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Research Article

Calculation the thermodynamic parameters of some imidazolidin-2,5-diones by using DFT method

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ABSTRACT

The aim of present studies is to focus on the structural optimization and thermodynamic properties of some 4-aryl-imidazolidin-2,5-diones (IMs) by using density functional theory (DFT). The collected data showed that the substitution on the aryl ring can be effective on the thermodynamic properties.

Keywords: Imidazolidin-2,5-dione; Thermodynamic; Density Functional Theory; Substitution

1. Introduction

Density functional theory (DFT) [1] has proved itself to be a valuable tool for the quantum mechanical description of electronic structure and properties of atoms, molecules, clusters and solids. The central theme of DFT is the use of the single-particle electron density [2] as the basic variable to express the energy of a many electron system as a unique functional of the density. Starting with the pioneering work of Hohenberg and Kohn [3], DFT has been elevated from its status of being a ground state theory to include excited states [4] and time-dependent phenomena [5]. Besides providing conceptual simplicity and computational economy, DFT has given birth to a number of important chemical concepts [1,6] and has also provided rigorous

foundation to many of the existing concepts, important examples being the concepts of electronegativity[7], chemical hardness [8], Fukui function [9] and several other chemical reactivity indices [10,11].

The importance of imidazolines in biochemistry has recently increased, since they are found in many biologically active compounds.[12] Preparation of 2-substituted imidazolines and oxazolines has become of great interest and importance because of their pharmaceutical1 and synthetic material applications.[13] In addition, these methodologies provide access to new derivatives of the imidazoline pharmacophore observed in many bioactive molecules, for example in the cardiovascular arena.[14]

They are also used in organic synthesis as synthetic intermediates,[15] chiral ligands,[16] chiral auxiliaries,[17] and so on. Furthermore, many oxidizing methods of imidazolines to imidazoles, which are also found in many biological compounds, have been reported.[18] However, it is essential to have reliable conventional methods at hand to study the geometry and conformational hyper surface of molecules with interesting biological properties. However, the characteristics studied in this work have not been studied so far.

2. Computational methods

Geometries of quinazolinone and its derivatives were optimized using density functional theory (DFT) B3LYP method with 6-31++G(d,p) and 6-311++G(2d,2p) basis sets. Compound **a** (with X = H) is considered as a reference to compound in the comparative investigation of the effect of the substitution on the aryl group at the 4 position on the optimized structures of 4-aryl imidazolin-2,5-diones (IMs)

Using Koopmans' approximation can be simplified to the calculation of the chemical potential energy (μ) and chemical hardness energy (η) by the following forms equations 2 and 3.

$\mu = (\varepsilon \text{ LUMO} + \varepsilon \text{ HOMO}) / 2$ (2)

$\eta = (\varepsilon \text{ LUMO} - \varepsilon \text{ HOMO}) / 2$; (3)

where the symbols have their usual meaning.

Using this simple idea, Parr et al. performed a variation calculation that led to the definition of the global electrophilicity index as ω=-ΔE(ΔN*), which may be recast into the more familiar form equation 4:

$$\omega = \frac{\mu^2}{2\eta} \qquad (4)$$

The global electrophilicity is defined in terms of the electronic chemical potential (μ) and the chemical hardness (η).

3. Results and discussion

The general structure of 4-aryl-imidazolin-2,5-diones (IMs) is shown in Fig. 1, where the numbering scheme used to describe these structures is also introduced.

