Theoretical spectroscopic investigation of 3,5-bis(trifluoromethyl) phenyl isothiocyanate

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Abstract

In this work, theoretical study by using the DFT method on 3,5-bis(trifluoromethyl) phenyl isothiocyanate is reported. The FTIR and FT-Raman spectra of title compound were noted in the regions 4000–400cm^{-1}; The HOMO, LUMO and Gap energy of these compounds have been calculated and reported in this paper. Thus, our aim to explain the spectroscopic properties on the basis of the DFT quantum chemical calculations and we are interested to explain the nonlinear optical analysis. The study of structural, vibrational spectroscopic studies and nonlinear optical properties for these compounds could help to design more efficient functional photovoltaic organic compounds.

Keyword: DFT, isothiocyanate, DOS, FT-IR, FT-Raman, HOMO – LUMO.

Introduction

Thiocyanate and their complexes are important functional groups for various applications. Such as Antimicrobial drugs[1,2] Antibiotics[3,4], Anti-phytopathogenic[5], organocatalyst[6] , Thus, it is of interest to obtain information about their characteristics like density of functional groups and its homogeneity across a substrate surface or a micro spot.

Density functional theory (DFT) established by the computational quantum chemistry for studying spectroscopic properties of the molecules.

DFT calculations of FT-IR spectra for many organic molecules have shown hopeful agreement with experimental results. Therefore, in this present DFT techniques are engaged to study the inclusive FT-IR spectra (B3LYP with 6-311++G (d,p)basis set.) of the title molecule and to classify the various normal modes with greater wave number accuracy.

In the present work, we report the theoretical vibrational analysis of thiocyanate based compound. In addition HOMO-LUMO, Thermodynamical and NLO properties also calculated.

Materials and Methods
Computational details

The DFT with the Becke's and Lee–Yang–Parr (B3LYP) three-parameter and hybrid functional method accepted as a cost-effective approach and it has been used to compute optimized structural geometrical parameters, vibrational frequencies FT-IR and FT-Raman of the heading molecule. For

all calculations are performed with Gaussian 09^5 suite of quantum chemical codes.

The structural parameters after optimized were employed calculations of the vibrational frequencies, isotropic chemical shifts and electronic properties by using B3LYP with 6-311++G(d,p)basis set.

Result and discussion
Molecular geometry
The optimized bond length and bond angles of 3,5-bis(trifluoromethyl) phenyl isothiocyanate molecules along with the intermolecular hydrogen bonds of various base set.
The corresponding minimum energy obtained by B3LYP/6-311++G(d,p) method were fall on -1397.0954361. From the optimized geometry the optimized structural parameters were tabulated on Table 1 & 2.
The Geometrical parameters are obtained by computationally. For isothiocyanate the N_{15}-C_{16}, C_{16}-S_{17} bond lengths are 1.199, 1.575.
For 3,5 bis Trifluoromethyl F_1-C_2, C_2-F_3, C_2-F_4, C_{11}-F_{12}, C_{11}-F_{13} and C_{11}-F_{14} bond lengths are 1.349, 1.350, 1.355, 1.350, 1.349 and 1.355. For phenyl ring C-C bond lengths are 1.391, 1.398, 1.401, 1.391 and 1.394.

Vibrational analysis

The vibrational spectral analysis of 3,5-bis (trifluoromethyl) phenyl isothiocyanate compound is based on FT-IR (Fig. 2) and Raman (Fig. 3) spectra. The 3,5-bis(trifluoromethyl) phenyl isothiocyanate compound consists of 20 atoms, which has 54 normal modes. The 54 normal modes of 3,5-bis (trifluoromethyl) phenyl isothiocyanate have been assigned according to the detailed motion of the individual atoms. This compound belongs to C_1 symmetry group. Table 3 represents the intensity and assignments of the title compound.

