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Synthesis, Geometry optimization, Mulliken, MEP, HOMO-LUMO and NLO properties of 2-aryl-3-(2,6-diisopropylphenyl)thiazolidin-4-one based on DFT calculations

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ABSTRACT

A novel compounds *2-(substitutedphenyl)-3-(2,6-diisopropylphenyl)thiazolidin-4-one* (**8-12**) were synthesized and characterized with the aid of spectral techniques. The molecular geometry of synthesized compound was calculated in the ground state by density functional theory (DFT/B3LYP) using 6-31G(d,p) basis set. The Mulliken and MEP analyses confirm the reactive sites in the designed compounds. The calculated HOMO and LUMO energies were used to analyze the charge transfer within the molecule. The electrical dipole moment (μ) and first hyperpolarizability (βo) values have been computed using DFT/B3LYP method. The higher first order hyperpolarizability of **12** found to be 1.20 $x10^{-30}$ esu indicating its use as non-linear optical (NLO) material.

***Keywords*:** Thiazolidin-4-one, FT-IR, hyperpolarizability, HOMO–LUMO

1. INTRODUCTION

Thiazolidinones have been known for a long time [1,2] and have been utilised for a diverse range of applications, including materials, [1,2] synthetic intermediates, [1] analysis, dyes, photography [2] etc. In addition, they also possess a wide range of biological activities like antibacterial [3-7], antifungal [8], and antituberculosis [9] activities.

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4-Thiazolidinones have been reported as novel inhibitors of the bacterial enzyme Mur B [10] which is essential in cell wall biosynthesis and this array of properties has resulted in a considerable number of reviews.

In parallel to the invention of new materials, it is also important to modify their properties either by adding or incorporating other functional groups for tailor made applications. The methodology was further utilized towards quantum chemical calculation and spectral analysis is powerful approaches for study of different aspects of compounds. Since, now a day's spectrographic analysis combined with quantum chemical computations are employed as an effective tool in the vibrational analysis of biological compounds [11,12]. However, literature surveys revealed that till date neither completes spectroscopic nor quantum chemical calculations for title compounds have been reported. Therefore the present investigation was undertaken to taking into account the molecular structural properties, electronic and polarizability data of thiazolidine, in gas phase, due to its pharmaceutical importance.

The ground state properties of the title molecules are calculated using DFT/B3LYP level of theory using 6-31G(d,p) basis set. In this attempt, we report synthesis, FT-IR, molecular structure, dipole moment, polarizability, first order hyperpolarizability, HOMO–LUMO, Mulliken population analysis along with the molecular electrostatic potential surface would possibly give a clear understanding of the structural and spectral characteristics of the compound chosen for study.

