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# Structural, electronic, optical and vibrational properties of 1-(5-chloro-6-fluoro-1,3-benzothiazol-2-yl)hydrazine&1-(6-chloro-1,3-benzothiazol-2-yl)hydrazine-A quantum chemical study

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## ABSTRACT

*We have done a comparative study of 1-(5-Chloro-6-fluoro-1, 3-benzothiazol-2-yl)hydrazine& 1-(6-Chloro-1,3-benzothiazol-2-yl)hydrazinewith B3LYP with 6-311 G (d, p) as the basis set. Here we have done a relative study of their structures, vibrational assignments, thermal, electronic and optical properties of 1-(5-Chloro-6-fluoro-1, 3-benzothiazol-2-yl)hydrazine& 1-(6-Chloro-1,3-benzothiazol-2-yl)hydrazine. We have plotted frontier orbital HOMO- LUMO surfaces, Molecular electrostatic potential surfaces to explain the reactive nature of 1-(5-Chloro-6-fluoro-1, 3-benzothiazol-2-yl)hydrazine& 1-(6-Chloro-1,3-benzothiazol-2-yl)hydrazine.*

**Keywords:**1-(5-Chloro-6-fluoro-1,3-benzothiazol-2-yl)hydrazine, 1-(6-Chloro-1,3-benzothiazol-2-yl) hydrazine, Vibrational analysis, DFT, HOMO- LUMO surfaces, Optical properties

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## INTRODUCTION

Hydrazine, an inorganic compound, is a colourless, flammable liquid.It smells like ammonia. Hydrazine is mainly used as a foaming agent in the preparation of polymer foams. Hydrazine is also used in various rocket fuelsand to prepare the gas precursors used in air bags. Hydrazine is used in both nuclear and conventional electrical power plantsteam cycles as an oxygen scavenger to control concentrations of dissolved oxygen in an effort to reduce corrosion. Hydrazineshave great significance in pharmaceuticalssuch as the anti-tuberculosis medication isoniazid and the antifungal fluconazole, as well as in textile dyes and in photography too [1, 2]. Hydrazine derivatives have been examined extensively due to their biological applications as well as metal-extracting properties.Acid hydrazides have shown reliable biological properties like bactericidal, anti-malaria, anti-cancer, anti-depressant, anti-HIV and vasodilator activities [3-8].

As a part of our ongoing research work [9-17], we report the comparative study of-(5-Chloro-6-fluoro-1, 3-benzothiazol-2-yl)hydrazine& 1-(6-Chloro-1,3-benzothiazol-2-yl)hydrazine by DFT study. To the best of our knowledge no comparative quantum chemical calculations of these molecules have been reported so far in the literature.

## MATERIALS AND METHODS

### Computational Details

### Structure and Spectra

The molecular structures of the 1-(5-Chloro-6-fluoro-1, 3-benzothiazol-2-yl)hydrazine& 1-(6-Chloro-1,3-benzothiazol-2-yl)hydrazine have been modelled. The model molecular structures of 1-(5-Chloro-6-fluoro-1, 3-benzothiazol-2-yl)hydrazine& 1-(6-Chloro-1,3-benzothiazol-2-yl)hydrazineareare given in Figures 1.Fourier Transform Infrared spectrum (Fig.-3)of 1-(5-Chloro-6-fluoro-1, 3-benzothiazol-2-yl)hydrazine& 1-(6-Chloro-1,3-benzothiazol-2-yl)hydrazinewas recorded with FTIR Perkin Elmerspectrometer in KBr dispersion in the range of 400 to4000 cm$^{-1}$for the title molecules.

### Computational methods

All the calculations were performed by the B3LYP [18, 19] method using the 6-311 G (d, p) basis setof Density functional theory [20]. All computations were carried out with the GAUSSIAN 09 package[21]. By combining the results of the GAUSSVIEW'S program [22] with symmetry considerations, vibrational frequency assignments were made with a high degree of accuracy.Vibrational frequencies for these molecules were calculatedwith these methods and then scaled [23] by 0.9613.

## RESULTS AND DISCUSSION

### Geometry Optimization

Optimized parameters of 1-(5-Chloro-6-fluoro-1, 3-benzothiazol-2-yl)hydrazine& 1-(6-Chloro-1,3-benzothiazol-2-yl)hydrazinecalculated by B3LYP method with 6-311 G (d, p) basis set are listed in Table 1 in accordance with the atom numbering scheme as shown in Figures 1. Local minimum energies are -1392.3958a.u, and -1293.1372a.u,for 1-(5-Chloro-6-fluoro-1, 3-benzothiazol-2-yl)hydrazine& 1-(6-Chloro-1,3-benzothiazol-2-yl)hydrazinerespectively. For1-(5-Chloro-6-fluoro-1, 3-benzothiazol-2-yl)hydrazine& 1-(6-Chloro-1,3-benzothiazol-2-yl)hydrazine,C–C bond distances are found to be in the range from 1.381-1.429 A$^0$ and 1.318-1.401 A$^0$ while for C-N, these values are 1.350-1.461 A$^0$and 1.429-1.461 A$^0$respectively.In case of C-H bond distances, they are found to be 1.07 A$^0$ in both the molecules whilein case of C-Cl bond distance, they are found to be 1.760 A$^0$ in both the molecules.Optimized structures of1-(5-Chloro-6-fluoro-1, 3-benzothiazol-2-yl)hydrazine& 1-(6-Chloro-1,3-benzothiazol-2-yl)hydrazine, by B3LYP/6-311G (d, p) method are shown in Figure 1.

### Assignment of Fundamentals

1-(5-Chloro-6-fluoro-1, 3-benzothiazol-2-yl)hydrazinehas 14 atoms with 48 normal modes of vibration while1-(6-Chloro-1,3-benzothiazol-2-yl)hydrazinehas 14 atoms with 48 normal modes of vibration.On the basis of our calculated data and experimental FTIR spectra, we observe similarities and differences between the experimental and the calculated frequencies byDFT/B3LYP method.Assignments are done using the animated view ofnormal mode description. A good agreement is found between thetheoretical and experimental data. Vibrational frequencies, calculated for 1-(5-Chloro-6-fluoro-1, 3-benzothiazol-2-yl)hydrazine& 1-(6-Chloro-1,3-benzothiazol-2-yl)hydrazineand experimental frequencies (FTIR) havebeen compared in Tables 2 and 3, respectively.

