NMR, Aromaticity and Energetic Property in $C_6H_4O_2M$ (M=C, S, O and N) Dicarbaldehyde Derivatives: A Computational Study

GOLDASTEH ZAREI, REZA SOLEYMANI* and REYHANEH DEHGHANIYAN DEJVEJEN

Department of Chemistry, Tehran Branch, Islamic Azad University, Tehran, Iran.
*Corresponding author E-mail: reza.soleymani@hotmail.com

ABSTRACT

By using density functional theory (DFT) in B3LYP/6-311G(d,p) level of theory, NMR properties, energetic parameters, aromaticity, HOMO and LUMO parameters, were identified for a group of dicarbaldehydes, namely furan-2,5-dicarbaldehyde, pyrrole-2,5-dicarbaldehyde, thiophene-2,5-dicarbaldehyde, and cyclopenta-3,5-diene-1,3-dicarbaldehyde. NMR parameters were examined through GIAO method by calculating NICS at different points for the structures mentioned above. In addition, HOMO and LUMO related properties, including chemical hardness, chemical potential, electrophilicity, and the max amount of electronic charge transferred. Furthermore, to investigate chemical reactivity of the structures, electrostatic potential was evaluated at different parts of each structure.

Key words: DFT; Aromaticity; NICS; Electrostatic Potential.

INTRODUCTION

Thiophene-2,5-dicarbaldehyde, pyrrole-2,5-dicarbaldehyde, furan-2,5-dicarbaldehyde, cyclopenta-3,5-diene-1,3-dicarbaldehyde are compounds from dicarbaldehydes family that previously have been synthesized experimentally [1]. Due to their structural characteristics and particular chemical properties, these compounds have found wide applications in different industries. Numerous reports indicate their applications in industry, pharmaceutics, agriculture, chemical industries, as well as uses in variety of mechanisms including complexomety. Given their particular

structure, these compounds are capable of going through substitution. Such substitution changes some of their properties, like reactivity or synthetic or thermodynamic parameters [2-10].

The present study attempts to examine the effects of halogen substituent on such parameters as aromaticity scale as well as NMR, HOMO and LUMO related parameters. The first parameter, Nucleus Independent Chemical Shift (NICS), was calculated for different parts of the ring. The difference in this parameter stems from delocalized electron in the ring. Magnetic shielding provides us with exactly those data on delocalized electrons

and aromaticity, known as NICS. Conventionally, NICS is defined as the negative value of the absolute magnetic shielding calculated at selected points in vicinity of molecules. Negative values of NICS (magnetic shielding) inside the ring or molecule cages indicate presence of diatropic ring currents or armoaticity while positive values of NICS (lack of magnetic shielding) shows existence of paratropic ring currents or anti-aromaticity [11-13].

NICS is defined as the negative value of the absolute magnetic shielding calculated at the ring centre. In general, NICS values are calculated using virtual nuclei (ghost atoms) at different parts of molecules. The more the negative value of this descriptor the greater is the aromatic character of the molecular system. It is usually better to calculate this parameter in vicinity of the ring center. To calculate this parameters, two virtual points where considered; one at the ring center and another one angstrom above the ring centre (Figures 1 and 2).

The next parameter, electrophilicity, is a parameter which is well correlated with HOMO and LUMO indices and some reported that it is proportional to compound stability [11]. This parameter is calculated using Equation (1). In fact, electrophilicity is proportional to ionization potential and electron affinity. In addition, (2) and (3) can be used to determine chemical potential and chemical hardness. These parameters are correlated with HOMO and LUMO indices as well and therefore differ from one compound to another. Indeed, as electronegativity varies, it is expected that chemical potential changes as well. Increase in electron potential or decrease in chemical hardness can result in a good electrophone species. Equation (4) can be used to calculate the largest amount of charge transferred by electrons [14,15].

$$\Omega = \mu^2 / 2\eta = \chi^2 / 2\eta \qquad ...(1)$$

$$\chi = -\mu(\delta_E / \delta_N)_{VT} \approx (1+A)/2 \approx -1/2(\varepsilon_{HOMO} + \varepsilon_{LUMO}) ...(2)$$

$$\eta = (\delta_{2E} / \delta_{N2})_{VI} = (1-A) \approx (\varepsilon_{HOMO} + \varepsilon_{LUMO}) \qquad ...(3)$$

$$\Delta N_{max} = -\mu / \eta \qquad ...(4)$$

Finally, a number of thermodynamic parameters together with electrostatic potentials were evaluated for the structures.

Computational details

All computations were performed in gaseous state, at the pressure of 1 atmospheric and temperature of 298 K. Pentium IV computer with a 4 Gigabyte of RAM in corei7 processor was used to make computations in XP® operation system. The structures were initially designed through Gauss view [16] and final optimization was carried out using the program package Gaussian 09w [17]. B3LYP/6-311G(d,p) level of theory was employed in the computations. Once final optimization was performed, GIAO was used for calculating NICS values and chemical shifts at the different parts of the structures [18]. To calculate NICS, two virtual points where considered; one at the ring center and another one angstrom above the ring centre. Chemical shifts for nitrogen nuclei were calculated using TMS as reference. Finally, electrostatic potential was examined for different parts of the structures using Molekel software [19-24].

RESULTS AND DISCUSSION

Once final optimization was carried out, overall results were extracted. First, thermodynamic parameters were extracted and then other associated parameters were calculated and analyzed.

Energetic property

Low energy levels indicate higher levels of stability. In other words, reduced level of electronic energy, rotational and vibrational results in more stable structures.

