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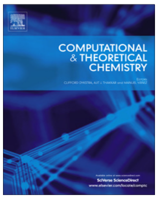

A study on the influence of intramolecular O—H···X (X = O and S) hydrogen bond formation on the aromaticity of heptafulvene derivatives, in which the methylene is replaced by AlH_2^-, BH_2^-, NH and O groups

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ABSTRACT

The influence of the intramolecular O—H···O and O—H···S hydrogen bond on the aromaticity of some heptafulvene derivatives, in which the methylene group is replaced successively by AlH_2^-, BH_2^-, NH and O groups, is investigated using magnetic (NICS(0), NICS(1) and $NICS(1)_{zz}$), geometrical (HOMA) and electronic (FLU and SA) criteria to consider the multidimensional character of aromaticity. It is found that the formation of intramolecular hydrogen bond changes aromatic character of heptafulvene derivatives. The variations of NICS indices due to the formation of intramolecular H-bonding significantly correlate with the properties of the considered hydrogen bonds, while the other indices do not give any meaningful results. It seems that the hydrogen bond influences the magnetic dimension of aromaticity in heptafulvenes. The influence of the O—H···O and O—H···S hydrogen bond on the aromaticity of these rings are also compared with each other.

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1. Introduction

Fundamental role of aromaticity in the current chemistry is undeniable. It is an important and useful concept in explaining the structures, stabilities, and reactivity of different molecules. [1]. Usually, aromaticity refers to electronic cyclic delocalization, which exists in all aromatic species and causes extra stabilization in this type of compounds [2]. Since this concept is not a directly observable quantity, it is usually evaluated indirectly by measuring a property that reflects the aromatic character of the whole or parts of the molecule. Thus the evaluation of aromaticity is usually performed by analyzing its different manifestations, including geometrical, electronic and magnetic dimensions, whereas most indices focus on just one aspect. On the other hand, the formation of intramolecular hydrogen bond is responsible for various molecular features and has a very pronounced effect on molecular structure and properties [3–5]. Furthermore, the intramolecular hydrogen bond has been subjects of many experimental as well as theoretical studies [6–9].

Heptafulvenes, unsaturated rings with one exocyclic C═C double bond, have intrigued chemists for several decades, especially in the context of the concept of aromaticity [10–15]. The substituted fulvenes represent an interesting group of systems for a systematic study of the extent of changes in the cyclic π-electron delocalization due to intramolecular interactions. Aromaticity of the fulvene rings depend on the electronic character of the exo-substituent. According to the unique cross conjugated structure, which can generate both (4n + 2) and (4n) π-electron species via bond polarization (See Scheme 1).

Recently Oziminski et al. investigated the effect of aromatization of pentafulvenes on the strength of intramolecular H-bonding [16]. Furthermore the impact of intramolecular H-bonding on the aromatic character of substituted pentafulvenes is also reported. It is found out that the hydrogen bond formation influences on the geometrical and electronic dimensions of aromaticity in substituted pentafulvenes [17]. It seems that intramolecular hydrogen could be also effected on the aromatic character of heptafulvenes. The main contribution of the present study is to explore the evolution of the aromaticity of some heptafulvene derivatives, in which the methylene group is replaced successively by AlH_2^-, BH_2^-, NH and O groups, as a function of intramolecular O—H···X (X = O and S) hydrogen bond formation. This study has been performed on the

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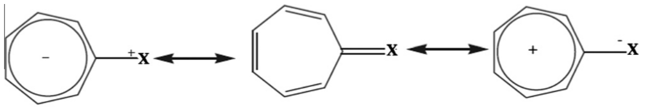

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Scheme 1. Canonical structures of hepta-fulvene.

basis of various aromaticity indices to consider the multidimensional character of aromaticity. Moreover the impact of O—H⋯O and O—H⋯S intramolecular hydrogen bonds on the aromatic character of the considered molecules are compared with each other.

2. Computational details

In this study different aromaticity indices are evaluated for the considered systems to investigate the aromaticity evolution upon intramolecular H-bonding formation. These indices are explained as follow.

Nucleus-Independent Chemical Shift (NICS) [18] as a magnetic-based aromaticity index is defined as the negative value of the absolute shielding calculated at the center of ring (NICS(0)). Also NICS(1) is defined as the negative value of the absolute magnetic shielding at 1 Å over the ring plane. Moreover the component of the shielding tensor perpendicular to the plane of the molecule ($\mathrm{NICS}(1)_{zz}$), is another NICS-based index of aromaticity [19]. The negative and positive NICS values denote aromatic and antiaromatic characters, respectively.

The Harmonic Oscillator Model of Aromaticity (HOMA) is applied as a conventional geometrical-based index, which is defined as [20]:

$$\mathrm{HOMA} = 1 - \left[\frac{\alpha}{n}\sum_{i=1}^{n}(R_{opt} - R_{av})^2\right] \tag{1}$$

where n is the number of considered bonds in the summation, R_{av} is the average bond length and α is a normalization constant (for C—C bonds $\alpha = 257.7$), fixed to give HOMA = 0 for a model of non-aromatic system and HOMA = 1 for the system with all bonds equal to the optimum value assumed to be achieved for fully aromatic system (for C—C bond $R_{opt} = 1.388$ Å).

