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Geometrical and electronic parameters of 2-arylamino-4-(3-coumarinyl)thiazoles by means of theoretical method

J Brindha, S Mahil Rani, V S Chithra & T F Abbs Fen Reji*

Department of Chemistry, Nesamony Memorial Christian College, Marthandam 629 165, India
E-mail: abbsfen@yahoo.com

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The geometrical and electronic parameters of 2-arylamino-4-(3-coumarinyl)thiazoles have been computed theoretically using the Gaussian 09W package of program using B3LYP/6-31G level of theory. The calculated geometrical parameters of 2-arylamino-4-(3-coumarinyl)thiazoles are comparable with the values reported for compounds of similar structure. Optimization reveals that the geometrical parameters are based on the size of the atom, bonding nature and charge transfer. The calculated MOs are supportive to establish the collective electronic properties of the optimized compounds. However, energy gap is an indicator of chemical reactivity, kinetic stability and polarizability.

Keywords: DFT, electronic properties, effective atomic charge, energy gap, hardness-softness

Coumarin and its derivatives have attracted much interest due to their optical[1] and biological properties[2]. A series of Coumarin derivatives were recently synthesized and found to have anticoagulant activity and cytotoxic activities[3]. The main advantage of the Coumarin is the low molecular weight oxygen heterocyclic which finds application as solvents and synthetic intermediates[4]. Density Functional Theory (DFT) calculations have become a popular tool in theoretical organic chemistry because of their efficiency[5]. B3LYP/6-31G (d) method is reliable and it is helpful for the understanding of vibrational spectrum and structural parameters[6]. The present work describes the studies on geometrical and electronic parameters of 2-arylamino-4-(3-coumarinyl)thiazoles supported by density functional theory (DFT) calculations. DFT calculations have been carried out using Gaussian 09W package. The optimized geometry of the molecule was found by optimizing all geometrical variables such as bond length, bond angle, *etc*. The electronic properties like frontier molecular orbital energy, ionisation potential, hardness, electronegativity, softness and dipole moment were calculated.

Experimental Section

Computational Details

All the computations were performed using Gauss-View molecular visualization program and Gaussian 09W quantum chemical software. The optimized structural and electronic parameters for the 2-arylamino-4-(3-coumarinyl)thiazoles molecule have been calculated by using B3LYP method with 6-31G basis set level.

Results and Discussion

Optimized Geometry

The optimized structure of 2-arylamino-4-(3-coumarinyl)thiazoles are presented in Figure 1 and the geometrical parameters are shown in Table I. The bond length is the average distance between the nuclei of two atoms bonded together in a molecule. Depending on the size of the atom the bond length will vary *i.e*., size of the atom increases bond length also increases. For example bond length of C – N is 1.40Å and bond length of C – S is 1.84 Å because size of the sulphur atom is greater than the nitrogen atom. The electronegativity of sp^2 hybridized carbon is greater than sp^3 hybridized carbon. Hence, the sp^2 hybridized carbons drag electrons more closely towards itself than the sp^3 hybridized atoms. Therefore, the bond length of single bond is greater than the double bond. For example bond length of C = C is 1.39 Å and C – C is 1.52 Å because the carbon atom in C = C is sp^2 hybridised and C – C is sp^3 hybridised. Moreover, adjacent atoms having similar charge, they repel each other and enlarge the bond length; likewise, adjacent atoms having opposite charge, they attract each other and shortening the bond length.

Mulliken Charges

In quantum chemical calculation, effective atomic charge changes somewhat more properties of molecular system such as dipole moment, polarizability, electronic structure, *etc*.[7] The effective atomic charge of 2-arylamino-4-(3-coumarinyl)thiazoles obtained from Mulliken population analysis is shown in Figure 2. The distribution of charges during compound formation is attributed to the charges of atoms and the charge will be either positive or negative. Negatively charged atoms are characterized by red colour and positively charged atoms are characterized by green colour. The highly charged atoms exist as bright in respective colours and atoms having small charge exist as dark in respective colours. The negatively charged atoms are electron acceptors and positively charged atoms are electron donors. The charges of the atoms will alter depending on the adjoining atoms. So 30H has high positive charge (0.3) due to the presence of the electronegative nitrogen. Mulliken population analysis reveals that, charge of all nitrogens and oxygens are negative (~-0.4 to-0.5) and act as electron acceptors. Some carbon atoms also (9C-13C, 18C-22C, 36C & 30C) having the negative charge and act as electron acceptors. Remaining carbons, sulphur and hydrogens exhibit positive charge and act as electron donors. Particularly nitrogen (16N) is having the most negative charge (~-0.78) and sulphur (1S) having the most positive charge (~+0.43) in all the compounds.