Relative energy and stability

Table 1 summarizes the results obtained through quantum computations. The findings indicate high levels of energy for compounds with Hydrogen substitution and low levels of energy for compounds with Bromine substitution. In addition, when Carbon element is used instead of M atom, a lower level of energy is achieved compared to the case where S, N, or O atoms are used. This can be attributed to the fact that when M is an atom other than Carbon, nonbinding pair of electrons interferes

Table 1. The values of electronic energies, E (Kcal/mol), relative electronic energies, E_{rel} (Kcal/mol), zero point vibrational energies, ZPVE (Kcal/mol) and dipole moments (Debye) of all of $C_6H_4O_2M$ (M=C, S, O and N) dicarbaldehyde derivatives calculated at the B3LYP/6-311G(d,p) level

Compound			E_0	E_{rel}	Order	ZPVE	Dipole
M	X	Entry					moment
C	Br	1a	-1878927.981	225230.932	4	63.585	3.762
	Cl	2a	-552442.194	1551716.718	8	63.995	3.605
	F	3a	-326316.710	1777842.203	13	64.970	3.835
	H	4a	-264025.311	1840133.601	16	69.883	4.673
N	Br	1b	-1889021.971	215136.942	3	57.456	2.987
	Cl	2b	-562535.905	1541623.007	7	57.828	2.835
	F	3b	-336408.762	1767750.151	12	58.709	3.038
	H	4b	-274120.996	1830037.916	15	63.765	3.964
O	Br	1c	-1901479.093	202679.820	2	49.145	5.212
	Cl	2c	-574992.900	1529166.013	6	49.525	5.002
	F	3c	-348865.769	1755293.144	11	50.452	5.107
	H	4c	-286579.191	1817579.722	14	55.474	6.021
S	Br	1d	-2104158.913	0.000	1	47.132	4.134
	Cl	2d	-777672.830	1326486.082	5	47.522	3.947
	F	3d	-551546.766	1552612.146	9	48.462	4.114
	H	4d	-489257.966	1614900.947	10	53.463	5.118

Table 2. Values of energies of the frontier molecular orbitals (ε_{HOMO} and ε_{LUMO}, eV), electronic chemical potential, µ (eV), chemical hardness, η (eV), electrophilicity, ε (eV) and maximum amount of electronic charge transfer for all of $C_6H_4O_2M$ (M=C, S, O and N) dicarbaldehyde derivatives calculated at the B3LYP/6-311G(d,p) level

Compound	HOMO	LUMO	µ	η	ω	ΔNmax
1a	-0.2684	-0.1203	-0.1944	0.1481	0.1275	1.3126
2a	-0.2705	-0.1209	-0.1957	0.1496	0.1280	1.3084
3a	-0.2698	-0.1182	-0.1940	0.1515	0.1242	1.2801
4a	-0.2652	-0.1125	-0.1888	0.1527	0.1168	1.2368
1b	-0.2619	-0.1027	-0.1823	0.1591	0.1044	1.1455
2b	-0.2646	-0.1035	-0.1841	0.1611	0.1051	1.1426
3b	-0.2643	-0.1016	-0.1830	0.1627	0.1029	1.1247
4b	-0.2598	-0.0943	-0.1771	0.1655	0.0947	1.0702
1c	-0.2778	-0.1141	-0.1960	0.1636	0.1173	1.1978
2c	-0.2808	-0.1152	-0.1980	0.1655	0.1184	1.1961
3c	-0.2813	-0.1140	-0.1976	0.1673	0.1167	1.1811
4c	-0.2767	-0.1067	-0.1917	0.1699	0.1081	1.1280
1d	-0.2762	-0.1213	-0.1987	0.1549	0.1275	1.2832
2d	-0.2799	-0.1221	-0.2010	0.1578	0.1280	1.2736
3d	-0.2807	-0.1201	-0.2004	0.1606	0.1251	1.2482
4d	-0.2787	-0.1135	-0.1961	0.1651	0.1164	1.1875

Table 3. NICS(0) and NICS(1) values for all of $C_6H_4O_2M$ (M=C, S, O and N) dicarbaldehyde derivatives calculated at the B3LYP/6-311G(d,p) level

Compound	Nucleic independent chemical shift (ppm)	
	NICS(0)	NICS(1)
1a	-3.5548	-5.5105
2a	-4.0763	-5.5643
3a	-5.9041	-5.6021
4a	-2.4991	-5.4926
1b	-12.4919	-10.0374
2b	-12.9353	-10.0839
3b	-14.5509	-10.1251
4b	-12.1694	-10.4342
1c	-11.5171	-9.6580
2c	-11.9401	-9.6641
3c	-13.4416	-9.6572
4c	-11.2771	-10.0178
1d	-11.7664	-9.8161
2d	-12.1260	-9.8148
3d	-13.5300	-9.8487
4d	-11.3356	-10.1376

with the resonance space, resulting in higher resonance stability, reduced level of energy, and increased stability (Figure 3).

Dipole moment

Dipole moment is caused by difference in electronegativity of elements, thus, creating difference in magnetic moment. This parameter was examined for the structures studied here. The parameter varies from 2.83 to 6.02 debye. This is attributable to M or halogen substitution. As seen in Table 1, the maximum value for this parameter is achieved when M is substituted with Oxygen while the minimum value is reached when Nitrogen substitutes.

