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Density Functional Theory Studies on Vibrational Spectra (E)-N-(4-carboxylphenyl)-2-(1-(pyrazin-2- yl)ethylidene)hydrazinecarbothioamide

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Abstract : The reaction of 2-acetylpyrazine with methyl hydrazinecarbodithioate (2) formed methyl-2-(1-(pyrazin-2-yl)ethylidene)hydrazinecarbodithioate (3). The condensation reaction of (3) with 4-aminobenzoic acid produced the title compound (E)-N-(4-carboxylphenyl)-2-(1-(pyrazin-2-ethylidene) hydrazinecarbothioamide (1). The ligand has been characterized using elemental analysis and FT-IR as well as melting point determination. The vibrational wavenumbers and corresponding vibrational assignments were examined theoretically using the Gaussion09. Theoretical vibrational wavenumbers using DFT of B3LYP/6-311 G (d,p) basis set was compared with experimental FT-IR spectra and they were found to support each other.

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Introduction

Thiosemicarbazones, their derivatives, as well as their transition metal complexes have aroused considerable interest in the areas of chemistry and biology [1]. The ligands have been used for metal analysis [2], for device applications relative to telecommunications, optical computing, storage and information processing [3]. Thiosemicarbazones are a versatile compound which exist in three structural isomer (E-, E'- and Z) [4] and can coordinate to the metal either as a neutral ligand or as deprotonated ligand through the NNS atoms [5-6]. The molecule adopts an E/Z configuration with respect to the C=N bond [7]. Therefore, thiosemicarbazone is selected in this study because it has diverse flexibility and able to form extensive networks in coordination polymer through hydrogen bonding and Л-Л bonding. Density functional theory (DFT) is a phenomenally successful approach to finding solutions to the fundamental equation that describes the quantum behaviour of atoms and molecules using Schrodinger equation in the setting of practical value [7].This approach has rapidly grown from being a specialized art practiced by a small number of physicists and chemists at the cutting edge of quantum mechanical theory to a tool that is used regularly by large numbers of researcher in chemistry, physics, materials science, chemical engineering, geology, and other disciplines [8]. DFT levels of theories was utilized to determine the optimized geometry, vibrational wave numbers in its ground state, dipole moment (μ), polarizability (α), hyperpolarizability (β), chemical potential, hardness (η), electrophilicity (ω) and the HOMO–LUMO energies [9]. This theory is reported to provide excellent vibrational frequencies of organic compounds if the calculated frequencies are scaled to compensate for the approximate treatment of electron correlation, for basis set deficiencies and for the anharmonicity [10]. This paper describes the theoretical study of vibrational wavenumber of this ligand comprehensively using DFT B3LYP/6-311G (d,p) basis which was compared with wavenumbers obtained experimentally from the corresponding FT-IR spectrum.

Experimental

Materials and methods

All the chemicals were reagent grade quality obtained from Merck, BDH and Systems. They were used without further purification. Melting points were determined using the Electrothermal 9300 Digital Melting Point Apparatus. The microelemental CHN-S data were performed using a Thermo Finnigan Model EA 112 series. Fourier Transform Infra-Red (FT-IR) spectrum in a range 4000 cm-1 to 370 cm-1 was recorded using a KBr pellet on a Perkin Elmer Model Spectrum GX apparatus.

Synthesis

A 2-acetylpyrazine (1 mmol) was added to methylhydrazinecarbodithiole (1 mmol) in 50 ml propanol. The mixture was stirred at room temperature for 2 hours and cooled at 5°C for 1day to formed methyl-2-(1-(pyrazin-2-hydrazinecarbodithioate. The methyl-2-(1-(pyrazin-2-yl)ethylidene)hydrazinecarbodithioate (1 mmol) was dissolved in butanol and 4-aminobenzoic acid (1 mmol) was added to the solution. The mixture was refluxed for 24 hours. The yellow precipitate was formed after the solution dried at room temperature for two weeks. Melting point, 128-129°. Elemental analysis (calc.), C, 54.47(55.96), H, 4.04(4.99), N, 22.91(20.39), S, 10.16(10.17) %.

Theoretical Calculation

The density functional theory (DFT) calculations were carried out using the GAUSSIAN09 program (11). The (DFT/B3LYP) at the 6-311G (d,p) basis set level was adopted to calculate the properties of the title molecule in this work. The optimized parameters of IR spectrum by the basis set are calculated and compared with the experimental data.