2. EXPERIMENTAL

Measurements

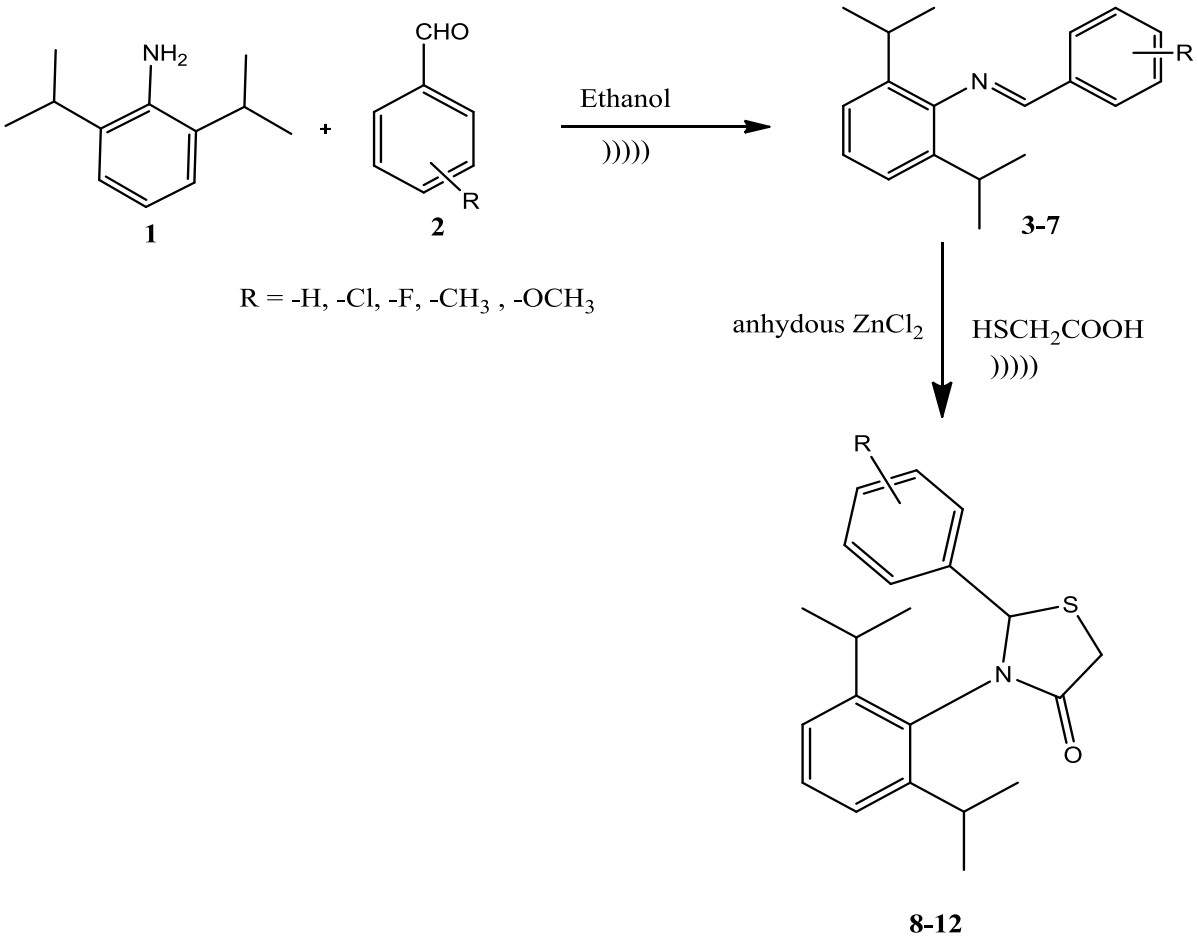
All the solvents were of spectral grade and used as such without further purification. The melting points of all the synthesized compounds were measured in open capillaries and are uncorrected. FT-IR spectra were recorded on the SHIMADZU FT-IR spectrometer (Thermo Nicolet) using KBr (pellet form).

Synthesis of 2-(substitutedphenyl)-3-(2,6-diisopropylphenyl)thiazolidin-4-one (**8-12**)

A mixture of (E)-2,6-diisopropyl-n-(4-substitutedbenzylidene)aniline(3-7) (0.01 mole) and mercaptoacetic acid (1.82 g, 0.02 mole) in DMF (30 ml), 2g of zinc chloride was added and placed in a small conical flask at room temperature then the mixture were placed in an ultrasound bath and irradiated for (25-30) minutes at room temperature, this reaction was monitored by TLC. The resultant solution was cooled and poured into cold water. The separated solid was filtered, crystallized from ethanol to give crystalline yellow.

*Synthesis of 3-(2,6-diisopropylphenyl)-2-phenylthiazolidin-4-one (**8**)*

White solid; Yield 83%, M.P: 188-192 °C, MF: $C_{21}H_{25}NOS$; elemental analysis: Calcd (%): C, 74.29; H, 7.42; N, 4.13; found (%): C 74.21; H 7.43; N, 4.24; IR (KBr, cm^{-1}): 3066 (νArC -H), 2991 (νC-H), 1687 (νC=O); 1649, 1600 (νC=C); 1510-947 (βC-H); 914-457 (ΓC-H).



Scheme 1. Synthetic route of compounds **8-12**

*Synthesis of 3-(2,6-diisopropylphenyl)-2-(4-fluorophenyl)thiazolidin-4-one (**9**)*

White solid; Yield 86%, M.P: 175-176 °C, MF: $C_{21}H_{25}FNOS$; elemental analysis: Calcd (%): C, 70.56; H, 6.77; F, 5.31; N, 3.92; found (%): C 70.42; H 6.43; N,3.84; IR (KBr, cm^{-1}): 3064 (νArC -H), 2914 (νC-H), 1751 (νC=O); 1697, 1581 (νC=C); 1492-960 (βC-H); 918-408(ΓC-H).

*Synthesis of 3-(2,6-diisopropylphenyl)-2-(4-chlorophenyl)thiazolidin-4-one (**10**)*

White solid; Yield 89%, M.P: 175-176 °C, MF: $C_{21}H_{25}ClNOS$; elemental analysis: Calcd (%): C, 67.45; H, 6.47; Cl, 9.48; N, 3.75; found (%): C 67.40; H 6.58; N, 3.74 IR (KBr, cm^{-1}): 3068 (νArC -H), 2993 (νC-H), 1693 (νC=O); 1647, 1604 (νC=C); 1479-989 (βC-H); 914-468 (ΓC-H).