HOMO and LUMO indices

HOMO and LUMO indices were studied for the compounds through quantum mechanics calculations. The results are presented in Table 2. These parameters can be used to describe chemical hardness, chemical potential, electrophilicity, and largest amount of transferred charge by electrons for the structures. The findings suggest that dependent parameters vary as HOMO and LUMO values change. Changes in HOMO and

Table 4. Computed B3LYP/6-311G(d,p) isotropic chemical shifts for ^{1}H in $C_6H_4O_2M$ (M=C, S, O and N) dicarbaldehyde derivatives respect TMS references

Methods	Isotropic Chemical Shift (TMS reference) B3LYP/6-311G(d,p)					
Entry	H1	H2	H3	H4	H5	H6
1a	10.40	10.22	6.99	-	3.53	3.53
2a	10.46	10.20	6.91	-	3.50	3.50
3a	10.48	10.23	6.96	-	3.45	3.45
4a	10.32	10.32	7.28	7.28	3.54	3.54
1b	10.10	9.90	6.68	-	9.20	-
2b	10.14	9.87	6.58	-	9.06	-
3b	10.16	9.90	6.38	-	8.82	-
4b	10.02	10.02	6.80	6.80	9.31	-
1c	10.23	9.99	6.88	-	-	-
2c	10.26	9.96	6.80	-	-	-
3c	10.26	9.96	6.72	-	-	-
4c	10.10	10.10	7.00	7.00	-	-
1d	10.31	10.13	7.25	-	-	-
2d	10.36	10.10	7.16	-	-	-
3d	10.43	10.14	7.10	-	-	-
4d	10.25	10.25	7.47	-	-	-

LUMO indices totally depend on M and type of halogen substituent attached to it. Figure 4 illustrates HOMO-LUMO gap in the form of DOS spectrum.

Figure 5 depicts the changes in electrophilicity. As seen in the figure, the minimum electrophilicity is reached when M is substituted with Nitrogen.

Aromaticity indices

Aromaticity is directly connected to stability. The more aromatic is a structure the higher levels of stability are expected. Changes in aromatic properties in the compounds were determined using NICS for different parts. The more negative is the NICS value, the higher levels of aromatic stability are expected. The index is, however, only considered for rings.

NICS indices

NICS indices for the structures were calculated using GIAO. The results are presented in Table 3. To investigate NICS values in the compounds we considered two points: one at the ring center and another one angstrom above the

ring centre. Figure 6 compares the results. As seen in the results, the parameter varies as M is substituted with another atom or as the substituent X is replaced. The figure indicates that in majority of compounds examined here, NICS value at the ring center is more negative compared to corresponding values obtained at one angstrom above the ring center. Therefore, higher levels of aromaticity are expected at the ring center compared to the space above the center. This can be attributed to higher resonance inside the ring which creates isotropic current.

^{1}H-NMR indices

Nucleus magnetic resonance (NMR) describes the chemical environment around nuclei and can be used to determine some chemical properties of compounds. In the structures studied here, chemical shift was investigated for hydrogen atom nucleus using DFT-GIAO in B3LYP/6-311G(d,p) level of theory. Isotropic chemical shift values of Hydrogen nuclei were studied as well (Table 4). All results were obtained using TMS as reference.

Table 5. Bond lengths (Å) for all of $C_6H_4O_2M$ (M=C, S, O and N) dicarbaldehyde derivatives obtained at the B3LYP/6-311G(d,p) level

Entry	Bond length (Angstrom)								
	C1-C2	C5-C6	C2-C3	C4-C5	C2-M	C5-M	C3-C4	C1-O1	C6-O2
1a	1.466	1.463	1.357	1.362	1.503	1.500	1.451	1.213	1.211
2a	1.466	1.462	1.357	1.362	1.500	1.502	1.450	1.211	1.214
3a	1.466	1.458	1.358	1.359	1.502	1.504	1.445	1.211	1.214
4a	1.463	1.463	1.361	1.361	1.501	1.501	1.449	1.213	1.213
1b	1.460	1.459	1.397	1.400	1.362	1.365	1.402	1.213	1.214
2b	1.460	1.458	1.396	1.400	1.362	1.365	1.401	1.213	1.215
3b	1.460	1.454	1.399	1.397	1.361	1.368	1.396	1.213	1.215
4b	1.457	1.457	1.398	1.398	1.364	1.364	1.453	1.214	1.214
1c	1.467	1.466	1.373	1.379	1.357	1.359	1.415	1.206	1.207
2c	1.468	1.465	1.373	1.380	1.354	1.357	1.414	1.206	1.208
3c	1.468	1.461	1.375	1.377	1.354	1.360	1.408	1.206	1.208
4c	1.465	1.465	1.376	1.376	1.356	1.356	1.415	1.207	1.207
1d	1.468	1.468	1.377	1.382	1.735	1.739	1.411	1.209	1.210
2d	1.468	1.467	1.377	1.383	1.735	1.738	1.410	1.208	1.210
3d	1.468	1.463	1.379	1.380	1.737	1.738	1.405	1.208	1.211
4d	1.465	1.465	1.381	1.381	1.737	1.737	1.410	1.209	1.209

Structural parameters

Once final optimization was carried out, length of structures were determined and analyzed. The results indicate that changing halogen substituent or M atoms leads to changes in bond length at some parts of the structure. Table 5 presents the results. As seen in the table, changes in vicinity of halogen substituent experience more variations as halogen substitution takes place.

Electrostatic potential map

To evaluate electric potentials in the structures, we first optimized the structures using B3LYP/6-311G(d,p) level of theory and then calculated electric potential for each structure [25]. Molecular electronic potential maps (MEPM) determine locations which are more likely to become the target for electrophilic attacks. In fact MEPM determines reactivity for different parts of molecules.

As seen in Figure 7, as we approach the blue region electric potential increases while areas near the red region represent smaller electric potentials. Electric potential is negative at the location of Oxygen atoms while for Carbon groups, electric potential becomes positive (*i.e.* closer to the blue region).

