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Spectroscopic and Nonlinear Optical Properties of Biologically Active 3-(2/3/4-Pyridyl)-4-amino-1,2,4-triazole-5-thiones by Density Functional Theory Method

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Abstract: In the present study, vibrational frequencies and gauge including atomic orbital (GIAO) 13C-NMR and 1H-NMR chemical shift values of 3-(2/3/4-pyridyl)-4-amino-1,2,4-triazole-5-thiones in the ground state have been calculated by using the density functional method (B3LYP) with 6-311G(d,p) basis set. The vibrational spectra of the title compounds which is calculated by DFT methods, reproduces vibrational wave numbers and intensities with an accuracy which allows reliable vibrational assignments. The title compounds have been studied theoretically in the 4000–400 cm^{-1} region and the assignment of all the observed bands were made. In the identification of calculated IR data was used the veda4f program. Theoretical infrared spectrums are formed from the data obtained according to B3LYP method. The calculated IR data of title compounds were calculated in gas phase by using of 6-311G(d,p) basis sets of B3LYP method and are multiplied with appropriate adjustment factors. Also, The ^{1}H- and ^{13}C- nuclear magnetic resonance chemical shifts values of 3-(2/3/4-pyridyl)-4-amino-1,2,4-triazole-5-thione molecules have been calculated by the gage including atomic orbital (GIAO) method. The calculated ^{13}C-NMR and ^{1}H-NMR chemical shift values compared with the experimental values. Experimental data were obtained from the literature. Furthermore, total static dipol moment (μ), the mean polarizability (<α>), the anisotropy of the polarizability (Δα), the mean first-order hyperpolarizability (<β>), of title compounds have been investigated by using B3LYP levels with the 6-311G(d,p) basis set.

Keywords: 1 2 4-Triazole-5-thione, GIAO, B3LYP, Polarizability, Hyperpolarizability

Introduction

The 1,2,4-Triazole compounds has showed widespread attention due to their different biological activities (Çiftçi et al., 2018), and the 1,2,4-Triazole containing amino group is also important for obtaining various Schiff bases with well-established antimicrobial properties as well. 1,2,4-Triazole skeleton are indeed known as important polar pharmacophore, both as a donor to hydrogen bond and as a acceptor, and thus readily to interact with a variety of partners in biological systems (Zhane et al.,2016). Several well- known pesticides containing 1,2,4-Triazole are Triadimefon (Crofton, 1996), Itraconazole, Voriconazole, Fluconazole, Diniconazole and Tebu- conazol (Küçükgüzel et al., 2015). 1,2,4-Triazole has an ambident nucleophilic centers and is a good starting material for the synthesis of several interesting N and S-bridged heterocycles (Aggarwal et al., 2011). Therefore, 1,2,4- Triazole is of significance for the design of new molecular entities with unique structural features. 1,2,4-Triazole and its derivatives are reported to possess a broad spectrum of biological activities such as antimicrobial, antifungal, antitumor, anti-HIV, antiviral, anticancer, anti-inflammatory, analgesic and antioxidant properties (Bayrak et al., 2010; Gürsoy Kol and Yüksek, 2010; Sancak et al., 2010; Çiftçi et al., 2018; Beytur et al., 2019; Turhan Irak and Beytur, 2019). Also, several articles reporting the synthesis of some 1,2,4-triazol derivatives have been published (İkizler and Yüksek, 1994; Yüksek et al., 2005; Yüksek et al., 2006; Turhan Irak and Gümüş, 2017; Beytur et al., 2019).

- Selection and peer-review under responsibility of the Organizing Committee of the Conference

In the present study, the optimized molecular structure, vibrational frequencies, spectroscopic parameters of the 3-(2/3/4-pyridyl)-4-amino-1,2,4-triazole-5-thiones have been calculated by using DFT/B3LYP method with 6-311G(d,p) basis set. All quantum chemical calculations were carried out by using Gaussian 09W (Frisch et al., 2009; Wolinski, Hilton & Pulay, 1990) program package and the GaussView molecular visualization program (Frisch, Nielson & Holder, 2003). The molecular structure and vibrational calculations of the molecule were computed by using Becke-3-Lee Yang Parr (B3LYP) (Becke, 1993; Lee et al.,1998) density functional method with 6-311G(d,p) basis set in ground state. IR absorption frequencies of analyzed molecule were calculated by density functional method. Then, they were compared with experimental data (Nadeem and Ashraf, 2012), which are shown to be accurate. The assignments of fundamental vibrational modes of the title molecule were performed on the basis of total energy distribution (TED) analysis by using VEDA 4f program (Jamroz, 2004). Furthermore, the mean polarizability (<α>), the anisotropy of the polarizability (Δα), the mean first-order hyperpolarizability (<β>) of titled compound have been investigated by using B3LYP and HF levels with the 6-311G(d,p) basis set.

