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Molecular structure, NBO, first order hyperpolarizability and HOMO-LUMO analysis of 7-Azathieno[2,3-c]cinnoline

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Abstract: In this work, we reported a theoretical investigations on molecular structure of 7-Azathieno[2,3-c]cinnoline(7AC). The molecular geometry and NBO have been calculated by using density functional theory B3LYP method with 6-311++G(d,p) basis set. Stability of the molecule arising from hyper-conjugative interactions and charge delocalization has been analyzed using natural bond orbital analysis (NBO). The calculated HOMO and LUMO energies show that charge transfer within the molecule. Molecular electrostatic potential(MEP) and the first order hyperpolarizability were also performed. The electron density-based local reactivity descriptor such as Fukui functions are calculated to explain the chemical selectivity or reactivity site in title compound. The molecule orbital contributions were investigated by using the total density of states (TDOS) and sum of α and β electron density of states ($\alpha\beta$DOS). The thermodynamical properties (heat capacity, entropy and enthalpy) of the 7AC at the different temperatures were calculated in gas phase.

Keywords: *DFT; NBO; Fukui function; Thermodynamic Properties.*

Introduction

The title compound (systematic name: pyrido[4,3-e]thieno-[2,3-c]pyridazine), C9H5N3S, consists of three fused heterocyclic rings [1].Cinnoline and related compounds pointed out that this ring system was the least known of the condensed, bicyclic aromatic heterocycles containing two nitrogen atoms. Some cinnolines have been screened and have received approval as bioactive drugs or are still under clinical trials[2].Cinnoline derivatives are an important class of compound possessing a wide variety of biological activities such as antibacterial and antifungi activities. Investigations on structures of Cinnoline derivatives have attracted the attention due to their peculiar properties and pharmacological uses. In DFT methods, Becke's three parameters exact-functional(B3) combined with gradient-corrected correlational functional of lee, Yang and parr (LYP) were the best predicting result for molecular geometry and NBO analysis of 7AC molecule. In addition, their non-linear properties have an importance for the design of various molecular electronic devices such as optical switches and optical data storage devices. NLO studies provide the key functions of frequency shifting, optical modulation, optical switching, optical logic, and optical memory for the emerging technologies in areas such as telecommunications, signal processing and optical interconnections.

Additionally, it was also planned to illuminate theoretical determination of the optimized HOMO-LUMO energy gap, MEP, NLO, Fukui functions and thermodynamical properties of the title compound by using density functional theory (DFT) with B3LYP/6-311++G(d,p) basis set. The other important quantities such as ionization potential(I), electron affinity(A), electrophilicity index(ω), chemical potential(μ), electronegativity (χ), hardness (η), and softness (S) are also evaluated in the way of molecular orbital framework.

Computational methods

Density Functional Theoretical (DFT) quantum chemical computations were carried out at the Becke3-Lee-Yang-parr(B3LYP) level with 6-311++G(d,p) basis set using Gaussion 09 program package [3] to get a clear knowledge of optimized parameters. NBO calculations [4] were performed using NBO 3.1 Program to understand inter and intra-molecular delocalization or hyperconjugation [5-8]. The first hyper polarizabilities and related properties (βtot α, Δα) of title compound 7AC were calculated using B3LYP/ 6-311++G(d,p) basis set. .The electronic properties such as HOMO and LUMO energies were determined by DFT approach. The total density of states (TDOS or DOS) and sum of alpha plus beta electrons (α橦DOS) spectra are prepared by using the program Gauss sum 2.2 [9].

Results and discussion

Molecular geometry

The optimized geometry structure of the title compound is shown in Fig. 1. The optimized structure parameter for this compound calculated by B3LYP with 6-311++G(d,p) basis sets are listed in Table 1.The theoretical values for the 7AC molecule were compared with XRD data of title molecules. The maximum bond length were calculated for C_3-S_{13}, C_{12}-S_{13} and found to be 1.726Å, 1.726Å(experimental) and 1.75Å, 1.726Å(theoretical)respectively. The reasoning for the larger bond length appear to be that the bond is repulsive and the forces of unlike charges are attractive. From the theoretical values, it is found that most of the optimized bond lengths are slightly higher than the experimental values due to the fact that the theoretical calculations belong to be isolated molecules in gaseous phase and the experimental results belong to molecule in solid state[10].The computed bond lengths and bond angles are in reasonable agreement with the corresponding experimental values. However, all bond lengths and computed with DFT-B3LYP levels show excellent agreement with the experimental structural parameters. Despite these differences, the calculated geometrical parameters represent a good approximation, and they are the basis for the calculation of other parameters such as polarizability, vibrational frequencies and thermodynamic properties.

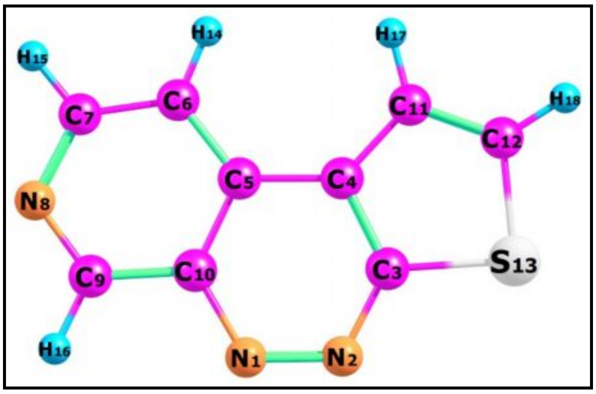

Fig 1.Optimized geometric structure with atoms numbering of 7AC

Table.1. Geometrical parameters optimized in 7-Azathieno[2,3-c]cinnoline bond length (A^o) and bond angle (^{o}) with 6-311++G (d, P) basis set.