M = C, N, O and S

X = F, Cl, Br and H
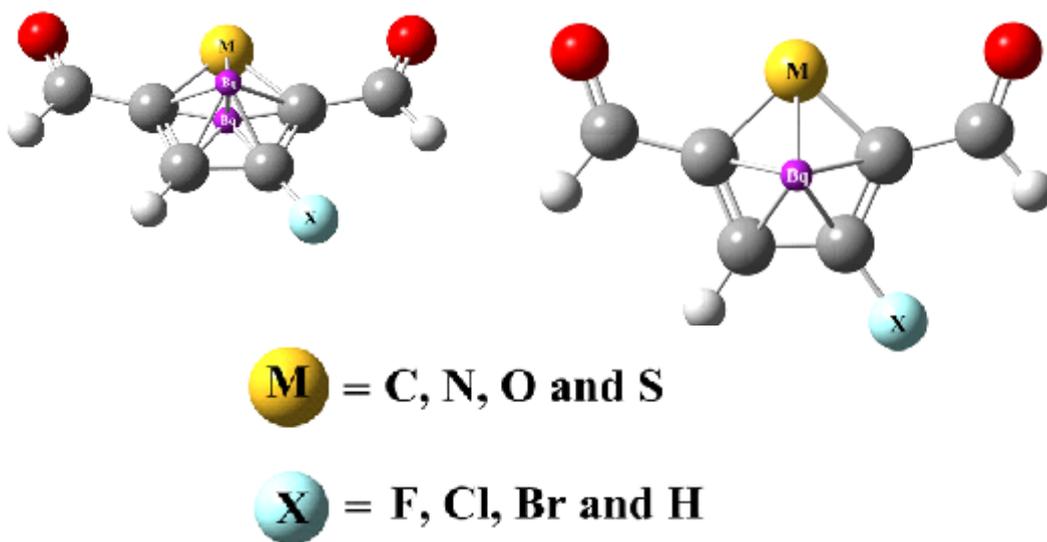
Fig.1: Definition of points at which the NICS values were calculated
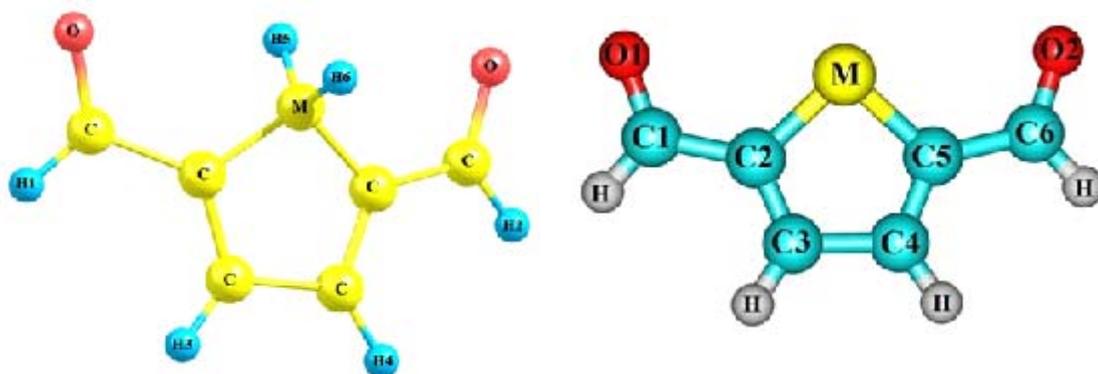
Fig. 2: Show C$_6$H$_4$O$_2$M (M=C, S, O and N) dicarbaldehyde derivatives including atom numbering
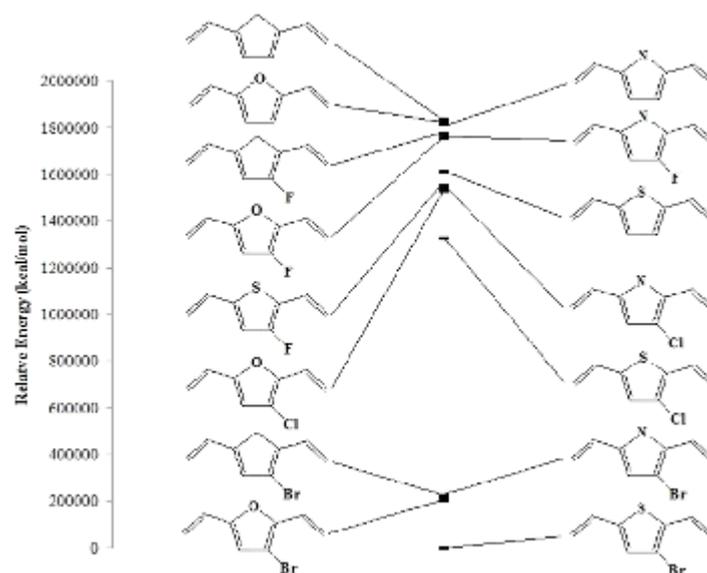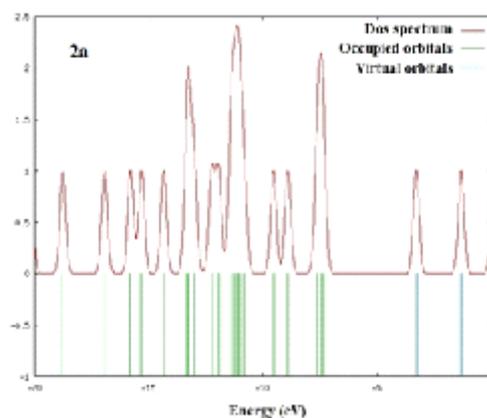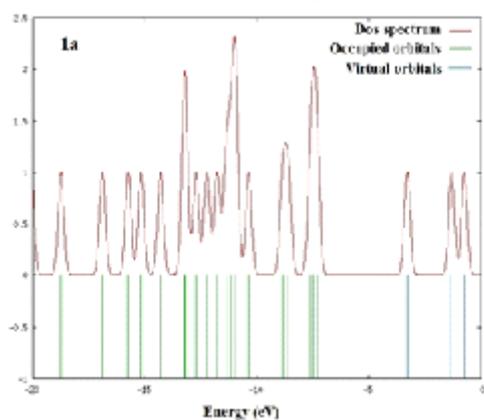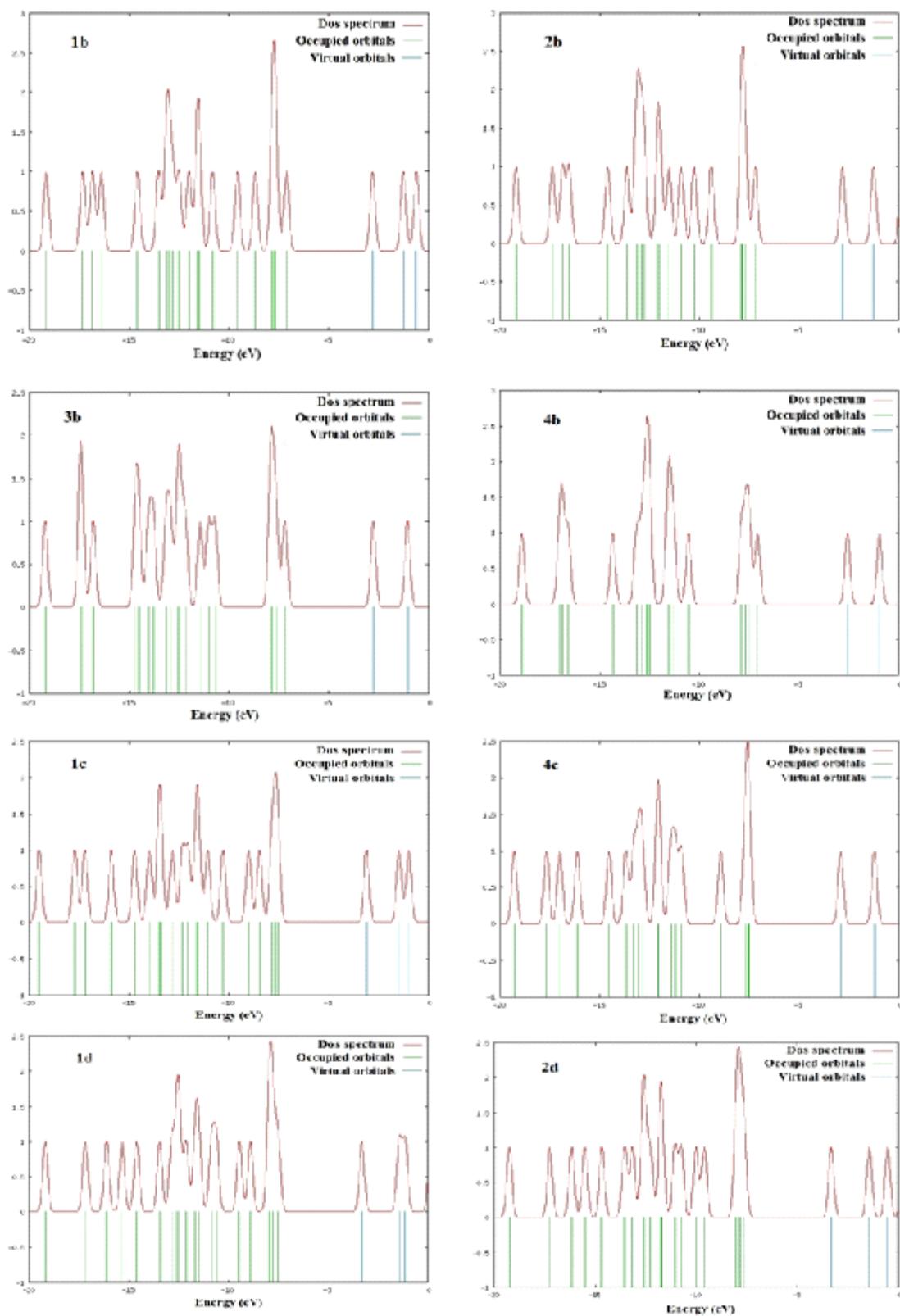