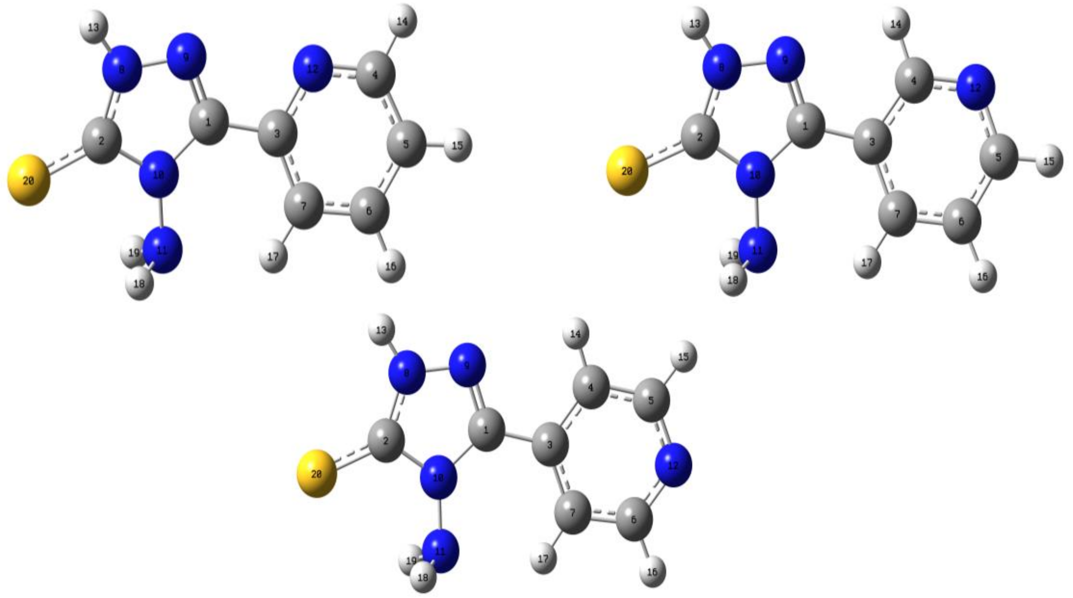


Figure 1. The optimized molecular structure (Gaussview Appearance) of compounds 1-3 with DFT/B3LYP 6-311G(d,p) level.

Method

The molecular structure of the title compound in the ground state is computed by performing both the density functional theory (DFT) and Hartree-Fock (HF) (Becke, 1993; Lee, 1998) at 6-311G+(d,p) level. Density functionals for all studies reported in this paper have been in the following form

$$E_{XC} = (1-a_0)E_X^{LSDA} + a_0 E_X^{HF} + a_X \Delta E_X^{B88} + a_C E_C^{LYP} + (1-a_C)E_C^{VWN}$$

where the energy terms are the Slater exchange, the Hartree-Fock exchange, Becke's exchange functional correction, the gradient corrected correlation functional of Lee, Yang and Parr, and the local correlation functional of Vosko, Wilk and Nusair (Vosko et al., 1980). The theoretical geometric structure of the title compound is given in Figure 1. Molecular geometry is restricted and the optimized geometrical parameters of the title compound in this study are carried out by using Gaussian 09W program package (Frisch et al., 2009) and the visualization parts were done with GaussView program (Dennington et al., 2009) on personal computer employing 6-311G+(d,p) basis set. Additionally, harmonic vibrational frequencies for the title compound are calculated with these selected methods and then scaled by 0.9516 and 0.9905, respectively (Avcı and Atalay, 2008) and these results were compared with the experimental data (Nadeem and Ashraf, 2012).

