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Charge transfer interaction and spectroscopic studies on analysis of 2-[2,4-bis(4-chlorophenylamino)thiazol-5-oyl]benzothiazole

***1 B Jini kumara, 2 TF Abbs Fen Reji**
[1] Assistant professor in chemistry, Department of Chemistry, Muslim Arts College, Thiruvithancode, Tamil Nadu, India
[2] Assistant professor in chemistry, Department of Chemistry & Research Centre, Nesamony Memorial Christian College, Marthandam, Tamil Nadu, India

Abstract

2-[2,4-Bis(4-chlorophenylamino)thiazol-5-oyl]benzothiazole is found to have antifungal and antibacterial activities promoting effect. These 2-[2,4-bis(4-chlorophenylamino)thiazol-5-oyl]benzothiazole derivatives are the subject of considerable pharmaceutical and chemical interest. Theoretical information on the optimized geometry, and IR intensities were obtained by means of Density Functional Theory(DFT) using standard B3LYP/6-31G basis sets with Gaussian 09 software package. The calculated geometries such as bond lengths, bond angle, dihedral angle atomic charges and intensities of Vibrational bonds of the titled compound were investigated. The IR spectra are obtained and assigned by vibrational analysis and found to be reliable compared with the experimental results. HOMO-LUMO energy gap shows the chemical stability of the molecule.

Keywords: gaussian, DFT, B3LYP, mullikencharges, HOMO, LUMO

Introduction

Benzothiazole derivatives are fascinating chemical products used in the field of medicine as they have been found to possess a wide spectrum of biodynamic properties [1]. Benzothiazole analogs of dendrodoine derivatives have attracted a great deal of interest due to their biological and commercial importance [2]. The study of benzothiazoles is, therefore, of practical and theoretical importance. A density functional theory of different benzothiazole derivatives have been calculated by using DFT/B3LYP method.

Marine organisms are known to contain several pharmacologically active compounds. Many marine natural products have unique structural features and substitutions, such as the presence of unusual heterocyclic ring systems or halogen substituents [3]. A few marine natural products or their synthetic analogs are in clinical use or at various stages of drug development. Many alkaloids are derived from marine organisms such as sponges, coelenterates, tunicates (ascuiduians), bryosoans, red algae and symbiotic bacteria [4]. Indole derivatives are quite common among marine alkaloids which possess excellent in vitro cancer cell cytotoxicity. In addition, benzothiazole exhibit several biological activities just as indoles.

Patil *et al.* reported[5] the DFT study on dihydroxyphenyl benzothiazole by using B3LYP/6-31G(d). The main objective of this paper is to present, more accurate vibrational assignments, bond lengths, bond angles, atomic charges and HOMO-LUMO of 2-[2,4-bis(4-chlorophenylamino)thiazol-5-oyl]benzothiazole using DFT/B3LYP method. A systematic study on vibrational spectra and structure of 2-[2,4-bis(4-chlorophenylamino)thiazol-5-oyl]benzothiazole.

Computational details

The DFT computation of 2-[2,4-bis(4-chlorophenylamino) thiazol-5-oyl]benzothiazole has been performed using Gaussian' 09 program package at the Becke-3Lee-Yang-Parr(B3LYP) level with standard 6-31G basis set. The optimized structural parameters are used in the vibrational frequency calculations at DFT level. At the optimized geometry of the title molecule no imaginary frequency modes are obtained, so there is a true minimum potential energy surface is found [6].

The assignments of the normal modes of vibration for the titled compound have been made by visual inspection of the individual mode using the Gauss view software. The optimized structure of 2-[2,4-bis(4-chlorophenylamino) thiazol-5-oyl] benzothiazole is given in figure 1. The optimized structural parameter calculated by B3LYP level with 6-31G basis set are given in Table 1.

