Indian J. Res. Found., (2015) 3, 1-5. ISSN 2454-6577

INDIAN JOURNAL OF RESEARCH FOUNDATION

www.indianjournal.net

RESEARCH ARTICLE

Synthesis, FT-IR analysis and DFT studies of 2-(4-amino-2-(4-ethoxyphenylamino)thiazol-5-oyl)benzofuran

T. Alwin*, T. F. Abbs Fen Reji

Department of Chemistry, Nesamony Memorial Christian College, Marthandam-629165, Tamil Nadu, India

Received 6 August, 2015; Accepted 10 October 2015
Available online 10 October 2015

Abstract

In the present study 2-(4-amino-2-(4-ethoxyphenylamino)thiazol-5-oyl)benzofuran was prepared from 1-(N-nitroamidino)-3-ethoxyphenyl thiourea and 2-bromo acetylbenzofuran in the presence of triethylamine and characterized by FT-IR spectra. The geometry of the molecule was investigated and optimized with the help of B3LYP/6-31G DFT method using Gaussian 09 software package. The vibrational frequencies which were determined experimentally from spectral data are compared with those obtained theoretically *Ab-initio* and DFT calculations. The calculated HOMO-LUMO energy gap reveals that charge transfer occurs within the molecule.

Keywords

Thiourea
FT-IR
DFT
Ab-initio
Homo-Lumo

Introduction

Heterocyclic compounds have been an interesting field for a long time in medicinal chemistry. A Heterocyclic compounds containing nitrogen and sulphur atom serve as unique and versatile scaffolds for experimental drug design [1]. Benzothiazole consists of thiazole ring fused with benzene ring and posses, multiple applications, 2-aminobenzothiazoles were intensively studied as central muscle relaxants with glutamate neuro trans mission in biochemical electro physiological and behavioral experiments benzothiazole ring [2] made thiazole ring fused with benzene ring. Benzothiazole derivatives have been studied and found to have various chemical reactivity and biological activity such as antiviral, anti bacterial, antimicrobial activity [3]. Benzofuran derivatives posses a wide range of biological activities such as antimicrobial, antitumor and anti inflammatory activity [4].

Experimental

The regents and solvents used were of AR grade. All chemicals were purchased from Merck and Sigma Aldrich.

*Corresponding author Tel. +9194442865090
E-mail : alwinchemistry@gmail.com

Published by GM SOFTWARE

Synthesis of 2-(4-amino-2-(4-ethoxyphenylamino) thiazol-5-oyl)benzofuran

A solution of 1-aryl/alkyl–3–N–nitroamidino) thiourea (1 mmol) in DMF (2 ml) was added to a solution of 2–bromoacetylbenzo furan (1 mmol) in DMF (2 ml). The reaction mixture was stirred well and triethylamine (1 mmol) was added. The reaction mixture was warmed at 80 – 85 °C for 15 min. It was then cooled and poured in to ice–cold water with constant stirring. A yellow orange precipitate thus obtained was filtered washed with water and dried. The crude product was recrystallized from methanol : water (2:1) ratio to give a yellow orange crystalline solid.

Results and Discussion

Theoretical computations of 2-(4-amino-2-(4-ethoxyphenylamino)thiazol-5-oyl)benzofuran have been performed using the B3LYP level of theory supplemented with standard 6-31G basis set using the Gaussian 09 software package [5]. Geometries have been first optimized structural parameters were used in the vibration frequency calculation at DFT level. The optimized structure is given in **Fig 1.**

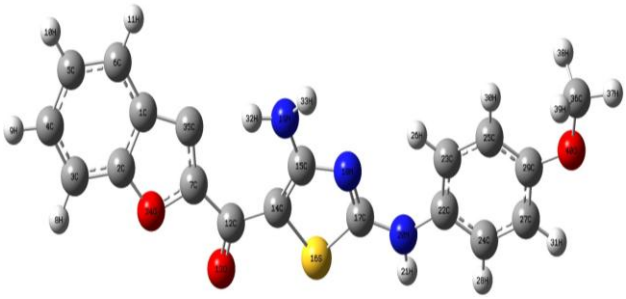


Fig 1 Optimized structure of 2-(4-amino-2-(4-ethoxyphenylamino)thiazol-5-oyl)benzofuran.

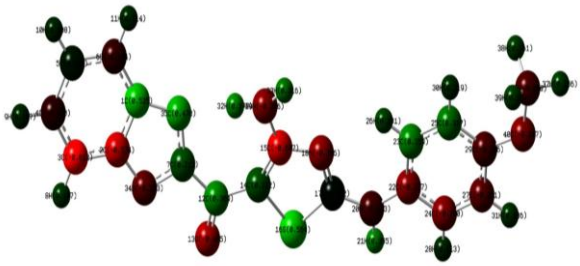


Fig 2 Mulliken atomic charges structure of 2-(4-amino-2-(4-ethoxyphenylamino)thiazol-5-oyl) benzofuran.