KN Parameters	Experimental[a] EXPRI	B3LYP/ 6-311++G(d,p)mn1
N1-N2	1.302	1.297
N1-C10	1.375	1.372
N2-C3	1.353	1.351
C3-C4	1.408	1.402
C3-S13	1.726	1.75
C4-C5	1.421	1.42
C4-C11	1.421	1.428
C5-C6	1.411	1.413
C5-C10	1.42	1.42
C6-C7	1.354	1.376
C6-H14	0.95	1.083
C7-N8	1.361	1.36
C7-H15	0.97	1.085
N8-C9	1.293	1.314
C9-C10	1.42	1.42
C9-H16	0.97	1.086
C11-C12	1.354	1.363
C11-H17	0.95	1.081
C12-S13	1.726	1.739
C12-H18	0.97	1.08
N2-N1-C10	119.47	119.8
N1-N2-C3	118.3	118.5
N1-C10-C5	124.6	124.5
N1-C10-C9	117.89	117.2
N2-C3-C4	126.65	126.7
N2-C3-S13	121.77	121.5
C4-C3-S13	111.58	111.8
C3-C4-C5	115.4	115.2
C3-C4-C11	111.93	112.2
C3-S13-C12	90.68	90.1
C5-C4-C11	132.5	132.6
C4-C5-C6	126.32	127.3
C4-C5-C10	115.4	115.3
C4-C11-C12	111.93	112.1
C4-C11-H17	125.4	124.7
C6-C5-H10	117.7	117.5
C5-C6-C7	118.27	118.7
C5-C6-H14	121.2	121
C5-C10-C9	118.27	118.3
C7-C6-H14	121.2	120.3
C6-C7-N8	124.6	124.3
C6-C7-H15	121.2	120.3
N8-C7-H15	115.1	115.4
C7-N8-C9	117.91	117.6
N8 C9-C10	123.69	123.6
N8-C9-H16	117.8	118.3
C10-C9-H16	117.7	118.2
C12-C11-H17	122.8	123.2
C11-C12-S13	114.11	113.9
C11-C12-H18	127.8	127.1
S13-C12-H18	118.1	119

[a] Taken from Ref [1]

NBO analysis

In order to investigate the intra and intermolecular interactions, the stabilizations energies of the title compound were performed by using second-order perturbation theory. The change in electron density (ED) in the (σ^*) antibonding orbitals and E(2) energies have been calculated by natural bond orbital (NBO) analysis[11,12] using DFT method to give clear evidence of stabilization originating from the various molecular interactions. The second-order Fock matrix was carried out to evaluate the donar-acceptors interactions in the NBO analysis[13]. The interactions result is a loss of occupancy from the localized NBO of the idealized Lewis structure into an empty non-Lewis orbital. For each donor (i) and acceptor (j), the stabilization energy E(2) associated with the delocalization i→ j is estimated as

$$\mathbf{E_2 = \Delta E_{ij} = q_i}\,\frac{F(i,j)^2}{\varepsilon_i - \varepsilon_j}$$

Were q_i is the donor orbital occupancy, ε_i and ε_j are diagonal elements and F(i,j) is the off diagonal NBO Fock matrix element. NBO analysis provides an efficient method for studying intra and intermolecular bonding and interaction among bonds, and also provides a convenient basis for investigation charge transfer of conjugative interaction in molecular systems. The larger the E_2 value, the more intensive is the interaction between electron donors and electron acceptors, i.e., the more donating tendency from electron donors to electrons acceptors and the greater the extent of conjugation of the whole system.

The strong intramolecularhyperconjugative interaction of the s and p electrons of C-C to the anti C-C bond of the ring leads to stabilization of some part of the ring as evident from table 2. For example the intramolecularhyperconjugative interaction of (C_4-C_{11}) distribute to σ^*(N_2-C_3, C_4-C_5)leading to stabilization of 5.55 kJ/mol. This enhanced further conjugate with anti-bonding orbital of π^*(C_5-C_{10}) which leads to strong delocalization of 17.38 kJ/mol respectively. As well as hyperconjugative interactions of the $\sigma \rightarrow \sigma^*$ and $\pi \rightarrow \pi^*$ transitions occur from various bonds in our molecule; particularly, (C_{12}-S_{13}) and π (C_5-C_{10}) having the bigger energetic contribution of their anti-bonding σ^*(N_2-C_3) and π^*(N_8-C_9) interactions at 8.97 and 29.45 kJ/mol. Theπ^*(C_5-C_{10})of the NBO orbital further conjugate with π^*(C_6 – C_7) resulting in an enormous stabilization of 155.14 KJ/mol as shown in Table 2. This is the highest energy from all interaction.

