

Research Article

A Theoretical Study on NLO Properties and Reactivity of Pyridazino Quinolines

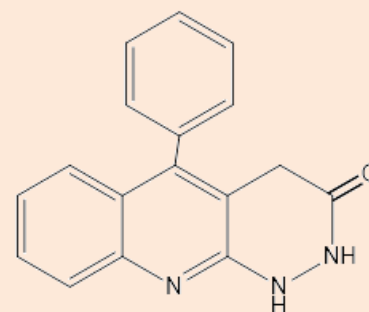
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Abstract

The density functional theory calculations were performed on 5-phenyl-1,4-tri hydro-2H-Pyridazino[3,4-*b*] quinolin-3-one. The computations were performed at DFT level of theory to get the optimized geometry and vibrational wave numbers of the normal modes of the compound. Mulliken population analysis on atomic charges is calculated. The calculated HOMO and LUMO energies show the reactive potential of the compound. The study has also extended to calculate the thermodynamic properties of the compound. Non linear optical behavior of the molecule was investigated by the determination of first hyperpolarizability.

Keywords: DFT, NLO, first hyper polarizability, HOMO and LUMO, Pyridazino quinoline.

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Introduction

Pyridazinones are important heterocyclic compounds which possess almost all types of biological activities such as antimicrobial, antifungal, antiviral [1-5], antifeedant, herbicidal [6, 7], antiinflammatory, analgesic and antipyretic [8-14], antidepressant, anti-anxiety [15-17], antihypertensive, antiplatelets, cardiotoxic, antidiabetic [18-24], diuretics, anticancer, antiasthmatic, anti-allergy and other anticipated activities [25-31]. In particular, a large number of pyridazinone derivatives are also used as intermediates for drugs and agrochemicals. Some pyridazinone compounds like indolidan, bemoradan, primobendan, levosimendan (antihypertensive), minaprine (antidepressant), emorfazone (anti-inflammatory), and azanrinone (cardiotonic), are used in the clinical marketed drugs [32]. Among the bi-functional molecules, hydroxyquinolines have been widely studied from both experimental and theoretical viewpoints. Early in 1968, Mason et al [33] had investigated the excited-state properties of 7-hydroxyquinolines (7-HQ) and pointed out that the OH group is more acidic and the ring nitrogen atom more basic in the excited state than in the ground state. Density functional theory (DFT) has become very popular in recent years. This is justified based on the pragmatic observation that it is less computationally intensive than other methods with similar accuracy. This theory has been developed more recently than other *ab initio* methods. The purpose of the present study was to theoretically optimize the geometry of the molecule through DFT using the Becke's three parameter Lee, Yang, and Parr functional (B3LYP [34] and then determine their spectral (IR), Mulliken charges, thermodynamic properties, frontier molecular orbital compositions, NLO properties, via Density Functional Theory (DFT). The DFT method was chosen for this study because it is faster, less computationally intensive, takes electron correlation into account and has a precise accuracy in reproducing experimental data [35]. In addition, DFT was developed especially for calculations [36]. DFT is generally considered to be a good compromise between accuracy and computational time.

Experimental

The quantum calculations of the physical properties (electronic and vibrational) were performed by using standard Gaussian 09W software package [37, 38] to optimize the molecular structures and to calculate the electronic and

vibrational properties of the study molecules. The geometry optimizations were carried out at the DFT level using the hybrid functional B3LYP based on Becke's three-parameter functional [38]. The molecular properties of the compounds had been computed by using the standard 6-31G(d, p) basis sets. Thus, all the parameters presented in this study: the best geometry, the total energy, frontier molecular orbital energies (HOMO and HUMO), energy gap, ionization potential, electron affinity, electronegativity, chemical hardness, chemical softness, electrophilicity, dipole moment and the harmonic vibration frequencies were calculated at B3LYP with 6-31G basis set [39-42].

Results and Discussion

Optimised geometrical parameters

The optimised structure and the scheme of numbering the atom of 5-phenyl-1,4-tri hydro-2H-Pyridazino[3,4-*b*]quinolin-3-one are represented in **Figure 1**.



