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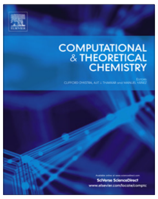

Assignment of aromaticity of the classic heterobenzenes by three aromatic criteria

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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 $NICS(max)_{\sigma zz}$ and $NICS(max)_{\pi zz}$ with respect to aromaticity are demonstrated, specifically between $NICS(max)_{\pi zz}$ 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 $NICS(max)_{\sigma zz}$ and ELF_σ. The σ aromatic order of the classic heterobenzenes ($C_5H_5N > C_6H_6 > C_5H_5P > C_5H_5As > C_5H_5Bi$, C_5H_5Sb) was proved *via* the level of electronic delocalization.

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 analogs of heterobenzens have been synthesized since the mid-16th century, the correspondence between aromatic character and electrons has not been fully characterized theoretically. In 2010, the Ring Critical Points, the magnetic susceptibility exaltation and different NICS types were studies 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 C_5H_5X (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

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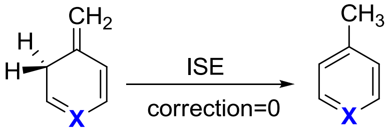

Scheme 1. The isomerisation stabilization energies were calculated by the nonaromatic isomer of the methyl derivative of the aromatic system.

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]

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

Both ELF$_\sigma$ and ELF$_\pi$ 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. The dual values are defined as

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

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

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

$$\mathrm{NICS(max)}_{\sigma zz} = \frac{\sum_{n=1}^{n_\sigma} NICS(\mathrm{max})_{\sigma zz}}{n_\sigma}$$

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. Miroslav et al. reported the outer-core region within the analysis of ELF, which can reveal valuable information about the participation of the inner-shell electrons in chemical bonding [26]. The average values of bonds imply the character of aromaticity, such as HOMA rule. ELF may be preferable to explain bonding character. Unfortunately, by comparison with NICS, a positive or a negative value cannot be obtained from the ELF method to judge aromaticity or anti-aromaticity. Empirical judgment thus plays a key role in the procedure. For typical organic compounds, if the average value of the sum of ELF$_\pi$ and ELF$_\sigma$ is larger than 0.70, then the molecule is globally aromatic [8].

2. Methods and calculations

Fig. 1 shows the structures of the classic heterobenzenes investigated. Their geometries were fully optimized without imposing any symmetry constraints [27–29]. The energies of the stationary points on the potential energy surface were calculated using the DFT (X3LYP) method [30–33] in conjunction with the 6-311++G(d,p) and LANL2DZ(d,p) (Los Alamos National Laboratory 2 double ξ) basis sets [33,34]. 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 [36], 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 [37] 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 [38]. 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$_{\mathrm{average}}$, ELF$_\sigma$, and ELF$_\pi$ were constructed with the Multiwfn2.4 software [39]. 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] [40,41] level for all molecules. Cartesian coordinates, energies for all stationary points and details of the calculation of ELF are available in the Supporting Information.

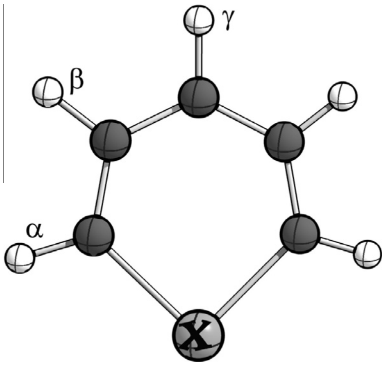

Fig. 1. The classic heterobenzenes investigated and their respective symmetry point groups. From left to right: benzene (C_6H_6, D_{6h}), pyridine (C_5H_5N, C_{2v}), phospha-benzene (C_5H_5P, C_{2v}), arsa-benzene (C_5H_5As, C_{2v}), stiba-benzene (C_5H_5Sb, C_{2v}) and bisma-benzene (C_5H_5Bi, C_{2v}).

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 [27]. They also found that nonlocal chemical shifts were consistent with smaller ring currents from N to Bi and hence a lower aromaticity than benzene [42]. 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 NICS(max)$_{zz}$ allows a separate analysis of π bonds in terms of ELF and NICS(max)$_{zz}$ to be readily carried out. Both Figs. 2 and 3 show the existence of good linear relationships between NICS(max)$_{zz}$ and ISEs and between ELF$_{\mathrm{average}}$ 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.