Result and discussion

Optimized geometry

The atom numbering scheme for the title compound is shown in Fig. 1. The bond distances and bond angles for the molecule are computed at DFT/6-311G (d,p) level. Since the crystal structure data of the title compound is not available at present, the optimized geometrical parameters was compared with other similar systems such 3-(2-Hydroxyphenyl)-1-{(*E*)- [1-(pyrazin-2-yl)ethylidene]amino}thioureamonohydrate [12] and 4,4’-Bipyridinium bis(perchlorate)–4-aminobenzoic acid–4,4 0 -bipyridine– water [13] for which experimental crystal data have been solved (Table 1). The title ligand showed that the N-N bond length is 1.35 Å (DFT) and 1.37 Å (XRD) respectively, which is similar to the N-N bond length of ligand thiosemicarbazone derivatives [14]. The bond length of C17-N15 and C17-N19 was found to be 1.37 Å thus showing partial double bond [15] character. These results can be explained by the existence of resonance in this part of the molecule. The ligand in the solid state exists as a thione form with bond lengths of C-S at 1.676 Å (DFT) 1.680 Å (XRD) [16], respectively. Comparing the theoretical values with the experimental ones indicates that most of the optimized bond lengths are very similar to each other but little difference than the experimental [12,13] values for bond angles because theoretical calculations are performed for isolated compound in the gaseous phase and the experimental results are for a compound in a solid state [17].

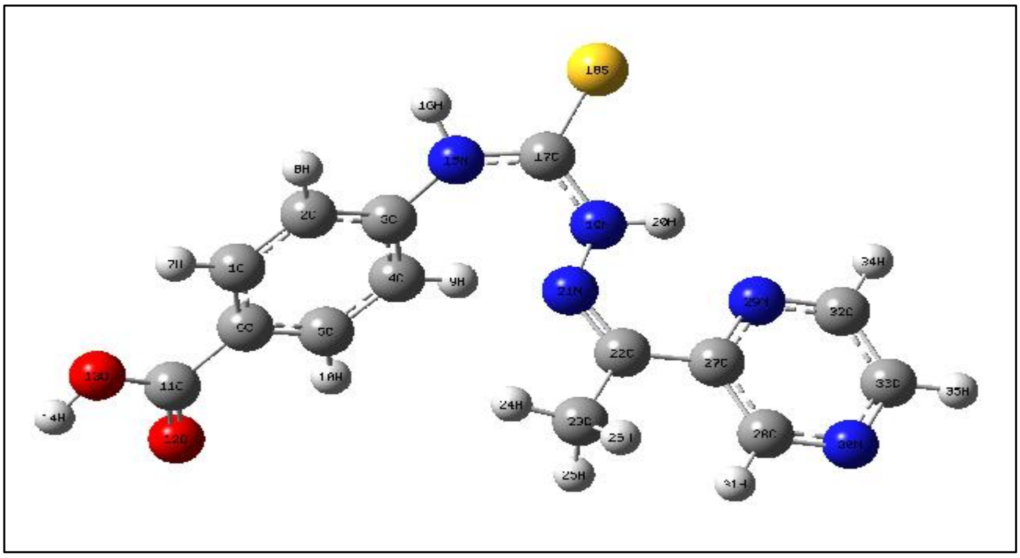

Figure 1 : Optimized structure for (E)-N-(4-carboxylphenyl)-2-(1-(pyrazin-2-yl) ethylidene)hydrazinecarbothioamide (1)

Table 1 : Selected structural parameters by theoretical calculations and experimental.