*Synthesis of 3-(2,6-diisopropylphenyl)-2-(p-tolyl)thiazolidin-4-one (**11**)*

White solid; Yield 79%, M.P: 118-119 °C, MF: $C_{22}H_{27}NOS$; elemental analysis: Calcd (%): C, 74.74; H, 7.70; N, 3.96; found (%): C 74.45; H 7.65; N, 3.84; IR (KBr, cm^{-1}): 3113

(νArC -H), 2852 (νC-H), 1681 (νC=O); 1598, 1506 (νC=C); 1361-945 (βC- H); 837-487 (ΓC-H).

*Synthesis of 3-(2,6-diisopropylphenyl)-2-(4-methoxyphenyl)thiazolidin-4-one (**12**)*

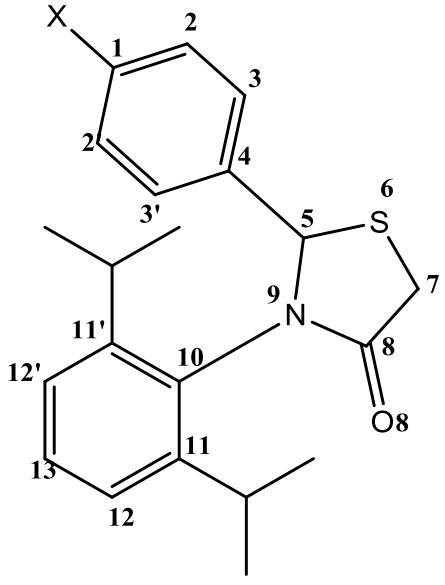
White solid; Yield 75%, M.P: 121-122 °C, MF: $C_{22}H_{27}NO_2S$; elemental analysis: Calcd (%): C, 71.51; H, 7.36; N, 3.79; found (%): C 71.50; H 7.45; N, 3.68; IR (KBr, cm^{-1}): 3095 (νArC -H), 2976 (νC-H), 1695 (νC=O); 1583, 1525 (νC=C); 1429-937 (βC-H); 881-422 (ΓC-H).

Computational details

The density functional theory (DFT) with B3LYP level theory using 6-31G(d,p) basis set in Gaussian-03 have been used for theoretical calculations [13-15]. He minimized structure used for geometry optimizations with B3LYP method. Mulliken atomic charges and Molecular Electrostatic Potentials (MEPs) of **thiazolidines** were plotted in 3D by using optimized structures at same level theory. Furthermore, HOMO and LUMO energy values and energy gap for thiazolidines were calculated by using B3LYP method with 6-31G(d,p) basis set. Moreover, in order to show nonlinear optical (NLO) activity of studied molecules, the dipole moment, linear polarizability and first order hyperpolarizability were obtained from molecular polarizabilities based on theoretical calculations.

3. RESULTS AND DISCUSSION

Geometry optimization



Entry	X
8	H
9	F
10	Cl
11	Me
12	MeO

Fig. 1. Numbering Pattern of **thiazolidines**.