Table.2.Second order perturbation theory analysis of Fock matrix in NBO basis for 7AC

Donor (i)	Type	ED/e	Acceptor(i)	Type	ED/e	^{a}E(2) (KJ mol^{-1})	^{b}E(J)-E(i)(a.u.)	^{c}F(I,j)(a.u.)
N_1-N_2	Π	1.8721	C_5-C_{10}	π^*	0.4472	11.88	0.34	0.062
N_2-C_3	Σ	1.9821	C_3-C_4	σ^*	0.0477	3.97	1.28	0.064
	Σ		C_2-S_{13}	σ^*	0.0228	3.39	1.40	0.062
C_3-C_4	Σ	1.9625	C_3-S_{13}	σ^*	0.0228	5.18	1.32	0.074
C_3-S_{13}	Σ	1.9782	N_2-C_3	σ^*	0.0502	5.98	1.40	0.082
	Σ		C_3-C_4	σ^*	0.0477	5.80	1.52	0.084
C_4-C_5	Σ	1.9721	C_4-C_{11}	σ^*	0.0195	4.79	1.26	0.070
C_4-C_{11}	Σ	1.9730	N_2-C_3	σ^*	0.0502	4.08	1.08	0.060
	Σ		C_4-C_5	σ^*	0.0315	5.55	1.24	0.074
C_4-C_{11}	Π	1.7123	C_3	LP(1)	1.2059	62.20	0.09	0.089
	Π		C_5-C_{10}	π^*	0.4472	17.38	0.28	0.065
C_5-C_{10}	Π	1.5198	N_1-N_2	π^*	0.3143	22.75	0.19	0.061
	Π		C_4-C_{11}	π^*	0.3854	20.48	1.22	0.063
	Π		C_6-C_7	π^*	0.2552	13.98	0.29	0.060
	Π		N_8-C_9	π^*	0.3287	29.45	0.26	0.081
C_6-C_7	Π	1.6790	C_5-C_{10}	π^*	0.4472	20.46	0.29	0.070
	Π		N_8-C_9	π^*	0.3287	15.28	0.28	0.058
C_6-H_{14}	Σ	1.9783	C_7-N_8	σ^*	0.0174	4.60	1.03	0.062
N_8-C_9	Π	1.7292	C_5-C_{10}	π^*	0.0447	14.87	0.31	0.063
	Π		C_6-C_7	π^*	0.2552	24.03	0.03	0.079
C_9-H_{16}	Σ	1.9779	C_5-C_{10}	σ^*	0.0401	5.37	1.03	0.067
C_{11}-	σ	1.9751	C_4-C_5	σ^*	0.0315	6.41	1.25	0.080

H_{12}								
C_{12}-S_{13}	σ	1.9798	N_2-C_3	σ^*	0.0502	8.97	1.40	0.101
	σ		C_{12}-S_{13}	σ^*	0.0135	5.25	1.94	0.090
	σ		C_{12}-S_{13}	π^*	0.6154	15.65	3.85	0.261
C_{12}-S_{13}	π	1.8740	C_3	LP(1)	1.2055	38.34	0.21	0.118
	π		C_4-C_{11}	π^*	0.3854	10.08	0.041	0.061
C_{12}-H_{18}	σ		C_{12}-S_{13}	σ^*	0.0135	7.71	1.48	0.096
	σ		C_{12}-S_{13}	π^*	0.6154	9.18	3.38	0.187
N_1	LP(1)	1.9453	N_2-C_3	σ^*	0.0502	8.00	0.79	0.071
	LP(1)		C_5-C_{10}	σ^*	0.0401	7.79	0.92	0.076
N_2	LP(1)	1.9567	N_1-C_{10}	σ^*	0.0350	7.08	0.83	0.068
	LP(1)		C_3-C_4	σ^*	0.0477	6.53	0.92	0.069
C_3	LP(1)	1.2059	N_1-N_2	π^*	0.3144	65.35	0.11	0.088
	LP(1)		C_4-C_{11}	π^*	0.3854	46.35	0.20	0.096
S_{13}	LP(1)	1.9434	C_3-C_4	σ^*	0.0477	8.18	1.02	0.082
	LP(1)		C_{11}-C_{12}	σ^*	0.0251	6.92	1.06	0.077
N_1-N_2	π^*	0.3143	C_5-C_{10}	π^*	0.0447	28.51	0.08	0.070
C_5-C_{10}	π^*	0.4472	C_6-C_7	π^*	0.2552	155.14	0.02	0.078
N_8-C_9	π^*	0.3287	C_6-C_7	π^*	0.2552	81.23	0.03	0.077

[a] $E^{(2)}$ means energy of hyper conjugative interaction (stabilization energy)

[b] Energy difference between donor and acceptor i and j NBO orbitals.

[c] F(i,j) is the Fock matrix element between i and j NBO orbitals

NLO Properties

The first order hyperpolarizability (β_{total}) of the title compound 7AC along with related properties (μ, α and Δα) are calculated by using DFT-B3LYP method with 6-311++G(d,P) basis set, based on the finite-field approach.NLO effects arise from the interactions of electromagnetic fields in various media to produce new fields altered in phase, frequency, amplitude or other propagation characteristics from the incident fields.

