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Crystal structure, FT-IR, FT-Raman, ^{1}H NMR and computational study of ethyl 2-{[(*Z*)3-(4-chlorophenyl)-3-hydroxy-2-propene-1-thione] amino} acetate

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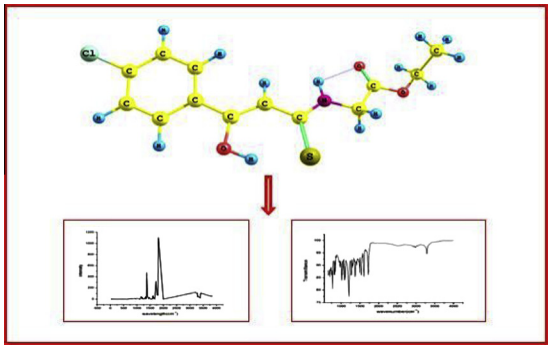
HIGHLIGHTS

- X-ray structure of ethyl 2-{[(*Z*)3-(4-chlorophenyl)-3-hydroxy-2-propene-1-thione] amino} acetate was analyzed.
- The geometry was compared with the calculated geometry of the molecule using RHF and B3LYP.
- FT-IR, ^{1}H NMR and FT-Raman spectra were recorded.
- *Z*-conformation of the thioamide group and the C—N bond is shortened.
- The conjugated *enol* form of the compound is found in the crystal.

GRAPHICAL ABSTRACT



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ABSTRACT

The molecular structure of a thioamide derivative ethyl 2-{[(*Z*)3-(4-chlorophenyl)-3-hydroxy-2-propene-1-thione] amino} acetate was determined by X-ray diffraction. The proton NMR (^{1}H NMR), Fourier Transform Infra-Red (FT-IR) and Fourier Transform Raman (FT-Raman) spectra of the compound were recorded and analyzed. The conjugated *enol* form of the compound was crystallized in the monoclinic space group $P2_1/c$, with unit cell dimensions $a = 12.514(2)$ Å, $b = 5.403(5)$ Å, $c = 21.233(3)$ Å, $\beta = 94.597(4)°$. The structure was solved by direct methods and refined to the *R* value of 0.0462. The thioamide moiety in the compound adopts the *Z*-conformation and the C—N bond shows a high rotational barrier. The geometry in the gas phase was optimized by B3LYP and RHF quantum mechanical calculations using Gaussian 09 programme and the vibrational frequencies were calculated. The experimental and theoretical data are in good agreement.

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Introduction

The compound ethyl 2-{[(*Z*)3-(4-chlorophenyl)-3-hydroxy-2-propene-1-thione] amino} acetate is a thioamide derivative. Thioamides are functional groups with general structures R1—CS—NR2 R3, where R1, R2 and R3 are organic groups, as shown in Fig. 1. Thioamides are analogous to amides with the oxygen atom in the amide replaced by sulphur atom in the thioamide [1] and they exhibit strong multiple bond character along the C—N bond resulting in a larger rotational barrier [2]. Regardless of the close structural analogy, there is a large difference in the chemical properties of the two species. Small difference in electronegativity between carbon and sulphur in C=S group compared to C=O group and larger size of sulphur atom allows greater charge transfer from nitrogen to sulphur in thioamides than nitrogen to oxygen in amides. Higher polarisability of sulphur relative to oxygen makes thioamide more reactive than its oxygen counterpart [3] and hence they take part in many reactions such as hydrolysis, reduction, oxidation and reaction with inorganic and organic amines [4]. Thioamides and their functionalized derivatives can be considered as highly flexible reagents due to their ability to react with both electrophiles and nucleophiles [5]. Hence they are useful synthons in the synthesis of heterocyclic compounds including regio – and stereo selective synthesis of natural products [6,7]. They are antithyroid drugs prescribed in the treatment of hyperthyroidism [8]. They block both the organification of iodine and coupling of iodotyrosil residues by inhibiting the thyroidal synthesis of thyroxine and 3,5,3′-triiodothyronine. Thioamide drugs are also clinically powerful in the treatment of *Mycobacterium tuberculosis*, *Mycobacterium leprae* and *Mycobacterium avium* complex infections, especially for drug resistant tuberculosis [9].

The conformation and planarity in the thioamide group and the deviation of sp^2 bond angles have been a subject of investigation [10]. In the present work, we report our investigations on the X-ray structure, ^{1}H NMR, FT-IR, FT-Raman and the results are compared with those calculated by theoretical DFT method for the ethyl 2-{[(*Z*)3-(4-chlorophenyl)-3-hydroxy-2-propene-1-thione] amino} acetate compound (Fig. 2).