Bond length			
F_1-C_2	1.349	C_8-C_9	1.391
C_2-F_3	1.350	C_8-H_{19}	1.082
C_2-F_4	1.355	C_9-C_{10}	1.394
C_2-C_5	1.509	C_9-C_{11}	1.509
C_5-C_6	1.391	C_{10}-H_{20}	1.081
C_5-C_{10}	1.393	C_{11}-F_{12}	1.350
C_6-C_7	1.398	C_{11}-F_{13}	1.349
C_6-H_{18}	1.082	C_{11}-F_{14}	1.355
C_7-C_8	1.401	N_{15}-C_{16}	1.199
C_7-N_{15}	1.382	C_{16}-S_{17}	1.575

Table 1: Bond length of 3,5-bis (trifluoromethyl) phenyl isothiocyanate

Bond Angle			
F_1-C_2-F_3	107.5	C_9-C_8-H_{19}	120.7
F_1-C_2-F_4	106.9	C_8-C_9-C_{10}	121.0
F_1-C_2-C_5	112.0	C_8-C_9-C_{11}	119.4
F_3-C_2-F_4	106.8	C_{10}-C_9-C_{11}	119.5
F_3-C_2-C_5	112.0	C_9-C_{10}-H_{20}	120.4
F_4-C_2-C_5	111.3	C_9-C_{11}-F_{12}	112.0
C_2-C_5-C_6	119.4	C_9-C_{11}-F_{13}	112.0
C_2-C_5-C_{10}	119.6	C_9-C_{11}-F_{14}	111.3
C_6-C_5-C_{10}	120.9	F_{12}-C_{11}-F_{13}	107.5
C_5-C_6-C_7	119.5	F_{12}-C_{11}-F_{14}	106.8
C_5-C_6-H_{18}	121.1	F_{13}-C_{11}-F_{14}	106.9
C_5-C_{10}-C_9	119.0	N_{15}-C_{16}-S_{17}	175.6
C_5-C_{10}-H_{20}	120.5	C_8-C_7-N_{15}	121.1
C_7-C_6-H_{18}	119.4	C_7-C_8-C_9	119.4
C_6-C_7-C_8	120.1	C_7-C_8-H_{19}	119.9
C_6-C_7-N_{15}	118.9	C_7-N_{15}-C_{16}	147.1

Table 2: Bond angle of 3,5-bis (trifluoromethyl) phenyl isothiocyanate

Carbon-hydrogen vibrations

The aromatic structure shows the presence of C–H stretching vibrations. The vibrations assigned at 3206, 3214 and 3219cm^{-1} by B3LYP/6-311++G(d,p) level. The value computed by B3LYP show good agreement with FT-Raman at 3219cm^{-1} and 3214 cm^{-1} and the FT-IR bands at 3206 and 3219 cm^{-1}.

Carbon–carbon vibrations

The ring carbon–carbon stretching vibrations occur in the region 1646–1476 cm^{-1}. The theoretically computed values by B3LYP/6-311++G(d,p) method at 1646, 1638,1487 and 1476 cm^{-1} for 3,5-bis(trifluoromethyl) phenyl isothiocyanate shows C-C stretching vibrations. The in-plane deformation vibration is at higher wavenumbers than the out-of-plane vibrations, Shimanouchi *et al.*[6] gave the wavenumber data for these vibrations for different benzene derivatives from normal coordinate analysis.

Trifluromethyl vibrations

The title molecule under consideration possesses one CF$_3$ group in the side substituted chain. For the assignments of CF$_3$ group frequencies one can expect that nine fundamentals can be associated to each CF$_3$ group. These vibrations are CF$_3$ symmetric stretching, CF$_3$ in-plane stretching, CF$_3$ in-plane bending, CF$_3$ symmetric bending, CF$_3$ in-plane rocking, CF$_3$ out of plane rocking, CF$_3$ twist, CF$_3$ out-of-plane stretching, CF$_3$ out-of-plane bending vibrations, respectively. Methyl groups are generally referred as electron donating substituent's in the aromatic ring system. The C–F methyl group stretching vibrations are highly localized and generally observed in the range 1300–1100 cm^{-1} [7,8]. The CF$_3$ symmetric stretching band obtained by computationally 1120 cm^{-1} and Antisymmetrical stretching is observed at 1158 to 1167 cm^{-1}.

