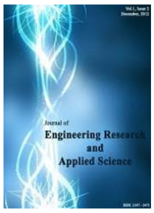
Journal of Engineering Research and Applied Science
Available at www.journaleras.com
Volume 10 (2), December 2021, pp 1843-1847
ISSN 2147-3471 © 2021



DFT studies of structural and nonlinear optical properties of 5-(Trifluoromethyl)pyridine-2-Thiol

H. Vural

Amasya University, Electrical and Electronics Engineering, aMASYA, Turkey.

Accepted 12 September 2021

Abstract

5-(trifluoromethyl)pyridine-2-thiol has been investigated quantum computationally by density functional theory (DFT) approach. The computational investigations were done using the B3LYP and HSEH1PBE hybrid functional combined with 6–311+G(d, p) basis set. Optimized geometry of 5-(trifluoromethyl)pyridine-2-thiol with bond angles and bond lengths has been obtained by using DFT theory. The B3LYP/6–311+G(d, p) and HSEH1PBE/6–311+G(d, p) functionals have been used to determine the molecular electronic dipole moment (μ), mean polarizability (α) and first order hyperpolarizability (β) of 5-(trifluoromethyl)pyridine-2-thiol. The first order hyperpolarizability (β) parameters show that 5-(trifluoromethyl)pyridine-2-thiol is an excellent candidate to NLO materials.

Keywords: DFT, NLO, 5-(trifluoromethyl)pyridine-2-thiol.

1. Introduction

Pyridine, which is a basic heterocyclic organic compound, is structurally related to benzene with one methine group (=CH−) replaced by a nitrogen atom. Due to their pharmacological properties such as antimicrobial [1], antifungal [2, 3] and antitubercular [4], pyridine and its derivatives are preferred in the synthesis of different compounds. Trifluoromethylated organic molecules are greatly used in material science [5], agrochemistry, and biological chemistry [6].

Nonlinear optical (NLO) materials are of great interest due to their potential applications in the field of optoelectronic [7]. DFT computations have made significant contribution to the understanding of the hyperpolarisabilities underlying the molecular NLO processes [8, 9].

Preferring computational methods to investigate many new properties while working on a molecule provides a great advantage in terms of time and cost. DFT has been increasingly used for calculating a wide variety of molecular properties that includes stability structure, charge transfer interactions, transition states, etc. DFT computations have made a significant contribution to the understanding of the quantum chemical properties of 5-(trifluoromethyl)pyridine-2-thiol. In the previous study, the 5-bromo-2-(trifluoromethyl)pyridine was characterized with FTIR and NMR techniques by Vural et al. [10]. They have also reported the effect of the molecule on pBR322 plasmid DNA and antimicrobial activities of 5-bromo-2-(trifluoromethyl)pyridine.

In this study, the molecular structure and nonlinear optical properties have been investigated on 5-(trifluoromethyl)pyridine-2-thiol. The optimized geometric parameters, the dipole moment (μ), mean polarizability (α), and first order hyperpolarizability (β) have been calculated using the DFT (B3LYP and HSEH1PBE) method with 6-311+G (d, p) basis set.

2. Computational details

The quantum chemical calculations for 5-(trifluoromethyl)pyridine-2-thiol were carried out by using GAUSSIAN 09W program packages [11]. The Gauss View 5.0 program was used to generate visual presentation [12]. The geometry of 5-(trifluoromethyl)pyridine-2-thiol was optimized by using the B3LYP [13] (Lee et al., 1988) and HSEH1PBE (The recommended version of the full

[a] Corresponding author; hatice.vural@amasya.edu.tr

Heyd-Scuseria-Ernzerhof functional, referred to as HSE06 in the literature) [14, 15] levels of DFT. The dipole moment (μ), mean polarizability (α), and first order hyperpolarizability (β) of 5-(trifluoromethyl)pyridine-2-thiol in the gas phase were investigated by using DFT (B3LYP and HSEH1PBE) method with the 6–311+G (d, p) basis set.