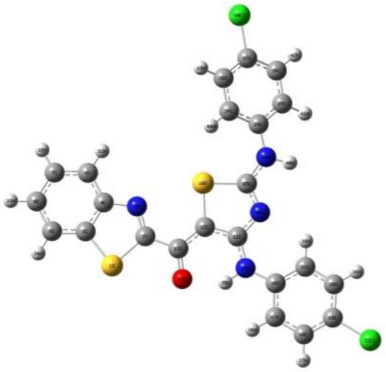

Fig 1: Optimized structure of 2-[2,4-bis(4-chlorophenylamino) thiazol-5-oyl]benzothiazole based on DFT B3LYP/6-31G basis set

Table 1: Optimized geometrical parameters of 2-[2,4-bis(4-chlorophenylamino)thiazol-5-oyl]benzothiazole at B3LYP with 6-31G level

Parameters	Bond lengths(Å)	Parameters	Bond angles(◦)	Parameters	Dihedral angle(◦)
	Calculated		Calculated		Calculated
S1-C2	1.8394	S1-C2-N3	115.523	S1-C2-N3-C4	0.006
C2-N3	1.3011	C2-N3-C4	112.857	C2-N3-C4-C5	0.013
N3-C4	1.3967	N3-C4-C6	124.950	N3-C4-C5-C9	-179.979
C4-C6	1.4039	C4-C6-H31	119.352	C4-C5-C9-H39	179.992
C6-H31	1.0836	C4-C6-C7	118.777	C5-C9-C8-H34	179.983
C6-C7	1.3921	C6-C7-H32	119.774	H34-C9-C8-H33	0.009
C7-H32	1.0846	C7-C8-H33	119.555	C9-C8-H33-C7	-179.972
C7-C8	1.4100	C8-C9-H34	120.692	H32-C7-C8-H33	-0.0029
C8-H33	1.0849	C8-C9-C5	118.182	C8-C7-H32-C6	-179.962
C8-C9	1.3974	C9-C5-S1	128.665	H32-C7-C6-H31	-0.057
C9-H34	1.0833	C5-C4-N3	114.946	C7-C6-H31-C4	-179.920
C9-H5	1.3962	N3-C4-C6	124.950	C7-C8-C9-C5	0.021
C5-S1	1.8148	S1-C2-C13	118.082	C9-C5-C4-C6	0.042
C2-C13	1.4704	N3-C2-C13	126.395	H31-C6-C4-C5	-179.878
C13-O14	1.2825	C2-C13-C12	120.552	H32-C7-C6-C4	-179.977
C13-C12	1.4175	C2-C13-O14	117.843	C9-C5-C2-S1	0.310
C12-S10	1.8353	C13-C12-C11	124.428	S1-C8-C9-C5	0.059
C12-C11	1.4156	C12-S10-C45	86.559	H34-C9-C5-S1	0.048
S10-C45	1.8264	S10-C45-N46	115.556	C5-C4-N3-C2	0.013
C45-N46	1.3236	C45-N46-C11	112.276	C4-N3-C2-S1	0.006
C11-N46	1.3769	N46-C11-N15	122.422	C4-H32-C7-C6	0.024
C45-N23	1.3599	C11-N15-C16	131.312	H31-C6-C4-N3	0.052
N23-H40	1.0138	C16-N15-H35	117.435	C2-C6-C4-N3	0.109
N23-C24	1.4147	N15-C16-C21	124.648	C4-N3-C2-C13	179.894
C11-N15	1.3593	C16-C21-H39	119600	N3-C2-C13-O14	-179.497
N15-H35	1.0288	C16-C21-C20	119.906	C2-N3-C4-C6	-179.921
N15-C16	1.4079	C21-C20-H38	120.023	C6-H31-C4-C5	0.189
C16-C17	1.4107	H38-C20-C19	120.229	C7-C6-C4-H31	179.922
C17-H36	1.0857	C20-C19-Cl22	119.348	C6-H31-C4-N3	179.957
C17-C18	1.3940	C18-C19-Cl22	119.232	N3-C2-C13-C12	0.345
C18-H37	1.0829	C19-C18-H37	120.611	C12-C13-C2-O14	179.841
C18-C19	1.3935	H37-C18-C17	120.490	N3-C2-C13-O14	-179.497
C19-Cl22	1.8282	H36-C17-C18	119.559	C13-C12-S10-O14	0.445
C19-C20	1.3917	H36-C17-C16	119.605	S10-C12-C11-N15	179.938
C20-C21	1.0833	C17-C16-C21	119.192	N23-H40-C45-N46	-175.607
C21-H39	1.3981	C45-N23-C24	131.140	C11-N46-C45-N23	-177.194
C21-C16	1.0793	C24-C25-H41	119.789	H35-N15-C11-N46	179.752
C24-C25	1.0793	C24-C25-C26	120.655	O14-C13-S10-C12	0.763
C25-H41	1.4075	C26-C25-H41	119.552	C12-C11-N15-H35	-0.0142
C25-C26	1.0857	C27-C26-H42	120.533	C45-N46-C11-N15	-179.951
C26-H42	1.3946	C26-C27-C28	121.392	C11-N46-C45-S10	0.042
C26-C27	1.0828	H43-C28-C27	120.395	C45-N23-C24-H40	-177.293
Cl30-C27	1.3939	H43-C28-C29	120.032	C24-N23-C45-N46	-177.573
C27-C28	1.8232	H44-C29-C24	120.985	C24-C45-N23-H40	-177.373
C28-H43	1.3916	C29-C24-C25	119.381	N23-C45-N46-C11	-177.194
C28-C29	1.0828	C29-C24-N23	123.262	C45-N46-C11-N15	-179.951
C29-H44	1.3985	C29-C24-C25	119.381\	N46-C11-N15-H35	179.752
C29-C24	1.0816	C19-C18-H37	115.556	N46-C11-N15-C16	-0.248
C28-C29	1.4047	H37-C18-C17	112.276	C11-N15-H35-C16	180.000
		H36-C17-C18	122.422	N15-C11-C16-C17	0.944
		H36-C17-C16	131.311	N15-C16-C17-H3	0.056
				N15-C16-C21-H39	-0.001
				C16-C21-H39-C20	179.977
				C21-H39-C20-H38	-179.999
				C21-C20-H38-C19	179.954
				H38-C20-C21-C19	-179.955
				C20-C19-H38-C18	0.109
				C20-C19-C18-H37	-179.978
				C20-H38-C19-Cl22	179.951
				C20-C19-C18-H37	-179.951
				C19-C18-C17-H37	-179.978
				C18-C17-H37-C16	179.987
				C17-H37-C16-H36	0.017