Isothiocyanates vibrations

The entire organic isothiocyanates exhibit a broad and very strong band centred around 2100 cm^{-1} due to the isothiocyanate group. At lower concentrations (smaller layer thickness) this band shows finer resolution and gives a strong peak or shoulder between 2080-2105 cm^{-1}. This is in agreement with the observation of williams [9] on phenyl isothiocyanate. Isothiocyanates strong stretching vibrations are obtained by computationally 2114 cm^{-1} range.
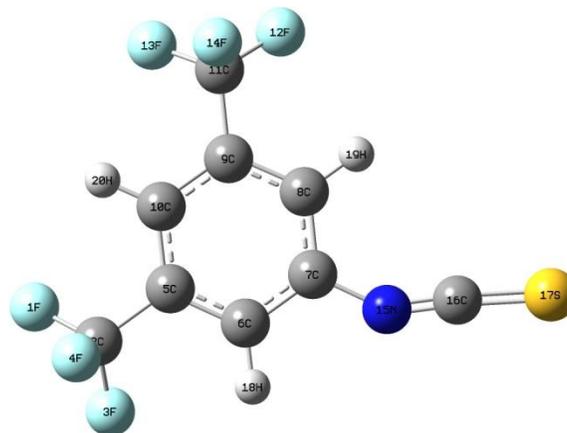
Figure 1: Optamized structure of 3,5-bis (trifluoromethyl) phenyl isothiocyanate

HOMO-LUMO analysis

The most important orbital's in molecule is the frontier molecular orbital's, called highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO). These orbitals determine the way of molecule interacts with other species. The frontier molecular energy gap

helps to characterize the chemical reactivity and kinetic stability of the molecule. A molecule with a small frontier orbital gap is more polarizable and is generally associated with a high chemical reactivity, low kinetic stability and is also termed as soft molecule[10].

The conjugated molecules are characterized by a small highest occupied molecular orbital-lowest unoccupied molecular orbital (HOMO–LUMO) separation, which is the result of a significant degree of intramolecular charge transfer from the end-capping electron acceptor groups through p-conjugated path [11].

The intramolecular charge transfer from the donor–acceptor group in a single-double bond conjugated path can induce large variations of both the dipole moment and the polarizability, making FTIR and FT-Raman activity strong at the same time. The analysis of wavefunction indicates that the electron absorption corresponds to the transition from the ground state to the excited state and is mainly described by one. An electron excitation from the high occupied molecular orbital to the lowest unoccupied molecular orbital (HOMO–LUMO). Generally, the energy gap between the HOMO and LUMO decreases, it is easier for the electrons of the HOMO to be excited. The higher energy of HOMO, the easier it is for HOMO to donate electrons whereas it is easier for LUMO to accept electrons when the energy of LUMO is low. The HOMO – LUMO energy diagram as shown in the figure 4.