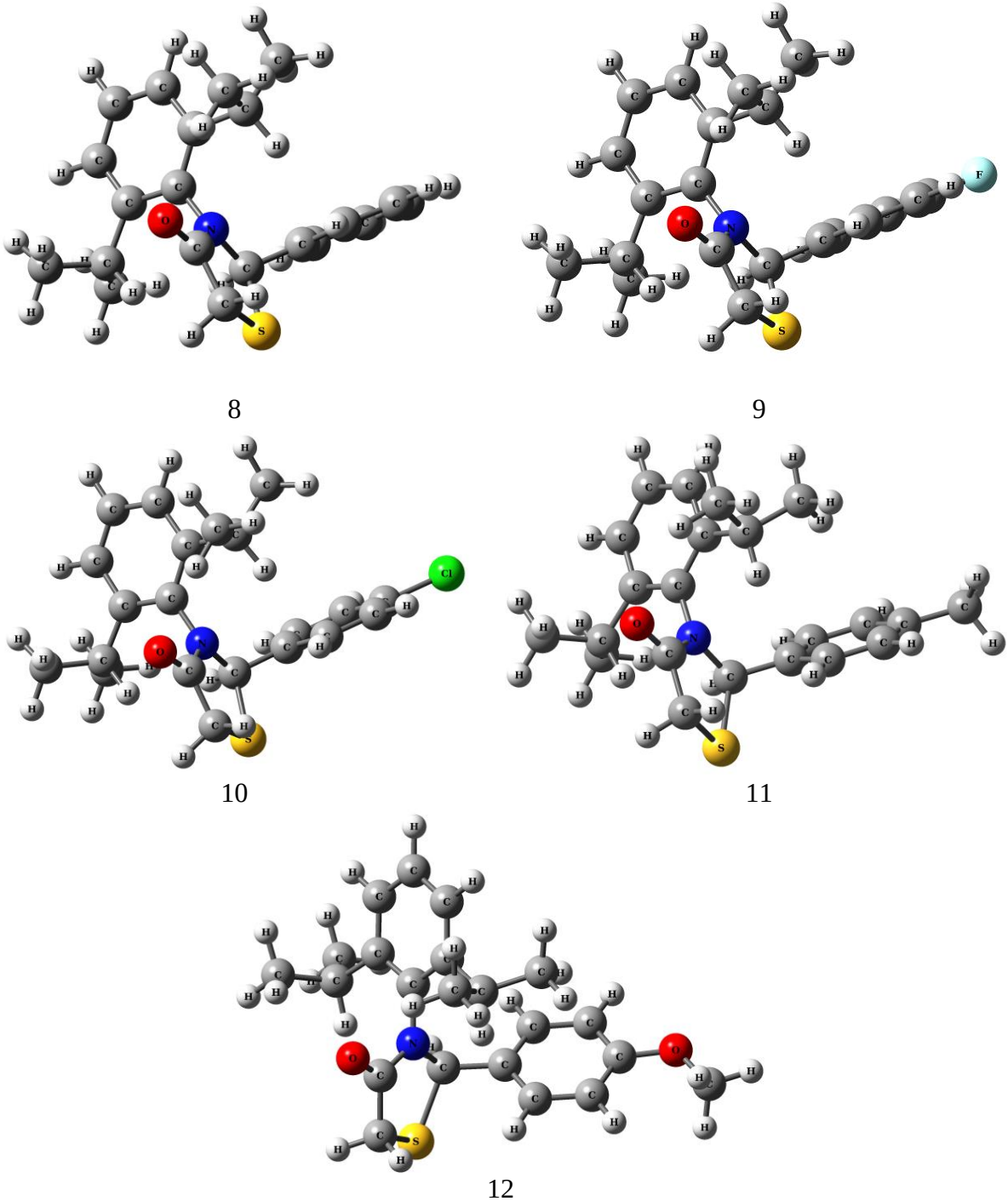
Table 1. Optimized parameters of compounds **8-12**

Bond length Å	8	9	10	11	12
C1-C2	1.3967	1.4027	1.3948	1.4088	1.4032
C1-X1	1.0696	1.3454	1.8257	1.5124	1.3883
C2-C3	1.3935	1.3997	1.3969	1.3939	1.3976
C3-C4	1.3971	1.4034	1.4048	1.4058	1.4020
C1-C2'	1.4000	1.4029	1.3913	1.4023	1.4024
C2'-C3'	1.4024	1.4051	1.4004	1.4001	1.3933
C3'-C4	1.4047	1.4022	1.4036	1.4018	1.4074
C4-C5	1.5411	1.5431	1.5155	1.5123	1.5116
C5-S6	1.9706	1.9789	1.9285	1.9321	1.9323
S6-C7	1.7613	1.7651	1.8861	1.8860	1.8856
C7-C8	1.5357	1.5393	1.5195	1.5200	1.5198
C8-O8	1.2611	1.2620	1.2620	1.2468	1.2472
C8-N9	1.3832	1.3769	1.3787	1.3776	1.3771
N9-C10	1.4636	1.4693	1.4534	1.4526	1.4526
C10-C11	1.4058	1.4071	1.4161	1.4163	1.4162
C11-C12	1.4012	1.4032	1.4045	1.4030	1.4031
C12-C13	1.4045	1.4046	1.4003	1.3954	1.3954
C10-C11'	1.4003	1.4000	1.3986	1.4133	1.4132
C11'-C12'	1.3986	1.4060	1.4028	1.4047	1.4046
C12'-C13	1.4028	1.3964	1.3964	1.3944	1.3944
Bond Angle°					
C2-C1-C2'	119.88	119.83	121.85	118.00	120.00
X1-C1-C2	119.92	119.91	119.02	121.32	124.34
X1-C1-C2'	120.20	120.27	119.12	120.67	115.66
C3-C4-C5	119.30	118.92	118.76	119.03	119.01

