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Assignment of Aromaticity of the Classic Heterobenzenes by Three Aromatic Criteria

Bo Hou^{a,b}, Pinggui Yi^{b,*}, Zhaoxu Wang^b, Shuqun Zhang^a, Jinhua Zhao^a, Ricardo L. Mancera^c, Yongxian Cheng^{a,*} and Zhili Zuo^{a,*}

^aState Key Laboratory of Phytochemistry and Plant Resources in West China, Kunming Institute of Botany, Chinese Academy of Sciences, Kunming 650201, China;

^bKey Laboratory of Theoretical Chemistry and Molecular Simulation of Ministry of Education, Hunan University of Science and Technology, Xiangtan, 411201, People's Republic of China;

^cSchool of Biomedical Sciences, CHIRI Biosciences, Curtin University, GPO Box U1987, Perth WA 6845, Australia

Abstract: Aromaticity is a key concept in physical organic chemistry. The aromatic order of the classic heterobenzenes was reported in experiment early. However, the unambiguous criteria used to validate the aromaticity of that were controversial or inadequate in theory. In this work, the global aromaticity of the compounds has been studied using the ELF, NICS and ISE. NICS(max)_{zz} was calculated based on the maximum NICS contribution to the out-of-plane zz tensor component. Two types of bonds are observed. The correlations between NICS(max)_{σzz} and NICS(max)_{πzz} with respect to aromaticity are demonstrated, specifically between NICS(max)_{πzz} and ELF_π (cc=0.98) for π bonds. For σ bonds, the different electron delocalization of σ bonds out of the plane of the ring predicted well the discrepancies between NICS(max)_{σzz} and ELF_σ. The σ aromatic order of the classic heterobenzenes (C₅H₅N > C₆H₆ >

* Corresponding author:

Prof. Dr. Zhili Zuo Tel./Fax: +86-871-65227196.

E-mail address: zuozhili@mail.kib.ac.cn

C₅H₅P > C₅H₅As > C₅H₅Bi, C₅H₅Sb) was proved *via* the level of electronic delocalization.

Keywords: NICS; ELF; Heterobenzenes; Global Aromaticity; π Aromaticity; σ Aromaticity

1. Introduction

A variety of chemical aromaticity indices have been developed on the basis of structural criteria, the harmonic oscillator model of aromaticity (HOMA)^[1-3] and ¹H NMR chemical shifts^[4], among others. The aromaticity or anti-aromaticity of a chemical compound defined using these indices is usually controversial.^[5-7] To have general applicability, the well-established definition of these concepts needs to be presented in a quantitative way.^[8-14] Aromaticity scales based on energy considerations have been developed, such as the aromatic stabilization energies (ASEs),^[15-18] which aims to measure the total stabilization energy of an aromatic ring by considering ring strain, hyperconjugation, differences in types of bonds, hybridization and the stabilization present in conjugated, non-aromatic systems. Ring strain and the presence of heteroatoms complicate the evaluation of ASEs and so the “isomerization method” was developed to consider the differences between the total energies of the methyl derivative of the aromatic system and its nonaromatic exocyclic methylene isomer, resulting in isomerisation stabilization energies (ISEs, correction = 0 kcal/mol, Scheme 1).^[19] Although analogues of heterobenzenes have been synthesized since the mid-16th century, the correspondence between aromatic character and electrons has not been fully characterised theoretically. In 2010, the

Ring Critical Points, the magnetic susceptibility exaltation and different NICS types were studied for hetero-benzenes of the group by Ebrahimi *et al.* Their observations confirmed magnetic and energetic criteria aromaticity were parallel in the present species.^[20] To further confirm the above conclusion, we also presented our investigation of the aromaticity of the classic heterobenzenes C₅H₅X (X=N, P, As, Sb and Bi) using the NICS(max)_{zz} and the “isomerization method”.^[21] Currently, however, the lack of correlation between σ bonds and π bonds was used for evaluation of aromaticity and has not been proved by other methods. We present here a solution to this problem, via analysis of the Electron Localization Function (ELF) used for studying on the inherent laws of different types of bonds, and comparison of their trend curves with the reported data.