The non-linear optical response of an isolated molecule in an electric field E_i (ω) can be represented as a Taylor series expansion of the total dipole moment, μ_{tot}, induced by the field:

$$\mu_{tot} = \mu_0 + \alpha_{ij}E_j + \beta_{ijk}E_jE_k + \dots,$$

Where α is the linear polarizability, μ_0 is the permanent dipole moment and β_{ijk} are the first hyperpolarizability tensor components. The isotropic (or average) linear polarizability is defined as :

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

First hyperpolarizability is a third rank tensor that can be described by 3×3×3 matrix. The 27 components of 3D matrix can be reduced to 10 components due to the Kleinman symmetry.Components of the first hyperpolarizability can be calculated using the following equation:

$$\beta_i = \beta_{iii} + \sum_{i \neq j}[(\beta_{ijj} + \beta_{jij} + \beta_{jji}])$$

Using the x, y and z components of β, the magnitude of the first hyperpolarizability tensor can be calculated by:

$$\beta_{tot} = \sqrt{(\beta_x^2 + \beta_y^2 + \beta_z^2)}$$

The complete equation for calculating the magnitude of β from Gaussian 03W output is given a follows:

$$\beta_{tot} = \sqrt{(\beta_{xxx} + \beta_{xyy} + \beta_{xzz})^2 + (\beta_{yyy} + \beta_{yzz} + \beta_{xxy})^2 + (\beta_{zzz} + \beta_{xxz} + \beta_{yyz})^2}$$

The calculations of the total molecular dipole moment (μ), linear polarizability (α) and first-order hyperpolarizability (β) from the Gaussian output have been explained in detail previously[14], and DFT has been extensively used as an effective method to investigate the organic NLO materials[15] . In addition, the polar properties of the title compound were calculated at the DFT (B3LYP)/6-311++G(d,p) level using Gaussian 09W program package.

The calculated dipole moment and hyperpolarizability values obtained from B3LYP/6-311G(d,p) methods are collected in Table 3. The total molecular dipole moment of 7AC from B3LYP with 6-311++G(d,p) basis set are 2.2733D. Which are 1.6 times greater than the value for urea (μ = 1.3732 D). Similarly the first order hyperpolarizability of 7AC with B3LYP/6-311++G(d,p) basis set is 2.2815 x 10^{-30} six times greater than the value of urea (β_o = 0.372 x10^{-30} esu). From the computation the high values of the hyperpolarizabilities of 7AC are probably attributed to the charge transfer existing between the phenyl rings within the molecular skeleton. This is evidence for nonlinear optical (NLO) property of the molecule.

Table.3. The values of calculated dipole moment μ (D), polarizability (α_0), first order hyperpolarizability (βtot) components of 7AC

Parameters	B3LYP/6-311++G(d,p)	Parameters	B3LYP/6-311++G(d,p)
μ_x	0.6727	β_{xxx}	21.7994
μ_y	-1.8863	β_{xxy}	234.0573
μz	-1.0758	β_{xyy}	-70.4906
μ(D)	**2.2733**	β_{yyy}	-15.0848
α_{xx}	209.0067	β_{zxx}	131.69
α_{xy}	-12.2541	β_{xyz}	-58.8599
α_{yy}	128.9775	β_{zyy}	43.2447
α_{xz}	-11.6344	β_{xzz}	-21.4797
α_{yz}	34.05789	β_{yzz}	3.9442
α_{zz}	88.1128	β_{zzz}	-51.9577
α_0 (e.s.u)	**2.1049X10^{-23}**	**βtot (e.s.u)**	**2.2815X10^{-30}**
α (e.s.u)	**5.5924X10^{-23}**		

HOMO-LUMO energy gap

The HOMO (highest occupied orbital)- LUMO (lowest unoccupied molecular orbital) energy gap of 7-Azathieno[2,3-c]cinnoline has been calculated at the B3LYP/6-311++G(d,p) basis set and their values shown in Table 4. Many organic molecules containing π conjugated electrons are characterized hyperpolarizabilities and were analyzed by means of vibrational spectroscopy[16,17]. The HOMO and LUMO are the main orbital taking part in chemical reaction. A molecule with a small frontier orbital gap is more polarizable and is generally associated with chemical reactivity, low kinetic stability and is also termed as soft molecule[18]. The frontier molecular orbital energies and corresponding density of state of the title compound are shown in Fig .2.

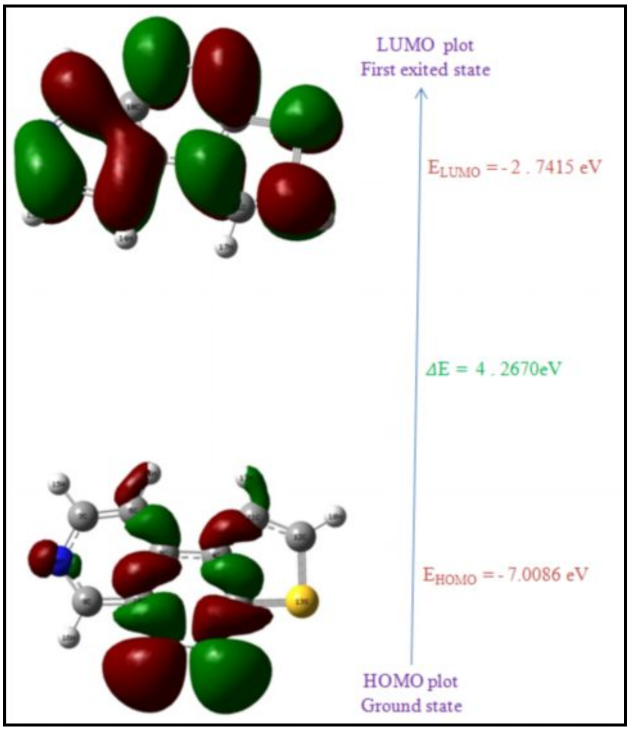

Fig 2. Atomic orbital HOMO – LUMO composition of the frontier molecular orbital for 7AC

