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A Comparative DFT Study on the Impact of Heteroatom (O, N, and S) Variation on Aromatic Character

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Abstract: ***Aromaticity cannot be measured or quantified directly by a single experiment. However, theoretical methods are used to assess aromaticity based on different magnetic, electronic, energetic, and structural indices. The aim of this study is to analyze, how the substitution of carbon with heteroatoms like O, N, and S effect the aromaticity of the cyclic conjugated systems. In the present DFT study, 28 considered systems are fully optimized using B3LYP/6-31G(d) basis set. NICS and HOMA indices were used to measure and quantify aromaticity, based on magnetic and structural criteria of the molecules. NICS and HOMA correlate well and provide reliable results. In our calculations, benzene shows the highest aromatic character. Five membered rings with heteroatom exhibit aromaticity while four membered cyclic system shows the anti-aromatic character. Furthermore, fused systems show high aromatic character and enhanced stability due to the delocalization of π-electrons. In three-ring fused system the middle ring shows anti-aromatic or slight aromatic character and outer ring exhibit higher aromatic character. This study provides better insights of aromaticity at undergraduate level to build the concept, enhance the quality of education, and deep understanding of this hypothetical concept.***

Keywords: Aromaticity, Anti-aromaticity, HOMA, NICS, Resonance, Theoretical Study

1. Introduction

Aromaticity is a key concept that accounts for the exceptional stability of cyclic conjugated systems resulting from the delocalization of π electrons over the molecular framework. It describes the stability induced by π-electron delocalisation of cyclic conjugated systems [1]. Despite its significance, there is no single clear definition of aromaticity, and it can be described using different models such as those of Hückel, which uses the (4n+2) rule, Mobius-aromaticity, metallo-aromaticty, etc [2,3]. In terms of calculating whether a planar cyclic system is aromatic or anti-aromatic, a planar cyclic system is said to be aromatic if it possesses (4n+2) number of π-electrons and antiaromatic if number of π-electrons are 4n (where, n = 0, 1, 2, ...). Aromaticity cannot be measured directly, but can be evaluated by means of theoretical indices that are derived from the magnetic, electronic, geometric, and energetic properties of the molecule [4-9]. Aromaticity is a multi-dimensional property, and to provide a reliable evaluation of aromaticity the use of various indices should be utilised. For example, magnetic criteria such as NICS (Nucleus independent chemical shift) can be used to measure ring currents in a sample of a molecule, with negative NICS values indicating aromatic character. Geometric criteria such as HOMA (Harmonic Oscillator Model of Aromaticity) can be used to measure how evenly distributed the bond lengths of the molecules are, which reflects the extent of the delocalisation of electrons. DFT is widely used for the evaluation of the indices that quantifies aromaticity due to its efficiency and accuracy in computations [10]. It is particularly beneficial when studying heterocyclic systems where aromaticity is difficult to evaluate experimentally. The addition of heteroatoms (N, O, and S) can change the degree of aromaticity due to differences in electronegativity and orbital overlaps [11-15]. Generally, nitrogen increases delocalisation, whereas oxygen and sulphur tend to decrease delocalisation. The objectives of the current study are as follows:

- To understand the concept of aromaticity in cyclic conjugated systems at the undergraduate level using computational approach.
- To measure and quantify aromaticity using two different aromatic indices, viz., NICS and HOMA.
- To analyze how the substitution of carbon with heteroatoms (N, O, and S) effect the stability and aromatic character of the cyclic conjugated systems.
- To validate the multidimensional property of aromaticity using theoretical approach.