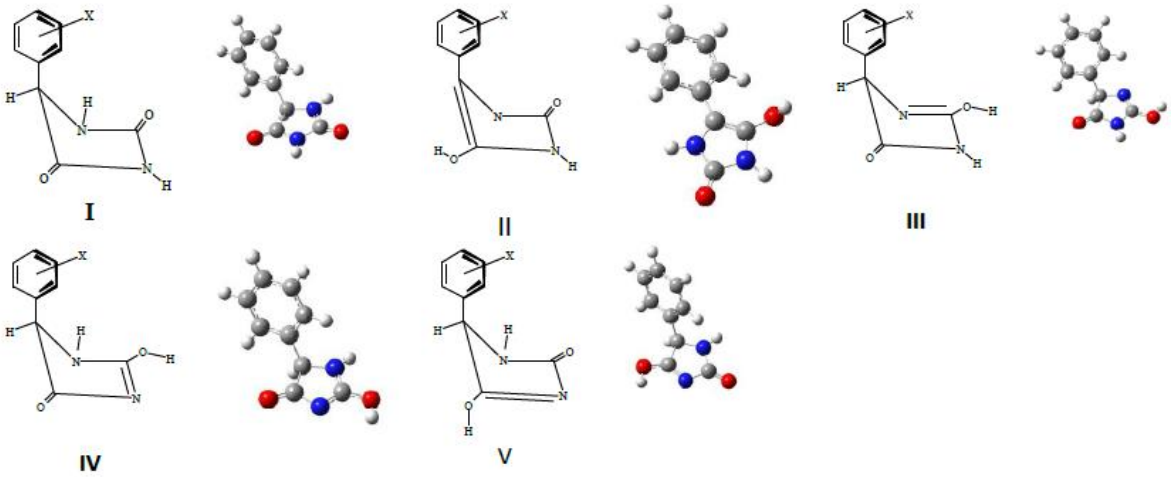

Fig 1: General structure of the imidazolidin-2,5-diones and derivatives with aryl-up conformation, and the numbering scheme used in this work. An example of the optimized structures imidazolidin-2,4-diones is given on the below. The red and blue balls represent the oxygen and nitrogen atoms, respectively

3.1. HOMO-LUMO energy

It is well-known that HOMO/LUMO (highest occupied or lowest unoccupied molecular orbital) and global electrophilicity/nucleophilicity energy interaction plays very important roles in chemical reaction. However, in this section, the HOMO and LUMO energies are calculated by B3LYP/6-311++G(d,p) method is shown below. According to equations (2), (3) and (4) one could calculate the chemical potential (μ), hardness (η) and global electrophilicity of these isomers. The data of this analysis are reported in the table 5. Furthermore, the orientationally averaged static polarizability were reported as:

$<\alpha 0> = (\alpha xx+\alpha yy+\alpha zz) / 3$ (5)

Which are calculated at HF/6-311++G(d,p) levels of theory. (Table1)

Table 1. Calculated HOMO, LUMO, chemical potential (μ), hardness (η) and global electrophilicity (ω) energy and averaged static polarizability (α) values of fives isomers of IMs using B3LYP/6-311++G(d,p) method. (Energies and averaged static polarizability are given in eV and a.u, respectively)

Isomer I													
Comp.	HOMO	LUMO	μ	η	ω	α	Comp.	HOMO	LUMO	μ	η	ω	α
a	-7.26	-1.21	-4.24	3.02	2.97	121.01	**k**	-7.07	-1.40	-4.24	2.84	3.17	144.09
b	-6.96	-1.05	-4.01	2.96	2.72	135.37	**l**	-7.17	-1.40	-4.28	2.88	3.14	142.55
c	-7.07	-1.05	-4.06	3.01	2.73	133.34	**m**	-6.96	-1.37	-4.16	2.79	3.10	140.80
d	-7.12	-1.02	-4.07	3.05	2.72	134.48	**n**	-7.25	-1.30	-4.28	2.98	3.07	120.88
e	-7.10	-1.16	-4.13	2.97	2.87	141.44	**o**	-7.36	-1.33	-4.34	3.02	3.13	120.91
f	-6.77	-1.11	-3.94	2.83	2.75	140.19	**p**	-7.31	-1.34	-4.33	2.99	3.14	120.85
g	-6.68	-1.03	-3.85	2.82	2.63	138.43	**q**	-7.57	-4.64	-6.10	1.46	12.74	141.28
h	-7.19	-1.39	-4.29	2.90	3.17	135.64	**r**	-7.75	-5.25	-6.50	1.25	16.95	138.79
i	-7.28	-1.39	-4.33	2.95	3.19	134.40	**s**	-7.65	-4.95	-6.30	1.35	14.72	138.18
j	-7.33	-1.35	-4.34	2.99	3.15	133.40							

