



Ab-initio study of '2-(3-bromo phenyl)1,3-dithian by density functional theory

Abhishek Bajpai¹, Anoop Kumar Pandey² and Vijay Narayan Mishra³

¹Govt P. G. College, Jagadapur C.G.

²Govt. D. P. G. College, Dantewada(C.G.)

³Shri Ram Shwaroop Memorial Group of Professional Colleges, Lucknow

ABSTRACT

In this paper we perform quantum chemical calculation on 2-(3-BROMO PHENYL)1,3-DITHIAN molecule. We designed this molecule by using X-ray diffraction method and geometry optimized by combination of DFT/B3LYP method and 6-311G(d,p) method with out any symmetry constrain. Normal mode analysis were done by animated gauss view. Calculated frequency were scaled by a scaling factor to compare with experimental one. Electronic properties of given molecule also predicated by using HOMO,LUMO, orbital and MESP surfaces. Our finding are experimental and calculated geometry are well matched with each other. Electronic parameter shows that benzene ring acts as most nucleophile charge center.

INTRODUCTION

Vibrational spectroscopy plays important role in field of physics and chemistry as well as in other areas of science. Its important applications are to study intra molecular and inter molecular forces, molecular structure determination, computation of degree of association in condensed phases, elucidation of molecular symmetries, identification and characterization of new molecules, deducing thermodynamical properties of molecular system, etc.[1-9]. A dithiane is a heterocyclic compound composed of a cyclohexane core structure wherein two methylene bridges (-CH₂- units) are replaced by sulfur centres. The three isomeric parent heterocycles are 1,2-dithiane, 1,3-dithiane and 1,4-dithiane. 1,3-Dithianes are protecting group of some carbonyl-containing compounds due to their inertness to many conditions. They form by treatment of the carbonyl compound with 1,3-propanedithiol under conditions that remove water from the system.[10]. Title compound is derivatives of 1,3-dithiane in which dithiane molecule are joined with phenyl ring as well as Bromine group are attached in 2,3 position of phenyl group. In this process the chemical as well physical and electronic properties are different from dithianemolecule. To study how these properties are change due to attachment of these group we study, Theoretical FT-IR and of the title molecule thermodynamic properties and electronic properties of title compound are reported with Density Functional B3LYP method. To gain a better understanding of the performance and limitation of DFT/B3LYP method, as a general approach to the vibrational problems of organic molecules, we calculated harmonic frequencies of 2-(3-BROMO PHENYL)1,3-DITHIAN by this method and compared these results with observed fundamental vibrational frequencies. The purpose of this study assumes importance because of the further work on 2-(3-BROMO PHENYL)1,3-DITHIAN, in which presumably some modification by chemical reaction such as oxidation/reduction on polyfunctional bioactive natural product will generate new reactive site in the molecule, which can be exploited for elaborating and appending pharmacophores to generate patentable compounds of biological

COMPUTATIONAL DETAILS

The DFT calculations have been performed at B3LYP/6-31G (d, p) [11-16] level has been employed for the computation of molecular structure, vibrational frequencies, HOMO-LUMO, and energies of the optimized structures, using G03 program [17], involving gradient optimized geometry [18]. The basis set 6-311G (d, p)

augmented by d polarization functions on heavy atoms and p polarization functions on hydrogen atoms as well as diffuse functions for both hydrogen and heavy atoms were used. Initial geometry was generated from standard geometrical parameters and was minimized without any constraint in the potential energy surface.