C3'-C4-C5	121.02	121.18	122.50	122.59	122.73
C4-C5-S6	112.53	112.76	112.53	113.22	113.25
C5-S6-C7	96.10	96.13	96.10	91.39	91.39
C7-C8-N9	111.00	110.74	111.00	113.44	113.44
C5-N9-C10	109.29	110.30	109.29	110.30	110.30
C11-C10-N9	120.30	120.68	120.30	113.44	113.44
C11'-C10-N9	119.67	119.39	119.67	119.39	119.39
Dihedral Angle°					
C3-C4-C5-S6	87.96	89.11	135.28	131.56	135.28
C3'-C4-C5-S6	-92.10	-90.98	-44.45	-48.16	-44.45
C4-C5-N9-C10	72.59	71.46	69.87	72.82	72.59
C11-C10-N9-C8	-47.38	-50.22	-93.14	-50.22	-47.38
C11'-C10-N9-C8	132.34	131.19	86.09	131.19	131.19
C11-C10-N9-C5	67.76	66.71	78.00	66.71	66.71
C11'-C10-N9-C5	-112.52	-111.88	-102.77	-111.88	-111.88

X= H, F, Cl, O and C for **8- 12** respectively

The optimized structural parameters such as bond lengths, bond and dihedral angles of **thiazolidines** were determined at B3LYP level theory with 6-311G(d,p) basis set and are presented in **Table 1** in accordance with the atom numbering scheme of the molecule shown in **Fig. 1** and the optimized structure of compounds are shown in **Fig. 2**. Bond distances in the phenyl ring show values ranges from 1.3948-1.4071Å. Likewise, bond angles are very similar as well (±0.2°). In the ring named thioazolidin in title molecules**.** The selected bond distances are C5-S6 1.9 Å, C5-N9 1.9 Å and C8-N9 1.38 Å, which is well matched with XRD values. The carbonyl carbon atom is sp^2 hybridised (three σ-bonds and one π-bond), and as a consequence, the carbonyl group is planar and has bond angles of around 113.56° (B3LYP) and 111.4° (XRD). The C=O bond is short (~1.2 Å) and also rather strong (ca. 690 kJ mol^{-1}). As oxygen is more electronegative than carbon, the electrons in the C=O bond are drawn towards the oxygen. This means that carbonyl compounds are polar and have substantial dipole moments. Due to pulling of electron from carbon C8, the bond strength changes which results in the lengthening of the bond (C7-C8 and C8-N9) compared with normal bond lengths of C-C and C-N. As seen in from selected dihedral angles of the molecule are C11-C10-N9-C8, C11'-C10-N9-C8, C11-C10-N9-C5, C11'-C10-N9-C5. These data reveal that the C=O group perpendicular to the phenyl group.



8 9

10 11

12

Fig. 2. Optimized structure of compounds **8-12**

Mulliken charge distribution analysis

Mulliken atomic charge calculation has an important role in the application of quantum chemical calculation to molecular system because of atomic charges effect dipole moment,

molecular polarizability, electronic structure and more a lot of properties of molecular systems [16]. The charge distributions over the atoms suggest the formation of donor and acceptor pairs involving the charge transfer in the molecule. The Mulliken charge distribution of the molecule is calculated on B3LYP at 6-31G(d,p) level theory. The calculated values of title molecules at gaseous phase are shown in **Table 2**.

Table 2. Mulliken atomic charges of compounds **8-12**

Atom	Charge a.u				
	8	9	10	11	12
C1	-0.117	0.292	0.232	0.118	0.288
X1	0.132	-0.331	-0.073	-0.483	-0.56
C2	-0.133	-0.146	-0.103	-0.16	-0.139
C3	-0.125	-0.127	-0.122	-0.126	-0.142
C2'	-0.125	-0.139	-0.097	-0.156	-0.124
C3'	-0.151	-0.155	-0.148	-0.152	-0.159
C4	0.175	0.183	0.18	0.184	0.185
C5	-0.334	-0.336	-0.335	-0.336	-0.336
S6	0.242	0.242	0.247	0.238	0.237
C7	-0.565	-0.566	-0.566	-0.564	-0.565
C8	0.549	0.548	0.55	0.548	0.548
O8	-0.447	-0.444	-0.443	-0.447	-0.449
N9	-0.61	-0.61	-0.61	-0.61	-0.61
C10	0.116	0.116	0.114	0.116	0.116
C11	0.182	0.182	0.182	0.182	0.182
C12	-0.198	-0.198	-0.199	-0.198	-0.198
C11'	0.195	0.194	0.194	0.195	0.195
C12'	-0.199	-0.198	-0.198	-0.199	-0.199
C13	-0.096	-0.097	-0.095	-0.096	-0.096

X= H, F, Cl, O and C for **8- 12,** respectively

The charge distribution of the title compound shows that all the nitrogen and oxygen atoms have maximum negative charges and Mulliken charges are less compared with natural charges. In addition negative charge spread over the C2, C2', C3, C3', C5, C7, C12, C12' and C13. This is due to the position of the atoms attachment with the molecule. From the above, we conclude that our designed candidate ready to nucleophilic substitution reactions.