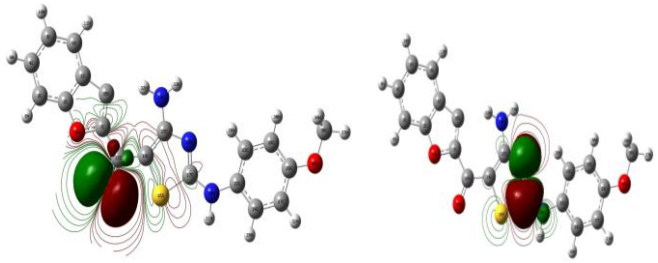
Table 1 Mulliken atomic charges

Atom	Mulliken charges	Atom	Mulliken charges
C_1	0.564	H_{21}	0.353
C_2	-0.574	C_{22}	-0.610
C_3	-0.816	C_{23}	0.875
C_4	-0.093	C_{24}	-0.720
C_5	0.056	C_{25}	0.333
C_6	-0.126	H_{26}	0.209
C_7	0.117	C_{27}	-0.272
H_8	0.148	H_{28}	0.114
H_9	0.109	C_{29}	-0.309
H_{10}	0.109	H_{30}	0.131
H_{11}	0.113	H_{31}	0.142
C_{12}	0.312	H_{32}	0.391
O_{13}	-0.466	H_{33}	0.320
C_{14}	0.380	O_{34}	-0.266
C_{15}	-0.627	C_{35}	0.507
S_{16}	0.540	C_{36}	-0.250
C_{17}	0.105	H_{37}	0.171
N_{18}	-0.388	H_{38}	0.137
N_{19}	-0.390	H_{39}	0.182
N_{20}	-0.138	O_{40}	-0.376

HOMO–LUMO

The optimized geometry of 2-(4-amino-2-(4-ethoxyphenylamino)thiazol-5-oyl)benzofuran at DFT/B3LYP/6-31G level is shown in **Fig 3.** The HOMO–LUMO energies is calculated values of HOMO (-0.25048 a.u), and LUMO (-0.06435 a.u) and energy gap (ΔE) is (-0.18613 a.u), 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.



HOMO UMO

Fig 3 HOMO and LUMO of 2-(4-amino-2-(4-ethoxyphenylamino)thiazol-5-oyl)benzofuran based on B3LYP/6-31G basis set

Molecular geometry

2-(4-amino-2-(4-ethoxyphenylamino)thiazol-5-oyl)benzofuran was subjected to optimization in the ground state. The optimized structural parameters was calculated by DFT/ B3LYP/6-31G basis set are listed in **Tables 1-3** in accordance with the atom Numbering scheme given in **Fig 1.** The bond length of 2-(4-amino-2-(4-ethoxyphenylamino)thiazol-5-oyl)benzofuran C_1-C_2, C_2-C_3, C_3-C_4, C_4-C_5, C_5-C_6, C_7-C_{12}, C_{12}-C_{14}, C_{14}-C_{15}, C_{22}-C_{24}, and C_{23}-C_{25} shows double character. The bond length of C_7-C_{35} is more than C_7-$C_{12;}$ this is due C_7-C_{12} double bond character, and C_7-C_{35} single bond character. The bond angle C_{14}-S_{16}-C_{17} (88.287) is very less than C_{17}-N_{20}-C_{22} (130.617) which is due to the fact that electro negativity of nitrogen is greater than sulphur. The dihedral angles show that the molecule consists of two planes.

Table 2 Bond length of 2-(4-amino-2-(4-ethoxyphenylamino)thiazol-5-oyl)benzofuran.

Atom	Bond length	Atom	Bond length
C_1-C_2	1.415	C_2-C_7	2.214
C_2-C_3	1.394	C_3-H_8	1.084
C_3-C_4	1.394	C_4-H_9	1.085
C_4-C_5	1.411	C_5-H_{10}	1.085
C_5-C_6	1.390	C_6-H_{11}	1.085
C_7-C_{12}	1.484	C_{24}-C_{27}	1.386
C_{12}-O_{13}	1.240	C_{24}-H_{28}	1.087
C_{12}-C_{14}	1.443	C_{25}-C_{29}	1.397
C_{14}-C_{15}	1.402	C_{25}-H_{30}	1.083
C_{14}-S_{16}	1.776	C_{27}-H_{31}	1.084
S_{16}-C_{17}	1.759	N_{19}-H_{32}	1.012
C_{17}-N_{18}	1.316	N_{19}-H_{33}	1.009
C_{15}-N_{19}	1.363	C_2-O_{34}	1.366
C_{17}-N_{20}	1.358	C_7-C_{35}	1.359
N_{20}-H_{21}	1.010	C_{29}-C_{36}	2.396
N_{20}-C_{22}	1.414	C_{36}-H_{37}	1.090
C_{22}-C_{23}	1.398	C_{36}-H_{38}	1.097
C_{22}-C_{24}	1.407	C_{36}-H_{39}	1.097
C_{23}-C_{25}	1.400	C_{29}-O_{40}	1.368
C_{23}-H_{26}	1.080		

Table 3 Bond angle of 2-(4-amino-2-(4-ethoxyphenylamino)thiazol-5oyl)benzofuran.