				C21-C16-C17-H36	0.022
				N23-C24-C25-H41	179.986
				C24-C25-C29-H44	1.996
				C28-C29-C24-H44	5.341
				H43-C28-C29-H44	179.274
				C29-C28-H43-C27	-1.721
				C27-Cl30-C28-H43	179.094
				C28-Cl30-C27-C26	179.342
				Cl30-C27-C26-C25	-179.770
				C27-C26-H42-C25	-179.478
				C26-H42-C25-H41	-179.443
				C26-C25-C24-H42	179.443
				C25-C24-N23-H41	0.114
				C25-C24-C26-H41	0.870

Results and discussion

Molecular geometry

The optimized structure of 2-[2,4-bis(4-chlorophenylamino) thiazol-5-oyl]benzothiazole is given in figure 1. The optimized structural parameter calculated by B3LYP level with 6-311G basis set are given in Table 1. The self-consistent field (SCF) energy of 2-[2,4-bis(4-chlorophenylamino)thiazol-5-oyl]benzothiazole at B3LYP level with the basis set 6-31G is found to be -2895.4955 a.u; with dipole moment 4.2765 Debye. The bond lengths of C4-C5, C5-C6, C6-C7, C7-C8, C8-C9 and C9-C4 shows double bond character (aromatic bond). similarly, the bond lengths of C16-C17,C17-C18,C18-C19, C19-C20, C20-C21 and C21-C22 shows double bond characters (aromatic bond).The bond angle (C12-S10-C45) is very less (86.559°) than the bond angle (C11-N15-C16)131.312° which is due to the fact that electronegativity of nitrogen is greater than sulphur [7].

Vibrational assignments

In order to obtain the spectroscopic signature of the title compound, we performed a frequency calculation analysis. Vibrational frequency were calculated by using B3LYP/6-31G, method. 2-[2,4-bis(4-chlorophenylamino)thiazol-5-oyl] benzothiazole molecules consists of 46 atom therefore it got 132 normal modes of vibrations. The scaling factor of 0.96 is used for getting theoretical vibrational frequency [8]. Comparison of the frequencies calculated at DFT method using 6-31G basis set with experimental values reveal that the B3LYP method shows very good agreement with the literature observation [9].

The hetero aromatic molecule containing an N-H group and [10-12] its stretching absorption occure in the region 3500-3220cm$^{-1.}$ Primary amine examined in dilute solution display two weak absorption bands one near 3500 cm^{-1} and the other near 3400 cm$^{-1.}$ These bands represent, respectively the asymmetric and symmetric N-H stretching modes. In the present work, the theoretical calculation indicate the scaled frequency values at 3484 and 3448cm^{-1} is assigned to N-H stretching vibration. Primary aromatic amines normally absorb at 1615-1580 cm^{-1}. The N-H in-plane bending vibration computed by B3LYP/6-31G method good agreement with literature values. The presence of aromatic N-H out-of-plane bending vibration are appeared with in the region 767-673cm^{-1}. In the present work, the theoretical calculation indicates, the scaled frequency values at 706 and 688cm^{-1} is assigned to N-H out-of-plane bending vibration.

