -3.4529 | -5.6450 | 6.85 |
| **HB14** | -8.0342 | -8.9755 | 6.51 |
| **HB15** | -8.7828 | -9.3871 | 5.95 |
| **HB16** | -1.4024 | -5.0556 | 7.89 |
| **HB17** | 8.0019 | 1.0392 | 2.74 |
| **HB18** | -7.0155 | -8.2562 | 6.67 |
| **HB19** | -9.1915 | -9.8445 | 6.34 |
| **HB20*** | -5.1153 | -6.1825 | 2.25 |
| **HB21** | -11.6831 | -11.6954 | 2.45 |

**Observation: HB20 was optimized using the basis set LanL2MB; also the NICS index for HB20 was computed at B3LYP/LanL2MB level (the calculations for the compound HB20 did not succeed when basis set LanL2DZ was used).*

**Table 6**
NICS VALUES (ppm) CALCULATED AT B3LYP/6-31G(D) LEVEL, FOR THE HB1-HB10 COMPOUNDS OPTIMIZED AT SEMI-EMPIRICAL LEVEL

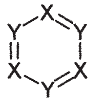
| HB | NICS(0) (ppm) | NICS(1) (ppm) |
|---|---|---|
| **HB11** | -2.1645 | -6.4899 |
| **HB12** | 8.6628 | 1.3526 |
| **HB13** | -0.4243 | -3.6243 |
| **HB14** | -3.1355 | -4.9396 |
| **HB15** | -4.3530 | -8.8837 |
| **HB16** | -0.8358 | -5.2709 |
| **HB17** | 8.7791 | 0.9996 |
| **HB18** | 3.2308 | -1.3591 |
| **HB19** | -3.7920 | -6.0389 |
| **HB20*** | - | - |
| **HB21*** | - | - |

** The optimization of the heterocycles HB20 and HB21 at semi empirical level did not succeed*

There are no significant differences between the results, so one may consider in the following discussions only the NICS values reported for the molecules optimized with *ab initio* methods. For the $(\lambda^3\text{-X})_6$ homocycles the benzene (HB1) geometry will be the reference and for the alternant heterocycles $(\lambda^3\text{-X-}\lambda^3\text{-Y})_3$ the reference will be the 1,3,5-triazine (HB2) molecule.

Accordingly to the literature data [15], for the systems that contain heteroatoms the NICS(1) index computation is preferred because the σ-bond contributions effects are avoided and the shifts caused by the σ-electrons are more accurately quantified.

The geometrical parameters of the *ab initio* optimized structures of heterobenzenes HB:



(1)

General formula of the heterobenzenes

For the HB2-HB10 heterobenzenes it may be observed that all the NICS(1) values are negative, proving the aromaticity of the compounds, and, by default, the continuous delocalization of the π-electrons. Greater NICS(1) values than the one corresponding to HB1, benzene, were obtained for the heterobenzenes HB9 and HB10. A similar value it was obtained for the HB5 compound. (The results are presented in table 3). The geometrical parameters presented in table 7 show that the heterobenzenes HB5, HB9 and HB10 have the closest geometry to the benzene ring (regarding the bond length equalization, a common feature for all the considered heterobenzenes, and especially regarding the same value of the bond angle of 120°). The other compounds from the HB2-HB10 series show NICS(1) values similar to the ones obtained for HB2, 1,3,5-triazine (also having geometries very similar to HB2, with differences of maximum 20° between XYX and YXY angles).