Figure 1

The optimized bond lengths and angles for the thermodynamically preferred geometry of determined at B3LYP/6-31g(d,p) levels are represented in **Table 1** in accordance with the atom numbering scheme of the molecule shown in Figure 1.

In the title compound 12-13,7-11,6-10,3-7,2-4 bond length are found to be about 1.42\AA and they found to be coincide with values shown by Singh Rajeev et al. 5-6 and 4-5 bond length are 1.363 and 1.313\AA respectively. The inner angle of 10-6-7, 11-7-6 and 7-3-2 are and outer angles of 12-13-17, 13-12-16, 7-3-22, 4-2-1, 2-4-9 are also found to be same as inner angle. The dihedral angle as 6-7-3-22, 7-3-22-2-, 3-2-4-9 are 180° , which suggest that molecule is planar.

Mulliken Charge Analysis

Atomic charge has been used to describe the processes of electronegativity equalization and charge transfer in chemical reactions [43] and to model the electrostatic potential outside molecular surfaces [44]. Effective atomic charge calculations have an important role in the application of quantum chemical calculation to molecular system because of atomic charges effect dipole moment, molecular polarizability, electronic structure, acidity–basicity behavior and a lot of properties of molecular systems.

Mulliken charge distributions were calculated by determining the electron population of each atom as defined by the basis set. The calculated Mulliken charge values using B3LYP levels of theory and basis set is listed in **Table 2**.

From the table it is concluded that all the H atoms have positive charges. N₅, N₉, N₁₈ and O₃₃ atoms also exhibit a negative charge, which are donor atoms. These atoms may also play an important role in the biological reactivity of the compound.

Table 1 The optimized geometrical parameters of the molecule.

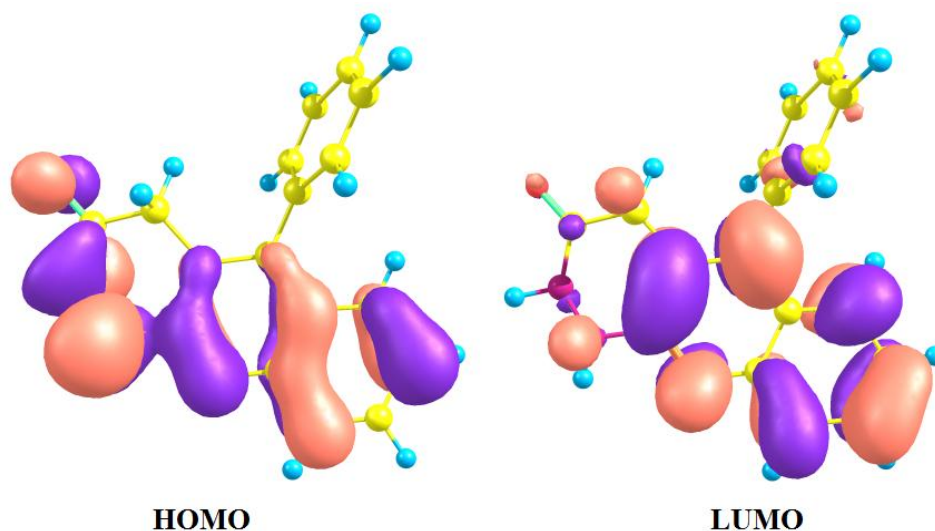
Bond in between	Bond length	Bond in between	Bond length	Bond in between	Bond angle	Angle in between	Bond angle	Angle in between	Bond angle
C1-C2	1.51	C10-H14	1.085	C2-C1-C8	114.4	N5-C4-N9	116.3	C12-C11-H15	120.2
C1-C8	1.522	C11-C12	1.378	C2-C1-H19	109.9	C4-N5-C6	117.4	C11-C12-C13	120.3
C1-H19	1.101	C11-H15	1.085	C2-C1-H34	112.5	C4-N9-N18	113.9	C11-C12-H16	119.9
C1-H34	1.091	C12-C13	1.414	C1-C2-C3	124.5	C4-N9-H20	108.9	C13-C12-H16	119.8
C2-C3	1.382	C12-H16	1.086	C1-C2-C4	117.7	N5-C6-C7	122.5	C12-C13-H17	119.7
C2-C4	1.427	C13-H17	1.086	C8-C1-H19	105.7	N5-C6-C10	118.3	C23-C22-C24	118.9
C3-C7	1.435	N18-H21	1.013	C8-C1-H34	107.7	C7-C6-C10	119.2	C22-C23-C25	120.5
C3-C22	1.496	C22-C23	1.403	C1-C8-N18	115.4	C6-C7-C11	118.7	C22-C23-C28	119.4
C4-N5	1.313	C22-C24	1.403	C1-C8-O33	123.3	C6-C10-H13	120.6	C22-C24-C26	120.5
C4-N9	1.404	C23-C25	1.395	H19-C1-H34	106.1	C6-C10-H14	117.6	C22-C24-H29	119.4
N5-C6	1.363	C23-C28	1.086	C2-C2-C4	117.6	C7-C11-C12	120.8	C25-C23-C28	120.1
C6-C7	1.432	C24-C26	1.395	C2-C3-C7	118.8	C7-C11-H15	119	C23-C25-C27	120.2
C6-C10	1.418	C24-H29	1.086	C2-C3-C22	120.9	N18-C8-O33	121.3	C23-C25-H30	119.7
C7-C11	1.42	C25-C27	1.396	C2-C4-N5	125.7	C8-N18-N9	120.3	C26-C24-H29	120.1
C8-N18	1.378	C25-H30	1.086	C2-C4-N9	118	C8-N18-H21	113.8	C24-C26-C27	120.2
C8-O33	1.221	C26-C27	1.396	C7-C3-C22	120.3	N18-N9-H20	109	C24-C26-H31	119.7
N9-N18	1.438	C26-H31	1.086	C3-C7-C6	117.9	N9-N18-H21	112.7	C27-C25-H30	120.1
N9-H20	1.016	C27-H32	1.086	C3-C7-C11	123.3	C13-C10-H14	121.9	C25-C27-C26	119.7
C10-H13	1.377			C3-C22-C23	120.5	C10-C13-C12	120.4	C25-C27-H32	120.1
				C3-C22-C24	120.6	C10-C13-H17	120	C27-C26-H31	120.1
								C26-C27-H32	120.1