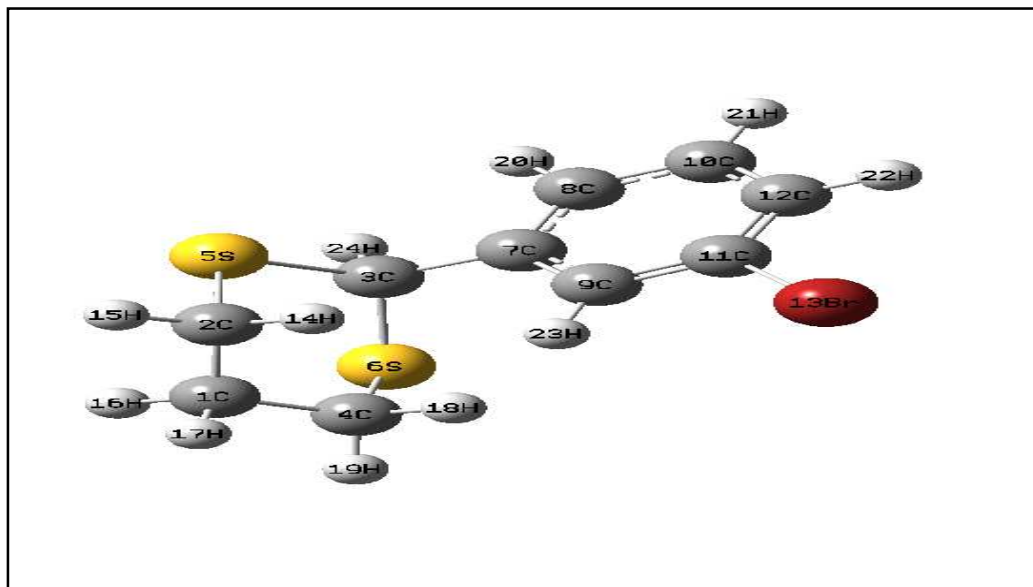


Fig-1 Molecular picture as molding of title molecule

RESULTS AND DISCUSSION

In the title compound, $C_{10}H_{11}BrS_2$, the 1,3-dithiane ring has a chair conformation with the 1,4-disposed C atoms being above and below the remaining four atoms. The bromobenzene ring occupies an equatorial position and forms a dihedral angle of $86.38(12)^\circ$ with the least-squares plane through the 1,3-dithiane ring. Experimental crystal structure taken from literature [11] Nearly all the calculated bond length match well with the experimental values. For example, the optimized bond lengths of C-C in ring R_1 falls in the range from 1.37\AA to 1.41\AA , which are in good agreement with the experimental bond lengths. The optimized bond lengths of C-S in ring R_2 falls in the range from 1.81\AA to 1.85\AA , which are also in good agreement with those of the experimental bond lengths. However, in the rings carbon-carbon bond lengths are not same (same type hybridization) this is due to antibonding repulsion between carbon and Sulfur atoms present in the ring and also the group attached to the ring. To achieve molecular stability they minimized strain so a compromised occurred consequently some bond length are enlarged however some bond lengths are contracted. Bond length in the ring has also shown characteristic variation but they have been small and less well pronounced as compared to the angular changes. The angular changes in benzene ring geometry have proved to be a sensitive indicator of the interaction between the substituent and the benzene ring [19].

Vibrational modes analysis

The molecule has C_1 point group symmetry and 24 atoms and 66 normal modes of fundamental vibration. Out of these N-1 are stretching modes and remaining are bending modes so 23 modes are corresponding to stretching and 43 modes are bending modes. Whole modes of frequencies are divided in two parts, above 1000 cm^{-1} are called functional region and below 1000 cm^{-1} are called fingerprint region. Detailed description of vibrational modes can be given by means of normal coordinate analysis. The calculated normal mode vibrational frequencies provide thermodynamic properties by way of statistical mechanics by combining the results of the GAUSSVIEW'S program [20]. It is well known that vibrational frequencies obtained by quantum chemistry calculation are typically larger than that of their experimental counterpart and thus experimental scaling factors of .9648 are usually employed to have better agreement with the experimental vibrational frequencies [21]. The scaling factor depends on both basis set and method used in the calculation and are determined from the mean deviation between calculated and experimental value of frequencies [22,23].

