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Five and nine membered (heteronines) heterocyclic molecules. Theoretical approach

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Abstract—The presence or absence of aromaticity in nine membered heterocyclic molecules (heteronines) has been studied from a theoretical point of view (B3LYP/6-311G(2d,p) level). For comparison, the aromaticity of pyrrole, thiophene and furan was analysed. The aromaticity of azonine and thionine is well established along with the problems that arise from the stabilisation of the latter. The origin of oxonine non-aromaticity is discussed in terms of atomic charges and electronegativity. Results for the ion cyclononatetraenide are also reported. Reaction coordinates leading to thionine derivatives are studied. Condensed Fukui functions derived from electronic structure calculations were computed for five and nine membered heterocyclic molecules. These reactivity indices explain the observed products with electrophiles. The stability and the reactivity of these molecules may be understood in terms of the present results. © 2001 Elsevier Science Ltd. All rights reserved.

1. Introduction

Large and medium sized rings have been a matter of controversy because their intrinsic flexibility may preclude the development of aromaticity.[1] In particular, the family of heteronines[2] presents several peculiarities that make this group of compounds very interesting. The most representative members of the heteronines are azonine (I), oxonine (II) and thionine (III) (see Fig. 1), all of them being nine member rings. Even though oxonine and thionine have the same number of valence electrons, there are big differences between these molecules.

The presence of lone pairs on the heteroatoms may be used to change the properties of a ring formed only by carbon atoms. Indeed, in some cases, this is the only way to obtain neutral aromatic rings with nine members. However, this condition is not a guarantee of aromaticity because it is necessary to fulfill the known requirements for aromatic character, i.e. electronic delocalisation, matching the Hückel rule and planarity. The systems in Fig. 1 can be classified as polyenes, thus fulfilling the requirement of electronic delocalisation. The fulfilment of the Hückel rule can be found in those cases where there are 10 π-electrons. Cyclononatetraene is a non-aromatic molecule ($4n$), but its anion cyclononatetraenide (IV in Fig. 1) is an aromatic species.[3,4] The addition of two electrons allows this ion to attain aromatic stability respect a non-aromatic unsaturated ring. This addition of electrons also can be attained with lone pairs on heteroatoms,[5,6] as in the aromatic series pyrrole, furan and thiophene. Azonine, oxonine and thionine have the same heteroatoms as pyrrole, furan and thiophene, respectively, but their behaviour is quite different. It has been reported that azonine and thionine are aromatic whereas oxonine is non-aromatic.[7,8] Experimental studies of Annastassiou et al. also led to this characterisation of nine membered heterocycles in which azonine is considerably more stable than oxonine.[9] Given that oxonine and thionine have the same number of valence electrons and the same heteroatoms of furan and thiophene, respectively, the reason for their contrasting behaviour is not clear. Moreover, thionine has been predicted to be an aromatic molecule but, to date, it has not been synthesised.[2,10–13] One of the goals of this work is to understand the anomalous behaviour of oxonine as compared with furan and thionine, and to give an explanation for the absence of a thionine synthesis.

On the other hand, it is well known that aromaticity is related to the thermodynamic stability of the systems. There is also a relation between hardness and stability. In 1987, Pearson concluded that, ‘there seems to be a rule of nature that molecules arrange themselves to be as hard as possible’. Parr and co-workers also reported this statement, called the principle of maximum hardness.[14] In addition, density functional theory (DFT) has the advantage of providing definitions of important universal concepts of molecular structure and reactivity. Recent work based on DFT[15,16] has developed the concepts of absolute electronegativity and absolute

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Keywords: heteronines; theoretical calculations; hardness; Fukui functions.