**Fig. 3: Show relative energy (Kcal/mol) in various
C$_6$H$_4$O$_2$M (M=C, S, O and N) dicarbaldehyde derivatives**
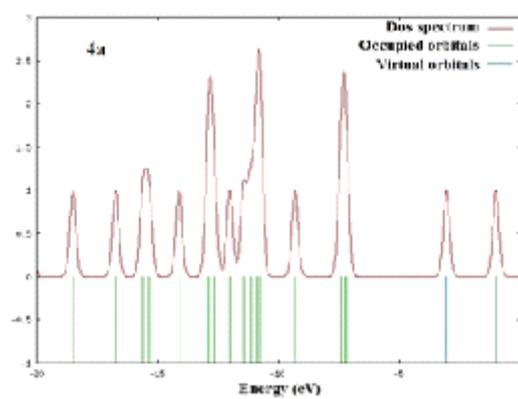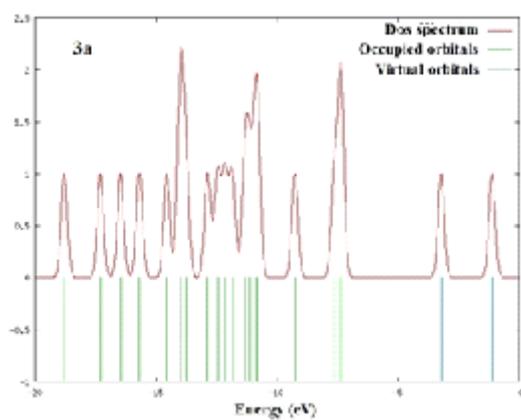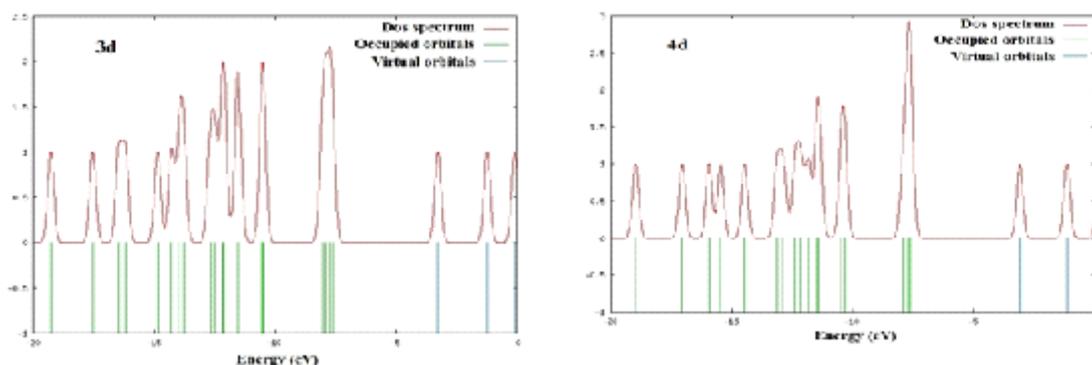
Fig. 4: Partial DOS diagram containing HOMO (left) and LUMO (right) plot of C$_6$H$_4$O$_2$M (M=C, S, O and N) dicarbaldehyde derivatives obtained by B3LYP/6-311G(d,p) level of theory
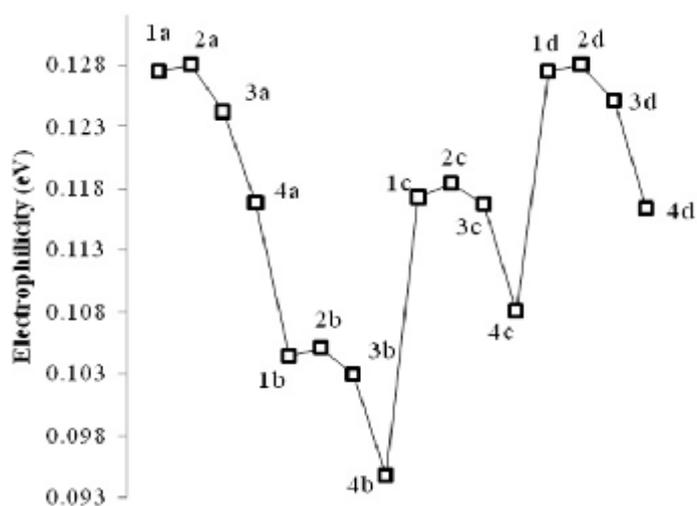