The aromatic structure shows the presence of C-H stretching vibrations in the region 3100-3000cm^{-1} which is the characteristic [13-15] region for the ready identification of the C-H stretching vibrations. The C-H stretching vibration computed by B3LYP/6-31G method good agreement with literature observations. The C-H in-plane bending vibrations were observed in the [9] region 1420-1000cm^{-1}.These bands represents, the C-H in-plane–bending vibrations. In the present work, the theoretical calculation indicate the scaled frequency value at 1395 cm^{-1} is assigned to C-H in-plane-bending vibration. The presence of C-H out-of plane vibrations were observed in the region 999-750cm^{-1}.In the present work, the C-H out-of-plane bending vibration computed by B3LYP/6-31G method good agreement with literature observation. Generally, the carbon-carbon stretching vibrations in aromatic compound from the band in the region 1650-1430cm^{-1}. In the present study, the scaled frequency value at 1478cm^{-1} are assigned to carbon-carbon stretching vibration. The assignments of methyl group vibration make a significant contribution to the titled compound. The asymmetric C-H vibration for methyl group usually occurs in the region between 2975 cm^{-1} and 2920 cm^{-1}. The theoretically computed values by B3LYP/6-311G method for C-H vibrations are found at 2964, 2864cm^{-1}. Thus the theoretically computed values for C-H vibrations nearly coincide with literature values. In the title compound the methyl in-plane bending modes occur in the range 1479-1411 cm$^{-1.}$ The C-H out-of plane bending vibrations occur at 888 cm^{-1} and 774 cm^{-1}. The assignments are in agreement with the literature values. The carbonyl group is present in a large number of different classes of compounds, for which a strong band [16]observed due to the C=O stretching vibration is in the region of 1850-1550 cm^{-}1.The intensity of these bands can be increase due to conjugation or formation of hydrogen bonds. The lone pair of electrons on oxygen also determined the nature of the carbonyl group. In our present study the theoretically computed wavenumber for C=O stretching vibrations occur at 1571 cm^{-1}.The in-plane and out-of plane C=O bending mode occur at 1522 cm and 849 cm^{-1}. The identifications of C-N, C=N vibrations is a difficult task, since the mixing of several bands are possible in the region. Silver-stein *et al*. assigned C=N stretching absorption in the region 1382-1226 cm^{-1} for aromatic amines. The identification of wavenumber for C-N stretching in the side chains is rather difficult since there are problems in differensiating wavenumber from others. The band at 1357 cm^{-1} corresponds C-N, C=N stretching vibrations. The C-S stretching vibration [17] is expected in the region 710-685cm-1. While DFT calculations give the C-S stretching vibration at 637cm-1 is assigned to C-S stretching vibration. The carbonyl group is important and its characteristic frequency has been extensively used to study a wide range of compounds.

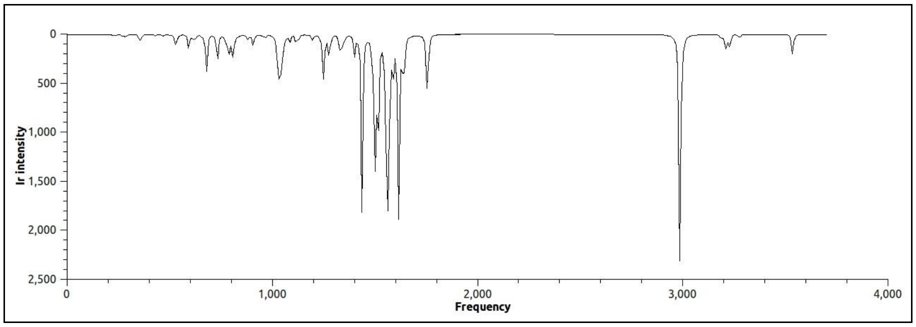

Fig 2: Theoretical FT-IR spectrum of 2-[2,4-bis(4-chlorophenylamino) thiazol-5-oyl] benzothiazole

Table 2: Selected theoretical vibrational assignments along with their intensities of 2-[2,4-bis(4-chlorophenylamino) thiazol-5-oyl] benzothiazole calculated at B3LYP/6-31G level