TABLE-1 Bond Length (Å) and Bond Angle Of 2-(3-BROMO PHENYL)1,3-DITHIAN

| S.NO. | PARAMETER | EXPERIMENTAL VALUE | CALCULATED VALUE |
|--------------------|------------|--------------------|------------------|
| Bond length | | | |
| 1. | (C1-C2) | 1.507 | 1.5179 |
| 2. | (C1-C4) | 1.515 | 1.5173 |
| 3. | (C1-H16) | 0.9700 | 1.093 |
| 4. | (C1-H17) | 0.9700 | 1.1092 |
| 5. | (C2-S5) | 1.803 | 1.8201 |
| 6. | (C2-H14) | 0.9700 | 1.107 |
| 7. | (C2-H15) | 0.9700 | 1.1079 |
| 8. | (C3-S5) | 1.810 | 1.8353 |
| 9. | (C3-S6) | 1.811 | 1.8317 |
| 10. | (C3-C7) | 1.505 | 1.4951 |
| 11. | (C3-H24) | 0.9800 | 1.12 |
| 12. | (C4-S6) | 1.803 | 1.8215 |
| 13. | (C4-H18) | 0.9700 | 1.1119 |
| 14. | (C4-H19) | 0.9700 | 1.1063 |
| 15. | (C7-C8) | 1.389 | 1.4007 |
| 16. | (C7-C9) | 1.383 | 1.3992 |
| 17. | (C8-C10) | 1.385 | 1.3913 |
| 18. | (C8-H20) | 0.9300 | 1.097 |
| 19. | (C9-C11) | 1.381 | 1.3788 |
| 20. | (C9-H23) | 0.9300 | 1.1011 |
| 21. | (C10-C12) | 1.371 | 1.3925 |
| 22. | (C10-H21) | 0.9300 | 1.0951 |
| 23. | (C11-C12) | 1.375 | 1.3803 |
| 24. | (C11-BR13) | 1.897 | 1.8684 |
| 25. | (C12-H22) | 0.3900 | 1.0945 |

Bond Angles

| | | | |
|-----|----------------|--------|----------|
| 26. | (C2-C1-C4) | 113.5 | 112.4779 |
| 21. | (C2-C1-H16) | 108.6 | 110.3231 |
| 22. | (C2-C1-H17) | 108.6 | 108.8631 |
| 23. | (C4-C1-H16) | 108.9 | 110.2763 |
| 24. | (C4-C1-H17) | 108.9 | 108.8979 |
| 25. | (H16-C1-H17) | 107.7 | 105.7613 |
| 26. | (C1-C2-S5) | 114.8 | 114.6868 |
| 27. | (C1-C2-H14) | 108.9 | 110.293 |
| 28. | (C1-C2-H15) | 108.9 | 110.2238 |
| 29. | (S5-C2-H14) | 108.6 | 110.3017 |
| 30. | (S5-C2-H15) | 108.6 | 104.6352 |
| 31. | (H14-C2-H15) | 107.5 | 106.2386 |
| 32. | (S5-C3-S6) | 113.16 | 114.1738 |
| 33. | (S5-C3-C7) | 109.74 | 112.2819 |
| 34. | (S5-C3-H24) | 107.9 | 103.1387 |
| 35. | (S6-C3-C7) | 110.01 | 114.4447 |
| 36. | (S6-C3-H24) | 107.9 | 102.9457 |
| 37. | (C7-C3-H24) | 107.9 | 108.5857 |
| 38. | (C1-C4-S6) | 113.8 | 114.5929 |
| 39. | (C1-C4-H18) | 108.8 | 110.133 |
| 40. | (C1-C4-H19) | 108.8 | 110.4234 |
| 41. | (S6-C4-H18) | 108.8 | 109.71 |
| 42. | (S6-C4-H19) | 108.8 | 105.0388 |
| 43. | (H18-C4-H19) | 107.7 | 106.5423 |
| 44. | (C2-S5-C3) | 98.61 | 103.8718 |
| 45. | (C3-S6-C4) | 98.59 | 103.3156 |
| 46. | (C3-C7-C8) | 121.5 | 118.8331 |
| 47. | (C3-C7-C9) | 119.3 | 112.1459 |
| 48. | (C8-C7-C9) | 119.2 | 119.02 |
| 49. | (C7-C8-C10) | 119.8 | 120.9814 |
| 50. | (C7-C8-H20) | 120.1 | 119.7839 |
| 51. | (C10-C8-H20) | 120.1 | 119.2345 |
| 52. | (C7-C9-C11) | 119.7 | 118.2824 |
| 53. | (C7-C9-H23) | 120.1 | 121.7517 |
| 54. | (C11-C9-H23) | 120.1 | 119.9584 |
| 55. | (C8-C10-C12) | 121.2 | 120.2004 |
| 56. | (C8-C10-H21) | 119.4 | 119.8713 |
| 57. | (C12-C10-H21) | 120.7 | 119.9284 |
| 58. | (C9-C11-C12) | 121.5 | 123.9205 |
| 59. | (C9-C11-BR13) | 118.53 | 117.8286 |
| 60. | (C12-C11-BR13) | 120.0 | 118.2508 |
| 61. | (C10-C12-C11) | 118.6 | 117.5934 |
| 62. | (C10-C12-H22) | 119.4 | 121.9382 |
| 63. | (C11-C12-H23) | 120.7 | 120.4683 |