HOMO = -0.27143 a.u

LUMO = -0.09897 a.u

HOMO – LUMO energy gap = -0.17246 a.u
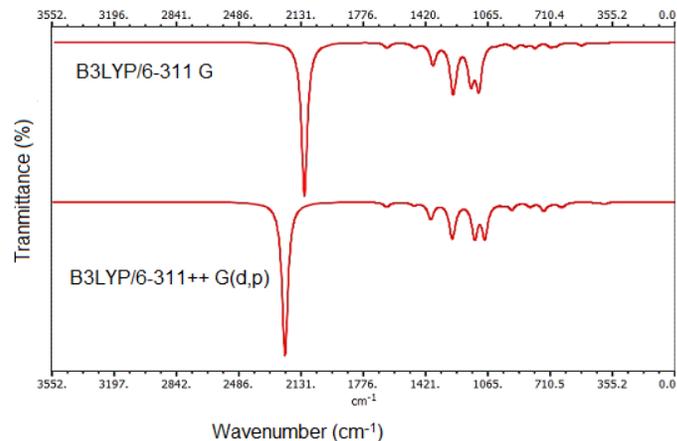
Figure 2: FT-IR spectrum of 3,5-bis (trifluoromethyl) phenyl isothiocyanate
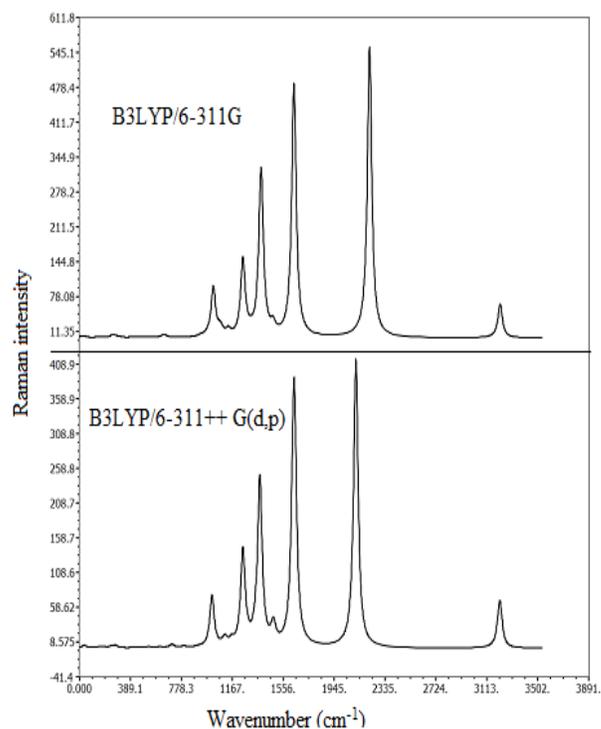
Figure 3: RAMAN spectrum of 3,5-bis (trifluoromethyl) phenyl isothiocyanate

Frequency	IR intensity		Raman intensity		Assignment
	B3LYP/ 6311G	B3LYP /6-311++ G(d,p)	B3LYP 6-311G	B3LYP 6-311++ G(d,p)	
798.1155	112.6328	66.6629	1.5503	3.1589	C-H bending
1012.6	21.8871	4.468	3.1304	25.8187	C-F Stretching
1120.434	5.6455	537.4498	2.5986	2.1401	C-F symmetric stretching band
1158.241	168.1496	152.8454	5.7053	1.899	CH$_3$ Antisymmetrical stretching
1167.633	296.8105	349.4353	6.7625	7.037	
1250.846	62.4255	105.7398	157.4162	150.8304	C-F Stretching
1476.784	3.3248	9.5972	13.6311	9.243	C-C stretching
1487.089	34.4528	48.8727	5.2469	20.8523	C-C stretching
1638.396	60.9808	21.1469	469.1823	226.6118	C-C stretching
2114.586	2089.6183	2011.791	602.2606	436.5377	S=C=N stretching
3206.077	1.4945	1.0061	30.5163	31.566	C–H stretching
3214.359	0.8897	1.7082	55.0325	63.5126	C–H stretching
3219.524	6.384	5.4632	65.4273	71.8624	C–H stretching

