

ELECTRONIC STRUCTURE OF MESOIONIC COMPOUNDS. THE CLASSIFICATION PROBLEM

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Mesoionic compounds are conventionally categorized into two types based on the primary origin of electrons within the conjugated system, specifically determined by the arrangement of heteroatoms in the five-membered ring. An examination of diverse mesoionic compounds has been undertaken to address the pivotal query surrounding their classification: does the primary origin of electrons hold significance, and does this criterion demarcate a definitive boundary between the two types of compounds? To comprehensively address this issue, the DFT calculations were performed for a set of mesoionic molecules. The electronic properties of the molecules were studied within the frameworks of quantum theory of atoms in molecules (QTAIM) and the Nuclear Independent Chemical Shift (NICS).

To comprehend the topological distinctions among representatives of the two types, we describe a set of indices designed to characterize the spatial distribution of electronic parameters within the molecular frameworks. The results obtained show that the existing classification is to a certain extent justified, with the main distinguishing factor between the two types being the nature of the distribution of the resulting ellipticities of bonds in five-membered ring and the structure of the molecular orbitals. At the same time, based on NICS calculations we concluded that both classes are not characterized by pronounced aromaticity of the mesoionic ring for the selected set of molecules.

Keywords: mesoionic compounds, density functional theory, quantum theory of atoms in molecules, nuclear independent chemical shifts.

Introduction

The mesoionic compounds typify dipolar molecules characterized by the delocalization of both positive and negative charges within the molecular framework. The structural representation of mesoionic compounds contradicts the classical covalent depiction and requires the introduction of integer charges assigned to specific atoms. Consequently, the mesoionic compounds are frequently illustrated as hybrids of various dipolar resonance structures.

Mesoionic compounds, characterized by substantial dipole moments, planar ring structures, and distinct charge regions, exhibit diverse applications. Notably, certain mesoionic compounds demonstrate antimicrobial and antitumor activities, particularly against sarcoma, melanoma, and hepatocarcinoma cells [1, 2]. In the agricultural domain, mesoionic derivatives of pyrido[1,2- α]pyrimidinones are employed as insecticides to control rice pests in several Asian countries [3,4]. High hyperpolarizability, ease of synthesis, stability, and tunable optical properties pose mesoionic compounds as promising materials for nonlinear optical devices, including optical switches and data storage elements [5].

In organic synthesis, palladium complexes of mesoionic compounds surpass triphenylphosphine complexes as catalysts for Shizuki-Miyauri cross-coupling reactions, leading to the synthesis of novel substances [6]. Cycloaddition reactions of mesoionic compounds find utility in polymer synthesis, yielding materials with high cross-linking density, thermal stability, and low dielectric constants [7]. In the liquid state, mesoionic compounds exhibit ionic liquid properties, competing favorably with other structures [8].

Within scholarly discourse, the term "mesoionic compound" has been established specifically for two types of five-membered heterocyclic mesomeric betaines (HMB) – type A and type B [9, 10] (see, however [11] where five separate classes of six-membered heterocyclic mesomeric betaines are discussed). The selective restriction of the term "mesoionic" to these two categories of five-membered

HMBs has been justified as a means to uphold the precision and utility of the nomenclature [10]. These are cyclic molecules having two or more heteroatoms in a five-membered ring and exocyclic heteroatoms. In both types of compounds, the molecules manifest a conjugated system of 8 π -electrons; however, the distinguishing factor between the classes lies in the origin of these π -electrons, as presented in Fig. 1. The categorization of HMB through an examination of their connectivity matrix reveals type A mesoionic compounds as conjugated HMB and type B as pseudo-semi-conjugated [12]. Nevertheless, upon the formation of a chemical bond in analogous molecules, a conjugated system emerges, leading to the assumption that all electrons are shared. Therefore, our objective is to dive into the electronic characteristics of mesoionic compounds, seeking to ascertain whether such a formal classification corresponds to Bader's theory (Quantum Theory of Atoms in Molecules, QTAIM).