TABLE-3 Calculated Wave Numbers and it's Respective IR Intensity of 2-(3-BROMO PHENYL)1,3-DITHIAN

| S.N. | Frequency | IR intensity | Vibrational Assignment |
|------|-----------|--------------|---------------------------------------|
| 1 | 30 | 0.9915 | τ (C2-C1-C4-S6) |
| 2 | 66 | 0.9412 | τ (C2-C1-C4-S6) |
| 3 | 86 | 0.3615 | ω (H14-C2-H15) |
| 4 | 118 | 4.1845 | τ (C4-C1-C2-S5) |
| 5 | 157 | 0.3045 | ω (C11-Br13) |
| 6 | 189 | 1.6223 | S(H15-C2-H14) + γ (C1-C2) |
| 7 | 228 | 1.8368 | S(H15-C2-H14) |
| 8 | 251 | 1.7949 | γ (C9-C11) |
| 9 | 280 | 1.7415 | γ (H17-C1-H16) |
| 10 | 304 | 2.3248 | ν (C1-H16) |
| 11 | 331 | 0.2342 | τ (C11-C9-C7-C3) |
| 12 | 333 | 2.691 | τ (H16-C1-C4-H19) |
| 13 | 392 | 0.832 | γ (C10-H21) |
| 14 | 400 | 1.5569 | γ (C10-H21) |
| 15 | 457 | 0.1361 | τ (H16-C1-C4-H18) |
| 16 | 531 | 0.9883 | γ (C12-H22) |
| 17 | 602 | 7.6831 | γ (C3-H7) + γ (C12-H22) |
| 18 | 636 | 17.8482 | γ (C8-H20) |
| 19 | 648 | 2.2422 | γ (C1-H17)+ γ (C8-H20) |
| 20 | 677 | 10.7149 | R(H17-C1-H16) |
| 21 | 682 | 20.4597 | β (C1-H17) |
| 22 | 728 | 18.8086 | ν (S5-C3) |
| 23 | 770 | 45.5193 | ν (S6-C3) |
| 24 | 800 | 3.9586 | β (C12-H22) |
| 25 | 830 | 2.1029 | S(H14-C2-H15) |
| 26 | 868 | 15.7285 | τ (C4-H19-H18-C1) |
| 27 | 911 | 2.0319 | β (C12-H22) |
| 28 | 926 | 16.874 | ω (C3-H24) |
| 29 | 936 | 5.0797 | ω (C9-H23) |
| 30 | 948 | 11.036 | τ (C1-H17-H16-C2) |
| 31 | 974 | 0.0678 | β (H14-C2-H15) |
| 32 | 985 | 1.2886 | β (C10-H21) |
| 33 | 1009 | 0.9926 | ω (C3-H24) |
| 34 | 1028 | 14.9869 | β (C3-H24) + β (C9-H23) |
| 35 | 1058 | 0.2887 | β (C3-H24) |
| 36 | 1069 | 0.79975 | β (C12-H22) |
| 37 | 1083 | 0.6843 | β (H16-C1-H17) |
| 38 | 1086 | 1.2813 | β (C10-H21) |
| 39 | 1109 | 0.3933 | β (H16-C1-H17) |
| 40 | 1123 | 1.3827 | β (C8-H20) + β (C10-H21) |
| 41 | 1128 | 0.589 | β (C2-H14) + β (C4-H18) |
| 42 | 1152 | 1.7359 | β (C3-H24) + β (C9-H23) |
| 43 | 1182 | 1.1101 | β (C9-H23) |
| 44 | 1196 | 31441 | β (C9-H23) |
| 45 | 1230 | 6.5523 | β (H18-C4-H19) |
| 46 | 1298 | 0.3442 | β (C9-C7) |
| 47 | 1303 | 1.3967 | S(H14-C2-H15) |
| 48 | 1349 | 4.2874 | S(H16-C1-H17) |
| 49 | 1351 | 28.4239 | S(H17-C1) |
| 50 | 1358 | 4.7522 | S(H17-C1-H16) |
| 51 | 1390 | 4.8241 | S(H19-C4-H18) |
| 52 | 1516 | 46.2083 | ν (C9-C11) + ν (C11-C12) |
| 53 | 1660 | 7.1159 | Butterfly motion in 6 membered ring |
| 54 | 1732 | 21.1627 | ν (C9-C7) |
| 55 | 1775 | 0.5853 | ν (C12-C10) |
| 56 | 2816 | 49.7385 | ω (C3-H24) |
| 57 | 2890 | 3.3643 | ν (H17-C1-H16) |
| 58 | 2900 | 16.3919 | ν (H19-C4-H18) |
| 59 | 2917 | 14.2707 | ν (H15-C2-H14) |
| 60 | 2966 | 7.8823 | ν (H17-C1-H16) |
| 61 | 2974 | 6.1848 | ν (C4-H19) + ν (C9-H23) |
| 62 | 2983 | 14.399 | ν (C8-H20) |
| 63 | 2987 | 15.7249 | ν (C2-H15) |
| 64 | 2991 | 48.4965 | ν (C9-H23) |
| 65 | 3002 | 25.5815 | ν (C10-H21) |
| 66 | 3018 | 47.2122 | ν (C12-H22) |