The HOMO and LUMO energies, the energy gap (ΔE), the ionization potential (I), the electron affinity (A), the absolute electro negativity (χ), the absolute hardness (η) and softness (S) for the 7AC molecule have been calculated at B3LYP/6-311++G(d,P) basis set(Fig 2) and the result are given in the Table 4.

By using HOMO and LUMO energy values for a molecule, electronegativity and chemical hardness can be calculated as follow:

$$\chi = \frac{I + A}{2}$$ (Electronegativity)

$$\mu = -\frac{(I + A)}{2}$$ (Chemical potential)

$$\eta = \frac{I - A}{2}$$ (Chemical hardness)

s=1/2η (chemical softness), $\omega=\mu^2/2\eta$ (Electrophillicity index)

Where I and A are ionization potential and electron affinity; I= E_{HOMO} and A= E_{LUMO}respectively . The calculated value of electrophilicity index describes the biological activity of the 7AC.

Table.4.Comparison of HOMO, LUMO, energy gaps and ionization potentials of 7AC

Basis set	**B3LYP/6-311++G(d, p)**
E_{Homo} (eV)	-7.0086
E_{Lumo} (eV)	-2.7415
Ionization potential	7.0086
Electron affinity	2.7415
Energy gap (eV)	4.2670
Electronegativity	4.8750
Chemical potential	-4.8750
Chemical hardness	2.1335
Chemical softness	0.2343
Electrophilicity index	5.5697

Molecular electrostatic potential map

In the present study, the molecular electrostatic potential(MEP) and contour plot of 7-Azathieno[2,3-c]cinnoline are illustrated in Fig. 3 and 4. The electron density surface can be used to located atoms, emphasize electron densities associated with chemical bond. However, it can be seen from the ESP figure that while the negative ESP are localized more over the molecules. The MEP is related to the electronic density which is a very useful descriptor for determining sites for electrophilic attack and nucleophilic reactions, the study of biological recognition processes and a hydrogen-bonding interactions[19,20].

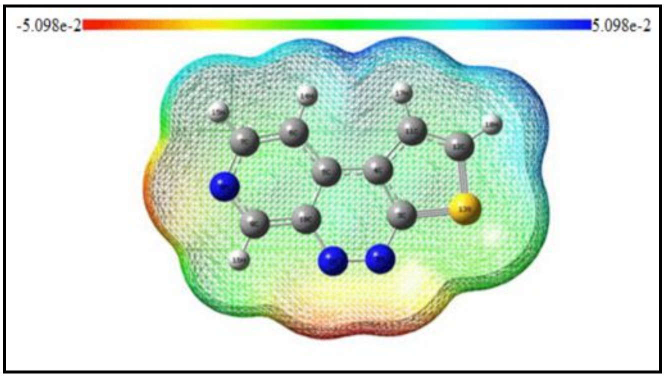

Fig.3. Total electron density mapped with molecular electrostatic potential surface of 7AC

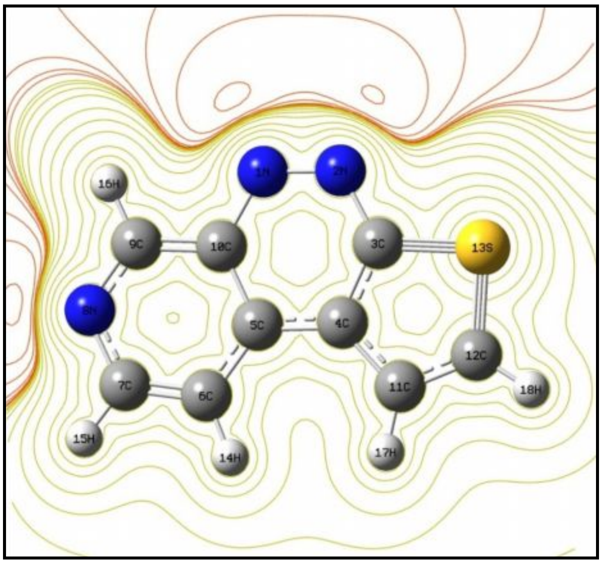

Fig.4. The contour map of electrostatic potential of the total density of 7AC.

To predict reactive sites for electrophilic and nucleophilic attack for the investigated molecule, molecular electrostatic potential(MEP) was calculated at B3LYP/6-311++G(d,p) optimized geometries. In the majority of the MEPs, while the maximum negative region which preferred site for electrophilic attack indications as red color, the maximum positive region which preferred site for nucleophilic attack symptoms as blue color. The importance of MEP lies in the fact that it simultaneously displays molecular size, shape as well as positive, negative and neutral electrostatic potential regions in terms of color grading and is very useful in research of molecular structure with its physiochemical property relationship. In the present study, 3D plots of molecular electrostatic potential(MEP) of 7AC has been drawn in Fig. 3.The MEP is a plot of electrostatic potential mapped onto the constant electron density surface.