Scaled frequency (cm-1)	Intensity (km)Mol-1	Assignments
3440	48.472	N23-H40 (str)
3166	52.3937	N15-H35 (str)
3151	8.6503	C20-H38, C21-H39 (str) sym
3124	0.4374	C29-H44, C28-H43 (str) sym
3115	2.3387	C26-H42, C25-H41, C29-H34 (str) asym
3112	3.0182	C17-H36, C18-H37, C20-H38 (str) asym
3109	17.5254	C6-H31, C7-H32, C8-H33, C9-H34 (str) sym
3109	1.6374	C28-H43, C29-H44 (str) asym
3104	4.0858	C20-H38, C21-H39 (str) asym
3101	22.0924	C6-H31, C7-H32, C8-H33, C9-H34 (str) asym
3089	10.4507	C6-H31, C7-H32, C8-H33, C9-H34 (str) asym
3075	2.1492	C6-H31, C7-H32, C8-H33, C9-H34 (str) asym
3075	11.261	C17-H36, C18-H37, C25-H45, C26-H42 (str) asym
1636	2.1121	N15-H35 (ip bend)
1590	678.2072	N15-H35 (ip bend), C6-H31, C7-H32, C8-H33, C9-H34 (ip bend),C-N (str),C-S (ip bend)
1589	7.0082	N23-C45 (str), C-S (ip bend), C-C(str), C29-H44, C28-H43, C25-H41(ip bend)
1585	24.1691	C21-H39, C20-H38,C18-H37, C17-H36(ip bend)
1585	23.0835	C-N (str), C-N (ip bend), C-C (str), C25-H41,C29-H44, C28-H43(ip bend)
1560	23.0835	C21-H39, C20-H38,C18-H37, C17-H36(ip bend), C19-Cl22(ip bend)
1552	121.3308	C-N(str), C-S (ip bend), C-N(ip bend), C29-H44, C28-H43(ip bend)
1551	198.7146	C6-H31, C7-H32, C8-H33, C9-H34 (ip bend)
1551	255.7146	C-N(str), C-S (ip bend), C-O (str), C-N (ip bend), C8-H33(ip bend),C-S 9str)
1510	19.5943	C-N(str), C-O(str), C-C(str), C-Cl (str0, C-H (ip bend), C-N(ip bend)
1498	952.4852	C27-Cl30(str0, C28-H43, C29-H44, C25-H41, C26-H42 (ip bend)
1489	231.8828	C21-H39, C20-H38,C18-H37, C17-H36(ip bend)
1486	105.0078	C6-H31, C7-H32, C8-H33, C9-H39(ip bend)
1456	14.5197	C28-H43, C29-H44, C25-H41, C26-H42, C-N (ip bend), C-O (str)
1435	380.1144	C6-H31, C7-H32, C8-H33, C9-H39(ip bend)
1427	51.8795	C-C(str), C-O (str), C-N(str),C-S (ip bend),C-N (ip bend),C-H(ip bend)
1422	676.6221	C-C(str), C-O (str), C-N(str),C-S (ip bend),C-N (ip bend),C-H(ip bend)
1408	702.6315	C-N(str),C-O (str), C-O(str), C-S(str), C-S, C-N, C-S (ip bend)
1393	90.9402	C-N(str),C-O (str), C-O(str), C-S(str), C-S, C-N, C-S (ip bend)
1392	7.703	C-N(str),C-O (str), C-O(str), C-S(str), C-S, C-N, C-S (ip bend)
1327	107.1836	C-N, C-S, C-C, C-O, C-Cl (str), C-H, C-N, C-Cl(ip bend)
1322	4.495	C-N, C-S, C-C, C-O, C-Cl (str), C-H, C-N, C-Cl(ip bend)
1318	20.183	C-S (str),C-C(str), C-N (str), C-H (ip bend)
1312	9.8261	C28-H43, C29-H44, C25-H41, C26-H42 (ip bend), C-N (ip bend), C-N, C-Cl(ip bend)
1309	1.876	C-C(str), C21-H39, C20-H38,C18-H37, C17-H36(ip bend)
1304	15.4561	C-C (str), C-S(str), C-N (str), C-N, C28-H43, C29-H44, C25-H41, C26-H42 (ip bend)
1282	9.7111	C6-H31, C7-H32, C8-H33, C9-H34 (ip bend), C-N(ip bend), C-C(str), C-S(str)
1259	77.477	C-C(str), C-S,C-N, C-O (str), C-N, C-H (ip bend)
1235	179.869	C-C(str), C-S,C-N, C-O (str), C-N, C-H (ip bend)