**Table 7**

THE GEOMETRICAL PARAMETERS OF THE HETEROBENZENES

| *($\lambda^3$-X- $\lambda^3$-Y)$_3$* | *d(X,Y) (Å)* | *∢XYX (°)* | *∢YXY (°)* |
|---|---|---|---|
| **HB1** | 1.385 | 120.00 | 120.00 |
| **HB2** | 1.317 | 114.50 | 125.50 |
| **HB3** | 1.716 | 106.37 | 133.62 |
| **HB4** | 1.829 | 105.54 | 134.47 |
| **HB5** | 1.284 | 120.00 | 120.00 |
| **HB6** | 1.604 | 109.15 | 130.85 |
| **HB7** | 1.733 | 109.71 | 130.29 |
| **HB8** | 2.094 | 120.00 | 120.00 |
| **HB9** | 2.205 | 119.50 | 120.50 |
| **HB10** | 2.309 | 120.00 | 120.00 |
| **HB11** | 2.025 | 103.94 | 136.11 |
| **HB12** | 1.921 | 101.62 | 138.39 |
| **HB13** | 2.458 | 116.06 | 123.94 |
| **HB14** | 2.555 | 121.93 | 118.07 |
| **HB15** | 2.741 | 120.00 | 120.00 |
| **HB16** | 2.090 | 103.46 | 136.54 |
| **HB17** | 1.992 | 102.81 | 137.21 |
| **HB18** | 2.507 | 115.71 | 124.29 |
| **HB19** | 2.602 | 117.28 | 122.72 |
| **HB20** | 2.927 | 118.05 | 121.95 |
| **HB21** | 2.832 | 120.00 | 120.00 |

*Observation 1: the results are obtained for the compounds optimized with ab initio methods (HF/6-311G(d,p) for the HB1-HB10 series and HF/LanL2DZ for the HB11-HB21 series. Exception: HB20, which was optimized using HF/LanL2MB)*

*Observation 2:* $Z_X < Z_Y$

In the case of the HB11-HB21 heterobenzenes, the greatest NICS(1) value are the ones obtained for HB14, HB15, HB18, HB19 and HB21. As in the former series, the geometry of these compounds shows equal bond lengths and bond angles of 120° (or very close values). Others negative values for NICS(1), which confirm the aromatic character, are obtained for HB11, HB13, HB16 and HB20. Positive values of NICS(1) index are obtained only for HB12 and HB17, showing a possible non-aromatic character. It may be observed that the smallest values of NICS(1) (table 3 and table 5) are obtained for the heterocycles where X=N, Y=P, As, Sb, Bi.

The heterobenzenes reactivity may also be used as an aromaticity criterion. The LUMO-HOMO difference $\Delta\varepsilon$ represents an approximation of chemical hardness, being used as an index for the stability of the compounds. Accordingly to a study realized in 1993 [16] regarding the aromaticity of a series of compounds that include phosphabenzene, arsabenzene and stibabenzene, the borderline between aromatic and non-aromatic compounds is the $\Delta\varepsilon$ value of 1.28 eV. The results for the heterobenzenes series HB1-HB21 show, in all of the cases, a $\Delta\varepsilon$ value higher than 2 eV (table 3 and table 5).

## Conclusions

NICS(0) and NICS(1) value were computed both for the semi-empirical and *ab initio* optimized geometries of the heterobenzenes series HB1-HB21. There is a similar trend of the NICS values computed for the geometries optimized at different levels.

The NICS index values are strongly influenced by the geometry and symmetry of the molecules. Only this way the NICS values (similar or greater than the ones corresponding to benzene, HB1) obtained for HB5, HB8, HB15 and HB 20 may be explained. These results, at least in the case of HB5 (hexazine) that is known as an instable compound, are not conform to the experimental data.

The geometric parameters presented in table 7 show that, regarding the bond length equalization, all of the studied heterobenzenes should have aromatic character.

The reactivity based descriptors predict a possible aromatic character for all the compounds, but due to the lack of more significant experimental data concluding statements regarding aromaticity are difficult to make.

The results of the theoretical study of the six-membered homocycles ($\lambda^3$-X)$_6$ (X = CH, N, P, As, Sb, Bi) and six-membered alternant heterocycles ($\lambda^3$-X- $\lambda^3$-Y)$_3$ (X, Y = CH, N, P, As, Sb, Bi) aromaticity (evaluated from the NICS criterion, the LUMO-HOMO gap and bond lengths equalization) outline the impossibility of using just one of the magnetic or reactivity based descriptors for the evaluation of heteroaromaticity.

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