3. Results and discussion

3.1. Geometry optimization

The optimized geometry of 5-(trifluoromethyl) pyridine-2-thiol was carried out using the B3LYP and HSEH1PBE hybrid functional combined with 6-311+G(d, p) basis set (Fig. 1) The comparative parameters of 5-(trifluoromethyl) pyridine-2-thiol for the DFT (B3LYP and HSEH1PBE) methods are presented in Table 1.

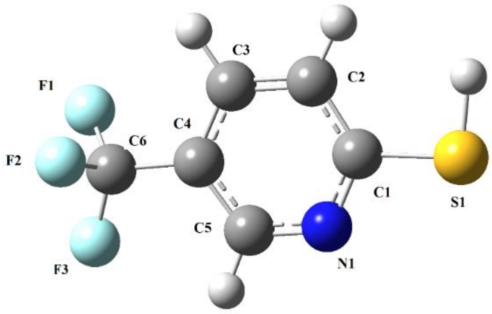


Figure 1. The optimized (with B3LYP/6-311+G (d, p) level) geometric structure of 5-(trifluoromethyl)pyridine-2-thiol.

The CC aromatic bond lengths of 5-(trifluoromethyl)pyridine-2-thiol are found to have longer values in the case of the DFT/B3LYP/6-311+G(d, p) calculation with respect to those of DFT/ HSEH1PBE/6-311+G(d, p) level. The C4–C6 bond length are computed as the longest CC bond distance because the substitution of electron donating trifluoromethyl group increases the electron density CC bonds.

The C1-N1 and C5-N1 bond lengths were computed as 1.331Å and 1.333Å for the B3LYP level. The corresponding lengths were calculated as 1.327Å and 1.328 Å for the HSEH1PBE level. The C1-S1 bond distance was predicted at 1.778 Å and 1.745 Å for the DFT/B3LYP and DFT/HSEH1PBE method. The S1/C1/C2 and S1/C1/N1 angles were calculated as 123.288° / 113.711° for the B3LYP level and 123.129° / 113.711° for the HSEH1PBE level. As can be seen from Table 1, the optimized parameters at the B3LYP/6-311+G (d, p) level of theory are in a good agreement with the computed values [10] of the similar molecule.

3.2. Nonlinear optical analysis

In order to investigate the nonlinear optical parameters of 5-(trifluoromethyl)pyridine-2-thiol, the B3LYP and HSEH1PBE level with 6-311+G (d, p) basis set were used. As values of the molecular electronic dipole moment (μ), mean polarizability (α) and first hyperpolarizability (β) of the Gaussian output are reported in atomic units (a.u.), these values have been converted into electrostatic units (esu) (α: 1 a.u.=0.1482 x10^{-24} esu and β: 1 a.u.= 8.639 x 10^{-33} esu). Obtained results are listed in Table 2.

In this study, the μ value is calculated as 3.2356 Debye (D) for B3LYP and 3.2023 Debye for HSEH1PBE level. The α value is computed at 14.611 $\times 10^{-24}$ esu and 14.341 $\times 10^{-24}$ esu for B3LYP and HSEH1PBE levels. The μ and α values of 5-(trifluoromethyl)pyridine-2-thiol calculated by the HSEH1PBE functional are found to be very close to the calculation made with the B3LYP functional.

Urea is one of the references molecules used to compare the NLO properties of molecular systems [16]. The μ value of urea is calculated as 1.671 D using the B3LYP functional [17]. The calculated μ values of 5-(trifluoromethyl)pyridine-2-thiol are larger than that of urea. In the previous study, the μ parameter for 5-bromo-2-(trifluoromethyl)pyridine calculated by DFT/B3LYP/6-31++G (d, p) method has been reported as 3.38 D for B3LYP [11].

Table 1. Selected theoretical bond lengths and angles for 5-(trifluoromethyl)pyridine-2-thiol.