The Electron Localization Function approach, based on properties of the electron delocalization defined by the ELF of Becke and Edgecombe,^[22,23] has been introduced to explain aromaticity.^[24,25] A separation of the ELF into σ and π components was shown to provide a useful scheme to discuss σ and π character in a molecular system.^[22,24] ELF is defined in terms of the excess of local kinetic energy density according to the Pauli exclusion principle, $T(\rho(r))$, and the Thomas-Fermi kinetic energy density, $T_h(\rho(r))$ ^[12]

$$\text{ELF} = \left[1 + \left(\frac{T(r)}{T_h(r)} \right)^2 \right]^{-1}$$

Both ELF_σ and ELF_π are defined as the ELF value at the relative bifurcation points that is the (3, -1) critical points (CPs) of the ELF basin that only contribute from different molecular orbitals (π orbitals or σ orbitals). The theoretical basis of these

indices is that the ELF value at the bifurcation point measures the interaction between adjoining ELF domains. A large ELF value indicates that electrons have a higher level of delocalization between these domains, which is commonly recognized as a feature of aromaticity. For typical organic compounds, if the average value of the sum of ELF_{π} and ELF_{σ} is larger than 0.70, then the molecule is globally aromatic.^[8] The dual values are defined as

$$ELF_{\pi} = \frac{\sum_{n=1}^{n_{\pi}} ELF_{\pi}}{n_{\pi}} \quad \text{and} \quad ELF_{\sigma} = \frac{\sum_{n=1}^{n_{\sigma}} ELF_{\sigma}}{n_{\sigma}}$$

Where n_{π} and n_{σ} are the total numbers of π orbital and σ orbital CPs in a molecule, respectively. According to Natural Localized Molecular Orbitals theory, $NICS(\max)_{\pi zz}$ and $NICS(\max)_{\sigma zz}$ can be derived separately as

$$NICS(\max)_{\pi zz} = \frac{\sum_{n=1}^{n_{\pi}} NICS(\max)_{\pi zz}}{n_{\pi}} \quad \text{and} \quad NICS(\max)_{\sigma zz} = \frac{\sum_{n=1}^{n_{\sigma}} NICS(\max)_{\sigma zz}}{n_{\sigma}}$$

The $NICS(\max)_{\pi zz}$ represents the zz tensor component of natural localized π molecular orbitals at the value of maximum NICS of the ghost atom position on the out of the ring center. The n_{π} is the number of π molecular orbitals. A similar definition for $NICS(\max)_{\sigma zz}$ is defined for σ bonds.

2. Methods and calculations

Fig. 1 shows the structures of the classic heterobenzenes investigated. Their geometries were fully optimized without imposing any symmetry constraints.^[26-28] The energies of the stationary points on the potential energy surface were calculated using the DFT (X3LYP) method^[29-31] in conjunction with the 6-311++G(d,p) and

LANL2DZ(d, p) (Los Alamos National Laboratory 2 double ξ) basis sets.^[32,33] The previous work indicated that the above basis sets can successfully be used in analysis of NICS indices.^[21,35] Employing an effective core potential (ECP) basis set such as LANL2DZ(d,p) or def2-TZVP for the X atom, while using all-electron basis sets for all other non-X atoms,^[35] was necessary for computations of the C_5H_5X (X=N, P, As, Sb, Bi) systems. The additional polarization functions have a more significant effect on the calculation of equilibrium geometries and accurate energies. At the stationary points, HF/[6-311++G(d,p) + LANL2DZ(d,p)] was used in the calculation of distributions of NICS using the NBO3.1 package^[36] as implemented in Gaussian 03, and then CCSD/[6-311++G(d,p) + LANL2DZ(d,p)] was used for better accuracy of the single-point calculation. Because the C_5H_5X molecules have small differences in ISEs, the different values of the electronic energies including both reactants and products (i.e. the isomerisation states) should be directly adopted by a high level of theory (CCSD method in this case). All the above calculations were carried out with the Gaussian03 package of programs.^[37] The σ and π orbitals were related to the σ and π delocalization by the corresponding critical points (CPs) values of ELF. The separate ELF_{average} , ELF_{σ} , and ELF_{π} were constructed with the Multiwfn2.4 software.^[38] In order to investigate the impact of basis sets, the relevant ELF were repeated at HF/6-311++G(3df,2pd) level for C_6H_6 , C_5H_5N and C_5H_5P compounds and at X3LYP/[6-311++G(d,p) + def2-TZVP]^[39-40] level for all molecules. Cartesian coordinates, energies for all stationary points and Details of the calculation of ELF are available in the Supporting Information.