12189	55.5435	N3-C4, C12-C11,C2-1S, C13-O14 (str), C-N, C-S, C-H(ip bend)
1197	42.6796	C-S, C-C, C-N (str), C28-H43, C29-H44, C25-H41, C26-H42(ip bend)
1190	11.9401	C28-H43, C29-H44, C25-H41, C26-H42 (ip bend)
1186	8.9855	C21-H39, C20-H38,C18-H37, C17-H36(ip bend)
1171	1.7923	C6-H31, C7-H32, C8-H33, C9-H34 (ip bend)
1119	3.7095	C-S, C-N, C-N(str), C-N, C-S, C-H (ip bend)
1118	2.5232	C-S, C-N, C-N(str), C-N, C-S, C-H (ip bend)
1115	4.4772	C-S, C-N, C-N(str), C-N, C-S, C-H (ip bend)
1094	7.1686	C-S, C-C, C-N, C-O(str), C-N, C-H(ip bend)
1069	69.6864	C-C(str),C27-Cl30(str), C6-H31, C7-H32, C8-H33, C9-H34 (ip bend)
1067	61.0524	C19-Cl22(str), C-C(str), C21-H39, C20-H38,C18-H37, C17-H36(ip bend)
1035	2.8724	C-N(str), C-N(ip bend), C-C (str), C-S (str), C6-H31, C7-H32, C8-H33, C9-H34 (ip bend)
1016	0.7049	C-N(str), C-S, C-C, C-O (str),phenyl,thiazole ring (op bend)
1008	3.6897	C-S,C-N,C-C(str), C6-H31, C7-H32, C8-H33, C9-H34 (ip bend)
1003	30.2356	C21-H39, C20-H38,C18-H37, C17-H36(ip bend), C19-Cl22 (str)
1002	49.6916	C27-Cl30(str), C28-H43, C29-H44, C25-H41, C26-H42(ip bend)
986	0.0381	C6-H31, C7-H32, C8-H33, C9-H34 (op bend)
975	3.7373	C7-H32, C8-H33, C9-H34 (op bend)
956	1.9331	C21-H39,C20-H38(op bend)
955	16.5118	C28-H43, C29-H44, C25-H41, C26-H42(op bend)
949	0.363	C17-H36, C18-H37, C25-H45, C26-H42, N15-H35, C29-H44 (op bend)
945	1.9349	C17-H36, C18-H37, C25-H45, C26-H42, N15-H35, C29-H44 (op bend)
912	140.9531	C6-H31, C7-H32, C8-H33, C9-H34 (op bend)
883	143.2883	N15-H35, C18-H37 (op bend)
864	0.1925	C-Cl(str), C-S(str), C-O (str), C-C(str), C-N, C-H (op bend)
859	17.2043	C6-H31, C7-H32, C8-H33, C9-H34 (op bend)
840	35.7445	C-Cl, C-S, C-O, C-C (str), C-N (str), C-N, C-H (op bend)
830	68.8378	C21-H39, C20-H38 (op bend)
816	6.3124	C26-H42,C25-H41, C29-H44, C28-H43 (op bend),C-N(op bend)
814	4.5729	C26-H42,C25-H41, C29-H44, C28-H43 (op bend),C-N(op bend)
809	35.0685	C17-H36,C18-H37 (op bend)
800	40.288	Phenyl, thiazole ring (op bend)
765	50.7697	C-S,C-Cl, C-O,C-N (str), C-C (str),C-N, C-H (op bend)
751	2.0505	C6-H31, C7-H32, C8-H33, C9-H34 (op bend)
747	1.102	C-S,C-Cl, C-O,C-N (str), C-C (str),C-N, C-H (op bend)
734	19.8928	C6-H31, C7-H32, C8-H33, C9-H34 (op bend)
706	8.4358	C26-H42,C25-H41, C29-H44, C28-H43 (op bend)
705	0.4394	N23-H40 (op bend), C2-1S (str), C-H (op bend),C-Cl (str)
695	59.4322	C6-H31, C7-H32, C8-H33, C9-H34 (op bend)
688	4.2404	N23-H40 (op bend), C2-1S (str), C-H (op bend),C-Cl (str)
680	4.0446	C-S (str), C27-Cl30 (str), C-N (op bend), C-H (op bend)
678	17.4809	C26-H42, C25-H41, C29-H44, C28-H43 (op bend),C-N (op bend0, C-O (op bend)
669	80.1742	Phenyl,thiazole ring vibration
659	0.4989	C-Cl(str), C-C (str), C-S (str), C-N(op bend), C-H (op bend)
639	4.2031	C-Cl(str), C-C (str), C-S (str), C-N(op bend), C-H (op bend)
630	14.3807	C-Cl(str), C-C (str), C-S (str), C-N(op bend), C-H (op bend)
607	19.205	C-Cl(str), C-C (str), C-S (str), C-N(op bend), C-H (op bend)
593	2.1629	N23-H40(op bend), C26-H42, C25-H41, C29-H44, C28-H43 (op bend)
583	19.2649	S10-C45 (str), C-H (op bend)
524	9.2663	C26-H42, C25-H41, C29-H44, C28-H43 (op bend), C-N (op bend)
512	15.5466	C21-H39, C20-H38, C17-H36, C18-H37 (op bend)
496	34.0112	C28-H43, C29-H44, C25-H41, C26-H42 (op bend)
485	0.2465	C5-1S-C2 (op bend), C6-H31, C7-H32, C8-H33, C9-H34 (op bend)
484	10.8848	C27-Cl30 (str), C2-1S-CS (op bend), C-H (op bend)
474	9.0854	C27-Cl30(str), C-C (str), C-N (op bend), C-H, C-O (op bend)
461	11.5993	C5-1S-C2, S10-Cl12 (str), C27-Cl30(str), C19-Cl22(str), C-H, C-O(str)
430	4.6774	C6-H31, C7-H32, C8-H33, C9-H34 (op bend)
421	37.5178	C19-Cl22, S10-C12 (str), C-S, Cl (op bend)
415	0.0036	C21-H39, C20-H38, C17-H36,C18-H37
412	2.0289	C26-H42, C25-H41, C29-H44, C28-H43 (op bend)
382	12.4976	C27-Cl30(str), C-O (op bend),C-S (op bend), C-H (op bend)
364	3.3433	C19-Cl22(str), C27-Cl30 (op bend), C-S (op bend)
349	1.315	Ring vibration