	B3LYP	HSEH1PBE	5-Bromo-2-(trifluoromethyl)pyridine[10]
Bond Lengths(Å)			
N1—C1	1.331	1.327	1.331
N1—C5	1.333	1.328	1.336
C1—C2	1.404	1.401	1.399
C2—C3	1.383	1.379	1.309
C3—C4	1.397	1.393	1.396
C4—C5	1.392	1.388	1.394
C4—C6	1.499	1.494	1.517
C1—S1	1.778	1.745	
C6—F1	1.354	1.345	1.350
C6—F2	1.357	1.347	1.358
C6—F3	1.349	1.340	1.350
Angles (º)			
S1—C1—C2	123.288	123.129	
S1—C1—N1	113.711	113.711	
F1—C6—F2	106.231	106.371	107.222
F2—C6—F3	106.867	107.025	107.383
F1—C6—F3	107.316	107.467	107.221
C3—C4—C6	120.237	120.201	
C5—C4—C6	121.462	121.470	
Torsion Angles (º)			
N1—C5—C4—C6	-178.325	-178.340	
C2—C3—C4—C6	178.373	178.383	
C3—C2—C1—S1	-179.929	-179.939	
C5—N1—C1—S1	179.947	179.950	

According to Table 2, the first hyperpolarizability value of 5-(trifluoromethyl)pyridine-2-thiol which is an indicator of NLO activity is equal to 318.780 $\times 10^{-32}$ esu for B3LYP and 308.932 $\times 10^{-32}$ esu for HSEH1PBE level. The β values are approximately eight times greater than that of urea (β = 0.3728 $\times 10^{-30}$esu) [18]. The large hyperpolarizability value of the 5-(trifluoromethyl)pyridine-2-thiol indicates that it has considerable NLO properties. Obtained value of the β with HSEH1PBE level is slightly different than these obtained with B3LYP level.

In the previous study, the β value for 5-bromo-2-(trifluoromethyl)pyridine calculated by DFT/B3LYP/6-31++G (d, p) method has been reported as 74.44 $\times 10^{-32}$ [11]. If the β values obtained in the previous study and the value obtained in our current study are compared, it can be seen that it increases. The relatively high values of the molecule suggest that 5-(trifluoromethyl)pyridine-2-thiol is a probable candidate for effective NLO materials.

Table 2 The dipole moment, mean polarizability and the mean first hyperpolarizability of 5-(trifluoromethyl)pyridine-2-thiol.

Property	B3LYP	HSEH1PBE
μ_x	1.6742 Debye	1.5599 Debye
μ_y	2.7682 Debye	2.7974 Debye
μ_z	-0.0576 Debye	-0.0499 Debye
μ	3.2356 Debye	3.2023 Debye
α_x	15.893×10^{-24} esu	15.611×10^{-24} esu
α_y	18.702×10^{-24} esu	18.354×10^{-24} esu
α_z	9.238×10^{-24} esu	9.058×10^{-24} esu
α	14.611×10^{-24} esu	14.341×10^{-24} esu
β_x	206.911×10^{-32} esu	201.873×10^{-32} esu
β_y	-242.254×10^{-32} esu	-233.651×10^{-32} esu
β_z	11.039×10^{-32} esu	9.661×10^{-32} esu
β	318.780×10^{-32} esu	308.932×10^{-32} esu

4. Conclusions

In the present paper, the optimized molecular structures of 5-(trifluoromethyl) pyridine-2-thiol were obtained at the hybrid functionals (B3LYP and HSEH1PBE) of the DFT. The electronic dipole moment (μ), mean polarizability (α) and first hyperpolarizability (β) parameters of 5-(trifluoromethyl) pyridine-2-thiol have been investigated by using the DFT/B3LYP/6-311+G (d, p) and DFT/ HSEH1PBE/6-311+G (d, p) methods. The NLO parameters calculated by the HSEH1PBE functional are found to be very close to the calculations made with the B3LYP functional. The first hyperpolarizability (β) value of 5-(trifluoromethyl)pyridine-2-thiol is eithy times higher than that of reference urea. Hence, 5-(trifluoromethyl)pyridine-2-thiol is promising candidate for nonlinear optical researches.