ν : Stretching; ν_s : symmetric stretching ν_{as} : asymmetric stretching, β : -in plane bending; γ : out of plane bending, w-wagging, τ : torsion, S: scissoring, R:rocking

C-H Vibrations

The hetero aromatic structure shows the presence of C-H stretching vibrations in the region 3000-3100 cm^{-1} , which is the characteristic region for the ready identification of the C-H stretching vibration [24]. In the present study the C-H stretching vibrations of the title compound are observed at 3018 and 3002 cm^{-1} , which polarized along ring R1. Some other C-H stretching vibrations are also calculated at 2991, 2987, 2951, cm^{-1} , which are also supported by the literature [25]. Some bending vibrations of C-H are also calculated and supported by literature. A strong band

appears due to mixing of several modes along with C-H in plane bending modes at 682 cm^{-1} , In the lower frequency region some significant intensity peaks of polarized IR due to out of plane bending in C-H.

Methylene Group Vibrations

The asymmetric CH_2 stretching vibrations are generally observed in the region $3100\text{-}3000\text{ cm}^{-1}$, while the symmetric stretching vibrations are generally observed between $3000\text{-}2900\text{ cm}^{-1}$ [26]. Two intense CH_2 antisymmetric stretching vibrations are calculated at 2987 and 2966 cm^{-1} , Whereas, CH_2 symmetric stretching vibrations are also calculated at $2917, 2983\text{ cm}^{-1}$. The bands corresponding to different bending vibrations of CH_2 group are summarized in Table 2 and are supported by literature [27].