2. Methodology

Becke three parameter hybrid and Lee-Yang-Parr correlation functional (B3LYP) based DFT calculations was used to geometry optimize all the 28 systems using the 6-31G(d) basis set [16-18]. The 6-31G(d) basis set contains polarization functions, which accurately describes how the electrons of the atom are distributed and the molecular geometries of the considered systems. The magnetic criterion of aromaticity was calculated using the calculation of NICS. It measures the negative of the absolute magnetic shielding. It was calculated by introducing a ghost atom (Bq) at a specific position relative to the ring centre and by performing the NMR calculation. In the present study, we calculated NICS(0), NICS(1), and $NICS(1)_{zz}$. The geometric criterion of the aromaticity was measured using HOMA. Unlike magnetic criteria, it is based on bond length equalization. It was calculated using formula:

HOMA $=1-\frac{\alpha}{n}\sum (R_{opt} - R_i)^2$

where, n is the number of bonds, α is a normalizing constant, R_{opt} represent ideal bond length and R_i is the optimized bond length. The optimized bond distance (R_i) for different types of bonds such as C-C, C-N, C-O, C-H within the particular ring system were extracted from the optimized output file. The values of R_{opt} and α for different bonds as mentioned in Table 1 were taken from the literature value [1]. HOMA were calculated by substituting the values of all the parameter in the above equation. All these calculations were done using MS-Excel. All DFT calculations were performed using the Gaussian 09 software.

Table 1: HOMA parameters for different bonds from ref. [1]

S. No.	Bond Type	R_{opt}	α
1	C-C	1.388	257.7
2	C-N	1.334	93.52
3	C-O	1.265	157.38
4	C-S	1.677	94.09

3. Results and Discussion

Total 28 molecules are selected in the present study to understand the concept of aromaticity. Four, five, six, seven membered rings, and fused rings as represented in Figure 3.1 are considered for the calculations. One of the C atoms is replaced by N, O, and S atom to see the effect of heteroatom on aromaticity. The aromatic character of the studied system was evaluated using two aromaticity indices, viz., NICS and HOMA. Since aromaticity cannot be explained using single index, a combination of magnetic and geometric criteria was used to provide the more reliable results.

3.1 HOMA Analysis of Selected Systems

All the HOMA values calculated using the formula mentioned under methodology section are presented in Figure 1. The optimized geometries of all the molecules along with selected bond lengths are depicted in Figure 2a and 2b. HOMA values are used to quantify aromaticity based on geometry criteria. HOMA values range from 0 to 1. The values close to zero show non-aromatic character and values close to 1 show highly aromatic character whereas negative values show anti-aromatic character.

In four membered heterocyclic **(1-4),** they show the most negative HOMA values, these values indicate high anti-aromaticity. These are the 4n electrons systems and show severe Bond Length Alternation (BLA), this result in rectangular geometry to minimize electronic destabilization. The introduction of heteroatoms such as (N, O, S) result in less negative HOMA values. These heteroatoms disrupt the anti-aromatic delocalization, and hence reduced the anti-aromatic character.

In five- membered heterocyclic **(5-8)**, aromatic character is primarily influenced by the size, electronegativity, and lone-pair availability of the heteroatom. According to HOMA values five- membered heterocyclic show order: Pyrrole > thiophene > furan. Pyrrole exhibit the highest aromatic character in this group, as nitrogen is sp^2 hybridised so its lone pair occupies p orbital, allowing effective participation in the delocalisation results in an aromatic sextet. Thiophene shows moderate aromaticity due to the lower electronegativity of sulphur, but due to its large atomic radii its orbitals are slightly diffused and induces slight geometric mismatch. Furan exhibits lowest HOMA value due to high electronegativity of oxygen. The oxygen atom holds its lone pair tightly, result in more localized electron density and show high bond length alteration.

In six-membered heterocyclic system **(9-12),** the benzene and pyridine both show HOMA values near 1.0 and represent the high aromatic character, ideal bond lengths, and complete delocalisation. They show ideal aromaticity due to high planarity as they have the perfect 120° bond angles for sp^2 hybridization. In contrast, Thiopyrylium **(12)** shows significant negative value which highlights the geometric alteration due to the large sulphur atom within a six-membered framework, which convert the aromatic character into anti-aromatic character.

Seven-membered heterocyclic systems **(13-16)** show HOMA values close to zero or even negative, indicating weak or non-aromatic character. It is because seven-membered rings often adopt non-planar (boat-like) conformations to avoid anti-aromaticity due to 8π electrons. Due to this loss of planarity, the π electron delocalisation disturbed that result into bond alteration and is effectively captured by the HOMA index.