Isomers II

Comp.	HOMO	LUMO	μ	η	ω	α	Comp.	HOMO	LUMO	μ	η	ω	α
a	-5.48	-1.44	-3.46	1.29	4.63	133.40	**k**	-5.65	-1.63	-3.64	1.19	5.53	159.71
b	-5.08	-1.29	-3.18	1.25	4.05	148.86	**l**	-5.70	-1.67	-3.69	1.18	5.78	156.95
c	-5.42	-1.42	-3.42	1.30	4.51	147.46	**m**	-5.63	-1.34	-3.49	1.47	4.14	151.22
d	-5.44	-1.42	-3.43	1.30	4.50	142.62	**n**	-5.59	-1.56	-3.57	1.24	5.15	132.75
e	-5.08	-1.29	-3.18	1.25	4.05	154.27	**o**	-5.67	-1.61	-3.64	1.22	5.42	134.06
f	-5.41	-1.41	-3.41	1.29	4.51	153.39	**p**	-5.51	-1.48	-3.50	1.28	4.79	134.00
g	-5.34	-0.88	-3.11	1.75	2.70	151.82	**q**	-5.93	-4.29	-5.11	0.82	15.92	167.88
h	-5.64	-1.61	-3.62	2.01	3.26	150.52	**r**	-5.95	-2.77	-4.36	0.21	45.41	154.21

Isomers III

Comp.	HOMO	LUMO	μ	η	ω	α	Comp.	HOMO	LUMO	μ	η	ω	α
a	-6.75	-1.55	-4.15	2.60	3.31	121.33	**k**	-6.75	-1.16	-3.96	2.80	2.80	144.40
b	-6.56	-0.86	-3.71	2.85	2.41	135.68	**l**	-6.93	-1.05	-3..99	2.94	2.71	143.03
c	-6.80	-0.76	-3.78	3.02	2.37	134.73	**m**	-6.95	-1.02	-3.98	2.96	2.68	141.31
d	-6.79	-0.77	-3.78	3.01	2.38	133.81	**n**	-6.84	-1.05	-3.94	2.89	2.68	120.94
e	-6.73	-0.95	-3.84	2.89	2.56	140.31	**o**	-6.97	-1.31	-4.14	2.83	3.03	121.05
f	-6.45	-1.54	-3.99	2.45	3.25	140.67	**p**	-6.77	-1.48	-4.13	2.65	3.22	121.33
g	**-6.28**	-0.80	-3.43	2.74	2.29	139.26	**q**	-7.24	-4.39	-5.81	1.43	11.85	141.93
h	**-6.83**	-1.14	-3.98	2.84	2.79	135.80	**r**	-7.49	-2.79	-5.14	2.35	5.63	139.87
i	**-7.04**	-1.04	-4.04	3.00	2.72	134.81	**s**	-7.15	-4.34	-5.57	1.40	11.76	138.68
j	**-7.02**	-1.00	-4.01	3.01	2.68	133.78							

Isomers IV

Comp.	HOMO	LUMO	μ	η	ω	α	Comp.	HOMO	LUMO	μ	η	ω	α
a	**-6.68**	-1.90	-4.29	2.39	3.85	123.18	**k**	-6.73	-2.05	-4.39	2.34	4.12	146.63
b	**-6.51**	-1.84	-4.18	2.34	3.74	137.64	**l**	-6.83	-2.06	-4.44	2.39	4.13	145.60
c	**-6.60**	-1.86	-4.23	2.37	3.77	136.97	**m**	-6.89	-1.19	-4.04	2.85	2.87	144.22
d	**-6.59**	-1.85	-4.22	2.37	3.37	135.61	**n**	-6.75	-2.02	-4.39	2.37	4.06	122.81
e	**-6.63**	-1.93	-4.28	2.35	3.90	143.47	**o**	-6.85	-2.04	-4.44	2.40	4.11	123.09
f	**-6.59**	-1.91	-4.25	2.34	3.86	143.08	**p**	-6.77	-1.93	-4.35	2.42	3.92	123.01
g	**-6.42**	-1.72	-4.07	2.35	3.53	141.87	**q**	-7.08	-4.55	-5.81	1.26	13.38	144.52
h	**-6.76**	-2.05	-4.40	2.36	4.12	137.79	**r**	-7.10	-4.55	-5.82	1.28	13.26	142.00
i	**-6.85**	-2.06	-4.45	2.40	4.13	137.28	**s**	-7.12	-4.49	-5.80	1.31	12.80	140.61
j	**-6.73**	-1.91	-4.32	2.41	3.87	136.12							

Analysis of the data that reported in the table 1 predicts the most stable isomer is isomer **I**, with no exception compounds, because this isomer has the less electrophilicity.

Analysis of the optimized structures of imidazolidin-2,4-diones that the five-membered ring adopts a envelope conformation, flattened at N1 toward an envelope conformation, with a pseudo-axial orientation of the C4 substituent. In Tables 1 the optimized lengths of the C2=O6, C5=O7, N1–H, N3–H, and C4–H bonds that play a role in the activities of IMs are listed. Furthermore, the optimum values of the N1-C2-N3and N1-C5-C4 triangles, denoted by α and β respectively reported in Tables 1.