3. Results and Discussion

3.1 Global aromatic character

Heterobenzenes have similar bond lengths, molecular orbitals, chemical stabilities and other properties. Ashe and co-workers reported many chemical properties of the classic heterobenzenes on the basis of spectral properties. They clearly demonstrated that a methine group of benzene can be replaced by isoelectronic nitrogen without disrupting its aromaticity to any significant extent.^[26] They also found that nonlocal chemical shifts were consistent with smaller ring currents from N to Bi and hence a lower aromaticity than benzene.^[41] However, the lack of a unique scale of aromaticity remains an essential limiting factor in providing a simplified assessment of aromaticity. The existence of a good linear correlation between ISEs and $\text{NICS}(\text{max})_{zz}$ allows a separate analysis of π bonds in terms of ELF and $\text{NICS}(\text{max})_{zz}$ to be readily carried out. Both Figs 2 and 3 show the existence of good linear relationships between $\text{NICS}(\text{max})_{zz}$ and ISEs and between $\text{ELF}_{\text{average}}$ and ISEs. Global aromaticity reflects the existence of a ring current which has important magnetic properties, such that the ghost-atom positions play a critical role in determining aromaticity.

A recent review also showed that the magnitude of the $\text{NICS}(\text{max})_{zz}$ tensor of heterobenzenes is markedly similar to both the molecular structure and the total number of valence electrons. The ^1H NMR spectra of stibabenzenes and bismabenzenes showed very low field signals for the α -protons due to the very large diamagnetic anisotropies of the Sb and Bi atoms.^[41,42] The α -proton chemical shift of

bismabenzene is larger (13.25 ppm) than that of stibabenzene (10.94 ppm),^[26] while the values of their corresponding NICS(max)_{zz} tensors are -25.264 and -25.721, respectively. It is important to take into account the magnetic properties of the relative heteroatom because they can influence the distribution of chemical shifts of α -protons.^[41] We note that the best fit curve of NICS(max)_{zz} vs ISEs (Fig. 2) fits the data somewhat differently to that of ELF_{average} vs ISEs. Comparing with ELF_{total}, we can directly resort to ELF_{average} as an efficient aromaticity probe, and hence it is applied here. Both tensor values of NICS(max)_{zz} and ELF_{average} are effective measurements for indices of aromaticity of the molecules studied in this work.

The delocalized p-MO in C₅H₅X renders its p-aromaticity according to the famous 4n+2 Hückel rule. As illustrated in Fig. 4, the main NICS(max) _{π zz} tensor of π orbitals including heteroatoms increase rapidly from -10.05 to -0.91, which is in agreement with the trend of α -proton shifts in experiment (e.g. the α -proton shift of C₅H₅Sb is less than that of C₅H₅Bi, 10.94 ppm < 13.25 ppm).^[41] The first and the third orbitals of the heteroatoms in red color indicate the estimated magnitude of the considerably inductive effects about the α -proton and β -proton.

3.2 The π and σ aromatic character

In order to establish adequately the determination of global aromaticity, the separation of the ELF into σ (ELF _{σ}) and π (ELF _{π}) contributions provided a useful scheme to assess the σ and π aromatic character in the molecules. Recently, the values of ELF_{average} (0.815), ELF _{σ} (0.717) and ELF _{π} (0.913) for benzene were reported by Santo *et al*^[42] and are in excellent agreement with our results (shown in **Table 1**).