In fused and polycyclic systems **(17-28)**, naphthalene analogues **(21-24)** show the HOMA index (> 0.7), highlights the effective delocalization across the bicyclic system. In five-six fusion ring systems **(17-20)**, asymmetry in aromaticity is observed. The benzene ring (0.686) retains more aromatic character than the furan ring, this is because the more stability attributed to benzenoid structures. In tricyclic Systems **(25-28)**, fluorene-type structures, the outer six-membered rings show highly aromatic character while the central ring often exhibits anti-aromatic or weakly aromatic character. This is because the outer ring tries to retain the benzenoid stability and hence result in redistribution of electron density that alter the delocalisation with in the ring.

3.2 NICS analysis of selected heterocyclic systems

In four membered heterocycle compounds (**1-4**), NICS(0), NICS (1) and NICS $(1)_{zz}$ values show that O and S containing compounds show slight aromatic character while the N containing compound show anti-aromatic character (refer Table 2, 3 and 4).

The behaviour of nitrogen containing compound (Azete '2') can be explained on the basis of Hückel's rule as it has 4π electrons. Here, the nitrogen is sp^2 hybridised and hence, its lone pair is localized and doesn't participate in delocalisation. As it follows the 4n rule, it is highly unstable and show anti-aromatic character. O and S containing compound (Oxete '3' and Thiete '4') are also 4π electrons system and are non-aromatic in nature but the slight aromatic character is shown by them. It can be due to σ contribution or orbitals interaction. Unlike azete, the lone pair present on oxygen and sulphur are not localised and they can interact partially with the π system. Moreover, the 3p orbitals in sulphur are slightly diffused which can overlap with the p orbitals of carbon in steric system like thiete and result in slight aromatic character.

In five-membered heterocycles (**5-8**), NICS parameter such as NICS(0), NICS(1), and NICS(1)$_{zz}$ show negative values for systems. Hence, they exhibit aromatic character (refer Table 2, 3 and 4). Cyclopentadiene is non-aromatic in nature due to the presence of sp^3 hybridised carbon, as they break the conjugation in a system. But the result shows aromatic character, it may be observed due to hyperconjugation or σ aromaticity. The C-H bond can exhibit pseudo resonance in the system due to hyperconjugation as it can donate the electron density to empty p orbital of carbon. The C-C and C-H σ bond can interact with the π electron system of the C=C bond. This result in σ aromaticity. The continuous movement of σ electron can induce a diamagnetic ring current, results in negative NICS value. The trend in aromaticity follows the order: thiophene > pyrrole > furan.