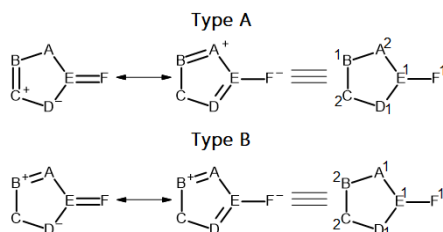


Figure 1. Resonance structures and the origin of π -electrons in mesoionic molecules

Calculation details

The objective of current investigation is the correlation between the electronic structure of mesoionic compounds and their classification. Geometric and electronic properties were computed for 10 mesoionic compounds (Fig. 2). Calculations were performed utilizing the density functional B3LYP within the 6-31++G(d,p) basis set employing Gaussian 09 software [13]. Our preliminary calculations have shown that the results remain quite stable when the chosen basis set is changed. A software package AIMAll [14] was used for consideration and analysis of electronic characteristics in QTAIM frameworks.

Among the studied molecules there are both conventional representatives of mesoionic molecules, such as münchnone 1A, derivatives of diazoles 2A and 1B, and tetrazole 2B, as well as previously unreported molecules 4B and 5B, which, to the best of our knowledge, have not been synthesized to date.

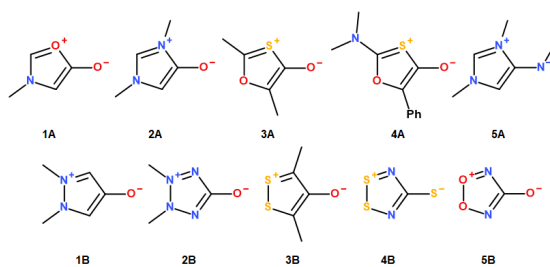


Figure 2. Systems under consideration.

Current investigation is guided by QTAIM, the main objects of which are atoms and bonds as inherent manifestations of the observed electron density distribution function ρ within the system. Simultaneously, the electron density distribution within the molecule describes the average way in which electronic charge is spatially distributed within the coulomb field created by the nuclei [15]. In accordance with the principles of QTAIM, the depiction of a molecular structure involves the identification of critical points within the electron density field, along with the delineation of gradient trajectories originating and terminating at these critical points (CPs). Furthermore, it is well known that the nature of chemical bond is discerned through the sign of the second derivative at a specific point. Thus, in addition to the electron density eigenvalue at CPs, the Laplacian of the electron density $\nabla^2\rho$ serves as a descriptor for bond characteristics. After all, a crucial parameter, particularly in the examination of conjugated systems, is the ellipticity of the bond ε . It is defined in relation to the

cylindricity of the electron density at the CP and quantitatively assesses the extent to which the electron density preferentially occupies a specific plane containing the bond axis.

The characteristics of bonds, such as electron density ρ , Laplacian of electron density $\nabla^2\rho$ and ellipticity ε at critical points are compared to reference molecules, which are furan, pyrrole, thiophene, pyrazole, isoxazole, isothiazole and tetrazol. Also we provide an analysis of geometrical parameters in studied molecules.

Results and discussion

Certain molecular characteristics of the investigated molecules are given in Table 1. The acquired data reaffirm the notably elevated dipole moments and polarizabilities of mesoionic compounds. These characteristics provide the optical nonlinearity outlined above, as well as environmental effects, such as solvatochromism [16]. It is pertinent to observe that, generally, type A compounds exhibit larger values of HOMO-LUMO gaps. Typically, a larger HOMO-LUMO gap indicates increased stability, although further research is warranted to delve into this aspect.

Table 1. Quantitative characteristics of the studied molecules.

	HOMO-LUMO gap, eV	Dipole Moment, D	Polarizability, a.u.
1A	4.44	7.90	63.689
2A	4.19	7.12	81.640
3A	3.51	5.38	91.835
4A	3.10	10.58	208.131
5A	3.35	6.29	106.910
1B	3.29	9.83	84.219
2B	3.73	10.91	72.060
3B	2.72	4.02	107.651
4B	1.66	5.93	98.618
5B	2.04	1.98	42.350

In type A compounds, the A-E bond is identified as the weakest, as indicated by the following facts: it is on average 0.2 Å longer than the corresponding bonds in the reference molecules, and displays relatively low electron saturation and ellipticity. These findings align with earlier research [17]. Conversely, the D-E bond in type A compounds tends to shorten, exhibiting high ellipticity and substantial negative Laplacian values, which indicates a strong electronic correlation. Finding general patterns in type B compounds may be challenging, but it can be said that both A-E and D-E bonds are characterized by the large negative values of the Laplacian, which indicates a high concentration of electron density on the interaction lines and strong electron sharing.