Atom	Bond angle	Atom	Bond angle
C_1-C_2-C_3	122.90	C_2-C_7-C_{12}	151.21
C_2-C_3-C_4	116.63	C_7-C_{12}-O_{13}	118.23
C_3-C_4-C_5	121.53	C_7-C_{12}-C_{14}	121.51
C_4-C_5-C_6	121.35	C_{12}-C_{14}-C_{15}	137.47
C_1-C_2-C_7	74.753	C_{12}-C_{14}-S_{16}	113.82
C_2-C_3-H_8	121.023	C_{14}-S_{16}-C_{17}	88.28
C_3-C_4-H_9	119.21	S_{16}-C_{17}-N_{18}	115.92
C_4-C_5-H_{10}	119.14	C_{14}-C_{15}-N_{19}	128.02
C_5-C_6-H_{11}	121.17	S_{16}-C_{17}-N_{20}	118.94

Bond angle	Value (°)	Bond angle	Value (°)
C_{17}-N_{20}-H_{21}	115.04	C_{24}-C_{27}-H_{31}	120.86
C_{17}-N_{20}-C_{22}	130.61	C_{15}-N_{19}-H_{32}	119.68
N_{20}-C_{22}-C_{23}	124.29	C_{15}-N_{19}-H_{33}	115.84
N_{20}-C_{22}-C_{24}	116.79	C_1-C_2-O_{34}	111.55
C_{22}-C_{23}-C_{25}	120.15	C_2-C_7-C_{35}	72.00
C_{22}-C_{23}-H_{26}	119.71	C_{25}-C_{29}-C_{36}	93.52
C_{22}-C_{24}-C_{27}	120.91	C_{29}-C_{36}-H_{37}	135.97
C_{22}-C_{24}-H_{28}	119.89	C_{29}-C_{36}-H_{39}	95.22
C_{23}-C_{25}-C_{29}	120.65	C_{25}-C_{29}-O_{40}	124.98
C_{23}-C_{25}-H_{30}	118.33		

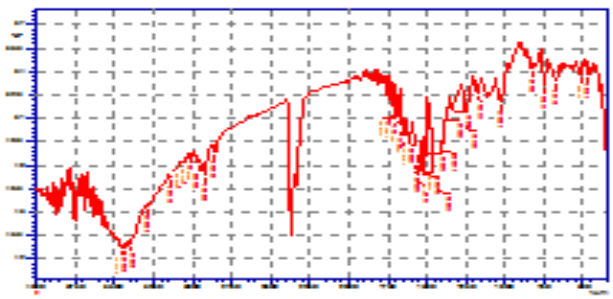
Table 4 Dihedral angle of bond length of 2-(4-amino-2-(4-ethoxyphenylamino)thiazol-oyl)benzofuran.

Atom	Dihedral angle	Atom	Dihedral angle
C_1-C_2-C_3-C_4	0.612	C_{12}-C_{14}-C_{15}-N_{19}	-5.657
C_2-C_3-C_4-C_5	-0.248	C_{14}-S_{16}-C_{17}-N_{20}	-179.68
C_3-C_4-C_5-C_6	-0.178	S_{16}-C_{17}-N_{20}-H_{21}	-0.618
C_6-C_1-C_2-C_7	179.67	S_{16}-C_{17}-N_{20}-C_{22}	179.54
C_1-C_2-C_3-H_8	-179.54	C_{17}-N_{20}-C_{22}-C_{23}	-1.869
C_2-C_3-C_4-H_9	179.71	C_{17}-N_{20}-C_{22}-C_{24}	178.36
C_3-C_4-C_5-H_{10}	179.86	N_{20}-C_{22}-C_{23}-C_{25}	179.76
C_4-C_5-C_6-H_{11}	179.98	N_{20}-C_{22}-C_{23}-H_{26}	0.214
C_1-C_2-C_7-C_{12}	-173.80	N_{20}-C_{22}-C_{24}-C_{27}	179.76
C_2-C_7-C_{12}-O_{13}	7.529	N_{20}-C_{22}-C_{24}-H_{28}	-0.2728
C_2-C_7-C_{12}-C_{14}	-172.84	C_{22}-C_{23}-C_{25}-C_{29}	0.0154
C_7-C_{12}-C_{14}-C_{15}	6.923	C_{22}-C_{23}-C_{25}-H_{30}	179.95
C_7-C_{12}-C_{14}-S_{16}	-177.55	C_{22}- C_{24} -C_{27} -H_{31}	-179.99
C_{12}-C_{14}-S_{16}-C_{17}	-177.14	C_{14}-C_{15} -N_{19}-H_{32}	15.79
C_{14}-S_{16}-C_{17}-N_{18}	0.325	C_{14}-C_{15}-N_{19}-H_{33}	165.84
C_6-C_1-C_2-O_{34}	179.68	C_{25}-C_{29}-C_{36}-H_{38}	55.05
C_1-C_2-C_7-C_{35}	1.15	C_{25}-C_{29}-C_{36}-H_{39}	55.04
C_{23}-C_{25}-C_{29}-C_{36}	179.96	C_{23}-C_{25}-C_{29}-O_{40}	179.99
C_{25}-C_{29}-C_{36}-H_{37}	179.97		