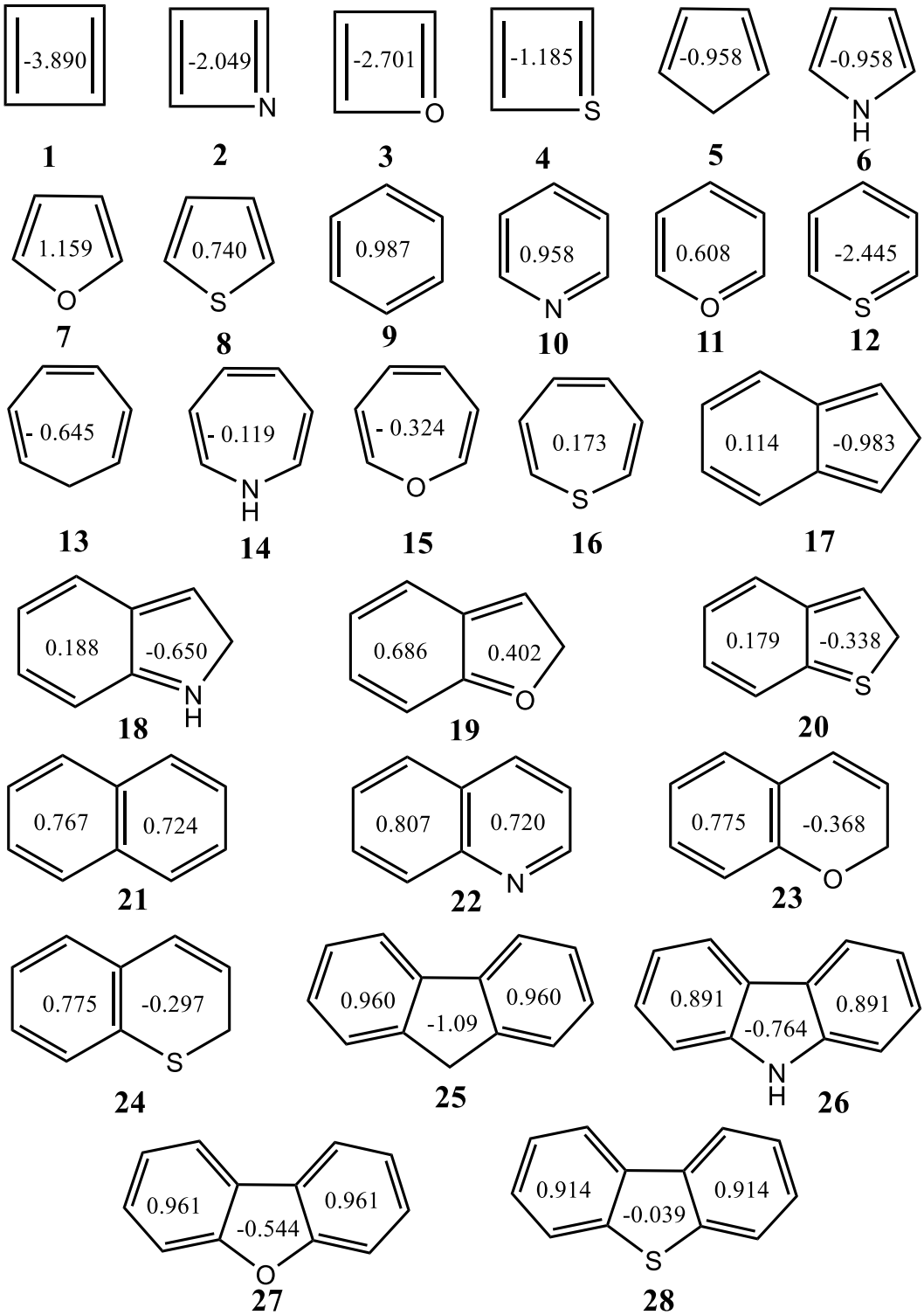

Figure 1: Structures of the 28 heterocyclic systems investigated in the study with HOMA values