PARAMETERS	B3LYP/ 6-311G (d,p)	XRD*	PARAMETERS	B3LYP/ 6-311G (d,p)	XRD*
Bond length (˚A)			**Bond Angle (˚)**		
C1-C2	1.39	1.37	N5-C3-C2	117.5	120.8
C1-C6	1.40	1.39	N5-C3-C4	122.9	120.6
C1-H7	1.08	0.95	C2-C3-C4	119.4	118.6
C2-C3	1.40	1.39	C5-C4-C3	119.8	120.4
C2-H8	1.09	0.95	C5-C4-H9	120.1	119.8
C3-C4	1.40	1.39	C3-C4-H9	120.1	119.8
C3-N15	1.41	1.41	C4-C5-C6	121.0	121.3
C4-C5	1.39	1.39	C4-C5-H10	120.5	119.4
C4-H9	1.08	0.93	C6-C5-H10	118.5	119.4
C5-C6	1.40	1.49	C5-C6-C1	119.1	117.9
C5-H10	1.09	0.93	C5-C6-C11	118.3	119.8
C6-C11	1.48	1.48	C1-C6-C11	122.5	122.3
C11-O12	1.22	1.22	O2-C11-013	121.9	122.0
C11-O13	1.36	1.37	O13-C11-C6	112.9	114.8
C13-H14	0.98	0.89	O12-C11-C12	125.1	123.2
H16-N15	1.01	0.88	C3-N15-H16	114.6	114.2
N15-C17	1.37	1.34	C3-N15-C17	131.7	133.3
C17-S18	1.68	1.68	H16-N15-C17	110.9	112.4
C17-N19	1.37	1.37	N15-C17-S18	121.3	127.4
N19-H20	1.02	0.87	N15-C17-N19	119.0	113.4
N19-N21	1.35	1.37	S18-C17-N19	119.7	119.2
N21-C22	1.30	1.28	C17-N19-H20	117.7	118.4
C22-C23	1.51	1.50	C17-N19-N21	121.7	118.0
C22-C27	1.48	1.49	H20-N19-N21	119.2	123.7
C23-H24	1.09	0.98	N21-C22-C23	114.4	126.6
C23-H25	1.10	0.98	N21-C22-C27	127.2	114.0
C23-H26	1.10	0.98	C23-C22-C27	118.4	119.4
C27-C28	1.41	1.41	C22-C23-H24	108.8	109.5
C27-N29	1.35	1.34	C22-C23-H25	117.8	109.5
C28-N30	1.33	1.35	C22-C23-H26	111.8	105.5
C28-H31	1.09	0.95	H24-C23-H25	108.4	105.5
N29-C32	1.33	1.34	H25-C23-H26	107.4	109.4
N30-C33	1.34	1.33	C22-C27-C28	121.3	122.8
C32-C33	1.40	1.38	C22-C27-N29	119.5	117.3

C32-H34	1.09	0.95	C28-C27-N29	119.0	119.1
C33-H35	1.09	0.95	C27-C28-N30	122.9	122.4
Bond Angle (˚)			C27-C28-H31	121.0	118.9
C2-C1-C6	120.2	121.3	N30-C28-H31	116.1	118.9
C2-C1-H7	120.1	119.3	C27-N29-C32	118.1	116.5
C6-C13-H13	119.7	119.3	C28-N30-C33	116.7	116.4
C1-C2-C3	120.5	120.6	N29-C32-C33	121.7	122.4
C1-C2-H8	120.1	119.7	N30-C33-C32	121.6	121.4
C3-C2-H8	119.4	119.7	N30-C33-H35	117.2	119.3
			C32-C33-H35	121.2	121.2

*ref 12,13

Charge distribution

The charge distribution of the molecule was calculated on the basis of the Mulliken method [18] using B3LYP/6-311G (d,p) level calculation. This calculation depicts the charges of the every atom in the molecule. Distribution of positive and negative charges is vital in increasing or decreasing bond lengths between the atoms. The survey of the literature revealed that effective atomic calculations plays an important role in the application of chemical calculation to molecular system because of atomic charges, dipole moment, molecular polarizability, electronic structure, acidity–basicity behaviour and more of other properties of molecular system [19]. Mulliken's atomic charges and plot are shown in Table 2 and Fig. 2. The Mulliken scheme places the negative charge on C1, C2, C4, C5, C6, O12, O13, N15, S22, N19, N21, C23, N29, N30 atoms, C3, C11, C17, C22, C27, C28, C32, C33 atoms split the positive charge and all the hydrogen atoms are in positive charge. Mulliken population analysis compute charges by dividing orbital overlap evenly between the two atoms involved [20].