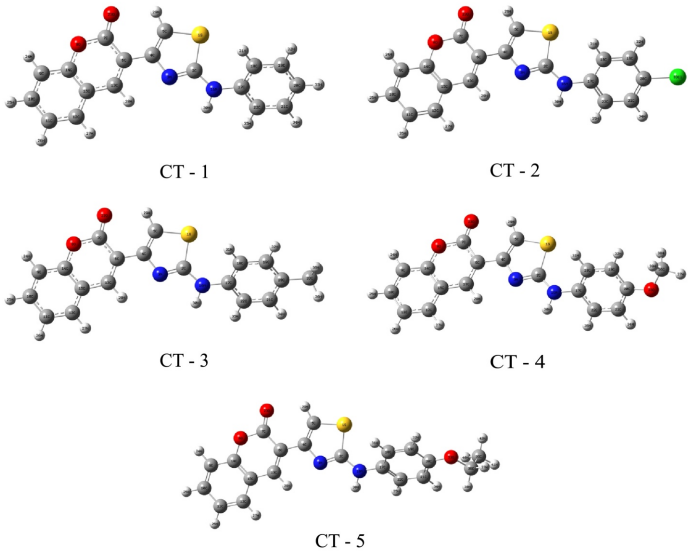

Figure 1 — Optimized structure of 2-arylamino-4-(3-coumarinyl)thiazoles

Table I — Bond Length data of 2-arylamino-4-(3-coumarinyl)thiazoles

Position	Atoms	Bond Length (Å)				
		CT-1	CT-2	CT-3	CT-4	CT-5
Thiazole	C – S	1.84	1.80	1.84	1.84	1.84
Thiazole	C – N	1.40	1.40	1.40	1.40	1.40
Thiazole	C = N	1.31	1.30	1.30	1.31	1.30
Thiazole	C – C	1.36	1.36	1.36	1.36	1.36
Thiazole	C – H	1.07	1.07	1.07	1.07	1.07
Coumarin	C – C	1.39	1.39	1.39	1.39	1.39
Coumarin	C – H	1.08	1.08	1.08	1.08	1.08
Coumarin	C – O	1.41	1.41	1.41	1.41	1.41
Coumarin	C = O	1.23	1.23	1.23	1.23	1.23
Chain	C - N	1.36	1.37	1.36	1.36	1.36
Chain	N – H	1.01	1.01	1.01	1.01	1.01
Chain	C – H	–	–	1.09	1.09	1.09
Chain	C – O	–	–	–	1.45	1.46
Phenyl	C – Cl	–	1.82	–	–	–
Chain	C – C	–	–	–	–	1.52

HOMO-LUMO

The frontier molecular orbitals are Highest Occupied Molecular Orbital (HOMO) and Lowest Unoccupied Molecular Orbital (LUMO) which are involved in the charge transfer. HOMO is the electron donor *i.e.* it has the potential to donate electron and LUMO is the electron acceptor *i.e.*, it has the potential to accept electron in a compound. Presence of HOMO and LUMO in 2-arylamino-4-(3-coumarinyl)thiazoles are confirmed that the charge transfer exist within the molecule. During the charge transfer electron donation process originates from the HOMO into the LUMO. According to Koopmans' theorem[8], the frontier molecular orbital energies are given by

$-\varepsilon_{HOMO} = I$ and $-\varepsilon_{LUMO} = A$. … [1]

Where, I is Ionization potential & A is Electron Affinity.

The equation [1] states that, HOMO energy is the Ionization Potential and LUMO energy is the Electron Affinity. Literature survey reveals that, the absolute electro negativity (χ), absolute hardness (η) and softness (S) of a compound can be calculated using the HOMO and LUMO energies. The operational definitions for the electronic parameters are,

$\chi = (I+A)/2$, $\eta = (I-A)/2$ and $S = 1/2\eta$ … [2]

Using the equation [2] we calculated the electro negativity, hardness and softness. The obtained parameters listed in Table II.

Hard molecules have a large HOMO-LUMO gap (ΔE), and soft molecules have a small HOMO-LUMO gap[9]. Hard molecules are stable because it requires more energy to the excitation of an electron. A small HOMO-LUMO gap means small excitation energies