Table 2 The calculated Mulliken charge values.

Atoms	Mulliken Charges	Atom	Mulliken Charges	Atoms	Mulliken Charges	Atom	Mulliken Charges
C1	-0.3202	N9	-0.4377	H17	0.08883	C26	-0.0866
C2	0.08055	C10	-0.0932	N18	-0.4064	C27	-0.08
C3	-0.0323	C11	-0.1409	H19	0.1577	C28	0.0963
C4	0.45044	C12	-0.0938	H20	0.2822	H29	0.0976
N5	-0.6035	C13	-0.0906	H21	0.28292	H30	0.09279
C6	0.22299	H14	0.0948	C22	-0.0066	H31	0.09446
C7	0.11359	H15	0.10024	C23	-0.0936	H32	0.09167
C8	0.58029	H16	0.08746	C24	-0.0952	O33	-0.5029
				C25	-0.087	H34	0.15572

Frontier molecular orbital analysis

FMO analysis is a physical property used to determine, ability to absorb light, electronic as well as optical properties of organic compounds [45]. In molecular interaction, the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) play the key role. HOMO is the orbital which has ability to donate electrons and its energy corresponds to ionization potential (I. P.), while LUMO has electrons accepting ability, and its energy corresponds to electron affinity (E. A.). FMO analysis was computed at the same level as used for optimization along with additional keyword pop = full, and HOMO-LUMO surfaces of all four molecules shown in **Figure 2** and energy is E HOMO = -5.69eV E LUMO = -1.44eV and $\Delta E = 4.25\text{eV}$

**Figure 2**

The calculated ionization energy and electron affinity that can be expressed through HOMO and LUMO orbital energy as $I = -E_{\text{HOMO}}$ and $A = -E_{\text{LUMO}}$.

The global hardness is $\eta = 1/2(E_{\text{LUMO}} - E_{\text{HOMO}})$. The hardness has been associated with the stability of chemical system. The electron affinity can be used in combination with ionization energy to give electronic chemical potential, $\mu = 1/2(E_{\text{LUMO}} + E_{\text{HOMO}})$. The global electrophilicity index, $\omega = \mu^2 / 2 \eta$, is also calculated and listed in **Table 3**.