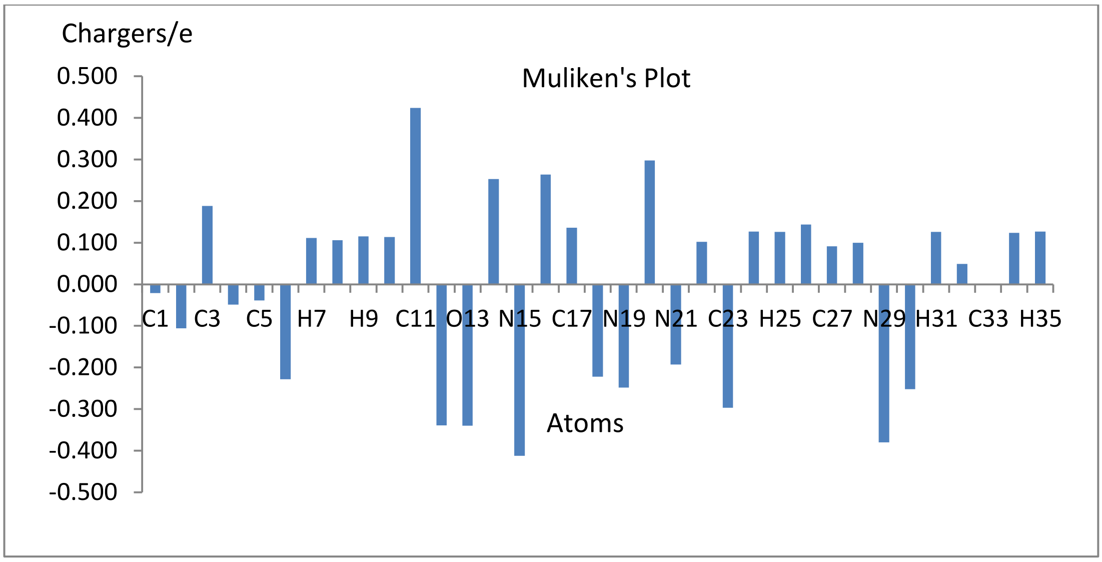

Figure 2 : The atomic charge plot of (E)-N-(4-carboxylphenyl)-2-(1-(pyrazin-2-yl) ethylidene)hydrazinecarbothioamide (1)

Table 2 : Mulliken atomic charges for (E)-N-(4-carboxylphenyl)-2-(1-(pyrazin-2-yl)ethylidene)hydrazinecarbothioamide (1

Atoms	Chargers	Atoms	Chargers
C1	-0.021	N19	-0.248
C2	-0.106	H20	0.298
C3	0.188	N21	-0.193
C4	-0.049	C22	0.102
C5	-0.039	C23	-0.297
C6	-0.228	H24	0.127
H7	0.111	H25	0.126
H8	0.106	H26	0.144
H9	0.115	C27	0.091
H10	0.114	C28	0.100
C11	0.424	N29	-0.380
O12	-0.339	N30	-0.252
O13	-0.340	H31	0.126
H14	0.253	C32	0.049
N15	-0.412	C33	0.000
H16	0.264	H34	0.124
C17	0.136	H35	0.127
S18	-0.222		

Vibrational frequency

The experimental IR spectrum is shown in Fig. 3. Vibrational frequencies calculated at the B3LYP/6- 311G (d p) level were scaled by a typical factor of 0.96. Some primary calculated harmonic frequencies are listed in Table 3 and compared with the experimental data. The descriptions concerning the assignments have also been indicated in Table 2. The Gauss-view program [21] was used to assign the calculated harmonic frequencies. As seen from Table 3, the predicted harmonic vibration frequencies and the experimental data were very similar to each other. From the theoretical and experimental wavenumber, it was found that the wavenumber for stretching O13-H14, stretching C21-N22; rocking N19-H20 and N15-H16, wagging CH_3; N19-C20 and N15-H16, scissoring pyrazil, twisting C22-N21 and wagging N19-N21 and $CH_{3,}$ which are at 3773, 1625, 1420, 1233 and 618 cm^{-1} respectively were found to be the same. The mismatch between the theoretical and the experimental wavenumbers is due to the fact that the former refers to an isolated molecule in the gas phase the later refers to compound in solid phase, where it may undergo inter and intramolecular interactions [22] .