The aromatic fluctuation index (FLU) [21] is an electronic-based index, in which considers the amount of electron sharing between contiguous atoms as well as considering the similarity of electron sharing between adjacent atoms. For a ring with N atoms, which the elements are ordered according to the connectivity of the atoms in the ring ($A = \{A_1, A_2, \ldots, A_N\}$), the FLU index is defined as follow:

$$\mathrm{FLU}(A) = \frac{1}{N}\sum_{i=1}^{N}\left[\left(\frac{V(A_i)}{V(A_{i-1})}\right)^{\alpha}\left(\frac{\delta(A_i, A_{i-1}) - \delta_{ref}(A_i, A_{i-1})}{\delta_{ref}(A_i, A_{i-1})}\right)\right]^2 \tag{2}$$

where $A_0 = A_N$, $\delta(A,B)$ denotes the delocalization index value between atoms A and B, and $V(A_i) = \sum_{A_j \neq A_i}\delta(A_i, A_j)$ is the atomic valence that for a closed shell system. Also α is 1 and -1 when $V(A_i) > V(A_{i-1})$ and $V(A_i) \leqslant V(A_{i-1})$, respectively, to ensure that the first term in Eq. (3) is always greater or equal to unity. Note that $\delta_{ref}(C,C) = 1.389$, which is obtained for benzene as reference at the B3LYP/6-311++G(d,p) level of theory. FLU close to zero indicates the aromatic character, and differs from, denotes nonaromatic one.

Shannon Aromaticity (SA) as another electronic-based aromaticity descriptor is defined as [22]:

$$\mathrm{SA} = 100\left[\ln(N) - \sum_{i=1}^{N}(p_i)\ln(p_i)\right] = 100(S_{\max}(r_c) - S_{\mathrm{total}}) \tag{3}$$

in which N is the number of considered bond critical points (BCPs) in the ring and p_i, which is defined as $p_i = \frac{\rho_i(r_c)}{\sum \rho_i(r_c)}$, is the normalized probability electron density ($\rho_i(r_c)$) at the ith BCP. The SA index for a given molecule is a measure of spatial localization of electron density and therefore less SA values are related to more aromatic molecule. The range of $0.300 < \mathrm{SA} < 0.500$ is also considered as the boundary between aromatic and anti-aromatic compounds; i.e. non-aromatic systems.

It is well-known that for the O—H⋯X intramolecular H-bonding, where O-H is the proton-donating bond and X (X = O and S) is an accepting center, the electron density of the H⋯X bond critical point ($\rho_{\mathrm{H \cdots X}}$) seems to be a reliable descriptor of the H-bonding strength [23]. The more $\rho_{\mathrm{H \cdots X}}$ at BCP as well as less hydrogen bond length ($R_{\mathrm{H \cdots X}}$) imply to stronger H-bonding. It is noticeable that the estimation of the overall energy associated with the intramolecular H-bond formation (E_{tot}) could be also computed using the so-called cis–trans method [24] as:

$$E_{tot} = E(\mathrm{closed}) - E(\mathrm{open}) \tag{4}$$

where E_{tot} indicates the total energy of the intramolecular hydrogen bond, whereas E(closed) and E(open) are the energies obtained after the geometry optimization procedures for closed and open conformations.

Previously it is reported that the influence of intramolecular H-bonding formation on the aromaticity could be investigated using the overall variation of each aromaticity index associated with the intramolecular H-bonding formation (AI_{HB}) which could be computed as follow:

$$AI_{HB} = AI(\mathrm{closed}) - AI(\mathrm{open}) \tag{5}$$

where AI(closed) and AI(open) are the each aromaticity index obtained after the geometry optimization for the closed and open conformations, respectively [17].

In this study, a set of 3-hydroxy-4-formylo and 3-hydroxy-4-thioylo heptafulvene derivatives, in which the CH_2 group is replaced by AlH_2^-, BH_2^-, NH and O groups as different substituents, in both closed and open forms are selected. It should be mentioned that the charged AlH_2^- and BH_2^- substituents are stronger electron-donating substituent than neutral BH and AlH ones. The geometries of all considered compounds are fully optimized using B3LYP method [25,26] and 6-311++G(d,p) [27–29] basis set and the nature of the stationary points are checked by frequency analysis at the same computational level. Moreover the NICS values are obtained from the NMR calculations at the HF/6-311++G(d,p) level of theory using the gauge-independent atomic orbital (GIAO) [30] formalism at the corresponding ring critical points. All calculations are performed using Gaussian 03 program [31]. All SA, FLU and HOMA aromaticity indices together with AIM analysis are obtained using the electronic wave functions and MULTIWFN user-friendly software [32].

3. Results and discussion

The canonical structures of heptafulvene are depicted in Scheme 1. The relative weights of the different resonance structures of heptafulvenes depend on the electronegativity of the X substituent. Following the Hückel 4n + 2 rule, more electronegative substituents increase the weight of 6π-electron resonance form of the seven-membered ring, which cause an increase in aromaticity. Hence for the considered compounds (see Scheme 1) a reliable aromaticity index should give the following order of aromaticity of these structures according to their substitutes as $AlH_2^- < BH_2^- < CH_2 < NH < O$.

In this part the influence of O—H⋯O intramolecular hydrogen bond formation is investigated. The optimized geometries of the

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