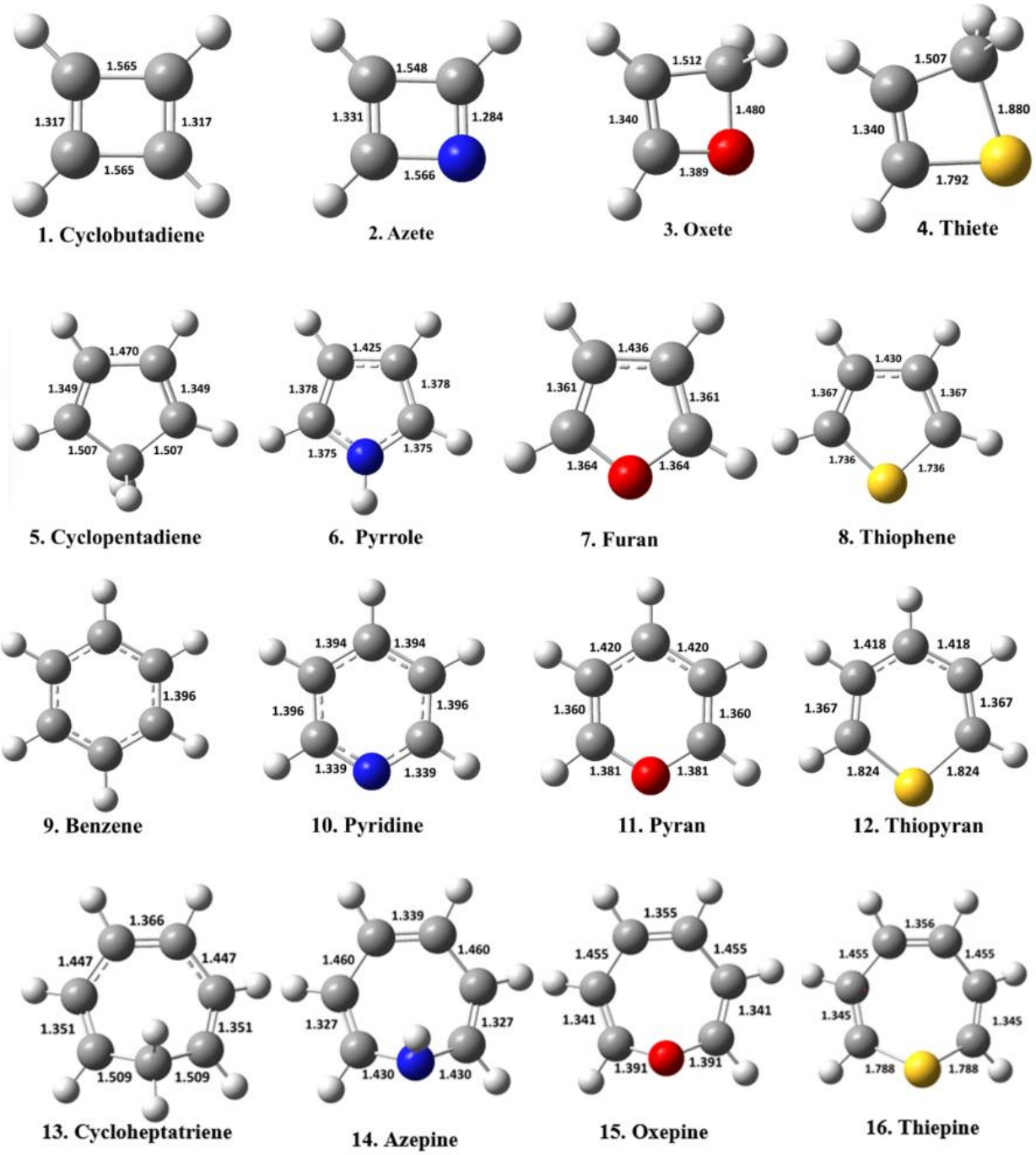

Figure 2a: Optimized geometries of the molecules (1-16) with selected bond lengths used for HOMA calculations (Color code: Grey: C, White: H, Blue: N, Red: O, Yellow: S)