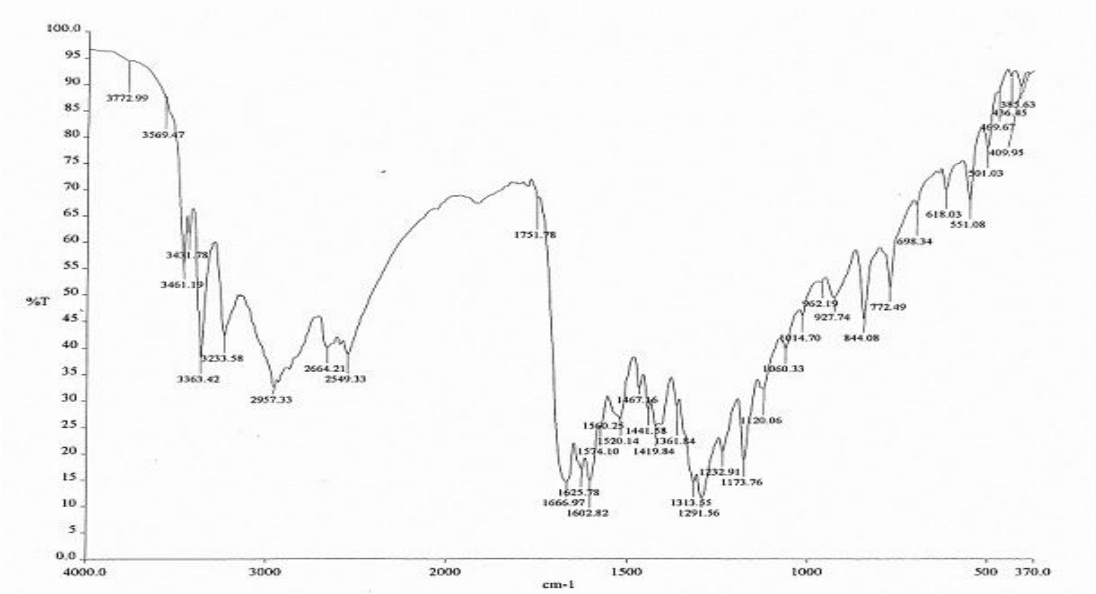

Figure 3 : The experimental IR spectrum of (E)-N-(4-carboxylphenyl)-2-(1-(pyrazin-2-yl) ethylidene)hydrazinecarbothioamide (1)

Table 3 : Comparison of the observed and calculated vibrational spectra of (E)-N-(4-carboxylphenyl)-2-(1-(pyrazin-2- yl)ethylidene) hydrazine carbothioamide

DFT 6-311G (d,p) (cm^{-1})	Exp (cm^{-1})	Vibrational assignments
3773	3773	νO13-H14
3594	3569	νN15-H16
3377	3363	νN19-H20
3212	3233	νC-H PHY
3023	2960	νCH_3
1797	1751	νC11-O12, ρO13-H14
1649	1666	νC1-C2, νC5-C4, C2H8-C1H7 SCI, δC4H5-C5H10
1625	1625	νC21-N22 , ρN19-H20, ρN15-H16
1609	1602	νPYZ
1566	1560	νN19-C17-N15, ρN19-H20, ρN15-H16
1541	1520	ωPHY
1443	1441	δPHY
1420	1420	ωCH_3, ωN19-C20, ωN15-H16
1376	1362	ωO13-H14, νC11-O13
1306	1313	ρC28-H31, ρC32-H34
1291	1264	νC3-N15 , ρN15-H16, ρPHY
1233	1233	δPYZ
1184	1173	ωN15-H16, ωN19-H20

1127	1120	νC17-S18 , ωN19-H20, ωN15-H-16, ρCH_3 ,νN19-N21
959	927	δN19-C17-N15, ρCH_3, ωC-H PHY
838	844	τC-H PHY
776	772	τPYZ, ρN19-H20
713	698	τPHY, ρN15-H16, ρO13-H14
618	618	τC22-N21, ωN19-N21, ωCH_3
549	551	τCH_3, ωN15-H16, ωC22-N21, ωN19-H20
501	502	ρPHY, ρN15-H16
423	436	τPHY
392	385	τPYZ

ν-stretching, δ-scissoring, ω-wagging, ρ-rocking, τ-twisting, PHY-phenyl, PYZ- pyrazil

Conclusion

Vibration spectra of (E)-N-(4-carboxylphenyl)-2-(1-(pyrazin-2- yl)ethylidene) hydrazinecarbothioamide (I) has been recorded and analysed. Density Functional Theory has been used to compute molecular geometry and vibrational wavenumber using B-3LYP 6-311 G (d,p) basis set. The theoretical results were found to support the experimental result obtained through FT-IR spectroscopy.