### Modes Description

### C–H Vibrations

We have seen in literature that the C–H stretchingvibrations are usually observed in 2800– 3200 cm$^{-1}$ region. In the study of1-(5-Chloro-6-fluoro-1, 3-benzothiazol-2-yl)hydrazine,the (C–H) functional group is present at 3084 and 3095 cm$^{-1}$ in the calculated spectra which is in good agreement with theexperimental data as given in Table 2.In the study of1-(6-Chloro-1,3-benzothiazol-2-yl)hydrazine,the (C–H) functional group is present at 3073, 3084 and 3088cm$^{-1}$ incalculated spectra which is in good agreement with theexperimental data as given in Table 3.

### N-H Vibrations

The N–H stretching vibrations are normally viewed in the region 3300-3600 cm$^{-1}$. For 1-(5-Chloro-6-fluoro-1, 3-benzothiazol-2-yl)hydrazine, the N-H stretching vibration is present at 3345, 3408 and 3444 cm$^{-1}$ while 3344, 3405 and 3445 cm$^{-1}$in 1-(6-Chloro-1,3-benzothiazol-2-yl)hydrazine. A strong scissoring vibrations of H-N-H is found at

1643cm$^{-1}$ for1-(5-Chloro-6-fluoro-1, 3-benzothiazol-2-yl)hydrazine while 1641cm$^{-1}$for 1-(6-Chloro-1,3-benzothiazol-2-yl)hydrazine. For 1-(5-Chloro-6-fluoro-1, 3-benzothiazol-2-yl)hydrazine, the twist $NH_2$ vibration, presented at 1300 cm$^{-1}$ while 842 cm$^{-1}$ in 1-(6-Chloro-1,3-benzothiazol-2-yl)hydrazine. Also the rocking $NH_2$ vibration, presented at 849 cm$^{-1}$for 1-(5-Chloro-6-fluoro-1, 3-benzothiazol-2-yl)hydrazine. All these bands are in good agreement with the experimental data as given in Tables 2 & 3.

**Table-1 Optimized geometrical parameters of 1-(5-Chloro-6-fluoro-1, 3-benzothiazol-2-yl) hydrazine & 1-(6-Chloro-1, 3-benzothiazol-2-yl) hydrazine by (B3LYP)/ 6-311 G (d, p) Method**

| S.NO. | 1-(5-Chloro-6-fluoro-1, 3-benzothiazol-2-yl) hydrazine | | 1-(6-Chloro-1,3-benzothiazol-2-yl) hydrazine | |
|---|---|---|---|---|
| | PARAMETERS | CALCULATED VALUE | PARAMETERS | CALCULATED VALUE |
| | **Bond Lengths** | | | |
| 1. | $C_1$-$S_8$ | 1.504 | $C_1$-$S_8$ | 1.504 |
| 2. | $C_1$-$N_9$ | 1.429 | $C_1$-$N_9$ | 1.429 |
| 3. | $C_1$-$N_{12}$ | 1.35 | $C_1$-$N_{10}$ | 1.35 |
| 4. | $C_2$-$C_3$ | 1.3818 | $C_2$-$C_3$ | 1.318 |
| 5. | $C_2$-$C_7$ | 1.429 | $C_2$-$C_7$ | 1.429 |
| 6. | $C_2$-$S_8$ | 1.504 | $C_2$-$S_8$ | 1.504 |
| 7. | $C_3$-$C_4$ | 1.403 | $C_3$-$C_4$ | 1.403 |
| 8. | $C_3$-$H_{17}$ | 1.07 | $C_3$-$H_{15}$ | 1.07 |
| 9. | $C_4$-$C_5$ | 1.3917 | $C_4$-$C_5$ | 1.3917 |
| 10 | $C_4$-$F_{10}$ | 1.35 | $C_4$-$Cl_{17}$ | 1.76 |
| 11. | $C_5$-$C_6$ | 1.4018 | $C_5$-$C_6$ | 1.4018 |
| 12. | $C_5$-$Cl_{11}$ | 1.76 | $C_5$-$H_{18}$ | 1.07 |
| 13. | $C_6$-$C_7$ | 1.3849 | $C_6$-$C_7$ | 1.3849 |
| 14. | $C_6$-$H_{18}$ | 1.07 | $C_6$-$H_{16}$ | 1.07 |
| 15. | $C_7$-$N_9$ | 1.4611 | $C_7$-$N_9$ | 1.4611 |
| 16. | $N_{12}$-$N_{13}$ | 1.4 | $N_{10}$-$N_{11}$ | 1.4 |
| 17. | $N_{12}$-$H_{16}$ | 1.0 | $N_{10}$-$H_{14}$ | 1.0 |
| 18. | $N_{13}$-$H_{14}$ | 1.0 | $N_{11}$-$H_{12}$ | 1.0 |
| 19. | $N_{13}$-$H_{15}$ | 1.0 | $N_{11}$-$H_{13}$ | 1.0 |
| | **Bond Angles** | | | |
| 20. | $S_8$-$C_1$-$N_9$ | 110.0484 | $S_8$-$C_1$-$N_9$ | 110.0484 |
| 21. | $S_8$-$C_1$-$N_{12}$ | 127.1965 | $S_8$-$C_1$-$N_{10}$ | 127.1965 |
| 22. | $N_9$-$C_1$-$N_{12}$ | 122.6978 | $N_9$-$C_1$-$N_{10}$ | 122.6978 |
| 23. | $C_3$-$C_2$-$C_7$ | 120.4689 | $C_3$-$C_2$-$C_7$ | 120.4689 |
| 24. | $C_3$-$C_2$-$S_8$ | 129.4825 | $C_3$-$C_2$-$S_8$ | 129.4825 |
| 25. | $C_7$-$C_2$-$S_8$ | 110.0486 | $C_7$-$C_2$-$S_8$ | 110.0485 |
| 26. | $C_2$-$C_3$-$C_4$ | 118.6716 | $C_2$-$C_3$-$C_4$ | 118.6716 |
| 27. | $C_2$-$C_3$-$H_{17}$ | 120.6642 | $C_2$-$C_3H_{15}$ | 120.6642 |
| 28. | $C_4$-$C_3$-$H_{17}$ | 120.6642 | $C_4$-$C_3$-$H_{15}$ | 120.6642 |
| 29. | $C_3$-$C_4$-$C_5$ | 120.895 | $C_3$-$C_4$-$C_5$ | 120.8955 |
| 30. | $C_3$-$C_4$-$F_{10}$ | 119.5522 | $C_3$-$C_4$-$Cl_{17}$ | 119.5522 |
| 31. | $C_5$-$C_4$-$F_{10}$ | 119.5522 | $C_5$-$C_4$-$Cl_{17}$ | 119.5522 |
| 32. | $C_4$-$C_5$-$C_6$ | 120.8927 | $C_4$-$C_5$-$C_6$ | 120.8927 |
| 33. | $C_4$-$C_5$-$Cl_{11}$ | 119.5536 | $C_4$-$C_5$-$H_{18}$ | 119.5536 |
| 34. | $C_6$-$C_5$-$Cl_{11}$ | 119.5536 | $C_6$-$C_5$-$H_{18}$ | 119.5536 |
| 35. | $C_5$-$C_6$-$C_7$ | 118.6055 | $C_5$-$C_6$-$C_7$ | 118.6055 |
| 36. | $C_5$-$C_6$-$H_{18}$ | 120.6972 | $C_5$-$C_6$-$H_{16}$ | 120.6972 |
| 37. | $C_7$-$C_6$-$H_{18}$ | 120.6972 | $C_7$-$C_6$-$H_{16}$ | 120.6972 |
| 38. | $C_2$-$C_7$-$C_6$ | 120.4657 | $C_2$-$C_7$-$C_6$ | 120.4657 |
| 39. | $C_2$-$C_7$-$N_9$ | 108.306 | $C_2$-$C_7$-$N_9$ | 108.3066 |
| 40. | $C_6$-$C_7$-$N_9$ | 131.2278 | $C_6$-$C_7$-$N_9$ | 131.2278 |
| 41. | $C_1$-$S_8$-$C_2$ | 103.2891 | $C_1$-$S_8$-$C_2$ | 103.2891 |
| 42. | $C_1$-$N_9$-$C_7$ | 108.3073 | $C_1$-$N_9$-$C_7$ | 108.3073 |
| 43. | $C_1$-$N_{12}$-$N_{13}$ | 109.4712 | $C_1$-$N_{10}$-$N_{11}$ | 109.4712 |
| 44. | $C_1$-$N_{12}$-$H_{16}$ | 125-2644 | $C_1$-$N_{10}$-$H_{14}$ | 125.2644 |
| 45. | $N_{13}$-$N_{12}$-$H_{16}$ | 125-2644 | $N_{11}$-$N_{10}$-$H_{14}$ | 125.2644 |
| 46. | $N_{12}$-$N_{13}$-$H_{14}$ | 120.0 | $N_{10}$-$N_{11}$-$H_{12}$ | 120.0 |
| 47. | $N_{12}$-$N_{13}$-$H_{15}$ | 120.0 | $N_{10}$-$N_{11}$-$H_{13}$ | 120.0 |
| 48. | $H_{14}$-$N_{13}$-$H_{15}$ | 120.0 | $H_{12}$-$N_{11}$-$H_{13}$ | 120.0 |