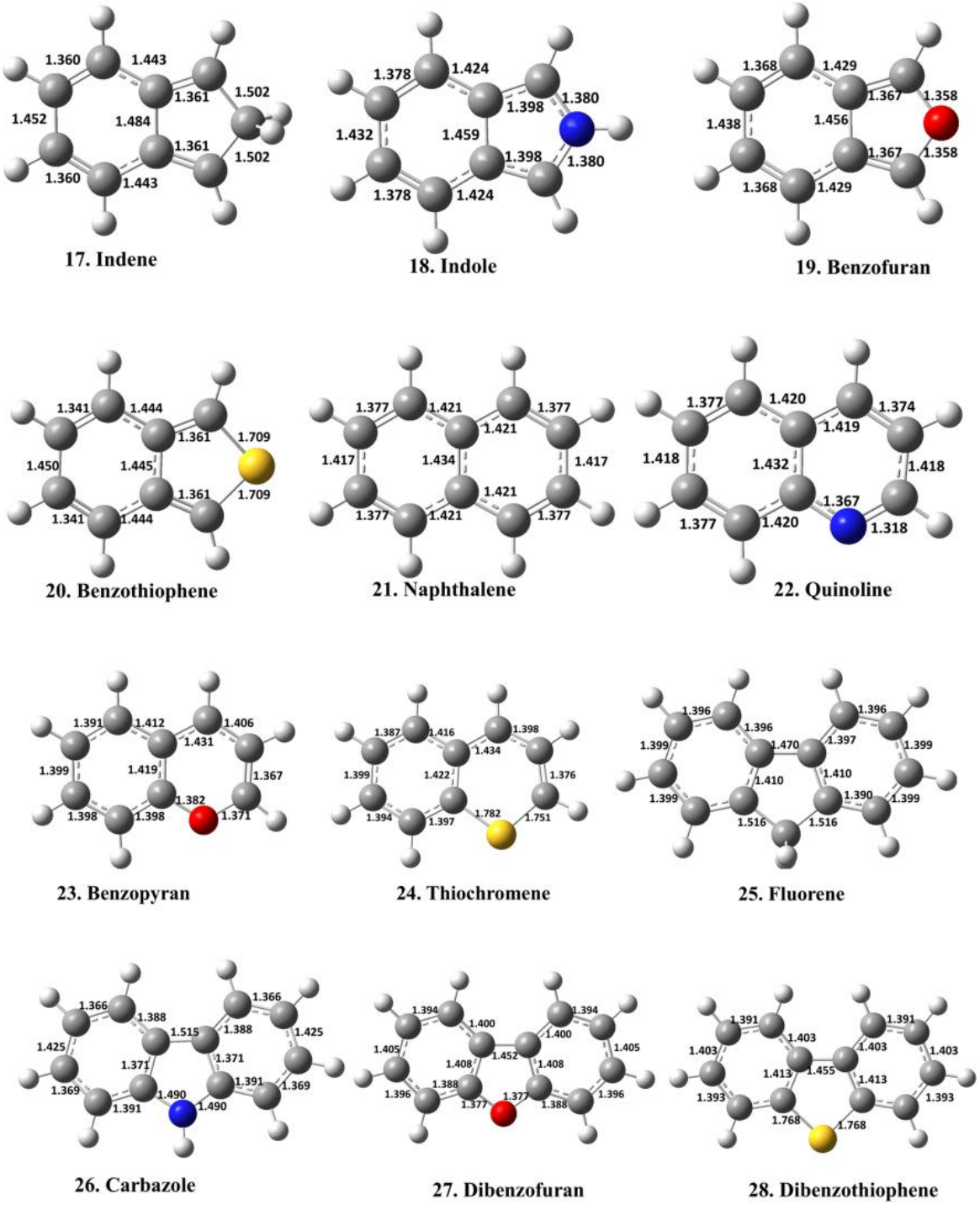

Figure 2b: Optimized geometries of the molecules (17-28) with selected bond lengths used for HOMA calculations

Thiophene shows the highest aromatic character because of less electronegativity of sulphur and the more diffused 3p orbital of sulphur. In the presence of magnetic field, the 3p orbital is more polarizable than the 2p orbital of nitrogen and oxygen which result in effective delocalisation of electrons. This leads to strong diamagnetic current, resulting in more negative NICS value.

Pyrrole shows intermediate aromatic character due to its low electronegativity than oxygen, the electrons are less localized on nitrogen and can more effectively participate in delocalisation. Additionally, the effective 2p-2p orbital overlap between nitrogen and carbon results in effective conjugation and high aromatic character. Furan shows the least aromatic character due to highest electronegativity of oxygen. Because of its high electronegative the lone pair of electrons more localized on oxygen. This results in less effective delocalisation across the ring and hence result in least negative NICS value.

For six-membered heterocyclic systems (**9-12**), benzene (‘**9**’) is taken as a reference to evaluate the effect of heteroatom on aromaticity in six-membered delocalized system as it is characterized by a perfectly 6π electron cloud. Like benzene, pyridine (‘10’) exhibit aromaticity while the other two system (‘**11**’ and ‘**12**’) show anti-aromatic character. In six membered ring, nitrogen atom is sp^2 hybridised. The sp^2 orbital is perpendicular to the π system; therefore, the lone

pair does not participate in delocalisation. When C-H is substituted with N, the (4n + 2) π-electron count remains intact (here n=1, 2e from each double bond) sustaining a diatropic ring current and thus, show negative NICS values. In contrast, the lone pair of oxygen and sulphur may involve in delocalisation and disrupt the 6π aromatic sextet. The contribution of these lone pair shifts the electronic structure into 4n π-electrons, and induced a paratropic current.