References

1. Jouad, E. M., Allain, M., Khan, M. A. & Bouet, M. (2005) *Polyhedron*, **24**, 327-332
2. Uesugi, K., Sik, L. J., Nisioka, H., Kumagai, T. and Nagahiro, T. (1994) *Microchem. J.*, **50**, 88-93
3. Yu-peng, T., Chun-ying, D., Cun-yuan, Z. & Xiao-zeng, Y. (1997) *Inorg. Chem.*, **36**, 1247-1252
4. West, D. X., Bain, G, A., Butcher, R. J., Jasinski, J. P., Yu Li., Pozdniakiv, R. Y., Martenez, J. V., Toscano, R. A. and Ortega, S. H. (1996) *Polyhedron*, **15**, 665- 674
5. Ayaan, U. E., Youssef, M. M. and Shihry, S. A. (2009) *Mol. Struct.*, **936**, 213-219
6. Ferrari, M. B., Fava, G. G., Pelizzi, C. and Tarasconi, P. (1992) *J. Chem. Soc., Dalton Trans.*, **2153**-2159
7. West, D. X., Padhye, S. B. and Sonowane, P. B. (1991) *Struct. Bond*., **76**,1
8. Sholl, D. S. and Steckel, J. A. (2009) “Density Functional Theory, A Practical Introduction” *Johns Wiley and Sons, Inc., Canada,* **1**
9. Thanikachalam, V., Periyanayagasamy, V., Jayabharathi, G., Manikandan, G., Saleem, H. and Subashchandrabose, S. (2012) *Spectrochim. Acta Part A*, **87**, 86– 95
10. Abramov, Y. A., Volkov, A. V. and Coppens, P. (1999) *Chem. Phys. Lett.*, **31**, 81–86
11. Frisch, M. J., Trucks, G. W., Schlegel, H. B., Scuseria, G. E., Robb, M. A., Cheeseman, J. R., Montgomery, J. A., Vreven, T., Kudin, K. N., Burant, J. C., Millam, J. M., Iyengar, S. S., Tomasi, J., Barone, V., Mennucci, B., Cossi, M., Scalmani, G., Rega, N., Petersson, G. A., Nakatsuji, M. H., Ehara, H, M., Toyota, K., Fukuda, R., Hasegawa, J., Ishida, M., Nakajima, T., Honda, Y., Kitao, O., Nakai, H., Klene, M., Li, X., Knox, J. E., Hratchian, H. P., Cross, J. B., Bakken, V., Adamo, C., Jaramillo, J., Gomperts, R., Statmann, R.E., Yazyev, O., Austin, A.J., R. Cammi, C., Pomelli, J. W., Ochterski, P. Y., Voth, A. K., Monokuma, G. A., Salvador, P., Dannenberg, J. J., Zakrzewski, V. G., Dapprich, S., Daniels, A. D., Stain, M. C., Farkas, O., Malick, D. K., Rabuck, A. D., Raghavachari, K., Foresman, J.B., Ortiz, J. V., Cui, Q., Baboul, A. G., Clifford, S., Cioslowski, J., Stefanov, B. B., Liu, G., Liashenko, A., Piskorz. P., Komaromi, I., Martin, R. L., Fox, D. J., Keith, T., Al-Laham, M. A., Peng, C. Y., Nanayakkara, A., Challacombe, M., Gill, P. M. W., Johnson, B., Chen, Wong, C. W., Wong, M. W., Gonzales, C., Pople,. J. A. (2004) *Gaussian 03, Revision C.02, Gaussian Inc., Wallingford, CT.*
12. Normaya, E., Farina, Y., Halim, A. S. N. and Tiekink E. R. T. (2011) *Acta Cryst.*, **67**, 0943–0944
13. Qun-Hui, M., Lu, H., Jian-Dong, H., Yi-Fan, L. and and Rong-Hua. Z. (2009) *Acta Cryst.*, **65**, 0132–0133
14. Singh, N., Kumar, A., Tiwari, R. P., Verma, D. and Vikas, B. (2010) *J. Mol. Struct*., **1016**, 97–108
15. Yesilkaynak, T., Binzet, G., Emen, F. M., Florke, N. K. and Arslan, H. (2010) *Eur. J. Chem.*, **1**, 1-5

16. Huan-Mei, G., Lin-Tong, W., Jing-Zhang, Pu-Su, Z. and Fang-Fang, J. (2008) *Molecules*, **13**, 2039-2048
17. Sidir, I., Sidir, Y. G., Kumalar, M. and Tasal, E. (2010) *J. Mol. Struct*., **964**, 134–151
18. Thanikachalam, V., Periyanayagasamy, V., Jayabharathi, J., Manikandan, G., Subashchandrabose, S. and Erdogdu, Y. (2012) *Spectrochim. Acta Part A*, **87**, 86– 95
19. Frish, A., Nielsen, A. B., Holder, A. J. (2000) “Gaussview User’s Manual” *Gaussian Inc., Pittsburgh, PA, USA*
20. John, C. J., Amalanathan, A. R., Twinkle, A. R., Srinivasan, P. and Joe, I. H. (2011) *Spectrochim. Acta Part A*, **151**– 161