**Table 2 Vibrational assignments of 1-(5-Chloro-6-fluoro-1, 3-benzothiazol-2-yl) hydrazine with B3LYP/6-311G (d, p)**

| S.NO. | Wave number Calculated | Wave number Exp. | IR INTENSITY | VIBRATIONAL ASSINGMENT |
|---|---|---|---|---|
| 1 | 65 | - | 5.563 | Twist in NH-$NH_2$ |
| 2 | 99 | - | 0.432 | Out of plane twisting in whole molecule |
| 3 | 121 | - | 11.29 | Twist in NH-$NH_2$ |
| 4 | 143 | - | 5.288 | Bending of NH-$NH_2$ |
| 5 | 204 | - | 4.221 | $\omega(C_5\text{-}Cl_{11})$ |
| 6 | 227 | - | 4.697 | Out of plane twisting in whole molecule |
| 7 | 261 | - | 1.856 | Twist in $NH_2$ |
| 8 | 267 | - | 27.85 | Twist in $NH_2$ |
| 9 | 299 | - | 53.16 | Twist in $NH_2$ |
| 10 | 320 | - | 10.10 | Twist in $NH_2$ |
| 11 | 322 | - | 2.300 | $\tau$ in whole molecule |
| 12 | 388 | - | 7.562 | Twist in $NH_2$ |
| 13 | 427 | 437 | 10.88 | $\tau(C_3\text{-}C_4\text{-}C_5\text{-}C_6)$ |
| 14 | 498 | 491 | 26.74 | Twist in $NH_2$ |
| 15 | 509 | 522 | 42.12 | Twist in $NH_2$ |
| 16 | 546 | - | 13.00 | Twisting in Benzene ring |
| 17 | 571 | 561 | 39.70 | Twisting in whole molecule |
| 18 | 585 | - | 8.007 | Butterfly motion at $C_1$ |
| 19 | 622 | 611 | 21.97 | $\beta(N_9\text{-}C_1\text{-}N_{12})$ |
| 20 | 640 | 655 | 2.961 | $\tau(C_5\text{-}C_4\text{-}C_3\text{-}H_{17})$ |
| 21 | 682 | - | 2.591 | Whole ring Torsion |
| 22 | 687 | 688 | 2.218 | Out of plane twisting in ring carbons |
| 23 | 707 | 719 | 31.22 | Ring breathing |
| 24 | 809 | - | 88.87 | $\tau$ (C-C-C-C) in whole ring |
| 25 | 818 | - | 11.36 | Out of plane Bending (C-C-H) both places |
| 26 | 849 | 831 | 116.0 | Rock $NH_2$ |
| 27 | 856 | 864 | 29.62 | Out of plane Bending (C-C-H) both places |
| 28 | 950 | 972 | 20.54 | Ring Breathing |
| 29 | 1039 | 1070 | 53.71 | $\beta$ (C-C-H) at both places + $\beta$ (C-C-C) in whole ring |
| 30 | 1102 | 1116 | 28.15 | $\beta$ $(C_1\text{-}N_{12}\text{-}N_{13})$ |
| 31 | 1174 | 1151 | 31.28 | $\beta$ (C-C-H) at both places |
| 32 | 1188 | 1201 | 1.947 | $\beta$ (C-C-H) at both places |
| 33 | 1246 | - | 2.214 | $\nu(C_2\text{-}C_7)+\nu(C_6\text{-}C_5)$ |
| 34 | 1257 | - | 14.84 | Twist $NH_2$ |
| 35 | 1287 | 1271 | 1.574 | Twist $NH_2$ |
| 36 | 1300 | 1292 | 89.75 | Twist $NH_2$ |
| 37 | 1368 | 1361 | 11.93 | $\beta$ (C-C-C) in whole ring |
| 38 | 1401 | 1396 | 45.09 | $\beta$ $(C_1\text{-}N_{12}\text{-}H_{16})$ |
| 39 | 1429 | 1452 | 278.9 | $\beta$ (C-C-H) at both places |
| 40 | 1529 | 1529 | 142.2 | Ring Deformation |
| 41 | 1550 | 1558 | 125.8 | $\nu(C_1\text{-}N_9)+\nu$(C-C) in whole ring |
| 42 | 1590 | 1597 | 75.81 | $\nu(C_1\text{-}N_9)+\nu$(C-C) in whole ring |
| 43 | 1643 | 1649 | 124.3 | S $(H_{15}\text{-}N_{13}\text{-}H_{14})$ |
| 44 | 3084 | 3068 | 1.2841 | $\nu(C_3\text{-}H_{17})$ |
| 45 | 3095 | 3091 | 0.0261 | $\nu(C_6\text{-}H_{18})$ |
| 46 | 3345 | 3373 | 1.4986 | $\nu(N_{13}\text{-}H_{14})+\nu(N_{13}\text{-}H_{15})$ |
| 47 | 3408 | 3398 | 42.9565 | $\nu(N_{12}\text{-}H_{16})$ |
| 48 | 3444 | 3450 | 8.7239 | $\nu(N_{13}\text{-}H_{14})+\nu(N_{13}\text{-}H_{15})$ |