In seven-membered heterocyclic systems (**13-16**), all the NICS parameter such as NICS (0), NICS (1), and NICS (1) zz show different results. NICS(0) show anti-aromatic character for oxygen and sulphur analogues. NICS (1) identifies all compound as aromatic system. It is because in large molecule like 7 membered, σ shielding between C-C and C-H σ bond creates a negative electron cloud that masks the true π character and result in negative NICS value. Therefore, for 7 membered ring NICS (1) is considered as the least reliable descriptor of aromaticity. NICS(1)zz show that carbon analogue is anti-aromatic in nature. For nitrogen, oxygen, and sulphur, it exhibits negative value and show that substituting heteroatom effect the paratropic current through electron localisation.

Table 2: NICS (0) values of the selected 28 heterocyclic systems

SYSTEM	NICS (0)			
	X = CH	X = N	X = O	X = S
C_3H_3X (1-4)	26.102	20.516	-9.176	-10.118
C_4H_4X (5-8)	-4.679	-15.638	-13.182	-17.121
C_5H_5X (9-12)	-9.645	-9.132	7.134	3.098
C_6H_6X (13-16)	-4.267	-2.265	1.788	1.185
C_8H_6X (17-20)	-25.902	-33.624	-20.208	- 15.743
C_9H_7X (21-24)	-41.702	-35.905	-29.638	-28.086
$C_{12}H_8X$ (24-28)	-8.798	-20.868	-21.075	-27.492

Table 3: NICS(1) values of the selected 28 heterocyclic systems

SYSTEM	NICS (1)			
	X = CH	X = N	X = O	X = S
C_3H_3X (1-4)	17.556	11.511	- 2.146	-2.900
C_4H_4X (5-8)	-5.184	-10.776	-10.226	-11.703
C_5H_5X (9-12)	-11.215	-11.343	3.166	1.629
C_6H_6X (13-16)	-4.928	-5.348	-1.724	-1.766
C_8H_6X (17-20)	-8.329	-14.889	-10.759	-10.416
C_9H_7X (21-24)	-17.597	-19.904	-9.981	-10.449
$C_{12}H_8X$ (24-28)	- 4.775	-11.658	-10.020	-9.844

Table 4: NICS $(1)_{zz}$ values of the selected 28 heterocyclic systems

System	NICS$(1)_{zz}$			
	X = CH	X = N	X = O	X = S
C_3H_3X (1-4)	59.224	44.124	- 3.003	- 1.753
C_4H_4X (5-8)	-11.514	-27.393	-26.745	-28.593
C_5H_5X (9-12)	-29.041	-28.975	15.076	10.930
C_6H_6X (13-16)	2.619	-6.080	-6.175	-5.981
C_8H_6X (17-20)	-4.909	-4.164	-25.256	-4.843
C_9H_7X (21-24)	-39.680	-43.138	-16.254	-17.355
$C_{12}H_8X$ (24-28)	-3.7446	-6.886	- 8.014	-7.450

In fused bicyclic systems (**17-20**), $NICS(1)_{zz}$ show contradictory results with NICS(0) and NICS(1). From the results tabulated in Table 2, 3, and 4, it can be seen that all the systems show aromatic character. The nitrogen analogue, indole (‘**18**’) exhibit the highest negative values in NICS(0) and NICS(1) analysis. This can be explained due to low electronegativity of nitrogen and the effective overlap between the 2p-2p orbitals. Because of this, the electrons are effectively delocalised all over the bicyclic ring and result in strong global diatropic ring current. However, the trend in $NICS(1)_{zz}$ is different, the oxygen analogue benzofuran (‘**19**’), shows the most negative value. It is due to high electronegativity of oxygen, it pulls the electron density towards itself and localized the electrons in five membered rings, as a result the local π electron density increase, it creates the local intense current that is best quantify by the zz component.