It is rather difficult to identify distinct trends in the electronic characteristics of the E-F exocyclic bond. For compounds 1A, 3A, and 5B, the positive Laplacian value in the CP of the E-F bond suggests an ionic character of given bond. The ellipticity in the CP of the E-F bond for compound 4A has a value 0.004, prompting a comparison with the ellipticity of a single σ -bond, such as C-H. Compounds 3A, 1B, and 3B also exhibit relatively low ellipticity values for the E-F exocyclic bond: 0.006, 0.075, and 0.057, respectively, which identifies them as single σ -bonds. However, in compound 5A, the exocyclic E-F bond displays an exceptionally low Laplacian value of -1.279 alongside a relatively high ellipticity of 0.277. The E-F bond in compound 2B is also unequivocally interpreted as double and covalent.

Table 2. Average values of the studied bond characteristics for two types of mesoionic compounds.

	r , Å		ρ , a.u.		$\nabla^2\rho$		ε	
	Type A	Type B	Type A	Type B	Type A	Type B	Type A	Type B
A-B	1.485	1.461	0.285	0.307	-0.596	-0.529	0.299	0.203
B-C	1.322	1.595	0.331	0.294	-0.419	-0.496	0.313	0.254
C-D	1.392	1.463	0.271	0.306	-0.185	-0.526	0.407	0.201
D-E	1.401	1.434	0.311	0.292	-0.828	-0.796	0.379	0.206

A-E	1.661	1.434	0.201	0.292	-0.356	-0.799	0.114	0.201
E-F	1.327	1.243	0.359	0.390	-0.292	-0.296	0.114	0.090

Mesoionic compounds of type A exhibit anomalous angular curvature near the exocyclic atom (Table 3). NBO analysis performed by Oziminski and Ramsden on compound 2A reveals a significant donor-acceptor interaction (34.6 kcal mol⁻¹) involving the lone exocyclic electron pair and the antibonding orbital related to the A-E bond. In contrast, the interaction with the adjacent D-E bond orbital is considerably weaker (15.4 kcal mol⁻¹). These interaction energies align with an observed compression of the A-E-F bond angle, leading to a concurrent weakening of the A-E bond and the reinforcement of the D-E bond [18].

Table 3. Calculated valence angles, formed by exocyclic bond

	1A	2A	3A	4A	5A	1B	2B	3B	4B	5B
A-E-F	118.4	122.4	121.9	118.5	131.3	129.5	126.2	123.4	122.2	129.3
D-E-F	140.3	135.1	135.1	135.5	126.6	129.5	126.2	124.7	122.2	129.3

To identify topological differences between representatives of the two types of mesoionic compounds, we propose indices summing the QTAIM characteristics of five-membered rings and five-membered rings along with the exocyclic atom. These indices are standard deviation (SD), and Kullback-Leibler divergence (KL).

$$SD = \sqrt{\frac{\sum_{i=1,5} (x_i - \bar{x})^2}{5}}, \quad (1)$$

$$KL = - \sum_{i=1,5} P \log_2 \frac{Q}{P}. \quad (2)$$

In the given formulas, \bar{x} represents the average value of the corresponding bond characteristic, P corresponds to the probability of a certain value and is calculated as $\frac{x_i}{S}$, where $S = \sum_{i=1,5} x_i$. The Kullback-Leibler index KL compares this distribution with the model (uniform) distribution, denoted as Q . The indices were computed both for the mesoionic five-membered cycle ($Q = \frac{1}{5}$) and for the conjugated system, including the mesoionic cycle and exocyclic atom ($Q = \frac{1}{6}$).

The ranges of the obtained index values are presented in Table 4. It is noteworthy that certain compounds demonstrate positive Laplacian values, both for endo- and exocyclic bonds. Due to the logarithmic limitations, the corresponding indices were not computed.