Table 3: Frequency and their assignments of 3,5-bis(trifluoromethyl) phenyl isothiocyanate
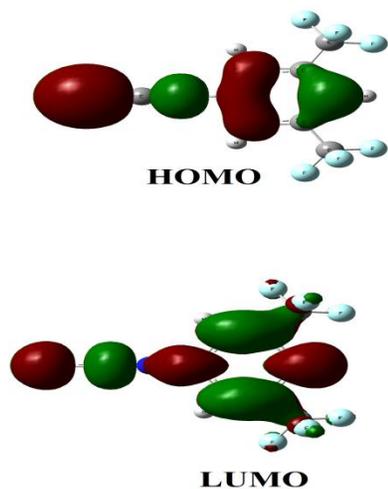
Figure 4: HOMO – LUMO
 energy diagram of 3,5-bis
(trifluoromethyl)
phenyl isothiocyanate
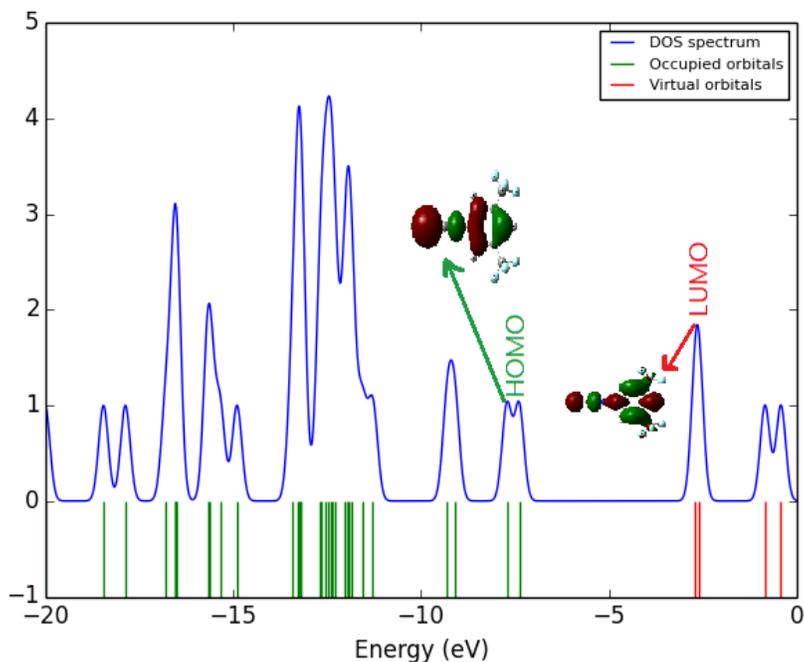
Figure 5. DOS of 3,5-bis(trifluoromethyl)
 phenyl isothiocyanate

The density of states (DOS) of the title compound is shown in Fig. 5. The DOS of the system defines the number of states per interval of energy at each energy level that are presented to be occupied by electrons. DOS diagram obtained by Gauss-sum program[21]. The density distributions are not discrete like a spectral density but they are endless. A high DOS at a specific energy level shows many states that are available for occupation.

Mulliken Analysis

The atomic charge in molecules is fundamental to physics and chemistry. For instance, atomic charge has been used to describe the processes of electronegativity equalization and charge transfer in chemical reactions[12], and to model the electrostatic potential outside molecular surface[13,14]. Mulliken atomic charges calculated at the B3LYP/6-311G++(d,p) method is collected in Table 4. The corresponding Mulliken's plot is shown in It is worthy to mention that C_2, C_8, C_{11} and C_{16} atoms exhibits positive charge, while C_5, C_6, C_7, C_9 and C_{10} atoms exhibit negative charges. However all the F atoms exhibit negative charges and all the H atoms exhibit positive charge. In isothiocyanate group S atom exhibit negative charge, C and N atoms exhibit positive charge.

Atom No.	Mulliken atomic charges obtained by B3LYP/6-311++G(d,p) method
F_1	-0.117787
C_2	0.944814
F_3	-0.080381
F_4	-0.041802
C_5	-0.767271
C_6	-0.218256
C_7	-0.570870
C_8	0.230528
C_9	-0.169717
C_{10}	-0.544445
C_{11}	0.823383
F_{12}	-0.092239
F_{13}	-0.106789
F_{14}	-0.041776
N_{15}	0.139153
C_{16}	0.224543
S_{17}	-0.170584
H_{18}	0.220378
H_{19}	0.133461
H_{20}	0.205655

Table 4: Mulliken charges of individual atoms of 3,5-bis(trifluoromethyl) phenyl isothiocyanate
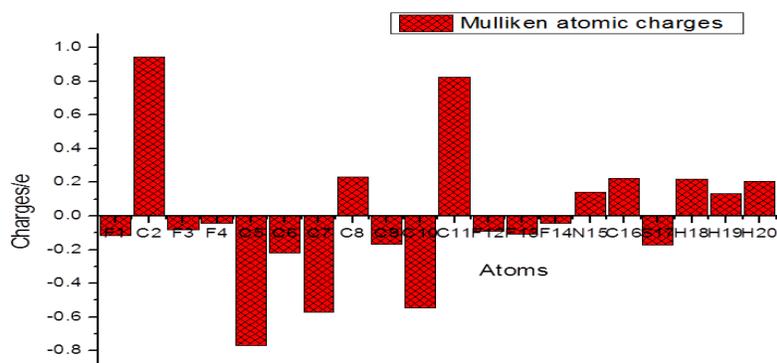
Figure 6: Mulliken atomic charges of 3,5-bis (trifluoromethyl) phenyl isothiocyanate