C-C Vibrations

The C-C aromatic stretch known as semi-circle stretching, calculated at $1732, 1775, 1516, 1303\text{ cm}^{-1}$ may be described as opposite quadrant of ring stretching. The theoretically calculated C-C-C bending modes and C-C torsional modes have been found to lower region of spectra

TABLE-3 Thermodynamic Properties of Title molecule

| PARAMETER | E (Thermal) Kcal/Mol | CV Cal/Mol-Kelvin | S Cal/Mol-Kelvin |
|---------------|----------------------|-------------------|------------------|
| Total | 122.500 | 47.345 | 113.665 |
| Translational | 0.889 | 2.981 | 42.722 |
| Rotational | 0.889 | 2.981 | 33.141 |
| Vibrational | 120.722 | 41.383 | 37.801 |

Electronic Properties:

The interaction with other species in a chemical system is also determined by frontier orbitals, HOMO and LUMO. It can also be determined by experimental data. The frontier orbital gap helps to distinguish the chemical reactivity and kinetic stability of the molecule. A molecule which has a larger orbital gap is more polarized having reactive part as far as reaction is concerted [28]. The frontier orbital gap in case of the given molecule is 0.239 eV for title molecule given in Table 4.

The contour plots of the HOMO, LUMO structure of the molecules are shown in Figure 2, 3. HOMO primary acts as donor and LUMO acts as acceptor. In title molecule both HOMO LUMO orbital lies on whole molecule except LUMO does not contain that carbon which connects bromine of benzene ring. The transition from HOMO \rightarrow LUMO in given molecule indicates charge transfer Benzene ring. The importance of MESP lies in the fact that it simultaneously displays molecular size, shape as well as positive, negative, and neutral electrostatic potential region in terms of grading and is very useful in the investigation of molecular structure with its physiochemical property relationship [29]. The MESP diagram is shown in Figure 4. The different values of the electrostatic potential at the surface are represented by different colors: red represents regions of most negative electrostatic potential, blue represents regions of most positive electrostatic potential, and green represents regions of zero potential. Potential increases in the order: red < orange < yellow < green < blue. In all cases, the shape of the electrostatic potential surface is influenced by the structure and charge density distributions in the molecule with sites close to the carbon atom of benzene ring, showing regions of most negative electrostatic potential

TABLE-4 Total energy, Dipole Moment, Homo, Lumo and Energy gap of 2-(3-BROMO PHENYL)1,3-DITHIAN

| PARAMETERS | VALUE |
|----------------------------------|-----------|
| Total Energy E (a.u.) | 0.6316949 |
| Dipole moment (Debye) | 1.4375 |
| Lumo | -0.05228 |
| Homo | -0.29167 |
| Frontier orbital Energy Gap (eV) | 0.239239 |