348	4.9321	Ring vibration
344	12.2754	Ring vibration
308	5.6974	C27-Cl30, C19-Cl22 (op bend)
301	1.5086	C27-Cl30, C19-Cl22 (op bend)
297	0.8125	C27-Cl30, C19-Cl22 (op bend), C-H (op bend)
262	2.7914	Ring vibration
252	1.6296	C27-Cl30, C19-Cl22 (op bend)
240	0.2107	C27-Cl30, C19-Cl22 (op bend)
225	2.2215	Ring vibration
192	0.07719	Ring vibration
183	0.5253	Ring vibration
168	0.6164	Ring vibration
150	0.3882	Ring vibration
137	0.3565	Ring vibration
122	0.5796	Ring vibration
111	0.5521	Thiazole ring vibration
106	0.8363	Ring vibration

Abbreviations: sym-symmetric, asym-asymmetric, str-stretching, ip bend-in plane bending, op bend-out of plane bending.

Mulliken atomic charges

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 polarisability, electronic structure and more a lot of properties of molecular systems. Atomic charge distributions were calculated by determining the electron population of each atom as defined by the basis set. In the title compound the magnitude of the carbon atomic charges was found to be positive and negative. The oxygen atom exhibit negative charge which are donar atom. Hydrogen atom exhibits a positive charge, which is an acceptor atom. To validate the reliability of our results, the mulliken population analysis of 2-[2,4-bis(4-chlorophenylamino)thiazol-5-oyl]benzothiazole has been calculated using B3LYP/6-31G basis set. The corresponding characteristics of the atomic charge populations of the constituent atoms are presented in table **3**. It was found that N (15) has more negative charge (-0.8270eV) and C(11) has more positive charge(0.5720eV). The mulliken atomic charge of all hydrogen and sulpur carries positive charge.