When the -CH group in benzene is replaced by N, P, As, Sb or Bi atoms, whose covalent radii increases in that same order (C, 73 ppm; N, 71 ppm; P, 107 ppm; As, 119 ppm; Sb, 139 ppm and Bi, 148 ppm),^[43] the trend in atomic size is reflected in the bond lengths from N to Bi (C—C, 1.397 Å; C—N, 1.345 Å; C—P, 1.773 Å; C—As, 1.872 Å; C—Sb, 2.059 Å; C—Bi, 2.124 Å).^[26,27,43] With increasing C—X bond length, the interactions of π bonds will also decrease. Although the C—N bond length in pyridine is shorter than the C—C bond length in benzene, bifurcation of benzene indicated that the corresponding p_z — p_z orbitals have maximal overlap. This is clearly reflected in the values $ELF_{\pi}=0.913$ (benzene) > $ELF_{\pi}=0.909$ (pyridine). As can be seen in **Table 1**, the ELF_{π} value of benzene is larger than in the other members of this group, with the aromatic rings presenting high bifurcation values ranging from 0.913 to 0.879. These values indicate the highly aromatic character of this molecular system (Fig. 5). The same conclusions can be drawn upon analysis of both $NICS(\max)_{zz}$ and $NICS(\max)_{\pi zz}$.

It is interesting to note that the values of ELF_{σ} do not always agree with the values of $NICS(\max)_{\sigma zz}$ in the linear growth model, as shown in Fig. 6. When X is CH, N, P, As, Sb and Bi the corresponding ELF_{σ} and $NICS(\max)_{\sigma zz}$ follow each other with a trend analogous to the vibration of a harmonic oscillator.^[44] For benzene and pyridine, the different metrics used resulted in greater differences. In our opinion, three possible reasons to this disagreement as following: 1) The maximum point is on the center of the ring and the xx , yy and zz tensor of components all contribute to the isotropic $NICS(\max)$. This is only one point of the $NICS$ indices, so the differences

are most likely due to an inadequate representation of all σ bond magnetic properties.

2) The maximum point which represents $\text{NICS}(\text{max})_{zz}$ at the ring center is far away from the σ bonds and both the bond lengths of C—C (1.397 Å) and C—P (1.773 Å) are longer than that of C—N (1.345 Å), resulting in the σ bonds becoming weaker and increasing the difference in the two metrics. 3) It is well known that the use of pseudopotentials can affect the ELF structure. The present study demonstrates that the basis sets give rise to large errors, such as the combination of 6-311++G(d,p) and LANL2DZ(d,p) at HF level (As evident in Fig. S2, Supporting Information). Analysis of the error line shows the components of ELF_σ need σ bonds need more inner shell electrons. It indicates that the values of ELF_σ are strongly influenced by using inconsistent pseudopotentials level. Theoretically, the more negative values of $\text{NICS}(\text{max})_{\sigma zz}$ are the more positive the values of ELF_σ . So both of 6-311++G(d,p) and LANL2DZ(d,p) are inappropriate or insufficient basis sets to study σ -bonds in the heterobenzenes system. As the red trace showed in Fig. 6, the calculation using 6-311++G(3df,2pd) basis set is consistent with the trend of $\text{NICS}(\text{max})_{\sigma zz}$.

To visualize the σ delocalization on the plane across $\text{C}_5\text{H}_5\text{As}$, $\text{C}_5\text{H}_5\text{Sb}$ and $\text{C}_5\text{H}_5\text{Bi}$ compounds, the contour maps of ELF_σ were calculated, which is characterised by the white regions on each molecular plane shown in Fig. 7. The upper region represents the heteroatom and the other one is located at the center of the heterocycle. The regions indicate that the delocalization of ELF_σ is zero regions. For $\text{NICS}(\text{max})_{\sigma zz}$, the adjacent grey regions increase between the two white regions when comparing $\text{C}_5\text{H}_5\text{Sb}$ with $\text{C}_5\text{H}_5\text{As}$, while the other regions decrease gradually from

C₅H₅As to C₅H₅Sb in the center of the ring, leading to an increase in the values of NICS(max)_{σzz} (C₅H₅Sb, -1.297 > C₅H₅As, -2.170). The depth of the grey regions seems decrease on the plane of C₅H₅Bi in the center of the ring, and these regions expand to both left and right. This leads to a low value of NICS(max)_{σzz} and is slightly lower than that of C₅H₅As [C₅H₅Sb (-1.297) > C₅H₅As (-2.170) and C₅H₅As (-2.170) > C₅H₅Bi (-2.185)]. For ELF_σ, the delocalization of the σ bond regions is clearly reduced.^[44] The blue area of C₅H₅Bi is smaller than the others. C₅H₅Sb has the greatest gray area as shown by the arrow in Fig. 7, resulting in the values of ELF_σ gradually decreasing from C₅H₅Bi to C₅H₅Sb [C₅H₅As (0.667) > C₅H₅Bi (0.636) ≅ C₅H₅Sb (0.625)]. In short, all the values of NICS(max)_{σzz} were negative, which indicates that the σ bonds of C₅H₅X molecules have σ aromatic character. The bifurcation in ELF_σ also succeeds in indicating the σ aromatic character of the classic heterobenzenes.