Experimantal Data

3-(2-Pyridyl)-4-amino-1,2,4-triazole-5-thione (1): IR (KBr, ν, cm^{-1}): 3430-3330 (NH_2), 1630 (Ar C=C), 1567 (C=N), 1238 (C=S). ^{1}H NMR (300 MHz, DMSO-d$_6$, δ, ppm): 13.8 (s, 1H, NH/SH), 8.60 (d, 1H, J=5.0 Hz, H-6), 8.03 (d, 1H, J=7.9 Hz, H-3), 7.81 (t, 1H, J=6.7 Hz, H-4), 7.37 (t, 1H, J=5.3 Hz, H-5), 5.54 (s, 2H, NH_2), (Nadeem and Ashraf, 2012).

3-(3-Pyridyl)-4-amino-1,2,4-triazole-3-thione (2): IR (KBr, ν, cm^{-1}): 3436-3334 (NH_2), 1627 (Ar C=C), 1570 (C=N), 1247(C=S). ^1H NMR (300 MHz, DMSO-d_6, δ, ppm): 12.6 (s, 1H, NH/SH), 9.13 (d, 1H, J=1.5 Hz, H-2), 8.68 (d, 1H, J=3.5 Hz, H-6), 8.36 (d, 1H, J=7.9 Hz, H-4), 7.56 (dd, 1H, J=7.9 Hz, J=4.9 Hz, H-5), 5.79 (s, 2H, NH2), (Nadeem and Ashraf, 2012).

3-(2-Pyridyl)-4-amino-1,2,4-triazole-5-thione (3): IR (KBr, ν, cm^{-1}): 3272 (NH_2), 1629 (Ar C=C), 1566 (C=N), 1218 (C=S). ^1H NMR (300 MHz, DMSO-d_6, δ, ppm): 13.7 (s, 1H, NH/SH), 8.82 (d, 2H, J=5.9 Hz, H-3, H-5), 7.83 (d, 2H, J=6.0 Hz, H-2, H-6), 5.53 (s, 2H, NH2), (Nadeem and Ashraf, 2012).