Table 2: Selected B3LYP/6-311++G(d,p) optimized geometrical parameters obtained for IMs (bond lengths and triangles are given in Å and degrees, respectively)

Comp.	C2=O6	C5=O7	N1-H	N3-H	C4-H	α	β
a	1.2079	1.2045	1.0096	1.0071	1.0962	105.35	105.59
b	1.2083	1.2047	1.0096	1.0070	1.0957	105.34	105.62
c	1.2083	1.2045	1.0096	1.0070	1.0955	105.34	105.61
d	1.2085	1.2052	1.0097	1.0076	1.0975	105.35	105.67
e	1.2084	1.2049	1.0096	1.0071	1.0957	105.32	105.67
f	1.2080	1.2046	1.0095	1.0070	1.0958	105.32	105.56
g	1.2092	1.2054	1.0091	1.0077	1.0955	105.62	105.57
h	1.2070	1.2042	1.0098	1.0077	1.0967	105.44	105.54
i	1.2066	1.2041	1.0098	1.0077	1.0965	105.43	105.51
j	1.2076	1.2044	1.0095	1.0068	1.0969	105.40	105.37
k	1.2069	1.2041	1.0098	1.0077	1.0967	105.44	105.54
l	1.2066	1.2041	1.0098	1.0078	1.0967	105.44	105.50
m	1.2076	1.2044	1.0095	1.0068	1.0970	105.39	105.31
n	1.2072	1.2043	1.0098	1.0076	1.0966	105.42	105.58
o	1.2067	1.2040	1.0098	1.0077	1.0965	105.43	105.50
p	1.2071	1.2048	1.0095	1.0073	1.0955	105.46	105.57
q	1.2055	1.2035	1.0100	1.0082	1.0967	105.50	105.41

A review of the data reported in table 1 shows that the C2=O6, C5=O7, N1-H, N3-H and C4-H bond lengths in the IMs compounds are very close, while they are dependent on the type of the substituent at the 4 position. The optimized structural parameters show that partial conjugation of the N1, N3 and N5 atoms with the carbonyl groups (C2=O6 and C5=O7) depends on the α and β angles, since approach of the 27=O6 group towards the coplanar conformation results in an increase in the C2=O6 bond lengths, and a decrease in the C5=O7 bond length. Analysis of the data reported in the table 1 show that the N1-C2-N3and N1-C5-C4 triangles are not flat because values of the N1-C2-N3and N1-C5-C4 triangles are <120°.

This parameter can be effect on the resonance of electron pair of N1 and N3 atoms with C=O groups.

3.2. Vibration analysis

Vibration analysis was carried out on the optimized geometries of the DHPMs at B3LYP/6-311++G(d,p) level of theory. The harmonic frequencies calculated for IMs along with their IR intensities (given in parentheses) are reported in Table 3.

Table 3: Calculated harmonic frequencies (cm-1) (IR intensities) obtained for the B3LYP/6-311++G(d,p) optimized structures of IMs.

Comp.	C2=O6	C5=O8	Comp.	C2=O6	C5=O8
a	1815.9 1020.6)	1851.2(278.9)	**k**	1817.6(1006.9)	1853.6(309.2)
b	1814.9(1029.6)	1849.9(284.6)	**l**	1818.1(980.6)	1854.8(293.1)
c	1814.3(1032.3)	1850.2(280.5)	**m**	1816.0(1005.4)	1852.0(246.1)
d	1816.1(1086.4)	1848.4(297.3)	**n**	1817.0(1007.0)	1853.0(278.6)
e	1814.3(1029.6)	1849.0(284.2)	**o**	1818.0(1007.1)	1854.6(281.8)
f	1815.4(1016.3)	1850.8(279.5)	**p**	1816.0(1056.0)	1852.6(257.0)
g	1810.5(1063.2)	1846.4(203.4)	**q**	1820.4(982.2)	1857.8(311.6)
h	1817.4(1007.6)	1853.5(299.8)	**r**	1819.3(934.3	1858.2(323.9)
i	1818.0(989.4)	1854.5(287.6)	**s**	1820.1(1046.9)	1858.9(226.2)
j	1816.4(1034.1)	1852.3(250.4)			

The C2=O67 and C5=O8 stretching frequencies in IMs core are normally lies between 1814.3-1820.4 and 1846.4-1858.9 cm-1, respectively. In this region, the bands are affected, appreciably by the nature of the substituents. A review of the data reported in Table 1 shows also that the vibrational frequencies of these carbonyl groups in the heterocyclic of IMs core dependence on the type and position of the substituent.

