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Aromaticity in Heteronins

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Hybrid density functional theory (B3LYP) calculations are performed on some of the heteronines (azonine, oxonine and thionine) in order to carry out a systematic estimation of aromaticity using structural, energetic and magnetic criteria. Optimized geometries predict a planer and puckered structures with no bond alternation for azonine and oxonine rings, respectively. A non-planer structure is obtained for thionine with bond alternation. A comparison has also been made between the difference of frontier molecular orbital energies of the cyclic and the chain-form analog of these molecules (ΔΔFMO). According to this quantity all of the proposed heteronines are aromatic. Results based on the Mulliken population analysis and computed NICS values predict the azonine, oxonine and thionine as aromatic, non-aromatic and antiaromatic, respectively.

Key Words: Aromaticity, Nucleus independent chemical shift, Heteronines, Density functional theory.

INTRODUCTION

Heterocyclic compounds have a major role in organic chemistry. The most important of the nine membered rings of these compounds (heteronines) are azonine, oxonine and thionine[1], which their chemistry and properties have been reviewed by Anastassiou *et al.*[2]. It has been reported that azonine and thionine are aromatic whereas oxonine is non-aromatic[3,4]. Experimental studies of Anastassiou *et al.*[5-7] showed that azonine is considerably more stable than oxonine. They also tried to synthesize thionine molecule using a photochemical procedure from episulphide of cyclooctatetraen, but they obtained thiobarbaralane as the final product[8-11]. To date all attempts to prepare thionine are failed and it has not been synthesized yet.

The aromaticity is one of the most important concepts in chemistry, which is related to the thermodynamic stability of the system and is recently reviewed by some authors[12-14]. No single measure of aromaticity exists; rather we associate a number of properties with aromaticity, principally planarity, bond non-alternation, resonance stabilization energy (RE) and magnetic effects.

Pearson and co-workers[15-17] showed that there is a relation between hardness and stability. Upon application of Koopman's theorem[18], the hardness corresponds to the energy gap between the HOMO and LUMO orbitals (ε_H and ε_L) and has the following simple operational form:

$$\eta = \frac{\varepsilon_L - \varepsilon_H}{2} \tag{1}$$

It shows that the harder molecules have the larger energy gaps. Since aromaticity is related to the stability of system, therefore it has something to do with hardness and hence the stability of aromatic hydrocarbons depends on their HOMO-LUMO energy gap. Jursic[19] showed that the molecular energy gap between HOMO and LUMO in conjugated polyenes is becoming narrower, with the increasing number of conjugated carbon double bonds. When a conjugated system is closed, the new-formed cyclic chemical system is either more stable (aromatic) or less stable (antiaromatic) than its open-chain analog. This should be reflected in widening or narrowing the frontier molecular orbital (FMO) energy gap. He defined ΔFMO(l) and ΔFMO(c) as the frontier orbital energy differences for linear and cyclic conjugated polyene, respectively and ΔΔFMO as:

$$\Delta\Delta\mathrm{FMO} = \Delta\mathrm{FMO(c)} - \Delta\mathrm{FMO(l)} \tag{2}$$

The calculated values for some selected cyclic compounds show that in all cases where a positive ΔΔFMO is obtained the cyclic chemical system is aromatic and when a negative energy is obtained the system is antiaromatic[19]. Therefore ΔΔFMO can be used as a measure of aromaticity.

Another measure of aromaticity is magnetic effects. The abnormal proton chemical shifts of aromatic molecules are the most commonly employed indicators of ring current effects[20-22]. Schleyer *et al.*[23] have proposed the negative of the computed magnetic shielding at or above the ring center as a simple and efficient probe for aromaticity. According to this probe, which is referred to Nucleus Independent Chemical Shift (NICS), negative values denote the presence of diatropic ring currents or aromaticity and positive values denote paratropic ring currents or antiaromaticity; while small NICS values indicate nonaromaticity. Since the introduction of NICS, many attempts have been made to use this criterion as a probe in the study of chemical reactions[24-27] or discussion about the stability of different organic and inorganic compounds[19,28-41].

Recently, Salcedo and co-workers[34] have studied heteronines (azonine, oxonine and thionine) from theoretical point of view. They have claimed that all the obtained stationary structures for these molecules are planer and the calculated values for NICS are all negative. Therefore they concluded that all of these heteronines are aromatic. But Schleyer *et al.*[42] calculated by *ab initio* and density functional methods aromatic stabilization energies as well as other properties for these heteronines and found that only azonine is planer and aromatic.

Our goal in this research is to analyze the aromaticity of azonine, oxonine and thionine molecules. We examine the aromaticity of these compounds using a number of properties, which are associated with aromaticity such as DFT structures, frontier molecular orbital energies, charge distribution and the magnetic property (NICS) of the proposed molecules. The differences in stabilities are explained in terms of the aromaticity.