Results and Discussion

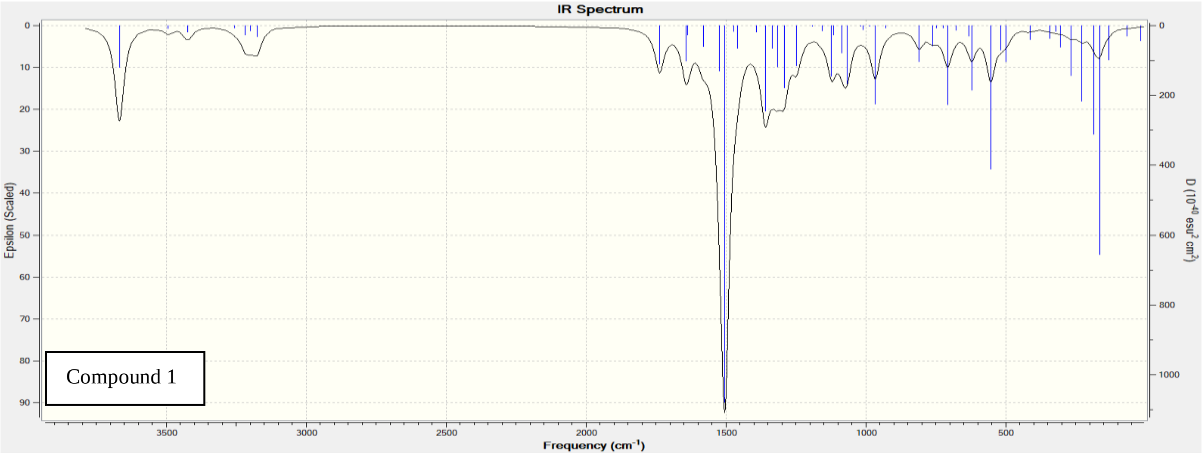
Analysis of vibrational modes

In spectroscopic field, the vibrational spectra of substituted benzene derivatives have been greatly investigated by various spectroscopic, since the single substitution can have a tendency to put greater changes in vibrational wavenumbers of benzene (Pir et al., 2013). In other words, molecular system of benzene is greatly affected by the nature of substituents. The number of potentially active fundamentals of non-linear molecule which have N atoms is equal to (3N-6) apart from three translational and three rotational degrees of freedom. The 3-(2/3/4-pyridyl)-4-amino-1,2,4-triazole-5-thiones contains 20 atoms and 54 normal vibration modes have C1 symmetry (Table 1). Experimentally (Nadeem and Ashraf, 2012), the investigated titled compound, as expected the IR spectra data, the NH_2 stretching vibration at the range of 3430-3330 cm^{-1} for compound 1, the range of 3436-3334 cm^{-1} for compound 2 and 3272 cm^{-1} for compound 3 respectively. The C=S peak at 1238, 1247 and 1218 cm^{-1} range was observed respectively. Theoretically and experimentally (Nadeem and Ashraf, 2012), the calculated vibrational frequencies for the 3-(2/3/4-pyridyl)-4-amino-1,2,4-triazole-5-thiones are summarized in Table 1. Finally, the experimental IR (Nadeem and Ashraf, 2012) and simulated spectra by using B3LYP/6-311G+(d,p) level of the titled compounds under investigation are given in Figure 2.

Table 1. The calculated scaled frequencies values of the titled compounds (1-3)

	Compound 1		**Compound 2**		**Compound 3**	
Vibration Types	**Experim.**	**skalalı DFT**	**Experim.**	**skalalı DFT**	**Experim.**	**skalalı DFT**
1		**17**		24		14
2		**67**		68		66
3		**130**		128		134
4		**163**		170		163
5		**183**		201		202
6		**227**		230		230
7		**265**		260		264
8		**302**		292		298
9		**319**		313		322
10		**341**		344		336
11		**409**		405		383
12		**494**		485		512
13		**513**		516		512
14		**549**		549		555
15		**616**		603		603
16		**626**		637		671
17		**671**		670		677
18		**701**		714		708
19		**717**		717		711
20		**742**		721		729
21		**754**		741		756
22		**802**		827		850
23		**921**		946		900

24			**957**		956		947
25			**975**		985		994
26			**1000**		1010		1002
27			**1008**		1019		1007
28			**1058**		1033		1029
29			**1075**		1057		1086
30			**1104**		1096		1096
31			**1112**		1116		1102
32			**1146**		1143		1129
33			**1179**		1214		1221
34	C=S	1238	**1236**	1247	1222	1218	1235
35			**1280**		1265		1259
36			**1304**		1274		1268
37			**1322**		1330		1332
38			**1347**		1352		1343
39			**1377**		1358		1356
40			**1446**		1414		1420
41			**1458**		1463		1446
42			**1490**		1478		1478
43			**1508**		1494		1511
44	C=N	1567	**1567**	1570	1560	1566	1548
45	Ar-C=C	1630	**1623**	1627	1602	1629	1594
46	Ar-C=C	1630	**1627**	1627	1617	1629	1621
47			**1720**		1694		1693
48			**3144**		3124		3121
49			**3168**		3149		3126
50			**3187**		3158		3181
51	NH_2	3330	**3225**		3198	3272	3204
52	NH_2	3330	**3390**	3334	3413	3272	3415
53	NH_2	3430	**3460**	3436	3474	3272	3477
54	NH_2	3430	**3632**	3436	3631	3272	3629