4. Conclusions

The ELF and NICS methods were used to characterize σ, π and global aromaticities of the nonmetallic and semi-metallic aromatic compounds of the classic heterobenzenes. These molecules were well characterized by linear relationships between the ELF and NICS metrics. The values of the σ bonds revealed their aromatic character, which is lower than that of the π bonds. ELF_π and NICS(max)_{πzz} were easily and efficiently applied to determine the overall aromatic character of the molecules. There was also excellent qualitative agreement with the electrons for maximum delocalization. The global aromatic order of the classic heterobenzenes

($C_6H_6 > C_5H_5N > C_5H_5P > C_5H_5As > C_5H_5Sb > C_5H_5Bi$) was revealed by calculation. For the σ bonds of C—X, the traces of ELF displayed the flip-up tendency and calculations of ELF_σ and $NICS(max)_{\sigma zz}$ permitted overall assignment of the σ aromatic character for all molecules.

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Scheme 1. The isomerisation stabilization energies were calculated by the nonaromatic isomer of the methyl derivative of the aromatic system.

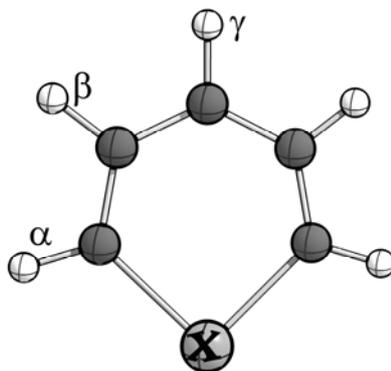


Fig. 1. The classic heterobenzenes investigated and their respective symmetry point groups. From left to right: benzene (C_6H_6 , D_{6h}), pyridine (C_5H_5N , C_{2v}), phospho-benzene (C_5H_5P , C_{2v}), arsa-benzene (C_5H_5As , C_{2v}), stiba-benzene (C_5H_5Sb , C_{2v}) and bisma-benzene (C_5H_5Bi , C_{2v}).

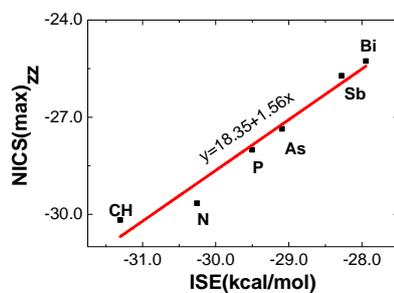


Fig. 2. Plot of the isomerization stabilization energies computed by the CCSD method vs the zz tensor component of NICS(max) as computed by the HF method for the set of six-membered heterocycles C_5H_5X (X = as shown, $cc=0.98$).

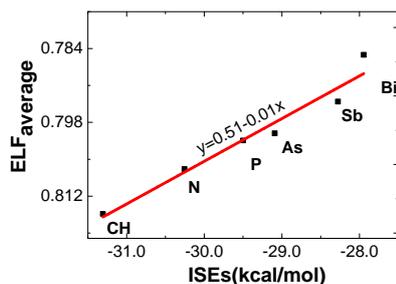


Fig. 3. Plot of the isomerization stabilization energies computed by the CCSD method vs the $ELF_{average}$ as computed by the HF method for the set of six-membered heterocycles C_5H_5X ($X =$ as shown, $cc=0.98$).

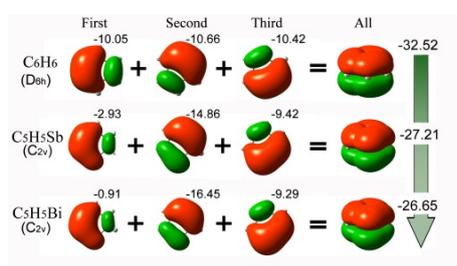


Fig. 4. The π orbitals to $NICS(max)_{\pi ZZ}$ tensor of benzene, stibabenzene and bimabenzene (Unit: the negative value of tensor).