Molecular electrostatic potential (MEP) analysis

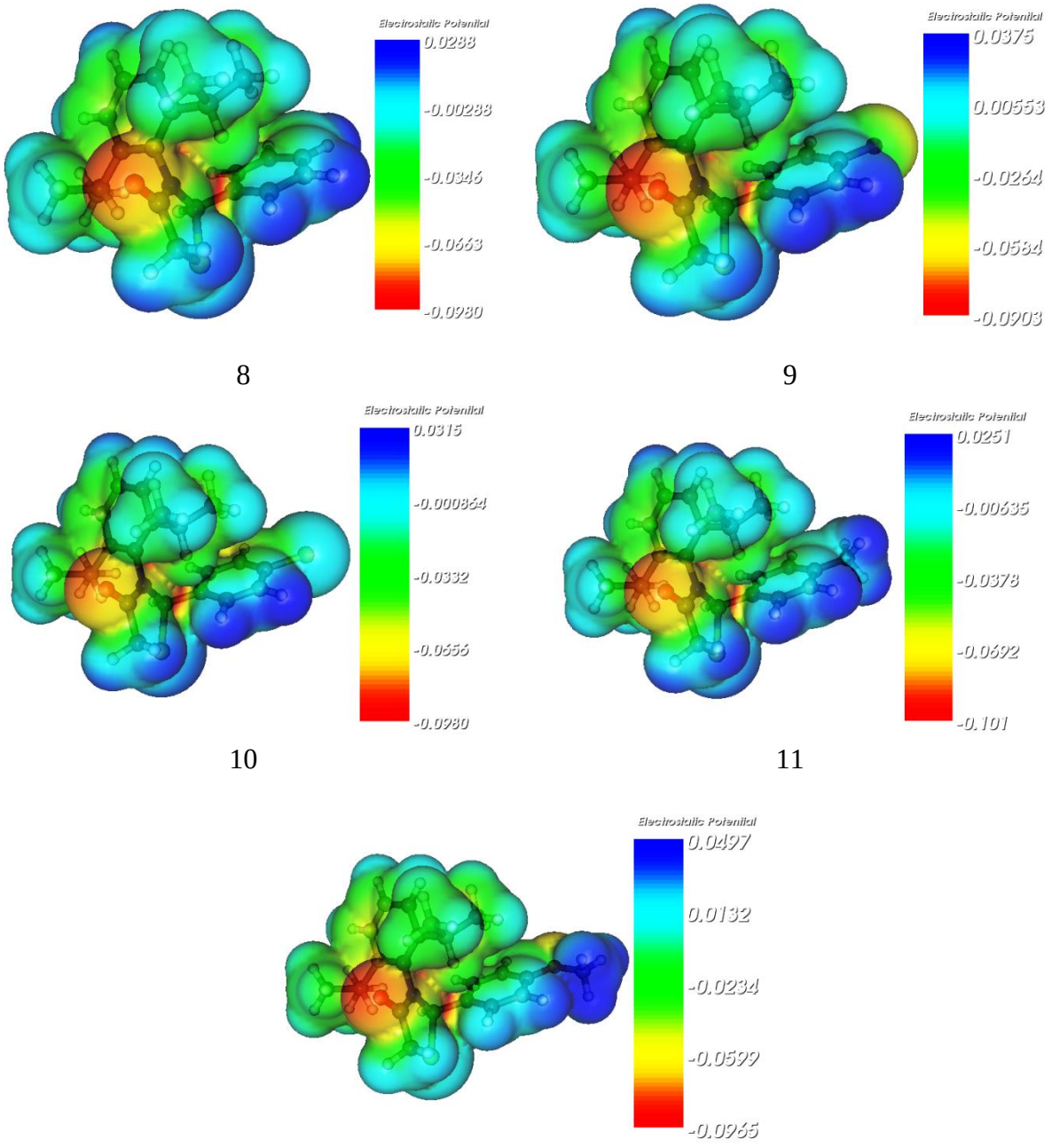


Fig. 3. Molecular electrostatic potential diagram of compounds **8-12**

The MEP is a crucial tool to grasp the molecular interactions in a given molecule. It is very useful for interpreting and predicting relative reactivity sites for electrophilic and nucleophilic attack and hydrogen bonding interactions [17,18]. The 3D plot of the MEP for the title molecules are shown in **Fig. 3**, which was calculated by using the optimized molecular structure at the B3LYP/6-31G(d,p) basis set.