The different values of the electrostatic potential at the surface are represented by different colors. Potential increases in the order red < orange < yellow < green < blue. The color code of these maps is in the range between –0.05098 a.u. (deepest red) and 0.05095 a.u. (deepest blue) in compound, where blue shows the strongest repulsion and red show the strongest attraction. According to these calculated results, the MEP map shows that the negative potential sites are on Sulphur and Nitrogen atoms and the positive potential sites as well are around the hydrogen atoms. The contour map of electrostatic potential of 7-Azathieno[2,3-c]cinnoline has been constructed by the DFT method and is shown in Fig.4 also confirms the different negative and positive potential sides of the molecule in accordance with the total electron density surface.

Local reactivity descriptors

Table.5.Condensed fukui function f_r and new descriptor $(sf)_r$ for 7AC.

Atoms	f_k^+	f_k^-	f_k^0	$s_k^+f_k^+$	$s_k^-f_k^-$	$s_k^0\ f_r^0$
N_1	-0.1462	-0.0886	-0.1174	0.0342	0.0208	0.0275
N_2	-0.1620	-0.0988	-0.1304	0.0380	0.0232	0.0306
C_3	0.1456	0.0852	0.1154	0.0341	0.0200	0.0270
C_4	-0.1897	-0.0925	-0.1411	0.0444	0.0217	0.0331
C_5	-0.1527	-0.0782	-0.1155	0.0358	0.0183	0.0271
C_6	-0.0336	-0.0540	-0.0438	0.0079	0.0127	0.0103
C_7	-0.0476	0.0024	-0.0226	0.0111	0.0006	0.0053
N_8	-0.0502	-0.0932	-0.0717	0.0118	0.0218	0.0168
C_9	0.0386	0.0358	0.0372	0.0091	0.0084	0.0087
C_{10}	0.0356	-0.0368	-0.0006	0.0083	0.0086	0.0001
C_{11}	0.0257	-0.1049	-0.0396	0.0060	0.0246	0.0093
C_{12}	-0.0696	-0.0264	-0.0480	0.0163	0.0062	0.0112
S_{13}	-0.0924	-0.1420	-0.1172	0.0216	0.0333	0.0275
H_{14}	-0.0532	-0.0389	-0.0461	0.0125	0.0091	0.0108
H_{15}	-0.0674	-0.0628	-0.0651	0.0158	0.0147	0.0152
H_{16}	-0.0650	-0.0553	-0.0602	0.0152	0.0130	0.0141
H_{17}	-0.0483	-0.0800	-0.0642	0.0113	0.0188	0.0150
H_{18}	-0.0678	-0.0708	-0.0693	0.0159	0.0166	0.0162

Fukui functions (f_k^+ , f_k^- , f_k^0) and local softness (s_k^+ , s_k^-, s_k^0)[21] for selected atomic sites in 7AC have been listed in Table 5. Using Hirshfeld atomic charges of neutral, cation, and anion states of 7AC, Fukui functions are calculated using the following equations.

$f_k^+ = q_k(N+1) \quad q_k(N)$ for nucleophilic attack

$f_k^- = q_k(N) - q_k(N-1)$ for electrophilic att*ack*

$$f_k^0 = \frac{q_k(N+1) - q_k(N-1)}{2} \quad \text{for radical attack}$$

In these equations, q_k is the atomic charge (evaluated from Mulliken population analysis, electrostatic derived charge, etc.)at the kth atomic site is the neutral(N), anionic(N+1), cationic(N-1) chemical species.kolandaival et al.[22] introduced the atomic descriptor to dermine the local reactive sites of the molecular system. The individual atomic charges calculated by Mulliken population analysis (MPA) have been used to calculated the Fukui function. Inorder to confirm that atomic descriptor would produce the reactive sites without disturbing the trend; we have performed the calculation for the reactive sites of the stable structures of 7AC.

The local softness is calculated using the following equations

$$s_k^+ = Sf_k^+ ,\ s_k^- = Sf_k^- ,\ s_k^0 = Sf_k^0$$

Where +, -, 0 signs show nucleophilic, electrophilic and radical attack at the respectively. It has been found that MAP schemes predict C_3 has higher f_k^+ value indicates the possible site for nucleophilic attack. In Table 5 it is reported the values of the Fukui function obtained from the Mulliken charges. From the values reported in Table(5), MAP schemes predict the reactivity order for the nucleophilic case was C_3> C_9> C_{10}> C_{11}. On the other hand, for electrophilic attack was C_3> C_9> C_7 site and the radical attack was predicted at C_3> C_9site. If one compares the three kinds of attack it is possible to observe that nucleophilic attack is bigger reactivity comparison with the electrophilic and radical attack.