Table 1

Computed values of $ELF_{average}$, ELF_{π} , ELF_{σ} , $NICS(max)_{ZZ}$, $NICS(max)_{\pi ZZ}$, $NICS(max)_{\sigma ZZ}$, and ISE^a ($kcal \cdot mol^{-1}$).

Molecules	ELF_{total}^b	$ELF_{average}^b$	ELF_{π}^b	ELF_{σ}^c	$NICS(max)_{ZZ}^b$	$NICS(max)_{\sigma ZZ}^b$	$NICS(max)_{\pi ZZ}^b$	ISE
C_6H_6	18.398	0.815	0.913	0.687	-30.173	-2.224	-32.522	-31.31
C_5H_5N	18.138	0.807	0.909	0.702	-29.657	-5.527	-31.579	-30.26
C_5H_5P	18.152	0.801	0.892	0.680	-28.007	-2.448	-29.390	-29.50
C_5H_5As	18.145	0.800	0.888	0.667	-27.361	-2.170	-28.706	-29.09
C_5H_5Sb	18.003	0.794	0.882	0.625	-25.721	-1.297	-27.211	-28.28
C_5H_5Bi	17.821	0.788	0.879	0.636	-25.264	-2.185	-26.652	-27.95

^aThe energies of the six-membered heterocycle compounds were calculated, with the difference of *anti-syn* diene mismatches using a correction=0 scheme being in good agreement with experimental values. ^bCalculated ELF_{total} , $ELF_{average}$, ELF_{π} , $NICS(max)_{ZZ}$, $NICS(max)_{\pi ZZ}$ and $NICS(max)_{\sigma ZZ}$ at HF/[6-311++G(d,p) + LANL2DZ(d,p)] level. ^cCalculated ELF_{σ} at HF/[6-311++G(d,p) + LANL2DZ(d,p)] level.

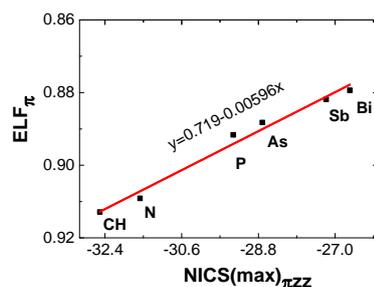


Fig. 5. Plot of the average values of $\text{NICS}(\text{max})_{\pi ZZ}$ vs the average values of ELF_{π} as computed by the HF method ($\text{cc}=0.98$).

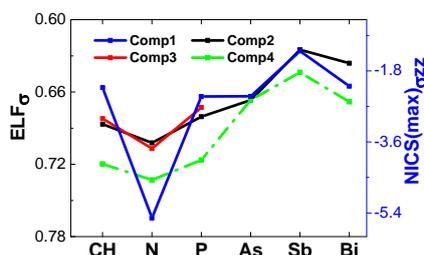


Fig. 6. HF and X3LYP methods with different basis sets are used for the study of the relationship between $\text{NICS}(\text{max})_{\sigma ZZ}$ (blue line) and ELF_{σ} (other lines). [—Comp1 at HF/[6-311++G(d,p) + LANL2DZ(d, p)] level; —Comp2 at HF/[6-311++G(d,p) + def2-TZVP] level; —Comp3 at HF/6-311++G(3df,2pd) level for C_6H_6 , $\text{C}_5\text{H}_5\text{N}$ and $\text{C}_5\text{H}_5\text{P}$; —Comp4 at X3LYP/[6-311++G(d,p) + def2-TZVP] level].

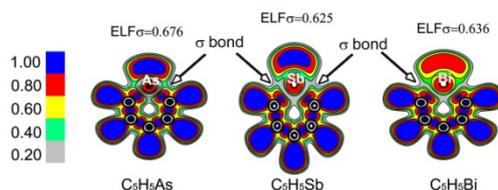


Fig. 7. ELF_{σ} bifurcation of the arsa-benzene ($\text{C}_5\text{H}_5\text{As}$), stiba-benzene ($\text{C}_5\text{H}_5\text{Sb}$) and bisma-benzene ($\text{C}_5\text{H}_5\text{Bi}$) in molecular planes at the HF/[6-311++G(d,p) + def2-TZVP] level.