Table 3

Molecular Property	B3LYP/6-31G(d,p)
E_{HOMO}	-5.69eV
E_{LUMO}	-1.44eV
Energy gap	4.25eV
Ionisation potential(I)	5.69eV
Electron affinity(A)	1.44eV
Global hardness(η)	2.125
Chemical potential(μ)	-3.565
Globalelectrophilicity(ω)	2.9904
Total energy	-895.13695

Table 3 summarised the important global chemical parameters. Ionisation energy is fundamental chemical parameters. Ionisation energy is a fundamental descriptor of the chemical reactivity of atoms and molecules high ionization energy indicates high stability.

Absolute hardness and softness are important properties to measure the molecular stability and reactivity it is apparent that the chemical hardness fundamentally signifies the resistance towards the deformation or polarization of the electron cloud of the atoms, ions or molecules under small perturbation of chemical reaction. A hard molecule has a large energy gap and a soft molecule has a small energy gap [46]. In this molecule the low value of global hardness indicates the reactive potential of the molecule.

TD Parameters

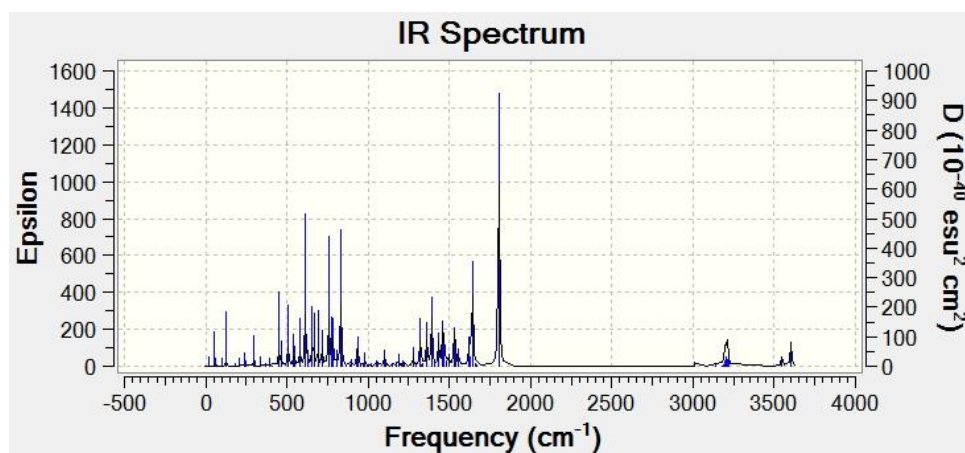
The dipole moment (μ in Debye) is another important electronic parameter which provides the information on the polarity and the reactivity indicator of the molecule. Dipole moment shows the molecular charge distribution and is given as a vector in three dimensions. Therefore, it can be used as a descriptor to depict the charge movement across the molecule. Direction of the dipole moment vector in a molecule depends on the centers of positive and negative charges. The calculated dipole moment of the compound is **2.2706**. The high value of dipole moment results stronger intermolecular interactions and high reactivity.

Analysis of the vibrational spectra

The infrared vibrational frequencies and intensities of the titled compound were calculated using the DFT B3LYP/6-311G (d,p) method and the results are given **Table 4**(**figure 3**). 1804cm^{-1} (C = O), 1642^{-1} (C = N), 3603^{-1} (NH), 3548^{-1} (NH) are the important IR absorption bands.