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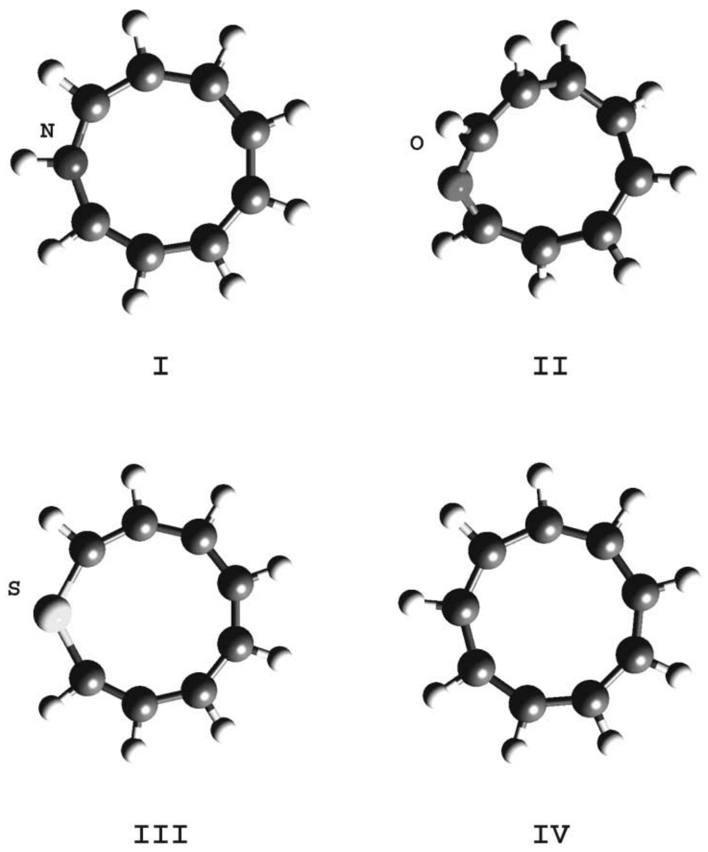


Figure 1. Optimised geometries (B3LYP/6-311G(2d,p) of azonine (I), oxonine (II), thionine (III) and anion cyclononatetraenide (IV).

hardness. Within this theory, the operational approximations are

Absolute electronegativity	Absolute (global) hardness
$X = 1/2(I + A)$	$\eta = 1/2(I - A)$

where I is the vertical ionisation energy and A is the vertical electron affinity. Upon application of Koopmans's theorem, the hardness corresponds to the energy gap between the HOMO and the LUMO. The principle of maximum hardness therefore confirms previous results[17] that claim that the stability of aromatic hydrocarbons depends on the HOMO–LUMO gap.

It is also possible to use DFT and molecular orbital theory to calculate local softness and condensed local softness in order to carry out a more detailed analysis of the effects that influence chemical reactivity. Local softness[18] is given by

$$s(r) = Sf(r)$$

where S is the global softness and $f(r)$ is the Fukui function.[19] Recently an alternative procedure to obtain information on $f(r)$ was reported.[20,21] This procedure condenses the values around each atomic site into a single value that characterises the atom in the molecule. With this approximation, the condensed Fukui function becomes

$$f^{+}_{\mathrm{A}K} = q_{\mathrm{A}K}(N_{\mathrm{A}} + 1) - q_{\mathrm{A}K}(N_{\mathrm{A}}) \quad \text{for nucleophilic attack}$$

$$f^{-}_{\mathrm{A}K} = q_{\mathrm{A}K}(N_{\mathrm{A}}) - q_{\mathrm{A}K}(N_{\mathrm{A}} - 1) \quad \text{for electrophilic attack}$$

$$f^{0}_{\mathrm{A}K} = 1/2[q_{\mathrm{A}K}(N_{\mathrm{A}} + 1) - q_{\mathrm{A}K}(N_{\mathrm{A}} - 1)] \quad \text{for radical attack}$$

where $q_{\mathrm{A}K}$ is the charge of the Kth atom in the molecule A. Systems with $N+1$, N and $N-1$ electrons are calculated with the ground state geometries of the N electron system. The simplest procedure to determine the charge is to make use of a Mulliken population analysis. In this work, a reactivity analysis of each compound will be presented.

The problem of aromaticity and reactivity in five and nine member ring molecules raises several questions that deserve to be studied carefully, this is in fact an old problem but to date there are not satisfactory answers even though we now have tools to search for solutions. The matter is also of interest for those chemists involved in heterocyclic and aromatic chemistry. The aim of the present study is to analyse these questions from a theoretical point of view. We have carried out (B3LYP/6-311G(2d,p)) DFT calculations on these molecules and some of their analogues. A comparison of aromaticity (using Nuclear Independent Chemical Shifts (NICS) as a criterion of measurement), atomic charges, HOMO–LUMO gaps and Fukui functions of these molecules is reported. Additionally, some interesting results about the nature of frontier orbitals of aromatic species are provided. It may be possible to explain experimental behaviour of these systems in these terms.