## Other modes of vibration

In 1-(5-Chloro-6-fluoro-1, 3-benzothiazol-2-yl) hydrazine, a ring deformation mode is calculated at 1529cm$^{-1}$ which is in good agreement with the experimental data i.e. 1529 cm$^{-1}$while in 1-(6-Chloro-1, 3-benzothiazol-2-yl) hydrazine,ring deformation mode is at 664cm$^{-1}$ having appropriate IR intensity which is in good agreement with experimental data i.e. 559 cm$^{-1}$.As expected, torsion modes along with wagging modes appear in the lower frequency range. For 1-(5-Chloro-6-fluoro-1, 3-benzothiazol-2-yl) hydrazine, strong torsion mode of C-C-C-C is at 427 cm$^{-1}$ in calculated spectrum which matches well with the experimental one, that is, 437cm$^{-1}$ while a strong torsion modes of C-C-C-C are at 472 cm$^{-1}$ in calculated spectrum for 1-(6-Chloro-1, 3-benzothiazol-2-yl) hydrazine which also matches well with the experimental one, that is, 472 cm$^{-1}$.In middle region, in and out of plane bending vibrations are found which matches well with their corresponding frequencies. Furthermore, the study of low frequency vibrations are of great significance, because it gives information on weak intermolecular interactions, which take place in enzyme reactions [24]. Knowledge of low frequency mode is also essential for the interpretation of the effect of electromagnetic radiation on biological systems [25].The aim of vibrational analysis is to acquire direct information on lower and higher frequency vibrations of 1-(5-Chloro-6-fluoro-1, 3-benzothiazol-2-yl) hydrazine and 1-(6-Chloro-1, 3-benzothiazol-2-yl) hydrazine.