Compound 1

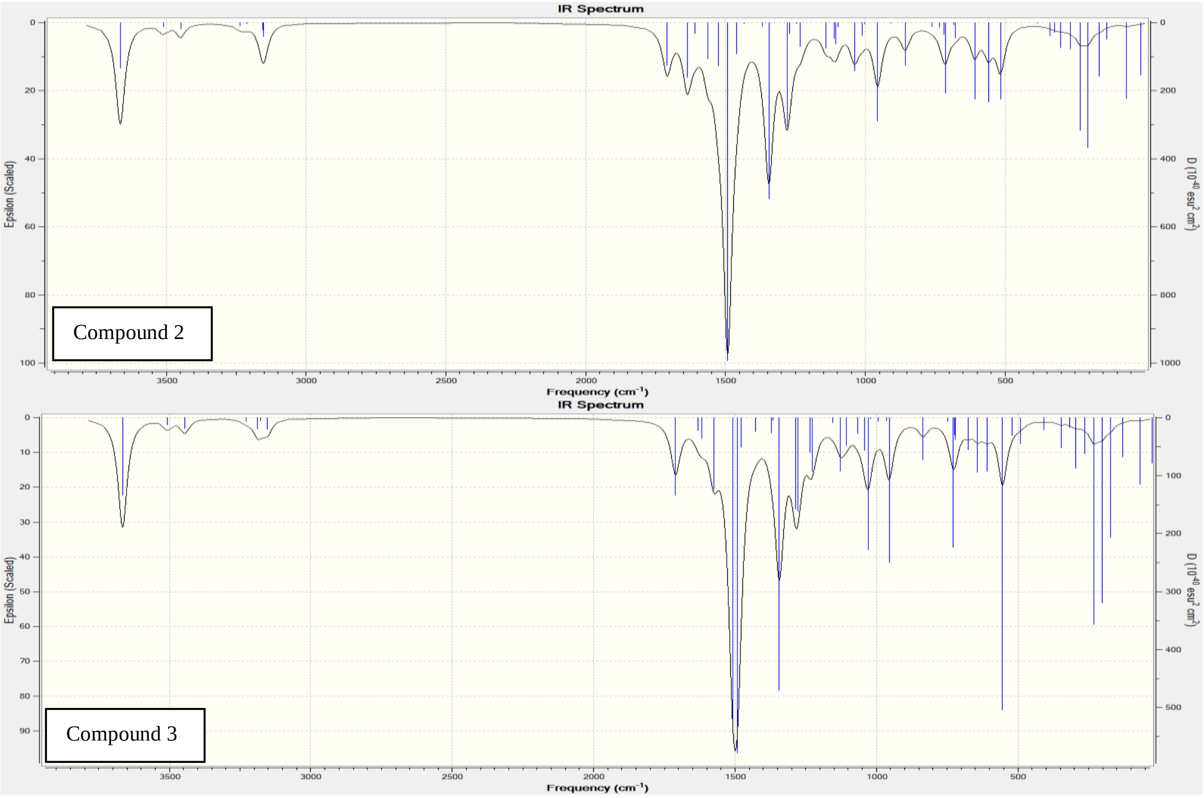


Figure 2. IR spectra simulated with DFT/B3LYP/6-311G+(d,p) level of the titled compounds (1-3)

NMR Spectral Analysis

The chemical shift analysis allows us to identify relative ionic species and to calculate reliable magnetic properties in nuclear magnetic resonance spectroscopy which provide the accurate predictions of molecular geometries, (Wade, 2006; Rani, et al., 2010; Subramanian et al., 2010). The optimized molecular geometry of the 3-(2/3/4-pyridyl)-4-amino-1,2,4-triazole-5-thiones were obtained by using B3LYP method with 6-311G+(d,p) basis level in DMSO solvent. The ^{1}H and ^{13}C NMR chemical shift values were calculated at the same level by using Gauge-Independent Atomic Orbital method (Table 2-4). Theoretically and experimentally values (Nadeem and Ashraf, 2012) were plotted according to δ exp=a. δ calc.+ b, Eq. a and b constants regression coefficients with a standard error values were found using the SigmaPlot program. The correlation graphics are given Figure 3. The (R^2) values (DFT) for ^{1}H NMR (DMSO) chemical shifts in different solvents have been found as 0.489, 0.585 and 0.448 for the 3-(2/3/4-pyridyl)-4-amino-1,2,4-triazole-5-thiones (1-3)respectively(Figure 3). In our study, the ^{1}H-NMR spectrum of the titled compounds were observed belong to H13 proton peak at 13.80, 12.60 and ppm, respectively because acidic show feature(Yüksek et al., 2005; Yüksek et al., 2006, Çiftçi et al., 2018).

Table 2. The calculated and experimental ^{1}H and ^{13}C NMR isotropic chemical shifts of the compound 1.

No	Experim.	DFT/6311+(d,p) DMSO	Diff./DMSO
1C		136,00	-136,00
2C		158,95	-158,95
3C		131,69	-131,69
4C		136,24	-136,24
5C		112,41	-112,41
6C		123,45	-123,45
7C		112,43	-112,43
13H	13,80	8,49	5,31
14H	8,03	8,46	-0,43
15H	7,37	7,08	0,29
16H	7,81	7,57	0,24
17H	8,60	8,87	-0,27
18H	5,54	3,72	1,82
19H	5,54	3,48	2,06

Table 3. The calculated and experimental ^{1}H and ^{13}C NMR isotropic chemical shifts of the compound 2