References

[1] Bhatt, A.H., Parekh, M.H., Parikh, K.A. and Parikh, A.R., Synthesis of pyrazolines and cyanopyridines as potential antimicrobial agents. J. Ind. Chem Soc, 2001, 40(6), 57-61.
[2] Patrick, G.L. and Kinsmar, O.S., Synthesis and antifungal activity of novel aza-d--homosteroids, hydroisoquinolines, pyridines and dihydropyridines. J.Med. Chem., 1996, 31, 615–624.
[3] Hishmat, O.H., Galil, F.M.A. and Farrag, D.S., Synthesis and antimicrobial activity of new benzofuranylpyridine derivatives. Pharmazie, 1990, 45, 793–795.
[4] Doshi, R., Kagthara, P. and Parekh, H., Synthesis and biological evaluation of some novel isoxazoles and cyanopyridines, a new class of potential anti-tubercular agents. Ind. J. Chem., 1999, 38, 348–352.
[5] Gryshuk, A., Chen, Y., Goswami, L.N., Pandey, S., Missert, J.R., Ohulchanskyy, T., Potter, W., Prasad, P.N., Oseroff, A., and Pandey, R.K., Structure-Activity Relationship Among Purpurinimides and acteriopurpurinimides: Trifluoromethyl Substituent Enhanced the Photosensitizing Efficacy. J. Med. Chem., 2007, 50, 1754–1767.
[6] Kirsch, P., Modern Fluoroorganic Chemistry, Wiley-VCH, Weinheim, Germany, 2004.
[7] Gümüş, H.P., Tamer, Ö., Avcı, D. and Atalay, Y., Effects of donor–acceptor groups on the structural and electronic properties of 4-(methoxymethyl)-6-methyl-5-nitro-2-oxo-1,2-

dihydropyridine-3-carbonitrilei. Spectrochim. Acta A, 2014, 132, 183-190.
[8] Prasad P.N. and Williams, D.J., Introduction to Nonlinear Optical Effect in Molecules and Polymers, Wiley, New York, 1991.
[9] Meyers, F., Marder, S.R., Pierce, B.M. and Bredas, J.L., Electric Field Modulated Nonlinear Optical Properties of Donor-Acceptor Polyenes: Sum-Over-States Investigation of the Relationship between Molecular Polarizabilities (.alpha., .beta., and .gamma.) and Bond Length Alternation. J. Am. Ceram. Soc.,1994, 116(23), 10703-10714.
[10] Vural, H., Kara, M., Spectroscopic, optical, DNA, antimicrobial and density functional theory studies of 5-Bromo-2-(trifluoromethyl)pyridine. Optik, 2017, 145, 479-488.
[11] Frisch M.J. et al., 2009. Gaussian 09, Revision A.1, Gaussian, Inc., Wallingford CT.
[12] Dennington R., 2009. GaussView Version 5, Roy, Todd Keith and John Millam, *Semichem Inc*., Shawnee Mission KS.
[13] Lee, C., Yang, W. and Parr, R.G., Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density. Phys. Rev., B37, 1988, 785-789.
[14] Heyd, J., and Scuseria, G.E., Efficient hybrid density functional calculations in solids: assessment of the Heyd-Scuseria-Ernzerhof screened Coulomb hybrid functional. J. Chem. Phys., 2004, 121, 1187-1192.
[15] Krukau, A.V., Vydrov, O.A., Izmaylov, A.F. and Scuseria, G.E., Influence of the exchange screening parameter on the performance of screened hybrid functionals. J. Chem. Phys. 2006, 125, 224106.
[16] Adant, C., Dupuis, M. and Bredas, J. L., Ab initio study of the nonlinear optical properties of urea: Electron correlation and dispersion effects. Int. J. Quantum Chem., 1995, 56, 497-507.
[17] Sayin, K., Karataş, D., Karakuş, N., Sayin, T.A., Zaim, Z. and Kariper, S.E., Spectroscopic investigation, FMOs and NLO analyses of Zn(II) and Ni(II) phenanthroline complexes: A DFT approach. Polyhedron, 2015, 90, 139-146.
[18] Cassidy, C., Halbout, J.M., Donaldson, W and Tang, C.L., Nonlinear optical properties of urea. Opt. Comm., 1979, 29 (2), 243–247.