Infrared Spectra

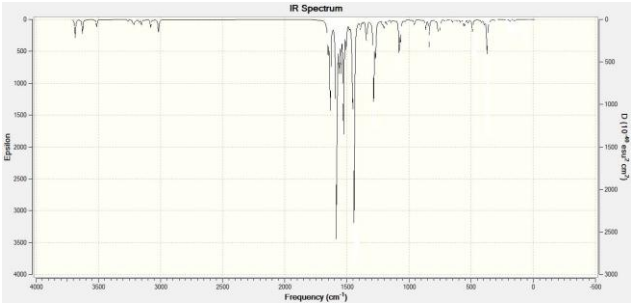
The compound 2-(4-amino-2-(4-ethoxy phenylamino)thiazol-5-oyl)benzofuran was obtained in 98% yield with melting point 155-158 °C. Based on the elemental analysis the molecular composition of the compound was found to be $C_{19}H_{14}N_3O_3S$. The IR (KBr) spectrum of the compound shows N-H peaks at 3454, 3425, and 3400 cm^{-1} respectively. The aromatic C-H bond gives peak at 3078 cm^{-1}, 3045 cm^{-1} 3078 cm^{-1}. The carbonyl group which occurred at 1649 cm^{-1}.

The vibration study of the molecule is compared with the calculated data and is shown in **Fig 4**. The calculated band at 3685 cm^{-1} is due to asymmetric N-H stretching of N_{19}-H_{32} and N_{19}-H_{33} but experimentally it is assigned at 3454 cm^{-1}. Calculated band at 3220 cm^{-1} is due to asymmetric C-H stretching of C_{23}-H_{26} and N_{20}-H_{21} calculated band at 3078 cm^{-1}, is due to asymmetric C-H stretching of C_{23}-H_{26}, C_{25}-H_{30}, C_{27} -H_{31}, C_{24}-H_{28}. The C=C stretching is experimentally observed around 1562 cm^{-1} which is close agreement with the calculated frequency 1566,1550, 1514 and 1502 cm^{-1} . The bands with in the range 1585-1015 cm^{-1} are assigned for C-H in plane bending vibrations which is in close agreement with the experimental values.



a) Experimental

Fig 4 Experimental and theoretical FT-IR spectrum of 2-(4-amino-2-(4-ethoxyphenylamino)thiazol-5-oyl)benzofuran.



b) Theoretical

Conclusions

2-(4-amino-2-(4-ethoxyphenylamino)thiazol-5-oyl) benzofuran has been synthesized and characterized by FT-IR spectrum. The structure of 2-(4-amino-2-ethoxyphenylamino thiazol-5oyl)benzofuran was optimized by DFT method using the basis set B3LYP/6-31G. The HOMO and LUMO energy gap reveals the activity of 2-(4-amino-2-(4-ethoxyphenylamino)thiazol-5-oyl)benzofuran.

Acknowledgement

One of the author Dr. T. F. Abbs Fen Reji thanks University Grants Commission, New Delhi for providing Financial Assistance in the form of Major Research Project [F. No. 41-229/2012 (SR)]. The authors thank Mohamed Sathak Engineering College, Kilakarai, Ramanathapuram and CDRI, Lucknow for measuring the spectral and analytical data results.

References

[1] N. B. Patel, F. M. Shaikh, *Sci. Pharm.*, 78, (2010), 753.

[2] M. Bryson, B. Fulton, P. Benfield, *Drugs*, 52, (1996), 549.

[3] S.P. Singh, S. Seghal, *Indian J. Chem*., 27B, (1988), 941.

[4] D. R. Harish Kumar, M. D. Karvekar, *Eur. J. Chem.*, 7, (2010), 636.

[5] R. F. Hunter, *J. Chem. Soc*., (1925), 2023.