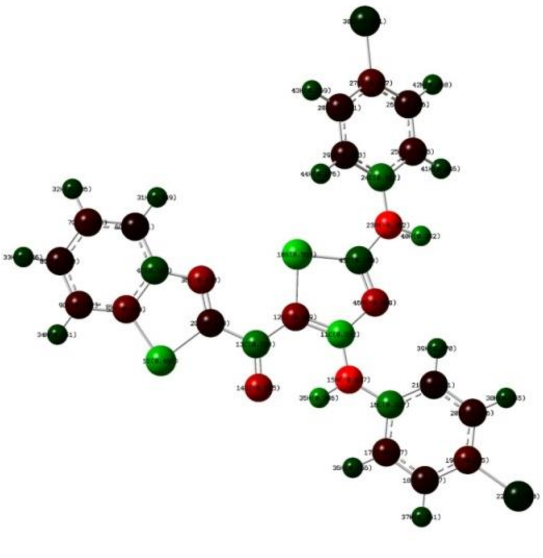

Fig 3: Mulliken charge distribution of 2-[2,4-bis(4-chlorophenylamino) thiazol-5-oyl]benzothiazole

Table 3: Mulliken atomic charges

Atom	Mulliken atomic charges	Atom	Mulliken atomic charges
S1	0.4970	Cl22	0.0595
C2	-0.1290	N23	-0.7817
N3	-0.0419	C24	0.3118
C4	0.1961	C25	-0.1448
C5	-0.288	C26	-0.1060
C6	-0.0614	C27	-0.2273
C7	-0.1553	C28	-0.1213
C8	-0.004	C29	-0.1029
C9	-0.1723	Cl30	0.0807
S10	0.5633	H31	0.1490
C11	0.05720	H32	0.1362
C12	-03490	H33	0.13603
C13	0.3176	H34	0.1511
O14	-0.5247	H35	0.3855
N15	-0.8270	H36	0.1563
C16	0.3269	H37	0.1609
C17	-0.1671	H38	0.15517
C18	-0.1066	H39	0.16995
C19	-0.2253	H40	0.3518
C20	-0.1255	C41	0.1459
C21	-0.0814	N42	0.1683

HOMO-LUMO energy gaps

The most important orbitals in a molecule are the Frontier molecular orbitals, called highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO). These orbitals determine the way the molecule interacts with other species. The lowering of the HOMO-LUMO band gap is essentially a consequence of the large stabilization of the LUMO due to the strong electron-acceptor ability of the electron-acceptor group. ΔE reveals the chemical activity of the molecule. LUMO as an electron acceptor represents the ability to obtain an electron and HOMO represents the ability to donate an electron. The calculated energy value of HOMO is -0.0955 a.u. and for LUMO is -0.2071 a.u. The value of energy separation ΔE between the HOMO and LUMO is 0.1115 a.u. The energy gap between HOMO and LUMO describes the chemical reactivity, optical polarisability, kinetic stability and chemical softness-hardness of a molecule. The chemical hardness is a good indicator of the chemical stability. The molecules having a small gap are known as soft and having a large gap are known as hard molecules. Figure 4 shows the HOMO-LUMO of 2-[2,4-bis(4-chlorophenylamino) thiazol-5-oyl]benzothiazole.

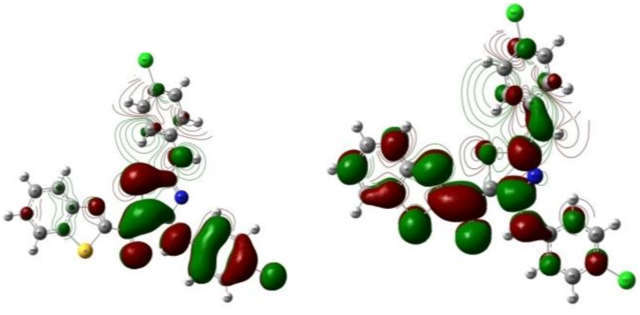

Fig 4: HOMO-LUMO of 2-[2,4-bis(4-chlorophenylamino)thiazol-5-oyl]benzothiazole

Table 4: HOMO-LUMO energy value calculated by B3LYP/6-31G level

Paremeters (a.u)	B3LYP/6-31G
HOMO	-0.0955
LUMO	-0.2071
HOMO-LUMO	0.1115

Conclusion

Attempts have been made in this paper to study the vibrational assignments of 2-[2,4-bis(4-chlorophenylamino)thiazol-5-oyl] benzothiazole using DFT method (B3LYP) with 6-31G basis set. The optimized molecular geometry, atomic charges in the ground state were also calculated. The results indicate that the B3LYP Method is able to provide satisfactory results for predicting vibrational frequencies and structural parameters. Atomic charge distributions were calculated by determining the electron population of each atom. The lowering in the HOMO and LUMO energy gap explains the eventual charge transfer interactions that take place within the molecule.

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