Fig. 3 indicates the electrostatic potentials at the surface for molecule which are shown by different colours. Therefore the red colour parts represent the regions of negative electrostatic potential, the blue lines represents the regions of positive electrostatic potential and green colours parts also represent the regions of zero potential. Negative electrostatic potential corresponds to attraction of the proton, while positive electrostatic potential corresponds to repulsion of the proton Furthermore, the red color of MEP are related to electrophilic reactivity and the blue color are related to nucleophilic reactivity. As seen from **Fig. 3**, the negative regions of MEP surface are localized on the O8 and N9 atoms. The positive regions of MEP surface are also localized in S6 atom. It is expected that former sites are the most reactive sites for electrophilic attack while the sulfur atoms are the most reactive for nucleophilic attack.

Frontier molecular orbital analysis

The frontier molecular orbitals (FMOs) are the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO). The shapes of these molecular orbitals, their energies as well as their energy gap have many applications in chemistry, physics and biology [19]. The molecular orbital of representative picture of compound 12 is shown in **Fig. 4**. The energies were calculated using DFT method at the B3LYP/6-31G(d,p) basis set.

The HOMO demonstrates the donor orbitals and the LUMO demonstrates acceptor orbitals [14,15]. The surface of FMOs is displayed to interpreting the bonding frame work of these compounds. Hence, significant molecular orbitals have been investigated i.e. LUMO, LUMO+1, HOMO, and HOMO-1 demonstrate the respective acceptor and donor levels.

The computed energy data of these molecular orbitals and the energy gaps of representative picture of compound 12 is shown in **Table 3**.

Table 3. Calculated energy values (eV) of compounds **8-12** in gas phase

B3LYP/6-31G(d,p)	8	9	10	11	12
E_{HOMO}	-6.41	-6.53	-6.58	-6.30	-6.08
E_{LUOMO}	-0.72	-0.88	-1.04	-0.65	-0.57
$E_{LUMO-HOMO}$	5.69	5.66	5.55	5.65	5.51
E_{HOMO-1}	-6.49	-6.58	-6.62	-6.46	-6.44
E_{LUMO+1}	-0.39	-0.64	-0.72	-0.35	-0.30

$EH_{OMO-1-LUMO+1}$	6.10	5.95	5.90	6.11	6.14
Electronegativity(χ)	-3.56	-3.70	-3.81	-3.48	-3.33
Hardness(η)	2.85	2.83	2.77	2.83	2.76
Electrophilicity index(ψ)	2.23	2.43	2.62	2.14	2.01
Softness(s)	130.12	130.90	133.48	130.81	134.32

The energies of FMOs (LUMO & HOMO) have been used to investigate the global reactivity descriptors [14] using the equations given in the supplementary information. The electro negativity (χ), global hardness (η), global softness (S) and global electrophilicity index (ψ) are known as global reactivity parameters [15]. These parameters are considered as highly successful descriptors for biological activity.