**Table 3 Vibrational assignments of 1-(6-Chloro-1, 3-benzothiazol-2-yl) hydrazine with B3LYP/6-311G (d, p)**

| S.NO. | Wave number Calculated | Wave number Exp. | IR INTENSITY | VIBRATIONAL ASSINGMENT |
|---|---|---|---|---|
| 1 | 65 | - | 5.521 | Twist NH-$NH_2$ |
| 2 | 108 | - | 9.7064 | Twist NH-$NH_2$ |
| 3 | 138 | - | 5.1037 | Twist NH-$NH_2$ |
| 4 | 187 | - | 3.9742 | Out of plane twisting in whole molecule |
| 5 | 199 | - | 3.1739 | Twist NH-$NH_2$ |
| 6 | 226 | - | 8.4174 | Twist NH-$NH_2$ |
| 7 | 282 | - | 71.7845 | Twist NH-$NH_2$ |
| 8 | 313 | - | 9.9433 | Twist $NH_2$ |
| 9 | 358 | - | 5.9474 | Twist $NH_2$ |
| 10 | 373 | - | 8.0188 | Benzene ring twist from joint |
| 11 | 421 | 423 | 11.5352 | Twist $NH_2$ |
| 12 | 472 | 472 | 8.3219 | Torsion in whole molecule |
| 13 | 498 | 487 | 43.3971 | Twist NH-$NH_2$ |
| 14 | 514 | 520 | 40.4365 | Twist NH-$NH_2$ |
| 15 | 549 | 557 | 22.2618 | Out of plane bending (C-C-H) |
| 16 | 579 | 580 | 15.2978 | Twist NH-$NH_2$ |
| 17 | 597 | - | 4.6665 | Butterfly motion at $C_1$ |
| 18 | 664 | 659 | 12.0686 | Ring deformation |
| 19 | 683 | 675 | 22.5229 | Twist NH-$NH_2$ |
| 20 | 707 | 715 | 0.12 | Out of plane bending in benzene ring |
| 21 | 734 | - | 39.243 | Torsion (C-C-C-C) whole |
| 22 | 801 | 800 | 31.4387 | Out of plane (C-C-H) whole |
| 23 | 834 | 817 | 15.3781 | Out of plane(C-C-H) whole |
| 24 | 842 | - | 119.8694 | Twist $NH_2$ |
| 25 | 860 | 866 | 43.8047 | β(C-C-C) whole |
| 26 | 924 | 958 | 0.3791 | Out of plane bending (C-C-H) |
| 27 | 1026 | 1035 | 5.8778 | β(C-C-H) whole |
| 28 | 1059 | 1051 | 18.3236 | Ring Breathing |
| 29 | 1105 | 1091 | 28.7061 | β(C-C-C)+ β(C-C-H) whole |
| 30 | 1110 | 1118 | 24.2967 | $\beta(C_4\text{-}C_5\text{-}H_{18})+ \beta(C_7\text{-}C_6\text{-}H_{16})$ |
| 31 | 1217 | - | 3.395 | $\beta(C_4\text{-}C_5\text{-}H_{18})+ \beta(C_7\text{-}C_6\text{-}H_{16})$ |
| 32 | 1241 | - | 65.5535 | $\beta(C_4\text{-}C_5\text{-}H_{18})+ \beta(C_7\text{-}C_6\text{-}H_{16})$ |
| 33 | 1256 | - | 11.2814 | Twist $NH_2$ |
| 34 | 1280 | 1267 | 25.1393 | ν (C-C) in benzene ring |
| 35 | 1301 | 1300 | 40.1762 | $\nu\ (C_1\text{-}N_{10})$ |
| 36 | 1376 | 1379 | 14.1543 | $\beta(C_4\text{-}C_3\text{-}H_{15})+ \beta(C_4\text{-}C_5\text{-}H_{18})$ |
| 37 | 1399 | 1402 | 39.2882 | $\beta(N_{11}\text{-}N_{10}\text{-}H_{14})$ |
| 38 | 1420 | 1425 | 168.599 | $\beta(C_4\text{-}C_3\text{-}H_{15})+ \beta(C_7\text{-}C_6\text{-}H_{16})$ |
| 39 | 1529 | 1527 | 82.181 | ν (C-C) in benzene ring |
| 40 | 1539 | 1551 | 121.3791 | ν (C-C) in benzene ring |
| 41 | 1586 | 1557 | 135.0449 | ν (C-C) in benzene ring |
| 42 | 1641 | 1651 | 127.1402 | $S\ (H_{13}\text{-}N_{11}\text{-}H_{12})$ |
| 43 | 3073 | 3074 | 2.5397 | $\nu\ (C_5\text{-}H_{18})+ \nu\ (C_6\text{-}H_{16})$ |
| 44 | 3084 | - | 0.7166 | $\nu\ (C_3\text{-}H_{15})$ |
| 45 | 3088 | - | 3.9547 | $\nu\ (C_5\text{-}H_{18})+ \nu(C_6\text{-}H_{16})$ |
| 46 | 3344 | 3356 | 1.6245 | $\nu\ (N_{11}\text{-}H_{13})+(N_{11}\text{-}H_{12})$ |
| 47 | 3405 | 3398 | 41.8012 | $\nu\ (N_{10}\text{-}H_{14})$ |
| 48 | 3445 | 3450 | 8.4869 | $\nu\ (N_{11}\text{-}H_{12}) + \nu\ (N_{11}\text{-}H_{13})$ |

## Electrical, Optical, Dipole moment and Thermo-dynamical properties

Frontier orbital energy gap, i.e. the gap between HOMO and LUMO shows theinteraction of that molecule with other species. Frontier orbital energy gap helps to differentiate thechemical reactivity of the molecules. In case of 1-(5-Chloro-6-fluoro-1, 3-benzothiazol-2-yl)hydrazine& 1-(6-Chloro-1,3-benzothiazol-2-yl)hydrazine, frontier orbital energy gap is 4.447and 4.555eV, respectively and are given in table 4. So it can be concluded that 1-(5-Chloro-6-fluoro-1, 3-benzothiazol-2-yl)hydrazine is the most reactive compound between them.The MESP is a map ofelectrostatic potential on uniform electron density. It is usedto visualize charge or electron density distribution withinthe molecule. The importance of MESP lies in the fact thatit simultaneously displays molecular size, shape as well aspositive, negative, and neutral electrostatic potential regions in terms of color grading.The pictures of HOMO, LUMO, and electrostatic potential for 1-(5-Chloro-6-fluoro-1, 3-benzothiazol-2-yl)hydrazine& 1-(6-Chloro-1,3-benzothiazol-2-yl)hydrazine are shownin Figures 2.

**Table 4 Lowest Energy, HOMO- LUMO Gap (Frontier orbital energy gap) and Dipole Moment of 1-(5-Chloro-6-fluoro-1, 3-benzothiazol-2-yl) hydrazine& 1-(6-Chloro-1, 3-benzothiazol-2-yl) hydrazine by (B3LYP)/ 6-311 G (d, p) method**

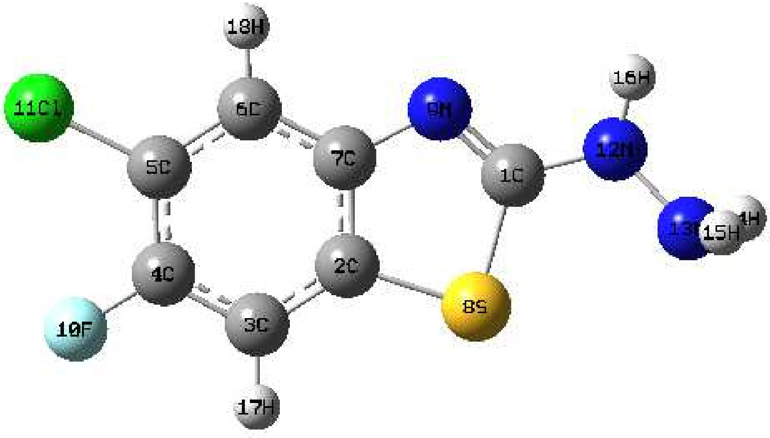
| S.NO. | PARAMETER | 1-(5-Chloro-6-fluoro-1, 3-benzothiazol-2-yl) hydrazine | 1-(6-Chloro-1, 3-benzothiazol-2-yl) hydrazine |
|---|---|---|---|
| 1. | Total Energy E (a.u.) | -1392.3959 | -1293.0702 |
| 2. | Homo | -0.20882 | 4.9019 |
| 3. | Lumo | -0.0439 | -0.03629 |
| 4. | Frontier Orbital Energy Gap | 4.447 eV | 4.555 eV |
| 5. | Dipole Moment | 6.6424 | 4.5551 |