COMPUTATIONAL DETAILS

Equilibrium geometries for the proposed heteronine molecules are obtained by optimizing within a density functional framework using the most popular 6-31G** basis set. Since Jursic and co-workers[43-48] have demonstrated that the B3LYP density functional theory[49-52] is a reliable method for the calculation of the geometries and energies of heterocyclic molecules, this exchange correlation functional is used for this purpose. Vibrational frequencies are also calculated at the same level mainly to check the number of imaginary frequencies (NIMAG). Absolute NMR shielding at ring center for each molecule is also calculated using the GIAO method[53] at B3LYP/6-31G** level of theory. The position of ring center is the (3+1) ring critical point of the electron charge density as defined within the atoms in molecules procedure[54]. All the calculations are performed with the GAUSSIAN 98W series of programs[55].

RESULTS AND DISCUSSION

The optimized geometries of azonine, oxonine and thionine are shown in Fig. 1. As it is shown, azonine molecule is planer whereas oxonine and thionine rings are not flat and their structures are puckered and boat shaped, respectively. Optimized bond lengths and angles of these molecules are given in Table-1. Structural analysis shows bond alternation in thionine (large variance in bond lengths and angles), whereas in each of the oxonine and azonine molecules the bond lengths are nearly the same, which implies to the conjugation of double bonds in these rings. Surprisingly, the average bond length in azonine (1.386 Å) is the same as benzene, which indicates to strong resonance in this molecule. It seems that thionine is non-planer in order to alleviate ring strain. It is recall that in all cases the calculated frequencies are positive and therefore the structures are minima on the potential energy surface. Any attempts to find a stationary planer structure for thionine were unsuccessful and the only obtained planer structure for this molecule has a negative vibrational frequency (-50.13214), which implies to the non stationary point of the structure. It seems that the previous reported planer structure for thionine[34] is only a local minima in the potential energy surface.

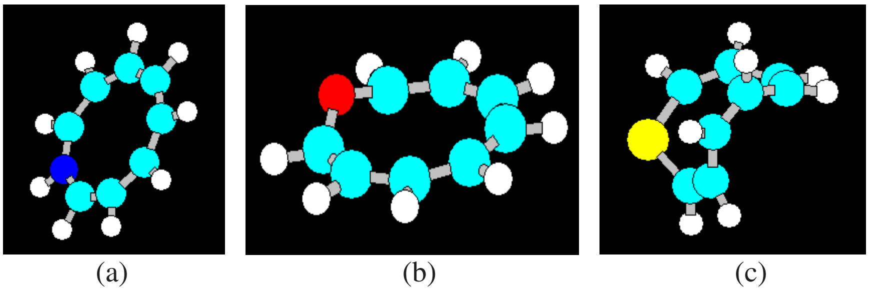
(a) (b) (c)

Fig. 1. Optimized structures for the proposed heteronins (a) azonine, (b) oxonine (c) thionine.

TABLE-1
OPTIMIZED BOND LENGTHS (Å) AND ANGLES FOR THE CONSIDERED HETERONINES

	Azonine	Oxonine	Thionine
Bond length			
X-C_1	1.36741	1.42380	1.76382
C_1-C_2	1.37299	1.36109	1.34031
C_2-C_3	1.41123	1.41984	1.46436
C_3-C_4	1.38026	1.37279	1.33958
C_4-C_5	1.40982	1.41618	1.47263
C_5-C_6	1.38013	1.37296	1.33686
C_6-C_7	1.41170	1.42068	1.47055
C_7-C_8	1.37218	1.36026	1.33398
C_8-X	1.36770	1.41923	1.78531
Average	1.38602	1.39614	1.47921
Variance	0.00033	0.00072	0.02835
Angle			
X-C_1-C_2	138.462	133.524	126.895
C_1-C_2-C_3	141.711	142.775	127.157
C_2-C_3-C_4	139.849	139.478	124.709
C_3-C_4-C_5	139.076	138.450	126.362
C_4-C_5-C_6	139.025	138.514	129.470
C_5-C_6-C_7	139.857	139.396	130.531
C_6-C_7-C_8	141.718	142.843	135.323
C_7-C_8-X	138.478	133.460	137.789
C_8-X-C_1	141.825	125.966	111.420
Average	140.000	137.156	127.740
Variance	1.749	25.546	49.750

We explore the frontier orbital energy change for the ring closing and production of azonine, oxonine and thionine. As it is shown in Fig. 2, there are five open-chain analogs that can be compared with these heterocycles. To obtain maximal conjugation of the carbon skeleton, the analog that has