Fig. 5: Show relative electrophilicity value for various C$_6$H$_4$O$_2$M (M=C, S, O and N) dicarbaldehyde derivatives
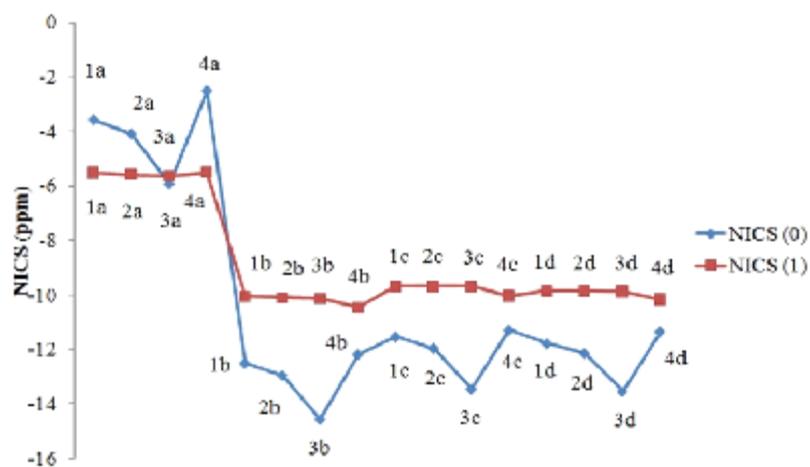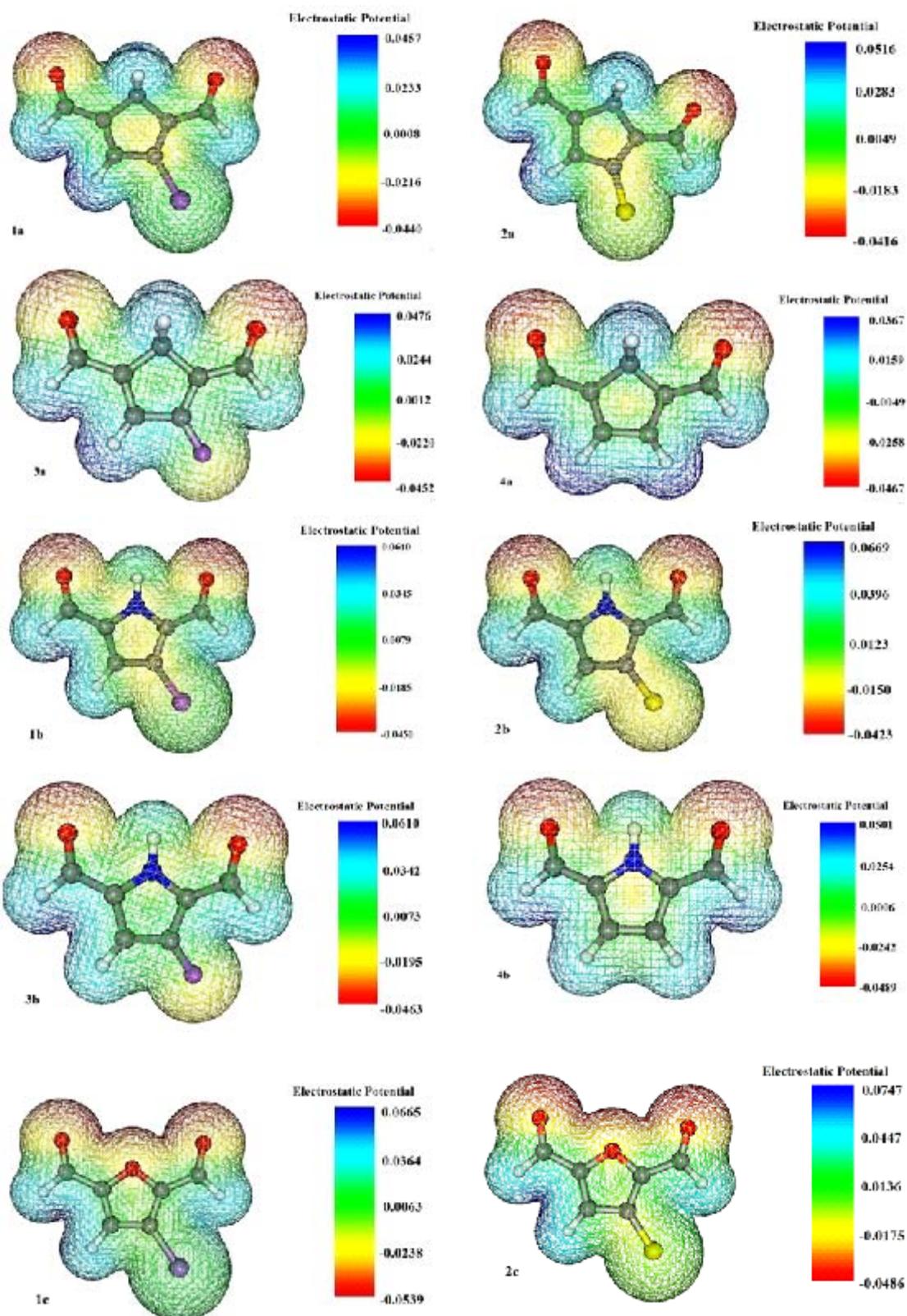