**Table 5 Polarizability and Hyper Polarizability of 1-(5-Chloro-6-fluoro-1, 3-benzothiazol-2-yl) hydrazine& 1-(6-Chloro-1, 3-benzothiazol-2-yl) hydrazine by (B3LYP)/ 6-311 G (d, p) methods**

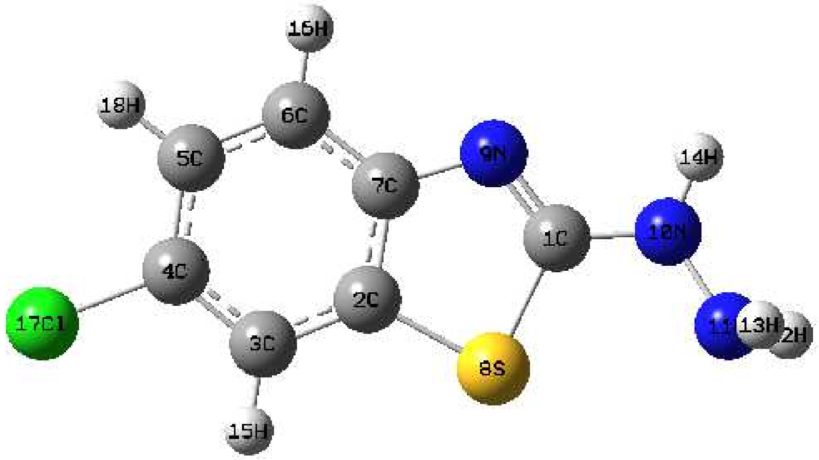
| S.NO. | 1-(5-Chloro-6-fluoro-1, 3-benzothiazol-2-yl) hydrazine | | 1-(6-Chloro-1,3-benzothiazol-2-yl) hydrazine | |
|---|---|---|---|---|
| | **PARAMETERS** | **POLARIZABILITY** | **PARAMETERS** | **POLARIZABILITY** |
| 1. | $\alpha_{xx}$ | -68.1287 | $\alpha_{xx}$ | -61.7672 |
| 2. | $\alpha_{yy}$ | -85.7497 | $\alpha_{xy}$ | -1.9320 |
| 3. | $\alpha_{zz}$ | -88.7856 | $\alpha_{yy}$ | -81.6095 |
| 4. | $\alpha_{xy}$ | 5.4876 | $\alpha_{yz}$ | 0.4604 |
| 5. | $\alpha_{xz}$ | -3.1162 | $\alpha_{zz}$ | -85.4339 |
| 6. | $\alpha_{yz}$ | -0.8495 | $\alpha_{zx}$ | 3.0954 |
| | $\alpha$ | 80.888 | $\alpha$ | 76.2702 |
| | **PARAMETERS** | **HYPER POLARIZABILTY** | **PARAMETERS** | **HYPER POLARIZABILTY** |
| 1. | $\beta_{xxx}$ | -195.4190 | $\beta_{xxx}$ | 199.8635 |
| 2. | $\beta_{yyy}$ | 8.5795 | $\beta_{xxy}$ | 10.4277 |
| 3. | $\beta_{zzz}$ | 2.7621 | $\beta_{xyy}$ | -7.3962 |
| 4. | $\beta_{xyy}$ | -1.8852 | $\beta_{yyy}$ | 0.0570 |
| 5. | $\beta_{xxy}$ | -39.8146 | $\beta_{zzz}$ | 2.4773 |
| 6. | $\beta_{xxz}$ | 12.5077 | $\beta_{xxz}$ | 12.6071 |
| 7. | $\beta_{xzz}$ | -4.2709 | $\beta_{xzz}$ | 14.3063 |
| 8. | $\beta_{yzz}$ | 2.0219 | $\beta_{yzz}$ | -3.3667 |
| 9. | $\beta_{yyz}$ | 1.1396 | $\beta_{yyz}$ | 0.6060 |
| 10. | $\beta_{xyz}$ | 3.2383 | $\beta_{xyz}$ | 1.1155 |
| | $\beta$ | 196.1749 | $\beta$ | 207.7139 |

**Table-6 Calculated Thermodynamic Properties of 1-(5-Chloro-6-fluoro-1, 3-benzothiazol-2-yl) hydrazine& 1-(6-Chloro-1, 3-benzothiazol-2-yl) hydrazine by B3LYP/6-311 G (d, p) methods**

| PARAMETER | E KCal/Mol | | CV Cal/Mol-Kelvin | | S Cal/Mol-Kelvin | |
|---|---|---|---|---|---|---|
| | 1-(5-Chloro-6-fluoro-1, 3-benzothiazol-2-yl) hydrazine | 1-(6-Chloro-1, 3-benzothiazol-2-yl) hydrazine | 1-(5-Chloro-6-fluoro-1, 3-benzothiazol-2-yl) hydrazine | 1-(6-Chloro-1, 3-benzothiazol-2-yl) hydrazine | 1-(5-Chloro-6-fluoro-1, 3-benzothiazol-2-yl) hydrazine | 1-(6-Chloro-1, 3-benzothiazol-2-yl) hydrazine |
| **TOTAL ENERGY** | 81.288 | 85.875 | 42.683 | 39.757 | 105.133 | 100.807 |
| **TRANSLATIONAL** | 0.889 | 0.889 | 2.981 | 2.981 | 42.027 | 41.769 |
| **ROTATIONAL** | 0.889 | 0.889 | 2.981 | 2.981 | 32.048 | 31.502 |
| **VIBRATIONAL** | 79.510 | 84.097 | 36.721 | 33.795 | 31.058 | 27.536 |