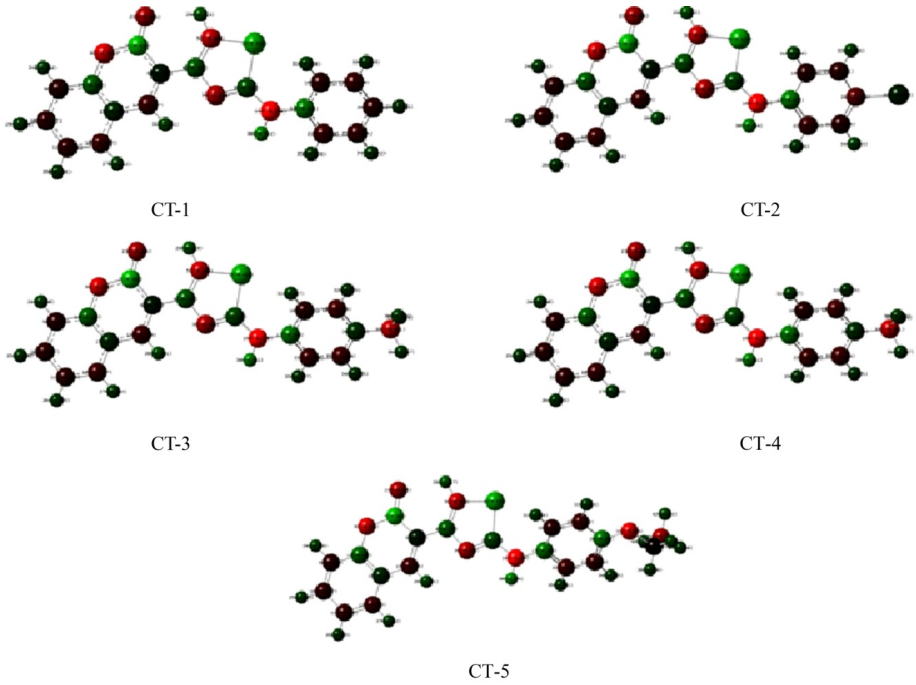

Figure 2 — Mulliken charge of 2-arylamino-4-(3-coumarinyl)thiazoles

Table II — Calculated electronic parameters of 2-arylamino-4-(3-coumarinyl)thiazoles

Parametres (a.u)	CT-1	CT-2	CT-3	CT-4	CT-5
Total Energy (a.u)	−1351.00	−1810.58	−1390.31	−1465.49	−1504.79
Dipole Moment (debye)	5.4046	5.5958	5.5752	4.7051	6.8884
E_{HOMO}	−0.20587	−0.26442	−0.24566	−0.2571	−0.25572
E_{LUMO}	−0.07812	−0.03222	−0.02383	−0.02331	−0.02253
ΔE	0.12775	0.23220	0.22183	0.23379	0.23319
Electronegativity (χ)	0.142	0.14832	0.13475	0.1402	0.13913
Ionisation Potential (I)	0.20587	0.26442	0.24566	0.2571	0.25572
Hardness (η)	0.0639	0.1161	0.1109	0.1169	0.1166
Softness (S)	7.8272	4.3066	4.5086	4.2772	4.2882

Table III — Abbreviation of 2-arylamino-4-(3-coumarinyl)thiazoles

Abbreviation	Compound Name
CT-1	2-Phenylamino-4-(3-coumarinyl)thiazole
CT-2	2-(4-Chlorophenylamino)-4-(3-coumarinyl)thiazole
CT-3	2-(4-Methylphenylamino)-4-(3-coumarinyl)thiazole
CT-4	2-(4-Methoxyphenylamino)-4-(3-coumarinyl)thiazole
CT-5	2-(4-Ethoxyphenylamino)-4-(3-coumarinyl)thiazole

to the multiple of excited states. Therefore, soft molecules, posses a small gap, is more polarizable than hard molecules. High polarizability was the most typical property attributed to soft acids and bases. Among these five compounds CT-1 has small energy gap (0.1277). Hence, it asserting CT-1 is a soft molecule and it has high polarizability (Table III).

The HOMO-LUMO energy gap is an indicator of kinetic stability. A large HOMO-LUMO energy gap point out low chemical reactivity and high kinetic stability because it is energetically unable to add electrons to a LUMO[10]. Among these five compounds CT-1 is kinetically unstable and has high chemical reactivity comparing with others because it has small energy gap (0.1277). The sequence of kinetic stability is CT-1 < CT-3 < CT-2 < CT-5 < CT-4. This declares CT-4 has high energy gap (0.23379) and it is a hard molecule. So it has high kinetic stability and low chemical reactivity. All the five compounds have the permanent dipole moment.

Conclusion

The geometrical and electronic parameters of 2-arylamino-4-(3-coumarinyl)thiazoles were calculated using B3LYP/6-31G basis set. Optimized geometrical parameters of 2-arylamino-4-(3-coumarinyl)thiazoles are comparable with the values reported for compounds of similar structure. The presence of HOMO - LUMO is confirmed that the charge transfer exist within the molecule. It is feasible for intramolecular charge transfer mechanisms between the atoms by comparing the charges. The charges of the atoms will alter depending on the adjoining atoms. So 30H has high positive charge (0.3) due to the presence of the electronegative nitrogen. Furthermore, CT-1 has small energy gap (0.1277). Hence, it asserting CT-1 is a soft molecule and it has high polarizability. This declares CT-4 has high energy gap (0.23379) and it is a hard molecule. So it has high kinetic stability and low chemical reactivity. All the five compounds have the permanent dipole moment.

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