Table 4. Topological indices describing the electronic structure of mesoionic compounds: (5) – for the cycle, (6) – for the conjugated system including the exocyclic atom.

	ρ		$\nabla^2\rho$		ε	
	Type A	Type B	Type A	Type B	Type A	Type B
SD(5)	0.030-0.074	0.028-0.073, <i>0.187</i>	0.197- 0.437	0.103-0.514, <i>0.712</i>	0.112- 0.176	0.007- 0.101
KL(5)	0.006-0.056	0.005-0.042, <i>0.213</i>	0.050-0.235, <i>0.589</i>	0.009- 0.189	0.080- 0.247	0.000- 0.083, 0.600
SD(6)	0.039-0.092	0.038-0.081, <i>0.172</i>	0.246- 0.410	0.185-0.476, <i>0.720</i>	0.129- 0.174	0.059- 0.092
KL(6)	0.009-0.071	0.008-0.062, <i>0.177</i>	0.100-0.105, <i>0.691</i>	0.069- 0.181	0.111-0.285, 0.415	0.070- 0.094, 0.486

Although type B mesoionic compounds inherently exhibit greater symmetry compared to type A compounds, all calculated index ranges are quite comparable for compounds of the two types, except

for the indices representing ellipticity distribution. Specifically, type A compounds are distinguished by corresponding indices values below 0.1, and type B exceeding 0.1. Values of indices approaching zero signify a uniform distribution of the given value within the bonds; as the index value increases, the corresponding distribution becomes more uneven. It is deduced that in type B compounds, the distribution of ellipticity values within the bonds is more uniform compared to type A compounds. Simultaneously, bonds in type A compounds exhibit higher ellipticity values (Table 2), indicating a higher level of conjugation than in type B compounds. The non-uniform distribution of ellipticity can be interpreted as a disruption of conjugation, a conclusion to some extent supported by the computed molecular orbitals (Fig. 2).

The Table 4 includes values in italic style that deviate from the specified ranges. Both types of compounds exhibit more ideal structures for which general trends can be found, as well as extreme structures with unique properties. Particular emphasis is placed on indices characterizing the distribution of electron density ρ . Upon examination of Table 4, it becomes apparent that the index ranges are nearly identical for compounds of both types. This observation leads to the conclusion that the initial origin of electrons has little influence on their subsequent distribution within the conjugated system. This perspective underscores the arbitrariness of the criterion used to categorize compounds into two types.

In the examination of aromaticity across two discrete classes of compounds, the NICS indices were determined at ring CPs and at a distance of 1 Å from the molecular plane, NICS(0) and NICS(1). The obtained values in Table 5 delineate that, at the specified 1 Å distance, compounds of type B manifest heightened shifts in contrast to type A compounds. However, despite these discernible distinctions, the computed indices for both classes substantiate a non-aromatic classification, with the noteworthy exception of compound 5B, wherein the computed value of -34.8 exceeds the corresponding benchmark for benzene (-29.2).

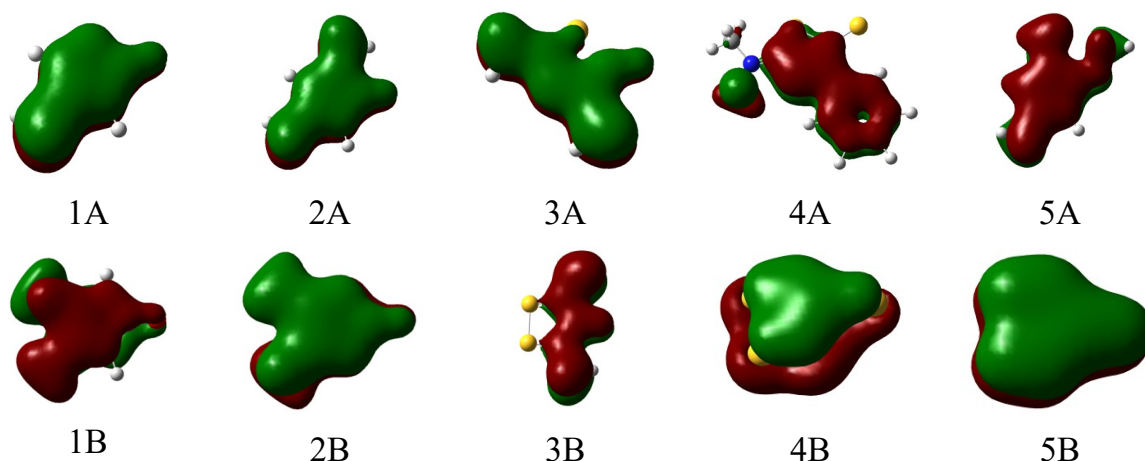


Figure 2. Molecular orbitals characterizing general molecular conjugation.