**1-(5-Chloro-6-fluoro-1, 3-benzothiazol-2-yl) hydrazine**



**1-(6-Chloro-1, 3-benzothiazol-2-yl) hydrazine**

**Fig1- Model Molecular structures of 1-(5-Chloro-6-fluoro-1, 3-benzothiazol-2-yl) hydrazine& 1-(6-Chloro-1, 3-benzothiazol-2-yl) hydrazine**

Dipole moment (μ), polarizability<α>and total first static hyperpolarizabilityβ[20, 21] can be expressed (table 5) in terms of *x*, *y*, *z* components and are given by following equations 1, 2 and 3-

$$\mu = (\mu_x^2 + \mu_y^2 + \mu_z^2)^{1\backslash 2} \text{-----------------------} [1]$$

$$<\alpha> = 1\backslash 3\ [\alpha_{xx} + \alpha_{yy} + \alpha_{zz}] \text{-----------------} [2]$$

$$\beta_{Total} = (\beta_x^2 + \beta_y^2 + \beta_z^2)^{1\backslash 2} = [(\beta_{xxx} + \beta_{xyy} + \beta_{xzz})^2 + (\beta_{yyy} + \beta_{yxx} + \beta_{yzz})^2 + (\beta_{zzz} + \beta_{zxx} + \beta_{zyy})^2]^{1\backslash 2} \text{---} [3]$$

The β components of Gaussian output are reported in atomic units.

Where (1 a.u. = 8.3693*10$^{-33}$e.s.u.).The calculated dipole moments for 1-(5-Chloro-6-fluoro-1, 3-benzothiazol-2-yl)hydrazine& 1-(6-Chloro-1,3-benzothiazol-2-yl)hydrazine are 6.6424, and 4.5551 Debye respectively.So, 1-(5-

Chloro-6-fluoro-1, 3-benzothiazol-2-yl)hydrazineis a better solvent between them.A greater contribution of $\alpha_{zz}$ is seen in 1-(5-Chloro-6-fluoro-1, 3-benzothiazol-2-yl)hydrazine&1-(6-Chloro-1,3-benzothiazol-2-yl)hydrazine both. For 1-(5-Chloro-6-fluoro-1, 3-benzothiazol-2-yl)hydrazine& 1-(6-Chloro-1,3-benzothiazol-2-yl)hydrazine, molecules are elongated more towards Z direction and more contracted in the X direction. $\beta_{xxx,}$ contributes alarger part of hyperpolarizibity in both the molecules. This shows that X-axis is more optically active.The values of hyperpolarizability indicate a possible use of these compounds in electro-optical applications.

Internal thermal energy (*E*), constant volume heat capacityCv, and entropy *S*, calculatedat B3LYP/6-311G (d, p) level, are listed in Table 6. We know that, conduction band isalmost empty at the room temperature, so electronic contribution in total energy isnegligible. Thermodynamic properties show thatvibrational motion plays an important role.