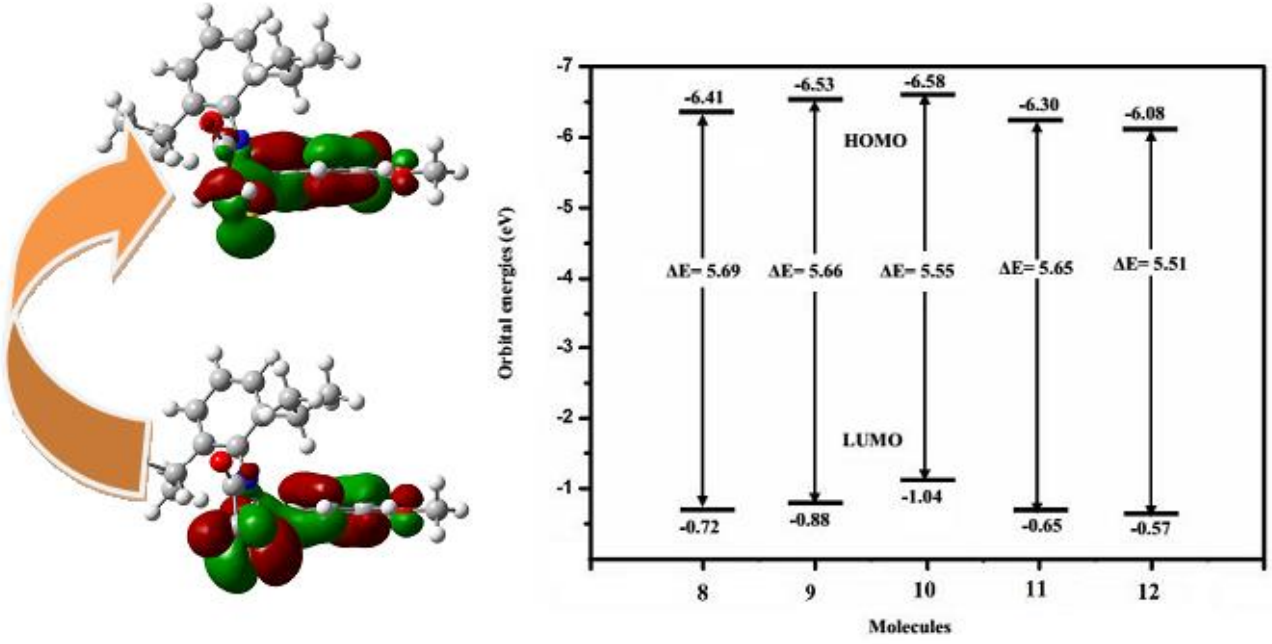


Fig 4. Molecular orbital diagram of compounds **8-12**

These reactivity parameters are also recently used in understanding the site selectivity and the reactivity [20-25]. Electro negativity is known as one of the most important chemical properties which define the power of specie to attract electrons towards itself. The large energy difference defines hard specie, which means specie is more stable and less reactive. While, small energy gap defines soft specie, which means specie is less stable and more reactive. The obtained findings indicate that the both molecules are less stable and more reactive see **Table 3**.

Non-linear optical (NLO) properties

The organic compounds have become the centre of attraction due to their unique characters and potent potential applications in nonlinear optics (NLO), photonics and electronics [26,27]. The sketch of dynamic organic compounds for utilization in NLO response is established on the basis of asymmetric polarization. It is directed through electron contributor and withdrawing groups on suitable location of the compound. The NLO response is enhanced with increasing the electron contributor and withdrawing group efficiency attached to the π-conjugated system [28]. Therefore, we also studied NLO parameters of the π-conjugated molecules (8 - 12) using B3LYP level of theory with 6-31G (d, p) basis set.

The total static dipolemoment (μ), the Mean polarizabilty (α), Anisotropy of the polarisabiltiy (Δα) and the first order hyperpolarizability (β_0) using the x, y, z components are calculated using the following equations.

$$\mu = (\mu_x^2 + \mu_y^2 + \mu_z^2)^{1/2}$$

$$\alpha_{tot} = \frac{1}{3}\alpha_{xx} + \alpha_{yy} + \alpha_{zz}$$

$$\Delta\alpha = \frac{1}{\sqrt{2}}\left[(\alpha_{xx} - \alpha_{yy})^2 + (\alpha_{yy} - \alpha_{zz})^2 + (\alpha_{zz} - \alpha_{xx})^2 + 6(\alpha_{xy}^2 + \alpha_{yz}^2 + \alpha_{xz}^2)\right]^{1/2}$$

$$\beta_0 = [(\beta_{xxx} + \beta_{xyy} + \beta_{xzz})^2 + (\beta_{yyy} + \beta_{yzz} + \beta_{yxx})^2 + (\beta_{zzz} + \beta_{zxx} + \beta_{zyy})^2]^{1/2}$$

Table 4. Non-linear optical properties of **thiazolidines** calculated using B3LYP method using 6-31G(d,p) basis set.

B3LYP	**8**	**9**	**10**	**11**	**12**
Dipole moment (D)	2.94	1.79	1.76	3.37	3.02
Polarisability α_o $\times 10^{-23}$ esu	2.20	2.34	2.47	2.29	2.35
Mean Polarisability $\Delta\alpha$ $\times 10^{-24}$ esu	2.94	4.10	4.53	3.01	5.23
Hyperpolarisability β_0 $\times 10^{-30}$ esu	0.38	0.40	0.53	0.72	1.20

Results from Table 4, the general ranking of NLO properties should be as follows: **12** > **11** > **10** > **9** > **8**. From the above results we can concluded that the presence of an electron donating group (methoxy) in the *para* position at the phenyl ring contributes to increase the dipole moments and first order hyperpolarizability of the **thiazolidines** probably because of an inductive competition between the methoxy and the electronic density available in the molecule. Therefore, the compound **12** has a potential use in the development of non-linear optical materials.

4. CONCLUSION

In this study, five **thiazolidin-4-ones** (**8-12**) were synthesized and characterized. The synthesied compounds subjected to computational studies by using DFT/B3LYP/6-31G(d,p) level theory. The geometry optimization has been obtained for the **thiazolidines** by using DFT method. The HOMO–LUMO energy gap has a substantial influence on the ICT. The lowering of HOMO–LUMO energy gap, a quantum–chemical descriptor, explains the ease with which charge transfer interactions take place within the molecule. The Mulliken and MEP maps show that oxygen and nitrogen atoms are the negative potential sites and the positive potential sites are around the hydrogen atoms. The total dipole moment, polarizability and hyperpolarizability of the compounds were calculated and the results show that the molecule could be good NLO material.

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