In fused bicyclic system (**21-24**), all the system shows aromatic character. Between the nitrogen, oxygen and sulphur analogue, nitrogen show the highest negative value indicating strong diatropic current. The high negative values for NICS(1) and $NICS(1)_{zz}$ in the nitrogen-containing analogues, relative to naphthalene, indicate a strong diatropic ring current induced by the substitution of the heteroatom in cyclic ring. By calculating the magnetic shielding at a distance 1 Å above the geometric ring centre and mainly focused on the zz tensor component i.e., $NICS(1)_{zz}$, the results reduced the σ - contribution and primarily reflect the effects of π electrons. The π cloud is polarized due to the high electronegativity of nitrogen cloud and strengthen the magnetic interaction perpendicular to the molecular plane. As a result, the heterocyclic systems exhibit a stronger aromaticity than the parent hydrocarbon, highlights that substitution of heteroatom can specifically intensify the induced diatropic current within these fused frameworks.

In the tricyclic series (**25–28**), all the system exhibits aromatic character. The heteroatomic substitution results in different order in different NICS parameter. The divergence in aromaticity among different NICS indices highlights the dependence of magnetic criteria on the electronic nature of the heteroatom. The sulphur analogue (‘**28**’) shows the most negative NICS(0) values, which explains the effect of σ - shielding and it mainly because of the core-electron contributions due to the larger size of sulphur atom rather than the π-delocalization. Additionally, the NICS(1) shows the highest negative value for nitrogen-containing carbazole (‘**26**’), suggesting an optimal balance of orbital overlap and diatropic ring current at the 1 Å distance. The $NICS(1)_{zz}$ index show oxygen analogue (‘**27**’) as the most aromatic system. This is attributed due to the high electronegativity of oxygen, as it induced polarization in the system and intensify the perpendicular magnetic response of the π-electron delocalization. Collectively, these results emphasize that while nitrogen provides the most balanced delocalization, oxygen induces the strongest π specific magnetic field in the fused tricyclic framework.

4. Conclusion

Assessment of aromaticity in 28 different types of heterocycles is done by comparing the NICS(0), NICS(1), and $NICS(1)_{zz}$ and HOMA values as part of this theoretical study at B3LYP/6-31G(d) level. Use of NICS value to evaluate aromatic character shown that the size of the ring and heteroatom (N, O, and S) substituent on the ring highly influenced the degree of aromaticity. For N-heterocycles, there is more consistent aromatic behaviour attributed to

optimum overlap of orbitals as well as delocalization of electrons. Conversely, O- and S- heterocycles exhibited varying degrees of localisation of electron density due to their different electronegativities and orbital sizes. All fused and larger systems have greater ability to exhibit aromaticity due to π-delocalisation being extended; however, the variability of the NICS(0), NICS(1), and NICS(1)$_{zz}$ values are observed. The analysis based on HOMA values suggested that the bond lengths become equalised with respect to the overall geometry of a molecule. Benzene and pyridine exhibited very strong aromatic character owing to planar structure and evenly sized bond length. Conversely, smaller multi-member rings or non-planar molecules either exhibited anti-aromatic or weakly aromatic character because of alternating bond lengths and/or distorted structure. The data provided evidence of changes to the aromaticity due to bonds of heteroatoms (N, O, and S). The overall conclusion of the analysis indicated that N appears to favour aromatic systems as compared to O and S. These findings suggested that aromaticity cannot be quantified by one single aromatic index, but rather requires an integrated approach in determining aromaticity. This study provides the better understanding of this hypothetical concept, highlight how the substitution of carbon with heteroatom, i.e., O, N, S effect the aromatic character and stability of heterocyclic systems. Furthermore, this comparative study explains, how aromaticity changes across a period in the periodic table. It also supports the ongoing work involving aromaticity assessment via computational methods.

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Author Contributions
All the authors have contributed significantly to this manuscript, participated in reviewing/editing and approved the final draft for publication. The research profile of the authors can be verified from their ORCID ids, given below:

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