Table 4

Frequency	IRintensity	Frequency	IRintensity	Frequency	IRintensity	Frequency	IRintensity
16.8512	0.1358	628.122	7.7408	1056.45	3.6114	1536.5	26.5633
51.007	1.4891	656.469	33.0461	1098.3	14.7757	1558.33	22.4498
60.2914	0.4002	665.828	29.8246	1106.01	4.0895	1623.53	40.9656
67.2286	0.0882	690.129	32.4672	1149.74	3.2248	1630.89	12.1981
99.1512	0.6659	715.23	6.1843	1170.54	3.4191	1642.08	145.964
125.28	5.7479	717.736	22.0385	1186.2	12.0123	1659.64	3.0481
181.927	0.4804	757.328	83.2155	1188.65	0.0486	1669.42	1.533
203.715	1.3787	778.7	32.0584	1207.6	0.7604	1804.14	417.97
242.719	2.6318	782.177	31.2431	1214.67	5.1009	3012.94	9.9993
250.344	1.2168	804.542	11.0136	1222.58	4.0622	3140.84	2.7046
295.346	7.5733	831.023	95.8005	1275.62	19.5136	3180.68	1.7635
302.611	1.4961	837.004	17.185	1294.16	1.98	3184.29	3.3555
339.525	2.6752	865.017	0.1262	1321.96	53.4427	3186.2	0.1992
365.805	0.8749	885.611	1.3499	1325.8	0.9126	3194.54	11.3429
394.87	2.6902	898.363	4.722	1339.01	3.1475	3197.72	13.5252
412.812	0.1233	929.401	13.2853	1358.72	0.6638	3201.28	25.1117
451.942	28.5423	938.322	23.5923	1362.29	50.5621	3210.04	16.8151
467.739	9.8611	951.014	1.0537	1391.38	80.9429	3212.4	15.9896
506.427	26.2271	966.902	0.4352	1410.47	4.4572	3216.47	16.041
511.184	11.0058	976.172	0.2839	1435.06	40.4056	3548.28	24.0707
542.112	14.7765	980.738	11.0093	1459.48	56.2584	3603.61	44.2302
549.195	9.2516	997.425	0.1476	1467.11	37.4673		
581.831	23.5821	1002.7	0.163	1482.78	5.9259		
612.97	79.4437	1016.12	2.514	1495.93	15.0347		
626.273	8.3839	1052.36	4.1427	1529.12	50.5482		

**Figure 3**

Non linear optical effects

The interactions of electromagnetic radiation in some molecules can give a non-linear optical (NLO) effect which shows the some alterations in- phase, frequency and amplitude from the incident field [37]. **NLO** is an important concept in current research scenario because of its vast applications to telecommunications, optical switching and signal processing [38-41]. The mean polarizability (α_0), the total static dipole moment (μ) and the first order hyperpolarizability (β_0) are calculated by using x,y,z components.

$$\begin{aligned}\mu &= (\mu_x^2 + \mu_y^2 + \mu_z^2)^{1/2} \\ \alpha_0 &= 1/3 (\alpha_{xx} + \alpha_{yy} + \alpha_{zz}) \\ \beta_0 &= (\beta_x^2 + \beta_y^2 + \beta_z^2)^{1/2} \\ &= [(\beta_{xxx} + \beta_{xyy} + \beta_{xzz})^2 + (\beta_{yyx} + \beta_{yxx} + \beta_{yzz})^2 + (\beta_{zzx} + \beta_{zxx} + \beta_{zyy})^2]^{1/2}\end{aligned}$$

The α_0 and β_0 values of the Gaussian 09 output are in atomic units (a.u) and these calculated values converted into electrostatic unit (e.s.u) (α_0 1a.u = 0.1482×10^{-24} esu; for β_0 1a.u = 8.639×10^{-33} esu) and the first order hyper polarizability is 0.51×10^{-30} esu. To study the **NLO** properties of molecule the value of urea molecule which is prototypical molecule is used as threshold value for the purpose of comparison. The first hyperpolarizability of the title molecule is found to be greater than the urea [μ and β of urea are 1.3732 Debye and 0.3728×10^{-30} cm⁵/esu] and from the resultant values we identified that 5-phenyl-1,4-tri hydro-2H-pyridazino[3,4-*b*] quinolin-3-one possess comparatively good NLO property indicating that this might a good OLED material.

Conclusion

The molecular geometry of the molecule in the ground state has been calculated by using DFT method. Thermodynamical parameters were obtained. The HOMO-LUMO energy gap helped in analyzing the reactive potential of the molecule. Mulliken atomic charges of the molecule were studied. The calculated dipole moment and first order hyperpolarizability results indicate that the molecule has a reasonably good non linear optical behaviour. The reasonably good **NLO** property 5-phenyl-1,4-tri hydro-2H-Pyridazino[3,4-*b*] quinolin-3-one might act as a good **OLED** material.

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