No	Experim.	DFT/6311+(d,p) DMSO	Diff./DMSO
1C		152,52	-152,52
2C		177,54	-177,54
3C		126,52	-126,52
4C		152,80	-152,80
5C		155,86	-155,86
6C		127,04	-127,04
7C		138,10	-138,10
13H	12,60	9,00	3,60
14H	8,68	9,50	-0,82
15H	8,36	8,85	-0,49
16H	7,56	7,54	0,02
17H	9,13	9,70	-0,57
18H	5,79	4,11	1,68
19H	5,79	3,84	1,95

Table 4. The calculated and experimental ^{1}H and ^{13}C NMR isotropic chemical shifts of the compound 3

No	Experim.	DFT/6311+(d,p) DMSO	Diff./DMSO
1C		151,53	-151,53
2C		178,56	-178,56
3C		136,29	-136,29
4C		122,73	-122,73
5C		154,73	-154,73
6C		155,23	-155,23
7C		121,79	-121,79
13H	13,70	8,52	5,18
14H	7,83	8,01	-0,18
15H	7,83	8,88	-1,05
16H	8,82	8,91	-0,09
17H	8,82	9,17	-0,35
18H	5,53	3,68	1,85
19H	5,53	3,67	1,86

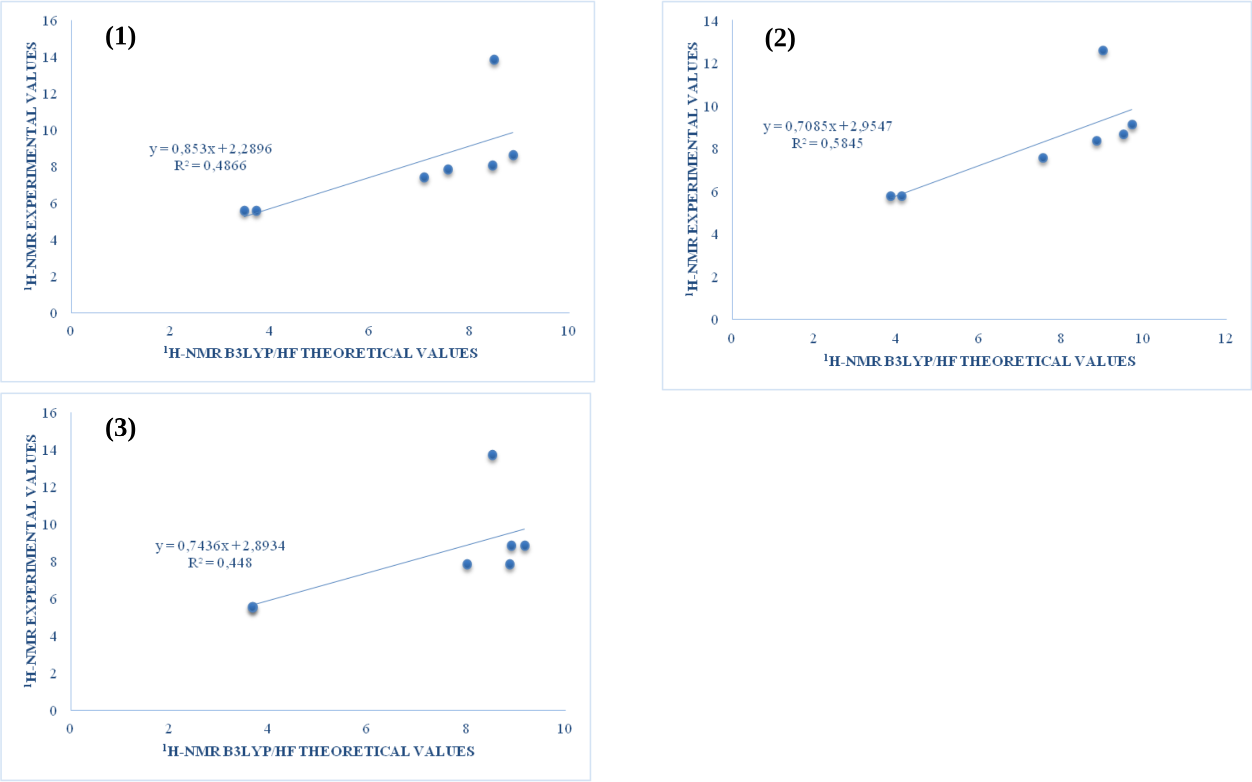


Figure 3. The correlation graphics for ^{1}H-NMR (DMSO) chemical shifts of the titled compounds (1-3)