Table 1. NICS, heteroatom atomic charges and HOMO–LUMO gap (in eV) of the five and nine member ring compounds

Compound	NICS	Heteroatom atomic charges	HOMO–LUMO gap
Azonine	−12.836	N=−0.11	4.57
Tionine	−12.393	S=−0.18	4.30
Oxonine	−2.774	O=−0.34	5.22
Pyrrole	−12.43 [−*15.1*][a]	N=−0.19	5.63
Thiophene	−11.90 [−*13.6*][a]	S=−0.05	6.12
Furan	−11.40 [−*12.3*][a]	O=−0.31	6.37
Anion cyclononatetraenide	−14.11	–	4.16

[a] Reported in Ref. 30.

2. Methodology

Full geometry optimisation was carried out at the B3LYP/6-311G(2d,p) level without symmetry constraints using the Gaussian 94-code.[22] The magnetic properties (NICS) also were calculated at this level using the continuous set of gauge transformation method.[23,24] The reaction coordinate calculations were done at the B3LYP/6-31G level using the QST2 method.[25] The initial geometries were approximated with the Cerius package[26] and a preliminary optimisation was obtained in each case using a molecular mechanics method.[27]

The good performance of density functional methods, in particular that of gradient-corrected hybrid functionals such as Becke3–Lee–Yang–Parr,[28] and their ability to reproduce highly accurate, ab initio results has led to their widespread application to many problems of chemical interest, even when B3LYP is not appropriate for determining the relative stabilities of olefinic and aromatic conformations of [10] annulene.[29] The energy difference between these two conformations is around 3–7 kcal/mol according to CCSD(T) calculations and less than the average errors obtained with B3LYP calculations.

Schleyer et al.[30] using the same or similar levels of theory as in the present work reported the NICS values of several systems as a simple and efficient probe of aromaticity and we have used this criterion in order to carry out the respective aromaticity comparisons. Furthermore in the same way we have taken the NICS value of benzene as −9.7[30] as a reference of our mesurements of aromaticity and we have adopted the same criterion that a low value of NICS should correspond to a non-aromatic compound.

3. Results and discussion

This section is organised into three subsections. Section 3.1 discusses the results of geometry optimisations and the relationships between thermodynamic stability and other properties of the systems. In Section 3.2, the difficultly of synthesizing thionine is discussed. Finally, in Section 3.3 some reactivity parameters for five and nine membered heterocyclic molecules are presented.

3.1. Geometry optimisation and the analysis of properties

The optimised geometries are shown in Fig. 1. The results are in good agreement with known experimental facts, viz. the azonine, the cyclononatetraenide ion and the thionine are planar, and the oxonine ring is puckered with a dihedral angle of 37°.

The main results for each molecule are shown in Table 1. Also for comparison, the NICS values for pyrrole, furan and thiophene are displayed with theoretical values reported previously.[30] As can be seen in Table 1, our results for the five-membered molecules are in good agreement with previous results.[30] The NICS indicate that pyrrole, furan, thiophene, azonine and thionine are aromatic whereas oxonine is non-aromatic. This conclusion agrees well with previous results of resonance energy[31] and MNDO calculations[32]

The ion cyclononatetraenide is not an heteronine but the description of this ion is useful since it has the most symmetric nine-member ring. It is possible to analyse its aromatic behaviour and the fulfilment of Hückel's rule and thereby establish some trends for these systems. Reports about this molecule,[3,4,33] indicate that its anion is a more stable than the neutral state. It was prepared first by LaLancette et al.[3] and Simmons et al.[4] reported the UV–visible spectra and made the first theoretical calculations at the Hückel level. The molecule belongs to the D_{9h} point group (a character table appears in Ref. 4) and the frontier orbitals are shown in Fig. 2. The HOMO belongs to the irreducible representation e_2'' with an eigenvalue of −0.855 eV, whereas the LUMO is e_3'' with an eigenvalue equal to 3.308 eV. The HOMO-1 orbital belongs to the e_1'' irreducible representation (eigenvalue=−3.929 eV) and

