Assessing the Mesoionic Compounds Definitions by QTAIM, NBO and Spackman charge models

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INTRODUCTION

The mesoionic compounds have been widely studied since late 19th century. Despite this, the definition of these compounds is still controversial. Most authors agree that mesoionic compounds have an important π-bonding delocalization and a large charge separation, but there is no agreement about how the π -bonds and the positive and negative charges are (de)localized throughout these compounds. The two main models commonly used to describe these molecules are shown in Figure 1.

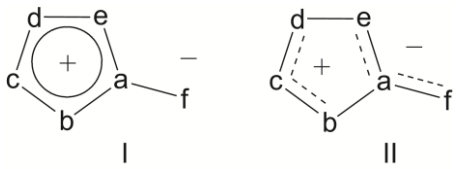

Figure 1. Mesoionic models I[1] and II[2]

In this work, we used three different charge models to evaluate the positive and negative charge distributions in these compounds: (i) Quantum Theory of Atoms in Molecules (QTAIM), (ii) Natural Bond Orbitals (NBO) and (iii) the Spackman's Geodesic scheme derived from Electrostatic Potential.

METHODS

We considered three different mesoionic rings: 1,3-diazole-4-thione (NNCS), 1,3-thiazole-5-thione (NSS) and 1,3-oxazol-5-one (NOO) and we also varied substituent groups to an overall of 48 structures. The structures were fully optimized to minimum geometries using M06-2X functional and cc-pVTZ basis set. Then, the charge calculations were performed with each method.

RESULTS AND DISCUSSION

The different charge models show some qualitative agreement in the mean charges of most atoms; but a few cases exhibit large differences. In addition, the absolute values differ much from a method to another, QTAIM charges, in general, have larger absolute values. Finally, the three methods disagree with both mesoionic models regarding the individual charges (Table 1) in these compounds.

Table 1. QTAIM, NBO and Spackman mean charges for the 48 mesoionic compounds

		d	c	b	e	a	f
QTAIM	NNCS	-1.273	1.297	-1.229	0.485	0.099	-0.161
	NSS	-1.267	0.529	0.380	0.526	-0.393	-0.032
	NOO	-1.286	1.267	-1.086	0.448	1.402	-1.245
		d	**c**	**b**	**e**	**a**	**f**
NBO	NNCS	-0.391	0.394	-0.337	0.049	-0.015	-0.372
	NSS	-0.370	0.041	0.458	0.046	-0.356	-0.232
	NOO	-0.366	0.386	-0.467	-0.125	0.676	-0.621
		d	**c**	**b**	**e**	**a**	**f**
Spackman	NNCS	-0.074	-0.095	0.333	0.233	-0.249	-0.467
	NSS	0.011	-0.100	0.151	0.172	-0.163	-0.360
	NOO	-0.036	0.057	-0.231	-0.138	0.500	-0.496

CONCLUSIONS

Therefore, the results show that mesoionic compounds have a complex electronic structure and do not follow the models I or II. Thus, a new and improved definition of mesoionic compounds is still needed.

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