Nonlinear Optic Properties

The materials having nonlinear activity possess a nonlinear response to the electric fields associated with the light of a laser beam. It is well known that the higher values of dipole moment, polarizability, and hyperpolarizability are important for more active NLO properties. In this study dipole moment, polarizability and first hyperpolarizability of the titled molecule were investigated by using B3LYP method at 6-311G+(d,p) basis set. The following formulas are used for calculating the magnitude of total static dipole moment (μ), polarizability (α) and first hyperpolarizability (β):

$$\mu = \left(\mu_x^2 + \mu_y^2 + \mu_z^2\right)^{\frac{1}{2}}$$

$$\alpha = \frac{1}{3}\left(\alpha_{xx} + \alpha_{yy} + \alpha_{zz}\right)$$

$$\beta = \sqrt{\left(\beta_{xxx} + \beta_{yyy} + \beta_{zzz}\right)^2 + \left(\beta_{yyy} + \beta_{xxy} + \beta_{yzz}\right)^2 + \left(\beta_{zzz} + \beta_{xxz} + \beta_{yyz}\right)^2}$$

Where, the total static dipole moment (μ), linear polarizability (α) and the first hyperpolarizability (β) using the *x*, y, *z* components are defined as (Abraham et al., 2008; Karamanis et al., 2008). The linear polarizability (α) and the first hyperpolarizability (β) values of conformer ct of the titled molecules (1-3) are investigated as a function of the two torsional angle using B3LYP/6-311G+(d,p) level of theory (Govindarajan et al., 2012) (Table 5).

Tablo 5. Calculated polarization and hyperpolarizability values of the molecules 1-3 (B3LYP/6-311G+(d,p))

B3LYP	**1**	**2**	**3**
α_{xx}	31,446 a.u.	32.472 a.u.	31.776 a.u.
α_{yy}	17.426 a.u.	18.157 a.u.	18.802 a.u.
α_{zz}	7.419 a.u.	8.484 a.u.	8.340 a.u.
A	18.76x10^{-24} esu	19.71x10^{-24} esu	19.64x10^{-24} esu
$\Delta\alpha$	20.90x10^{-24} esu	20.90x10^{-24} esu	20.34x10^{-24} esu
β_x	9352.32 a.u.	-7046.56 a.u.	-8440.32 a.u.
β_y	2191.08 a.u.	-3524.06 a.u.	-2571.32 a.u.
β_z	113.45 a.u.	59.77 a.u.	-0.81 a.u.
β_{xxx}	8936.28 a.u.	-6049.28 a.u.	-7886.06 a.u.
β_{xxy}	1732.66 a.u.	-2301.53 a.u.	1949.72 a.u.
β_{xyy}	480.00 a.u.	-768.52 a.u.	-384.46 a.u.
β_{yyy}	183.67 a.u.	-745.51 a.u.	-172.86 a.u.
β_{xxz}	85.44 a.u.	46.20 a.u.	-0.80 a.u.
β_{xyz}	-44.36 a.u.	-64.36 a.u.	0.27 a.u.
β_{yyz}	-80.13 a.u.	-120.10 a.u.	0.50 a.u.
β_{xzz}	-63.96 a.u.	-228.76 a.u.	-169.80 a.u.
β_{yzz}	274.76 a.u.	-477.03 a.u.	-448.75 a.u.
β_{zzz}	108.14 a.u.	133.68 a.u.	-0.51 a.u.
B	9.61x10^{-30} esu	7.88x10^{-30} esu	8.82x10^{-30} esu

Conclusion

In this study, The vibrational frequencies, ^{1}H and ^{13}C NMR chemicals shifts of 3-(2/3/4-pyridyl)-4-amino-1,2,4-triazole-5-thiones obtained have been calculated by using DFT/B3LYP methods. By considering the results of experimental works it can be easily stated that the ^{1}H chemical shifts, and vibrational frequencies spectroscopic parameters obtained theoretically are in a very good agreement with the experimental data. Finally, The nonlinear optical properties of the investigated compounds were calculated theoretically. It was found that the molecule concerned had a higher hyperpolarizability value than urine (0.77x10^{-30}esu) (Zyss, 1994). It was found that molecules whose structures were examined theoretically had higher hyperpolarizability values than urea. The sequence is 1> 3> 2> urea.

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