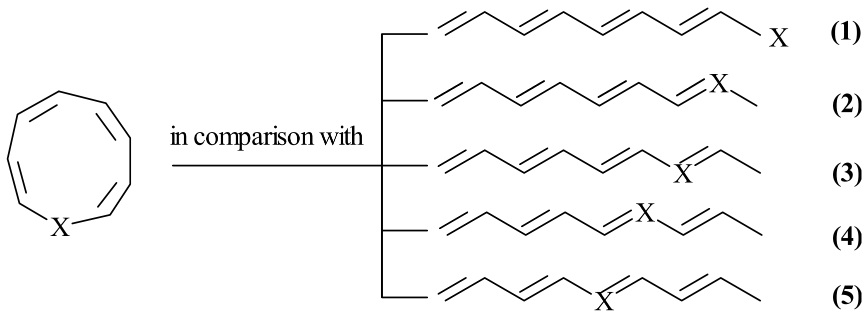

Fig. 2. Comparison of the cyclic forms of heteronins with the open-chain analogs

a hetero atom on the end of chain [analog (1)] is preferred. That is also demonstrated in the computed energies of these chain molecules, which three samples of them are given in Table-2 (the first open-chain analog has the lowest energy). The differences in FMO for the open-chain analogs [ΔFMO(l)] and the cyclic forms [ΔFMO(c)] for each heterocycle are calculated and gathered in Table-2. In all cases (with one exception) ΔΔFMO values are positive, which imply to more stability of cyclic forms of these molecules with respect to the chain analogs. Therefore according to this parameter (ΔΔFMO) all of the heteronines are aromatic.

TABLE-2
CALCULATED FRONTIER MOLECULAR ORBITAL ENERGIES AND THE RELATED DIFFERENCES (ΔFMO AND ΔΔFMO) FOR THE SELECTED OPEN-CHAIN ANALOGS AND THE CYCLIC FORMS OF THE CONSIDERED HETERONINES (Fig. 2)*

Molecule	E	ε_H	ε_L	ΔFMO	ΔΔFMO
1	-366.09997	-0.17705	-0.04680	0.13205	0.03935
3	-366.09100	-0.18253	-0.04077	0.14176	0.02784
5	-366.08936	-0.18486	-0.03535	0.14951	0.02009
Azonine	-364.88009	-0.20506	-0.03546	0.16960	
1	-385.97775	-0.18978	-0.05516	0.13462	0.00195
3	-385.80499	-0.16821	-0.06902	0.09921	0.03736
5	-385.95717	-0.20531	-0.03753	0.16785	-0.03128
Oxonine	-384.74814	-0.21419	-0.07762	0.13657	
1	-708.95781	-0.19736	-0.06739	0.12997	0.04518
3	-708.94151	-0.20430	-0.05140	0.14290	0.03225
5	-708.93997	-0.20712	-0.05237	0.15475	0.02040
Thionine	-707.72733	-0.20913	-0.03389	0.17515	

*All energies are in atomic units.

Atomic charges of the considered molecules are also calculated by using Mulliken population analysis, which are given in Table-3. Surprisingly, the charge of sulfur atom in thionine is positive, whereas the charges of nitrogen and oxygen atoms in two other heteronines are negative. It seems that sulfur's electrons are more contributed into ring currents than the electrons of nitrogen and oxygen atoms. But the charges of carbon atoms in azonine are nearly the same, which imply to the symmetric distribution of electrons on the ring and therefore aromaticity in this molecule. In the other hand in thionine, the variation of atomic charges is so that it is concluded the electronic distribution is not symmetric and hence this ring is not aromatic.

TABLE-3
THE CALCULATED ATOMIC CHARGES FOR THE HETERONINE MOLECULES BY USING MULLIKEN POPULATION ANALYSIS

Molecule	X	C_1	C_2	C_3	C_4
Azonine	-0.32722	0.03946	-0.10370	-0.11582	-0.15277
Oxonine	-0.23498	0.12025	-0.08941	-0.11556	-0.18450
Thionine	0.16189	-0.25463	-0.11272	-0.05830	-0.28550

The aromaticity of the proposed compounds is also studied by using magnetic effects. The calculated NICS values for azonine (-12.509), oxonine (-3.823) and thionine (+1.544) predict aromatic, non-aromatic and antiaromatic characteristics for these heteronines, respectively. It is mentioned that the calculated values of NICS for these molecules which are recently reported by Salcedo *et al.*[34] are -12.836, -2.774 and -12.393, respectively. It is obvious that in the azonine and oxonine cases the NICS values are nearly the same in these two works and the small differences are raised from differences in basis sets which are used. But there is a considerable difference between the NICS values of thionine in these two works (+1.544 and -12.393). It seems that using a planar structure for thionine which is not a stationary point in the potential energy surface by Salcedo *et al.*[34] makes this difficulty. To show this, the NICS is calculated for the non-stationary planer structure of thionine, which has one negative frequency. Surprisingly the obtained value is -12.971, which is similar to the value that is reported Salcedo and co-workers[34] for this molecule (-12.393). Therefore, the reported planer structure for thionine by Salcedo group[34] is not a stationary point.

Conclusion

Different criteria of aromaticity have been used to characterize the heteronines from the aromaticity point of view. According to structural, charge and NICS analysis the azonine, oxonine and thionine are aromatic, non-aromatic and anti-aromatic, respectively. But frontier molecular orbital studies predict all of these molecules as anti-aromatic compounds.

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