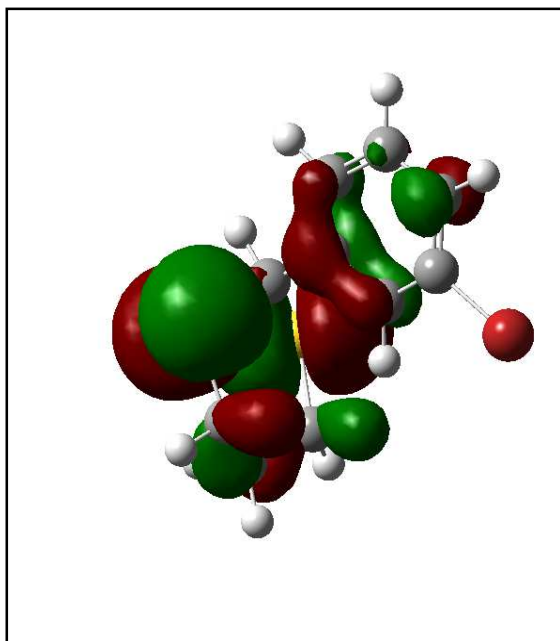


FIG-2 HOMO

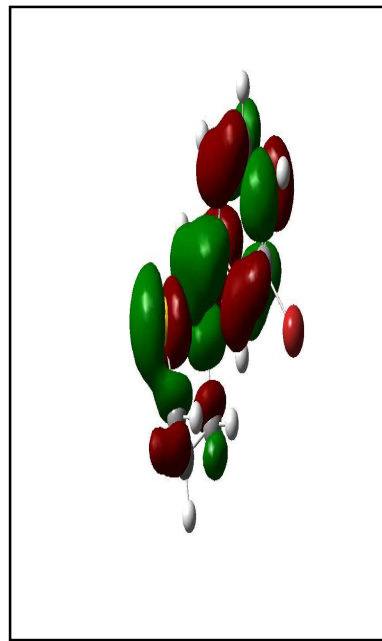


FIG-3 LUMO

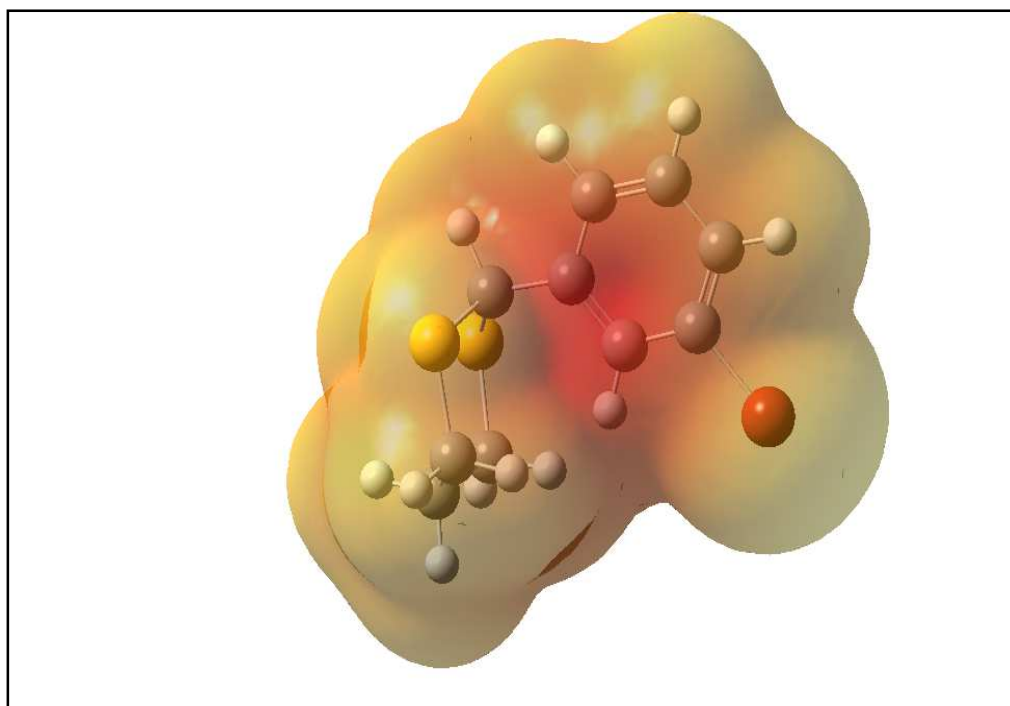


FIG-4 MESP Plot

CONCLUSION

The frequency assignments for 2-(3-BROMO PHENYL)1,3-DITHIAN have been made for the first time. The equilibrium geometry and harmonic frequencies 2-(3-BROMO PHENYL)1,3-DITHIAN were determined and analyzed at the DFT level of the theory using the 6-311G (d, p) basis set. Electronic properties show the reactivity of molecule with the help of HOMO-LUMO gap. Electronic parameter shows that benzene ring shows most nucleophile charge center. Thermodynamical parameter shows that vibrational motion plays significant role in thermal properties.

Acknowledgment

One of author A. K. Bajpai gave special thanks to provide financial support of UGC, New Delhi, by Minor research project.