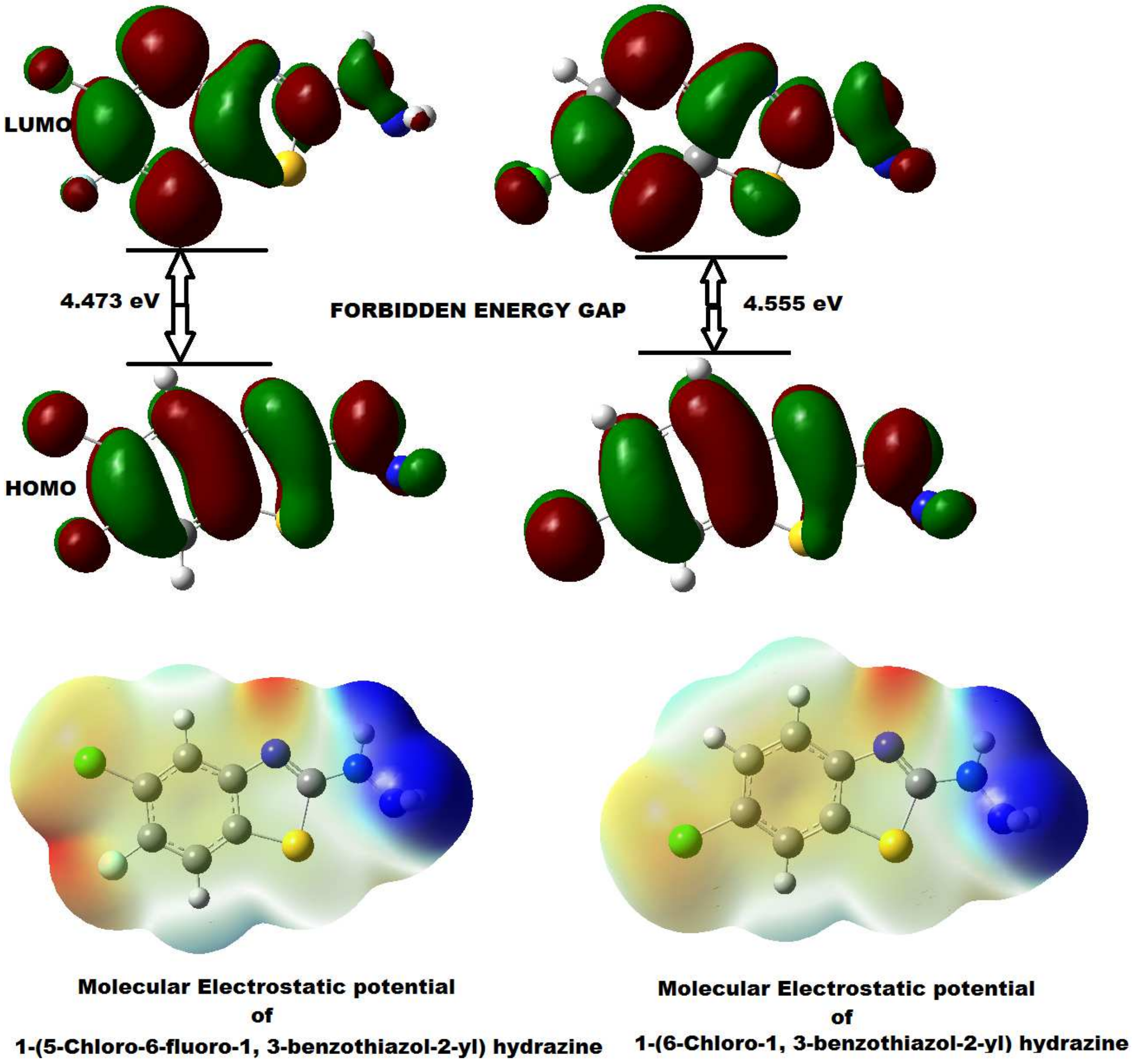


**Fig-2 Pictures of HOMO-LUMO and Molecular Electrostatic Potential of 1-(5-Chloro-6-fluoro-1, 3-benzothiazol-2-yl) hydrazine& 1-(6-Chloro-1, 3-benzothiazol-2-yl) hydrazine**

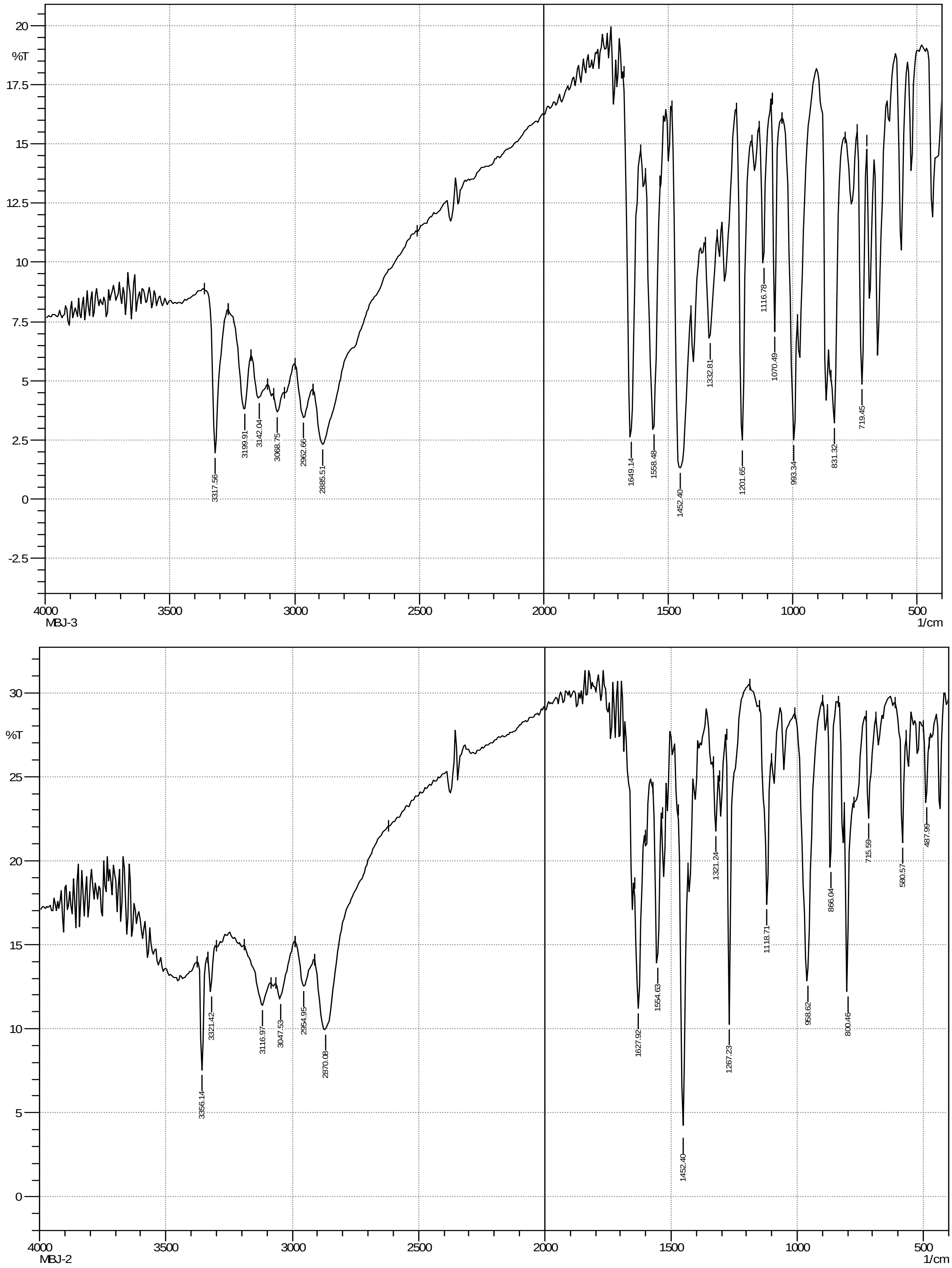


**Fig-3 Experimental FTIR spectra of 1-(5-Chloro-6-fluoro-1, 3-benzothiazol-2-yl) hydrazine& 1-(6-Chloro-1, 3-benzothiazol-2-yl) hydrazine**

## CONCLUSION

We have carried out a density functional theory calculation on 1-(5-Chloro-6-fluoro-1, 3-benzothiazol-2-yl) hydrazine &1-(6-Chloro-1, 3-benzothiazol-2-yl) hydrazine both. The calculated parameters show a good correlation with the corresponding experimental data thereby showing the validity of calculations. We have presented a complete normal mode analysis (vibrational assignments) using DFT/B3LYP/6-311 G (d, p) as the basis set. Normal modes are compared with the experimental data i.e. FTIR spectrum. The chemical reactivity is discussed by HOMO-LUMO as well as MESPanalysis.The lower value of frontierorbital energy gap of 1-(5-Chloro-6-fluoro-1, 3-benzothiazol-2-yl) hydrazine suggestsitsmore reactive nature as compared to1-(6-Chloro-1, 3-benzothiazol-2-yl) hydrazine. Mostly Hyper polarizability is controlled by bond length alteration,the donor and accepter strength and theplanarity of the molecules. The values of hyper polarizability show a probable use of these compounds in electro-opticalapplications.

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