Table 5. NICS values obtained for studied molecules

	NICS(0) _{iso}	NICS(0) _{zz}	NICS(1) _{iso}	NICS(1) _{zz}
1A	-14.2	-0.9	-5.0	-15.4
2A	-10.4	4.0	-6.0	-16.7
3A	-9.1	4.6	-6.1	-12.5
4A	-6.9	18.5	-3.7	-3.4
5A	-8.5	9.9	-4.3	-12.3
1B	-10.5	1.9	-7.4	-17.1
2B	-8.7	1.7	-7.4	-18.0
3B	-12.7	-3.1	-8.9	-18.9
4B	-8.1	-1.0	-5.3	-11.6
5B	-34.7	-59.7	-18.6	-34.8
furan	-12.1	-8.2	-9.3	-27.1
pyrrole	-14.0	-12.0	-10.0	-30.8
thiophene	-13.1	-7.9	-10.1	-27.5

pyrazole	-13.9	-15.0	-11.3	-32.8
isothiazole	-13.5	-12.5	-11.0	-29.9
isoxazole	-12.3	-11.2	-10.3	-28.4
benzene	-8.0	-14.5	-10.2	-29.2

Conclusions

The central aim of presented research was to ascertain the significance of electron origin classifying criterion in influencing the electronic properties of the two identified types of mesoionic compounds – type A and type B. According to our investigation, the formal classification of mesoionic compounds finds some confirmation within the QTAIM framework with the principal distinguishing factor between the two types being the distribution pattern of ellipticities (i.e conjugation). Notably, type A compounds exhibit specific geometric attributes leading to a breach of conjugation. Despite possessing higher ellipticities, which can be treated as enhanced conjugation compared to type B compounds, the distribution of these ellipticities within type A molecules is non-uniform. Conversely, type B compounds, characterized by a more uniform distribution of ellipticities, display elevated NICS(1) values, albeit less conjugation than type A compounds.

Ultimately, it is imperative to acknowledge that, in comparison to reference molecules, compounds from both types exhibit markedly lower NICS(1) values, warranting their classification as non-aromatic. It is noteworthy that, notwithstanding distinctive patterns discernible in compounds of both types, certain exceptional structures deviate from these trends, showing unique properties.

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Мезоіонні сполуки умовно класифікують на два типи на основі первинного походження електронів у спряженій системі, зокрема визначеного розташуванням гетероатомів у п'ятичленному кільці. В представленій роботі було проведено дослідження різноманітних мезоіонних сполук, щоб відповісти на ключове запитання щодо їх класифікації: чи має значення первинне походження електронів і чи цей критерій визначає остаточну межу між двома типами сполук? Щоб вирішити цю проблему були проведені квантовохімічні розрахунки методом функціоналу густини (DFT) для ряду типових мезоіонних молекул. Електронні властивості молекул досліджувалися в рамках квантової теорії атомів у молекулах (QTAİM) і ядерно-незалежного хімічного зсуву (NICS). Для опису відмінностей між представниками двох типів мезоіонних сполук запропоновано набір індексів, призначених для характеристики електронних QTAİM параметрів у молекулах. Отримані результати показують, що існуюча класифікація є певною мірою виправданою, головним фактором відмінності між двома типами є характер еліптичностей зв'язків у п'ятичленному кільці та структури молекулярних орбіталей. На основі розрахунків NICS дійшли висновку, що обидва класи сполук обраного набору не характеризуються вираженою ароматичністю мезоіонного кільця.

Ключові слова: мезоіонні сполуки, теорія функціонала густини, квантова теорія атомів у молекулах, ядерно-незалежні хімічні зсуви.

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