REFERENCES

- [1] D.H.Williams, L.Fleming, Spectroscopic Methods in organic chemistry, Tata Mcgraw Hill publishing Company Ltd, V edition **1998**.
- [2] C.N. Banwell, Elaine M. McCash, Fundamental of molecular spectroscopy, Tata Mcgraw Hill publishing Company Ltd, V edition **1995**.
- [3] Apoorva Dwivedi, Ambrish Srivastava, Abhishek Bajpai, *spectrochimica acta part A: molecular and biomolecular spectroscopy*, 149, (2015), 343-351.
- [4] Apoorva Dwivedi, Anoop Kumar Pandey, Neeraj Misra, *Spectroscopy: An International Journal* Volume 27 (2012), Issue 3, Pages 155–166 doi:10.1155/2012/486304.
- [5] Apoorva Dwivedi, Anoop Kumar Pandey, Neeraj Misra, *Spectroscopy: An International Journal* 26 (2011) 367–385.
- [6] Apoorva Dwivedi and Neeraj Misra, *Der Pharma Chemica*, **2010**, 2(2): 58-65. [ISSN 0975-413X].
- [7] Neeraj Misra, Apoorva Dwivedi, Anoop Kumar Pandey, Sanjeev Trivedi, *Der Pharma Chemica*, **2011**, 3(3):427-448.
- [8] Anoop Kumar Pandey, Apoorva Dwivedi, Neeraj Misra, *Spectroscopy*, Volume **2013** (2013), Article ID 937915, 11 pages.
- [9] Anoop Pandey, Shamoona Siddiqui, Apoorva Dwivedi, Neeraj Misra, Kanwal Raj, *Spectroscopy* 25 (2011) 287–302.
- [10] E. J. Corey, D. Seebach (1988). *Org. Synth.*; Coll. Vol. 6, p. 556
- [11] Crystal structure of 5-(1,3-dithian-2-yl)-2H-1,3-benzodioxole Julio Zukerman-Schpector, et al. *Acta Cryst.* (2015). E71, o167–o168
- [12] R.O. Jones, O. Ounnarson, *Rev. Mol. Physics* 61 (1989) 689.
- [13] T. Ziegler, *Che. Rev* 91 (1991) 651.
- [14] W. Kohan, L.J. Sham, *Phys. Rev A* 140 (1965) 1133.
- [15] A.D. Becke, *J. Chem. Phys* 98 (1993) 5648.
- [16] C. Lee, W. Yang, R.G. Parr, *Phys. Rev B* 37 (1988) 785.
- [17] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, J.A. Montgomery Jr., T. Vreven, K.N. Kudin, J.C. Burant, J.M. Millam, S.S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G.A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J.E. Knox, H.P. Hratchian, J.B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, P.Y. Ayala, K. Morokuma, G.A. Voth, P. Salvador, J.J. Dannenberg, V.G. Zakrzewski, S. Dapprich, A.D. Daniels, M.C. Strain, O. Farkas, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J.V. Ortiz, Q. Cui, A.G. Baboul, S. Clifford, J. Cioslowski, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, M. Challacombe, P.M.W. Gill, B. Johnson, W. Chen, M.W. Wong, C. Gonzalez, J.A. Pople, Gaussian 03 Revision C.02, Gaussian Inc., Pittsburgh, PA, **2003**.
- [18] H.B. Schlegel, *J. Comput. Chem* 3 (1982) 214.
- [19] A. Kovacs, I. Hargittai, *Structural Chemistry* 11 Nos.2/3 (2000).
- [20] A. Frisch, A.B. Nelson, A.J. Holder, GAUSSVIEW Inc. Pittsburgh PA, **2000**.
- [21] J.P. Merrick, D. Moran, L. Radom, *J. Phys. Chem. A* 111 (2007) 11683e11700.
- [22] G. Rauhut, P. Pulay, *J. Phys. Chem* 99 (1995) 3093.
- [23] P. Sinha, S.E. Boesch, C. Gu, R.A. Wheeler, A.K. Wilson, *J. Phys. Chem. A* 108 (2004) 9213.
- [24] A.D. Becke, *J. Chem. Phys* 98 (1993) 5648
- [25] N. Sundaraganesan, H. Saleem, S. Mohan, M. Ramalingam, V. Sethuraman, *Spectrochimica Acta Part A* 62 (2005) 740–751
- [26] V. Krishnakumar and R. John Xavier, *Indian J. Pure Appl. Phys.*, 41, 597-601 (2003).
- [27] V. Krishnakumar, R. John Xavier and T. Chithambarathanu, *Spectrochimica Acta*, A62, 931-939 (2005).
- [28] I. Fleming, *Frontier Orbitals and Organic Chemical Reactions*, John Wiley & Sons, New York, NY, USA, **1976**.
- [29] J. Spöner and P. Hobza, *International Journal of Quantum Chemistry*, vol. 57, no. 5, pp. 959-970, **1996**.