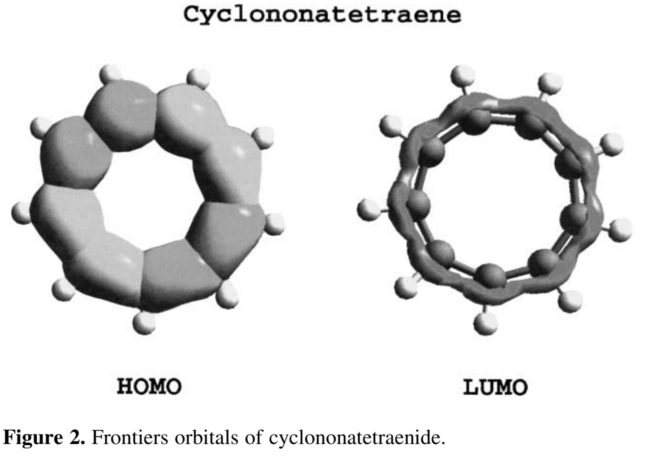


Figure 2. Frontiers orbitals of cyclononatetraenide.

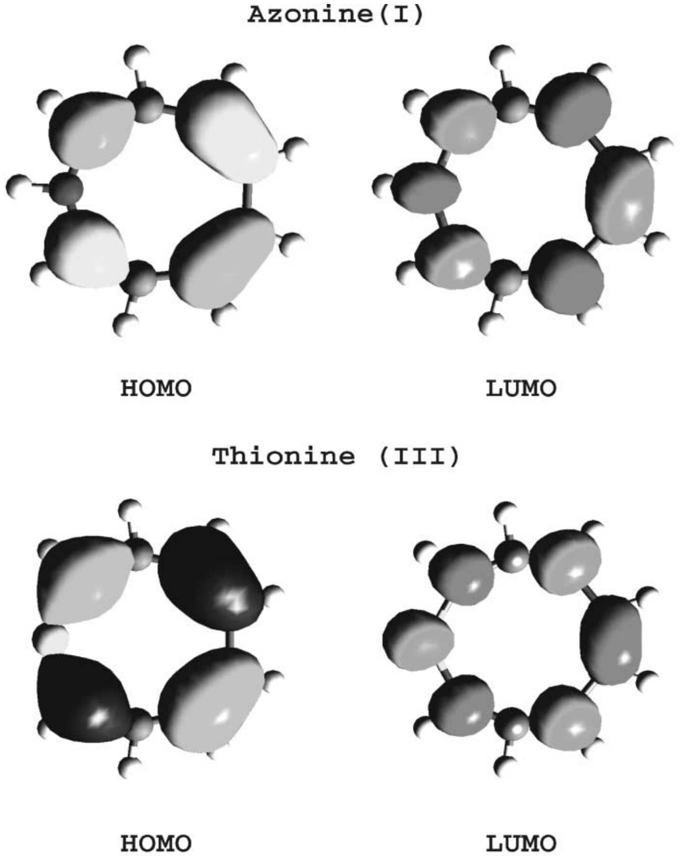


Figure 3. Frontiers orbitals of azonine and thionine.

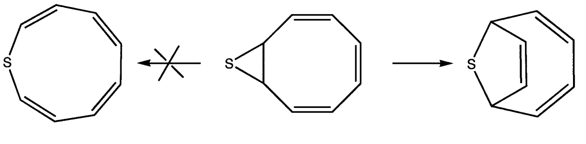
HOMO-2 belongs to a_2'' (eigenvalue$=-4.375$ eV). This description is similar to that proposed by Simmons. The degenerate orbitals (HOMO and HOMO-1) together with one non-degenerate molecular orbital (HOMO-2) are very important for the description of the Hückel's electron counting rule ($4n+2$) for aromaticity. The NICS value obtained for cyclononatetraenide (-14.11) is the largest among the species studied here and therefore confirms the Hückel's rule. Hence, IV is the most aromatic molecule of this study.

The other nine-member aromatic molecules are azonine and thionine. Azonine belongs to the C_{2v} point group with the HOMO located at -5.715 eV and the LUMO at -1.146 eV. The molecular orbital order presents five non-degenerate eigenfunctions that can accept the 10 π-electrons of the resonance cloud. The HOMO and LUMO belong to the a2 and $b1'$ irreducible representations, respectively. The same picture was found for the thionine molecule (see Fig. 3).