3.3. Thermochemical analysis

Standard formation enthalpies (ΔH°f) of the 4-aryl-the imidazolidin-2,5-diones compounds were calculated by using the B3LYP/6-311++G(d,p) level and below reaction. (Eq. 1) The results of the calculations are reported in table 2.

a C (s) + *b* H2 (g) + *c* N2 (g) + *d* O2 (g) → product 1

Table 4: Standard enthalpies of the formation of some IMs calculated based on the B3LYP/6-311++G(d,p) optimized structures IMs compounds.

Comp.	$\Delta H°_f$	Comp.	$\Delta H°_f$	Comp.	$\Delta H°_f$	Comp.	$\Delta H°_f$
a	-261.33	**f**	-462.83	**k**	-228.52	**p**	-454.87
b	-273.84	**g**	-462.25	**l**	-228.27	**q**	-425.59
c	-273.67	**h**	-290.60	**m**	-214.13	**r**	-425.12
d	-263.33	**i**	-290.44	**n**	-459.45	**s**	-401.39
e	-463.20	**j**	-279.39	**o**	-459.64		

The analysis of the data reported in Table 2 shows that the synthesis of MIs are exothermic and ΔH0f also depends on the type and position of the substituent on the aryl ring.

4. Conclusions

The B3LYP/6-311++G(d,p) calculations show that the heterocyclic ring in all IMs has a flat *envelope* conformation, and the aryl rings substituted at the 4 position are not perpendicular to heterocyclic ring of IMs. Calculated harmonic frequencies of the CO bond stretching show the general order υC5=O8>υC2=O6. Furthermore, the balance between donor-acceptor interactions of different bonds/atoms of the aryl ring and those of the heterocyclic ring plus induction and resonance effects determines the differences in the formation of enthalpies of IMs compounds.

References

[1] R.G.Parr, W.Yang, Density Functional Theory of Atoms and Molecules; Oxford University Press, New York, 1989.

[2] N.H.March, B.M.Deb, Single Particle Density in Chemistry and Physics.Academic Press, London, 1987.

[3] P.Hohenberg, W.Kohn, *Phys. Rev*. 136 (1964) B864.

[4] A.Theophilou, *J. Phys.* C12 (1979) 5419.

[5] E.Runge, E.K.U. Gross, *Phys. Rev. Lett*. 52 (1984) 99.

[6] P.Geerlings, F. De Proft, *Phys. Chem. Chem. Phys*. 10 (2008) 3028.

[7] R.G.Parr, R.A.Donnelly, M. Levy, W.E. Palke, *J. Chem. Phys*. 68 (1978) 3801.

[8] R.G.Parr, R.G. Pearson, *J. Am. Chem. Soc*. 105 (1983) 7512.

[9] R.G.Parr; W.Yang, *J. Am. Chem. Soc*. 106 (1984) 4049.

[10] P.K. Chattaraj, (Ed.), Chemical Reactivity Theory, A Density Functional View, CRC, Boca Raton, 2009.

[11] P.K Chattaraj, S.Giri, *Prog. Chem. C: Phys. Chem*. 105 (2009) 13.

[12] M.Anasatassiadou, S.Danoun, L.Crane, G.Baziard-Mouysset, M. Payard, D. Caignard, M. C.Rettori, P. Renard, *Bioorg. Med.Chem*. 9 (2001) 585.

[13] M. E.Jung, A.Huang, *Org. Lett*. 2 (2000) 2659.

[14] R. R.Ruffolo, W. E.Bondinell, J.P.Hieble, *J. Med. Chem*. 38(1995) 3681-3716.

[15] H.Du, Y.He, R. Sivappa, C.Lovely, *Synlett*. 28 (2006) 965.

[16] A.Bastero, C.Claver, A.Ruiz, S.Castill_on, E.Daura, C.Bo, E.Zangrando, .*J Chem. Eur*. 10 (2004) 3747.

[17] Y.Langlois, P. I. Dalko, *J. Org. Chem*. 63 (1998) 8107.

[18] M.Ishihara, H. Togo, *Synlett*. 28 (2006) 227.