Total, sum of alpha plus beta electrons DOS

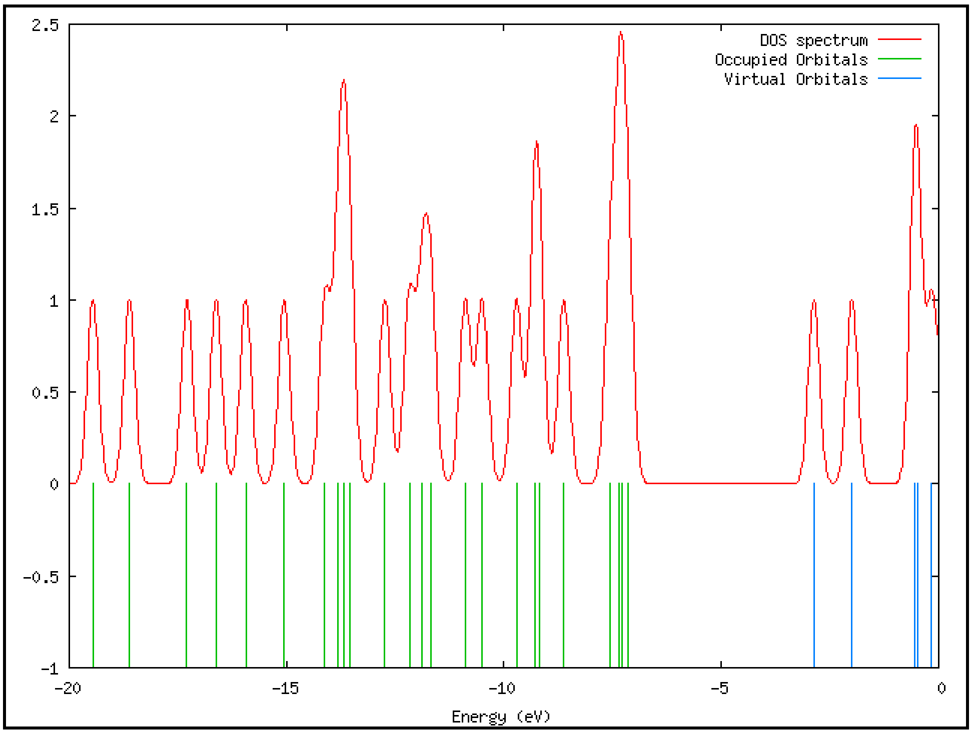

Fig.5.Calculated total electronic density of states (TDOS) for 7AC

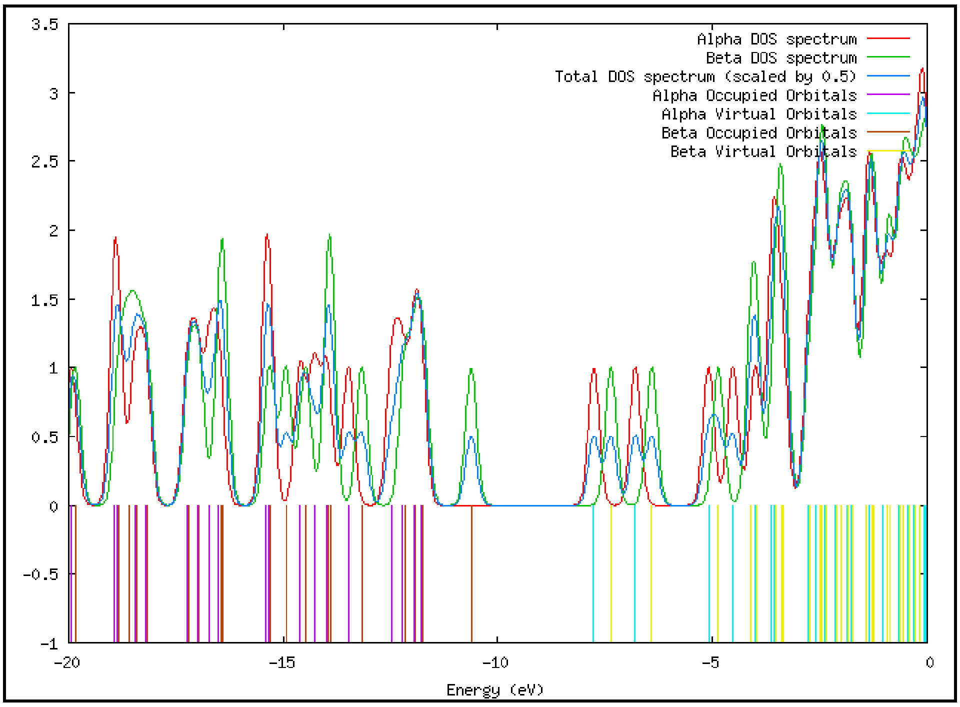

Fig. 6. The sum of alpha plus beta electrons DOS diagram of 7AC

In the boundary region, neighboring orbitals may show quasi degenerate energy levels. In such cases, consideration of only the HOMO and LUMO may not yield a realistic description of the frontier orbitals. For this reason, the total (TDOS), sum of and β electron density of states, in terms of Mulliken population analysis are calculated and created by convoluting the molecular orbital information with the Gaussian curves of unit height and full width at half maximum (FWHM) of 0.3 eV by using the Gauss Sum 2.2 program[23,24]. The TDOS, $\alpha\beta$DOS of the 7-Azathieno[2,3-c]cinnolineare plotted in Fig.5 and 6. They provide a pictorial representation of MO (molecule orbital) compositions and their contributions to chemical bonding. The most important application of the DOS plots is to demonstrate MO compositions and their contributions to the chemical bonding through the positive and negative charges provide $\alpha\beta$DOS, TDOS diagrams. The $\alpha\beta$DOS show the bonding, sum of positive and negative electron with nature of the interaction of the two orbitals, atoms or groups. The 7AC consists of 48 α-electrons and 48β-electrons, totally 96 electrons are occupied in density of states. The way we designate a pictorial representation for cations and anions is essentially similar to that for neutral atoms in their ground state. Because of the short range of absorption, alphas are not, in general, dangerous to life unless the source is ingested or inhaled, in which case they become extremely dangerous[25]. A positive value of the $\alpha\beta$DOS indicates a bonding interaction, negative values means that there is an anti-bonding interaction and zero values indicates non-bonding interactions [26].