Thermodynamic properties

On the basis of vibrational analysis and statistical thermodynamics, the standard thermodynamic functions: heat capacity ($C^0_{p,m}$), entropy (S^0_m) and enthalpy (H^0_m) were calculated using perl script THERMO.PL [15]. Thermodynamical functions are calculated for B3LYP/ 6-311++ G(d,p) base set. As observed from Table 5, the values of $C^0_{p,m}$,S^0_m and H^0_m all increase with the increase of temperature from 100 to 1000 K , which is attributed to the enhancement of the molecular vibration as the temperature increases. Figure 7 represents the correlation graph of thermodynamical functions.

T (K)	S (J/mol.K)	Cp (J/mol.K)	ddH (kJ/mol)
100	383.1	114.7	7.89
200	484.97	186.6	23
298.15	571.3	248.01	44.43
300	572.84	249.05	44.89
400	651.58	298.5	72.37
500	722.37	335.57	104.17
600	786.11	363.09	139.17
700	843.71	383.81	176.56
800	896.04	399.72	215.77
900	943.87	412.2	256.39
1000	987.84	422.16	298.13
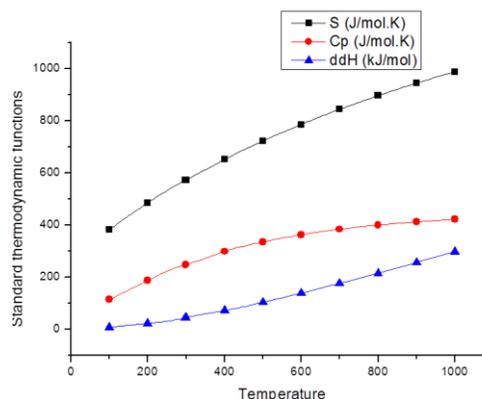
Figure 7: Thermodynamic correlation graph of 3,5-bis(trifluoromethyl) phenyl isothiocyanate

Table 5: Thermodynamic properties of 3,5-bis(trifluoromethyl) phenyl isothiocyanate

NLO properties

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[16]. NLO is at the forefront of current research because of its importance in providing 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[17-20]. Table 6 represents the Polar, Hyperpolar coordinates and they are calculated for B3LYP/ 6-311++ G(d,p) base set.

3,5-Bis(trifluoromethyl)phenyl isocyanate					
	Polar for au	Polar for esu		HyperPolar for au	HyperPolar for esu
α_{xx}	131.0575741	19.42273248	β_{xxx}	-9.0623915	-78.292719
α_{xy}	15.1438871	2.244324068	β_{xxy}	-48.6406002	-420.22074
α_{yy}	228.0268173	33.79357432	β_{xyy}	-148.765641	-1285.231
α_{xz}	2.9433399	0.436202973	β_{yyy}	-379.74493	-3280.7304
α_{yz}	8.1870814	1.213325463	β_{xxz}	-2.3890186	-20.639448
α_{zz}	78.7408886	11.66939969	β_{xyz}	-8.2957946	-71.669858
			β_{yyz}	-24.4752733	-211.44923
			β_{xzz}	6.7190387	58.047791
			β_{yzz}	53.1691939	459.344617
			β_{zzz}	-8.4604542	-73.092402
Polarizability			**Anisotropy of polarizability**		
$\alpha_{Tot\ for\ au}$	**145.94176**		**$\Delta\alpha$ for au**		**134.64125**
$\alpha_{Tot\ for\ esu}$	**21.628569**		**$\Delta\alpha$ for esu**		**19.953833**