Fig. 6: Compared NICS(0) and NICS(1) ppm, value for various C$_6$H$_4$O$_2$M (M=C, S, O and N) dicarbaldehyde derivatives
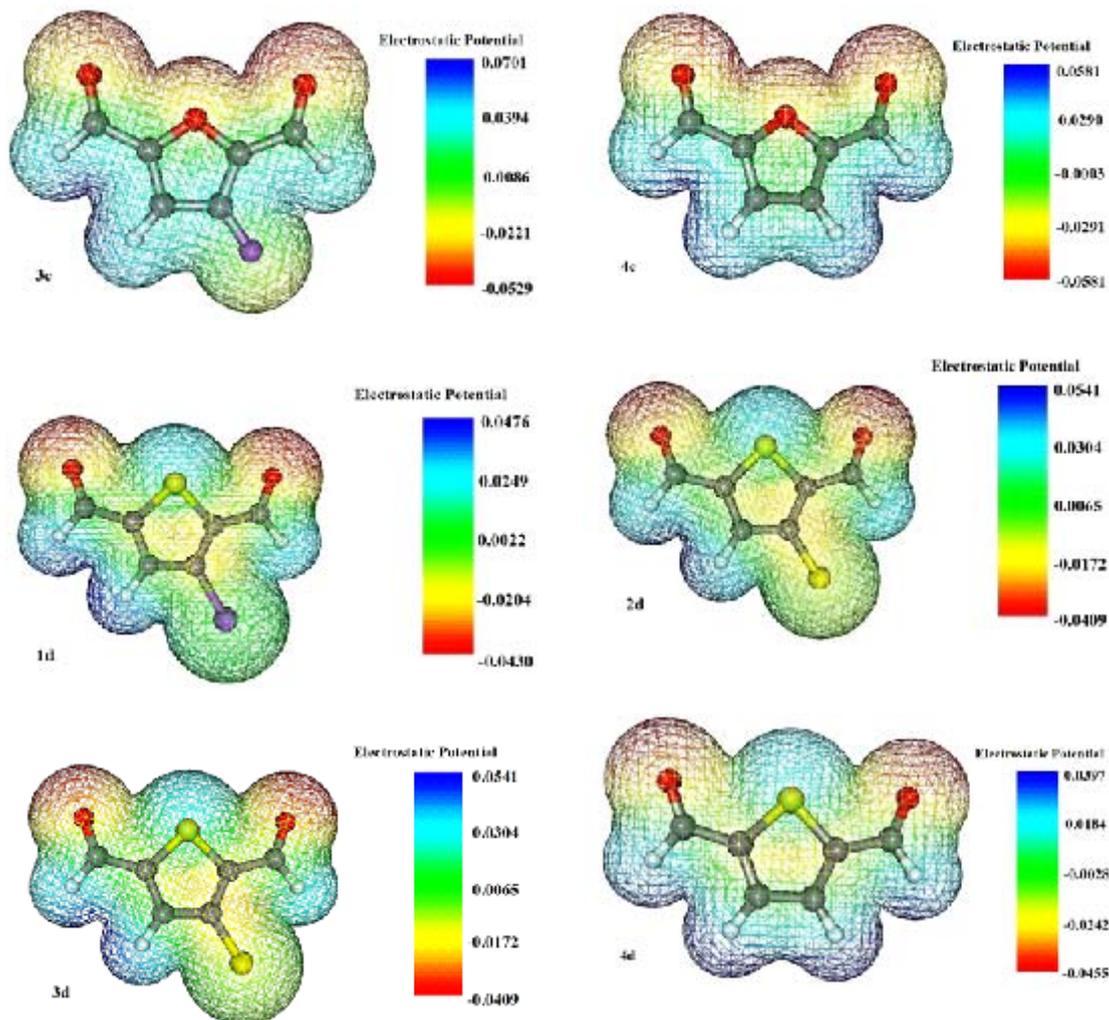
Fig. 7: B3LYP/6-311G(d,p) calculated 3D molecular electrostatic potential maps of C$_6$H$_4$O$_2$M (M=C, S, O and N) dicarbaldehyde derivatives (isosurface value 0.01 a.u.)