If we compare azonine with cyclononatetraenide we can see a strong difference in the eigenvalues of azonine with respect to cyclononatetraenide, as was expected due to the anionic nature of cyclononatetraenide. However, the HOMO–LUMO gap for both cases is very similar, 4.16 eV for cyclononatetraenide and 4.57 eV for azonine. The molecular orbitals cannot be compared because there are big differences in energy and symmetry.

These results represent a good description of the experimental (i.e. azonine and the ion cyclononatetraenide are thermodynamic stable species). However, the important question is why oxonine is non-aromatic and puckered? Trying to find an explanation, we looked at the atomic charges of each heteroatom. As can be seen in Table 1, the values are -0.11 for N on azonine, -0.34 for O on oxonine, and -0.18 for S on thionine. The negative charge on the oxygen atom of oxonine is bigger than the negative charge on nitrogen and sulphur of azonine and thionine, respectively. This result correlates well with the electronegativity. Oxygen is more negative because its electronegativity is bigger than the electronegativity of sulphur and nitrogen. This means that two π-electrons are localised on the orbitals near to the oxygen atom. Therefore they do not participate in the resonance phenomenon, and the double bonds are not delocalised onto the hereroatoms. The global result is a puckered ring and an atropic molecule. Despite this explanation of the non-aromatic behaviour of oxonine, it is important to note that the heteroatom atomic charges of the five membered molecules are similar. The oxygen is also negative in furan, but the distortion of the molecule is not possible due to the size of the ring. Furan may remains planar in spite of the heteroatom atomic charge.

The principle of maximum hardness establishes that the system would be more stable if the global hardness, related to the HOMO–LUMO gap were a maximum. As can be seen in Table 1, the HOMO–LUMO gap does not correlate well with the aromaticity and the expected stability of these



III V VI

Figure 4. Anastassiou[10,12,13] tried to synthesise thionine (III) in a photochemical procedure from episulphide of cyclooctatetraene (V), but he obtained as a final product thiabarbaralane (VI), a bicyclic molecule.

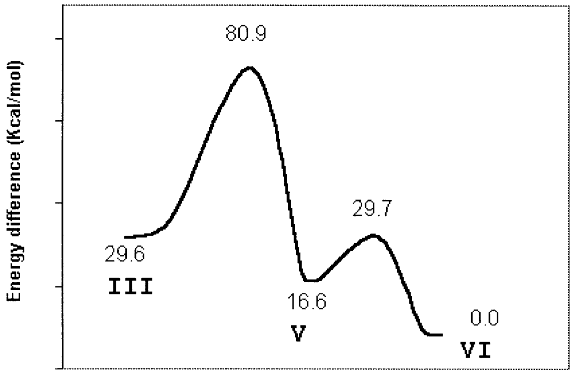


Figure 5. The reaction coordinate for the three sulphur heterocycles: thionine (III), episulphide of cyclooctatetraene (V) and thiabarbaralane (VI). The most stable complex is thiabarbaralane. The energy difference is with respect to thiabarbaralane.

molecules. Therefore, it is not possible to use hardness as a criterion of stability or aromaticity.

3.2. Can thionine be synthesised?

The results in Table 1 and Fig. 1 show that thionine should be a stable planar and aromatic molecule, but all attempts to prepare it have failed.[2,10–13] As an example, Anastassiou tried to synthesise this molecule[10,12,13] using a photochemical procedure from episulphide of cyclooctatetraene (structure V in Fig. 4), but these workers obtained thiabarbaralane (structure VI in Fig. 4), a bicyclic molecule as the final product. Therefore, the main problem is that thionine is probably less stable than the bicyclic molecule.[12] In order to explain this result, we studied the three sulphur heterocycles following a reaction coordinate. This is not a simulation of the photochemical procedure but a thermodynamic study in order to clarify this experimental result. The differences in energy values for the three isomers and the reaction coordinate are shown in Fig. 5. The energy differences were calculated with respect to the most stable complex, (thiabarbaralane (structure VI)). Since the aromaticity analysis of thiabarbaralane shows that the molecule presents a lower degree of aromaticity (the NICS value measured in the centre of the cage is −7.756) we can conclude that the aromaticity cannot be considered to be an important factor in this equilibrium.