Table 6: NLO parameter table of 3,5-bis(trifluoromethyl) phenyl isothiocyanate

Conclusion

We have carried out density functional theory calculations on the structure, vibrational spectrum, hyperpolarizability and HOMO–LUMO, NLO analyses of title compound. The equilibrium geometry by B3LYP/6-311++G(d,p) level for both the bond lengths and bond angles is performed better. The electric dipole moments and first hyperpolarizability of the compound studied have been calculated by DFT method with 6-311++G(d,p) basis set. This result shows the NLO behaviour of title compound. The DFT calculated non-zero l value of this ligand shows that the title compound might have microscopic first hyperpolarizability with non-zero values obtained by the numerical second derivatives of the electric dipole moment according to the applied field strength. The thermodynamic functions (heat capacity, internal heat energy, Gibbs energy and entropy) from spectroscopic data by statistical methods were obtained for the range of temperature 100–1000 K.

References

1. K. Nagai, T.A. Davies, M.R. Jacobs, P.C. Appelbaum, Antimicrob. Agents Chemother.46 (2002) 1273e1280.
2. R. Leclerq, P. Courvalin, Agents Chemother. 46 (2002) 2727e2734.
3. J.C. Post, N.L. Hiller, L. Nistico, P. Stoodley, G.D. Ehrlich, Curr. Opin. Otolaryngol. Head. Neck Surg. 15 (2007) 347e351.
4. F. Gotz, Mol. Microbiol. 43 (2002) 1367e1378.
5. Henry, Martin. U.S. Patent No. 3,151,023. 29 Sep. 1964.
6. Herrera, Raquel P., et al. *Angewandte Chemie International Edition* 44.40 (2005): 6576-6579.
7. Gaussian 09, Revision D.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R.Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P.Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J.Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta,F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K.Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E.Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R.Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J.Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox,Gaussian, Inc., Wallingford CT, 2009.
8. T. Shimanouchi, Y. Kalkiuti, I. Gamo, J. Chem. Phys. 25 (1956) 1241–1245.
9. T. Karthick, V. Balachandran, S. Perumal, A. Nataraj, Spectrochim. Acta 107A (2013) 72–81.
10. M. Karnan, V. Balachandran, M. Murugan, M.K. Murali, A. Nataraj, Spectrochim. Acta 116A (2013) 84–95.
11. WILLIAMS D., J. Chem. Phys. 1940 8 513.
12. B.J. Powell, T. Baruah, N. Bernstein, K. Brake, R.H. McKenzie, P. Meredith, M.R. Pederson, J. Chem. Phys. 120 (2004) 8608–8615.
13. C.H. Choi, M. Kertesz, J. Phys. Chem. A 101 (1997) 3823–3831.
14. S.Fliszar, Charge Distributions and Chemical Effects, Springer, New York, 1983.
15. P.E .Smith, J.Am.Chem.Soc.,113 (1991) 6029-6037.
16. J. Gao, J.Chem. Phys., 98(1993) 1975-1981.
17. K.K. Irikura, THERMO.PL, National Institute of Standards and Technology, 2002.
18. Y.X. Sun, Q.L. Hao, W.X. Wei, Z.X. Yu, L.D. Lu, X. Wang, Y.S. Wang, J. Mol. Struct.Theochem. 904 (2009) 74–82.
19. C. Andraud, T. Brotin, J. Am. Chem. Soc. 116 (1994) 2094–2102.
20. V.M. Geskin, C. Lambert, J.L. Bredas, J. Am. Chem. Soc. 125 (2003) 15651–15658.
21. M. Nakano, H. Fujita, M. Takahata, K. Yamaguchi, J. Am. Chem. Soc. 124 (2002) 9648–9655.
22. D. Sajan, I.H. Joe, V.S. Jayakumar, J. Zaleski, J. Mol. Struct. 785 (2006) 43–53.
23. N. M. O'Boyle, A. L. Tenderholt and K. M. Langner. J. Comp. Chem., 2008, 29, 839-845.