CONCLUSION

Density functional theory (DFT) and B3LYP/6-311G(d,p) were used to optimize 16 dicarbaldehyde compounds and several parameters, including energetic parameters, aromaticity, HOMO and LUMO indices, and electrophilicity, for these structures were compared to those of the stable and symmetric structure of benzene. The findings can be summarized as follows:

´ Investigation of energetic level reveals that among the 6a structures studied here, 3-bromothiophene-2,5-dicarbaldehyde has the lowest level of energy, and therefore, is the most stable compounds while cyclopenta-3,5-diene-1,3-dicarbaldehyde is the least stable structure with the highest energy level.

´ NICS analysis indicates that in all compounds studied here isotropic effect at the ring center is more significant than the effect observed at one angstrom above the

ring center. This can be attributed to increased resonance induced by nonbonding pair of electrons is some compounds with M group. In compounds where M atom is substituted with M, electrophilicity is lower compared to compounds with other substituents.

´   As halogen substituent or M atoms are changed, bond lengths experience some variations. These variations are larger at regions directly engaged with M atom or halogen substituent. In addition, changing

the halogen substituent leads to changes in dipole moment and electrostatic potential both depending on electron donating withdrawing power of substituent.

ACKNOWLEDGEMENTS

REFERENCES

1. B.L. Feringa, R. Hulst, R. Rikers, L. Brandsma, *Synthesis*, **15**: 316 (1988).
2. J. Lewkowski, *ARKIVOC*, (**i**): 17 (2001).
3. K. B. Kokoh, E. M. Belgsir, *Tetrahedron Letters*, **43**: 229 (2002).
4. S.P. Verevkin, V.N. Emel'yanenko, E.N. Stepurko, R.V. Ralys, D.H. Zaitsau, *Ind. Eng. Chem. Res*, **48**: 10087 (2009).
5. Sh. Takekuma, K. Tone, M. Sasaki, T. Minematsu, H. Takekuma, *Tetrahedron*, **63**: 2490 (2007).
6. H. Adams, N.A. Bailey, D.E. Fenton, P.D. Hempstead, G.P. Westwood, *Journal of Inclusion Phenomena and Macrocyclic Chemistry*, **11**: 63 (1991).
7. Sh. Takekuma, S. Hori, T. Minematsu, H. Takekuma, *Research Letters in Organic Chemistry*, **2009**: 5 (2009).
8. A. Michaleviciute, G. Buika, J.V. Grazulevicius, F. Tran-Van, C. Chevrot, V. Jankauskas, *Molecular Crystals and Liquid Crystals*, **468**: 107 (2007).
9. E. Aqad, P. Leriche, G. Mabon, A. Gorgues, M. Allain, A. Riou, A. Ellern, V. Khodorkovsky, *Tetrahedron*, **59**: 5773 (2003).
10. V.A. Knizhnikov, N.E. Borisova, N.Y. Yurashevich, L.A. Popova, A.Y. Chernyadev, Z.P. Zubreichuk, M.D. Reshetova, *Russian Journal of Organic Chemistry, C/C of Zhurnal Organicheskoi Khimii*, **43**: 855 (2007).
11. C. Yohannan Panicker, Hema Tresa Varghese, B. Hari Kumar and Asha Chandran. *Orient. J. Chem.* **27**(4): 1705-1709 (2011).
12. R. Soleymani, H. Rajabzadeh, *Asian Journal of Chemistry*, **24**: 4614 (2012).
13. S. Gumus, *Comput. Theor. Chem*, **963**: 263 (2011).
14. J. Kruszewski, T.M. Krygowski, *Tetrahedron Lett*, **13**: 3839 (1972).
15. R.G. Parr, L.V. Szentpaly, S. Liu, *J. Am. Chem. Soc*, **121**: 1922 (1999).
16. E. Chamorro, M. Duque-Norea, P. Perez, *J. Mol. Struct. (THEOCHEM)*, **896**: 73 (2009).
17. R. Dennington, T. Keith, J. Millam, K. Eppinett, W.L. Hovell, R. Gilliland, GaussView, Version 3.07, Semichem, Inc., Shawnee Mission, KS, (2003).
18. M.J. Frisch et al, GAUSSIAN 09w, Gaussian, Inc, Pittsburgh, PA, (2010).
19. Y.J. Beevi, H.T. Varghese, C.Y.Panicker, G. Rajendran, *Orient. J. Chem.*, **27**: 1109 (2011).
20. B. Semire, O.A. Odunola, *Orient. J. Chem.,* **25**: 841 (2009).
21. C.Y. Panicker, H.T. Varghese, A. Chandran, *Oriental journal of chemistry,* **27**: 1771 (2011).
22. C.Y. Panicker, H.T. Varghese, B. Harikumar, A. Chandran, *Orient. J. Chem.,* **27**: 1705 (2011).
23. Y.J. Beevi, H.T. Varghese, C.Y.Panicker, G. Rajendran, *Orient. J. Chem.,* **27**: 1109 (2011)
24. M.A. Boughdiri, O. Fliss, T. Boubaker, B. Tangour, *Oriental journal of chemistry,* **22**: 39052 (2006).
25. M. Taheri, R. Soleymani, B. Hosn, H. Rajabzadeh, M.R. Darvish, *Orient. J. Chem.*, **28**: 387 (2012).
26. P. Politzer, D.G. Truhlar, Chemical Application of Atomic and Molecular Electrostatic Potentials, Plenum, New York, (1981).