Thermodynamic properties

Table.6.Temperature dependence of thermodynamic properties of 7AC at B3LYP /6-311++G(d, P)

T(K)	S^{0}_{m} (J/ molK)	$C^{0}_{p,m}$ (J/ molK)	H^{0}_{m} (kJ/ mol)
100	282.18	60.1	4.32
200	337.57	107.23	12.58
298	390.06	159.01	25.66
300	391.05	159.96	25.95
400	443.8	207.76	44.4
500	494.52	246.75	67.2
600	542.32	277.31	93.47
700	586.94	301.2	122.44
800	628.44	320.13	153.55
900	667.06	335.39	186.35
1000	703.06	347.87	220.53

On the basis of vibrational analysis, the statistical thermodynamics and the standard thermodynamic function, heat capacity $\left(C^{0}_{p,m}\right)$, entropy $\left(S^{0}_{m}\right)$ and enthalpy changes $\left(H^{0}_{m}\right)$ were computed at B3LYP/6-311++G(d,p) basis set by using Perl script THERMO.PL and are listed in Table 6. It can be observed that these thermodynamic functions areall values increasing with the temperature ranging from 100 to 1000K due to the fact that the molecular vibrations intensities increase with temperature. The correlation equation between heat capacities, entropies, enthalpy changes and temperatures were fitted by quadratic formulas and the corresponding fitting factors (R^2) these thermodynamic properties are 0.9999,0.9995 and 0.9994 respectively. The correlations plot of those shown in Fig 7. The thermodynamic correlation fitting equation is follows:

$$\left(C^{0}_{p,m}\right) = -4.7501 + 0.6418T - 2.9112 \times 10^{-4}T^{2} \qquad (R^{2} = 0.9990)$$

$$\left(S^{0}_{m}\right) = 220.6279 + 0.6110T - 1.2769 \times 10^{-4}T^{2} \qquad (R^{2} = 0.9999)$$

$$\left(H^{0}_{m}\right) = -7.2963 + 0.0691T - 1.6141 \times 10^{-4}T^{2} \qquad (R^{2} = 0.9990)$$

The thermodynamic parameters provide very helpful information for the further study on the title molecule. They can be used to compute the other thermodynamic energy, according to the relationship of thermodynamic functions and evaluate directions of chemical behavior, according to the second law of thermodynamics in the thermo chemical field [27].

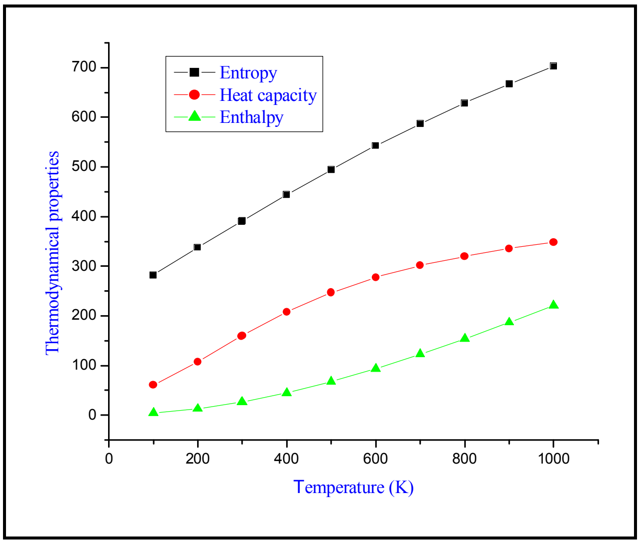

Fig 7.Correlation plot of thermodynamic properties at different temperature of the title compound.

Conclusions

The optimized molecular structure, thermodynamic and electronic properties of 7-Azathieno[2,3-c]cinnolineare calculated by DFT method using B3LYP++G(d,p) basis set. The optimized geometric parameters (bond lengths and bond angles) are theoretically determined by DFT theory and compared with experimental data. The NBO analysis indicates the intermolecular charge transfer between the bonding and antibonding orbitals. The electronic dipole moment, polarizabilities and the hyperpolarizabilities of the compound studied. The lowering of the HOMO-LUMO energy gap value has substantial influence on the intermolecular charge transfer and bioactivity of the molecule. The MEP map shows the negative potential sites are on Nitrogen and Sulphur atoms as well as the positive potential sites around the hydrogen atoms. Fukui function helps to identifying the electrophilic/nucleophilic nature of a specific site within a molecule and thermodynamic properties in the range from 100 to 1000K are obtained. The gradients of $C_{p,m}$, S_m andH_m increases with increase of temperature.

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