As can be seen in Fig. 5, episulphide of cyclooctatetraene (molecule V) is placed in the middle valley of the plot and can yield thionine (structure III) or thiabarbaralane (structure VI). The thiabarbaralane is more stable than the thionine by 29.6 kcal/mol. The energy barrier between V and VI is 13.1 kcal/mol, while the energy barrier between V and III is 64.3 kcal/mol. This explains the experimental facts about the preference of thiabarbaralane against thionine. The reaction leads to compound VI because it is more stable than III in a thermodynamic fashion. Furthermore, the energy barrier for this path is lower than the energy barrier for the synthesis of thionine. Therefore, with these results we can say that thionine exhibits aromatic stability and its preparation is only a matter of finding an appropriate synthetic route.

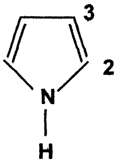
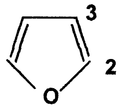
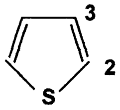
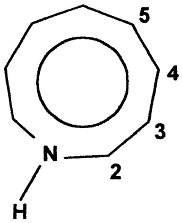
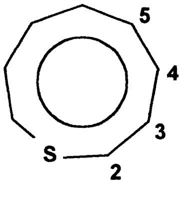
3.3. Reactivity parameters for five and nine membered heterocyclic molecules

Reactivity indexes derived from the DFT have been successfully applied in many cases in describing and understanding chemical reactivity.[34] As was presented in the Introduction, one can define regional or atomic reactivity indices such as the condensed Fukui function for a given atom in a molecule. For instance, for an electrophilic attack on the heterocyclic molecules, the condensed Fukui function is obtained according to

$$f_{AK}^{-} = q_{AK}(N_A) - q_{AK}(N_A - 1) \quad \text{for electrophilic attack}$$

The Mulliken population analysis was used to estimate the condensed reactivity indexes. In Table 2, the condensed Fukui function for electrophilic attack is shown for the relevant atoms in the heterocyclic compounds. It can be

Table 2. Calculated Fukui functions, f_j^-, for electrophilic attack at the qth atom, from the Mulliken population analysis

	N	−0.034		O	−0.10		S	−0.15
	C2	−0.154		C2	−0.14		C2	−0.17
	C3	−0.097		C3	−0.10		C3	−0.06
	N	−0.01					S	−0.19
	C2	−0.08					C2	0.02
	C3	−0.04					C3	−0.08
	C4	−0.06					C4	0.01
	C5	−0.05					C5	−0.12

observed that the largest (absolute value) f_k^- belongs to C2 in the five membered heterocyclic compounds. This means that C2 should be the most reactive site towards an electrophilic attack for these molecules. Theoretical results from the reactivity indexes are in complete agreement with the observed reactivity (furan, thiophene and pyrrole are chiefly substituted at C2[35]). For the nine-membered heterocyclic molecules, as far as we are aware, there is no experimental information about electrophilic attacks. For azonine, the reactivity indices are small and almost the same for the different atoms. Towards an electrophilic attack, there will be no preference. For thionine, the theoretical reactivity indices indicate that the most reactive site towards electrophilic attack is the sulphur atom. More experimental information is necessary to corroborate the predictions regarding the nine-membered heterocyclic molecules.

4. Conclusions

The heteronines are nine member ring compounds that are expected to be aromatic and planar. However, only azonine, i.e. the molecule with nitrogen as heteroatom, is aromatic. Oxonine is not planar and non-aromatic. Our results show that the negative charge and electronegativity of the oxygen atom leads to localised electron pairs, which compel the ring to be puckered. The theoretical results show that thionine should be a planar and aromatic molecule, in spite of having the same number of valence electrons as oxonine. According to our results, the existence of a more stable bicyclic isomer (thiabarbaralane) is the reason for the failure to obtain thionine via a photochemical procedure. The reaction coordinate presents a lower energy barrier for the synthesis of thiabarbaralane than for the synthesis of the thionine. The ion cyclononatetraenide is the most aromatic species of this study. Symmetry considerations allow analysis of this ion's aromaticity in a classical manner. Density functional theory reactivity indices are shown to be useful in understanding the observed reactivity of the five membered heterocyclic species and in predicting the presently unknown reactivity behaviour of the heteronines.

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