The ^{1}H NMR data shows the presence of both the *keto* and *enolic* forms of the compound. The possibility of the *enolic* form arises from the thiocarbonyl group or the *β-keto* group of the compound. The identity of the *enolic* form and related structural features were confirmed by X-ray crystallography.

Experimental

Synthesis of ethyl 2-{[(*Z*)3-(4-chlorophenyl)-3-hydroxy-2-propene-1-thione] amino} acetate.

Dithiocarboxylate derived from *para*-chloroacetophenone was taken as a model substrate for the reaction with glycine ester. Triethylamine (2 equiv.) was added to a mixture of dithiocarboxylate and ethyl glycinate hydrochloride taken in absolute ethanol.

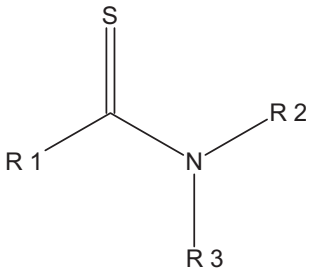

Fig. 1. General structure of thioamides.

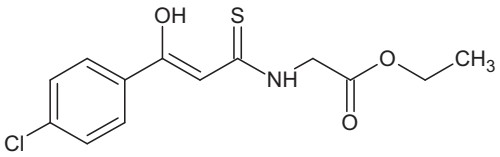

Fig. 2. Structure of ethyl 2-{[(*Z*)3-(4-chlorophenyl)-3-hydroxy-2-propene-1-thione] amino} acetate.

The reaction mixture was stirred at room temperature for 4 h and after the completion of reaction verificate by TLC, the mixture was added to ice cold water. The prepared solid was filtered, washed with water and dried to get the crude thioamide in 97% yield which was further purified by recrystallizing from hexane:ethyl acetate (7:3) (Fig. 3a) [11]. The ^{1}H NMR spectrum of the synthesized compound showed the presence of *keto* and *enol* forms in solution (Fig. 3b). When crystallized, the *enol* form of the racemate alone was incorporated in the crystal and was used for the X-ray structure analysis.

The FT-IR spectrum was recorded on a Shimadzu Model IR Prestige 21, with ZnSe ATR crystal (Pike technologies) spectrometer. The Raman spectrum was obtained on a Horiba Jobin Yvon LabRam HR system excitation wavelength: 514.5 nm of Argon ion laser. ^{1}H NMR spectrum was recorded on a Bruker spectrometer at 500 MHz. The compound was dissolved in chloroform ($CDCl_3$) and the chemical shifts were reported in ppm relative to tetramethylsilane (TMS).

Computational details

The vibrational frequencies were calculated using Gaussian09 software [12]. The calculations were performed at RHF/6-31G (d) and B3LYP/6-31G (d) level of theory to get the optimized structure. The optimized parameters of geometry have been used as the inputs for the frequency calculations [13]. Scaling factors were used for a better agreement with the experimental data (0.96 for B3LYP and 0.93 for RHF). DFT calculations were carried out with the hybrid B3LYP method. In the optimized structure, there is no negative frequency that indicates the optimized geometry is a global minimum of the potential energy curve. Apart from the vibrational frequency, reduced masses, force constants, infrared intensities, Raman activities, Raman intensities and depolarization ratio were calculated.

Results and discussion

Crystallization and data collection

Single crystals of the compound suitable for X-ray diffraction were grown by slow evaporation from chloroform–hexane solution. The pale yellow crystals were prismatic. The dimensions of the crystal used for data collection were 0.25 × 0.25 × 0.20 mm. The crystals belong to the monoclinic system with space group $P2_1/c$, the unit cell dimensions were $a = 12.514(2)$ Å, $b = 5.403(5)$ Å, $c = 21.233(3)$ Å, $\alpha = 90°$, $\beta = 94.597(4)°$ and $\gamma = 90°$. The cell parameters were determined by full-matrix least square refinement. The ranges of h, k, l are $-13 \leqslant h \leqslant 14$; $-6 \leqslant k \leqslant 6$ and $-26 \leqslant l \leqslant 26$ respectively. Intensity data were collected up to a maximum 2θ value of 51.96° with ω-scans using graphite monochromated Mo Kα radiation, on 'Mac Science DIP Labo 32001' [14]. The cell parameters were refined by SCALEPACK [15] and the intensity data were corrected for Lorentz, polarization and absorption corrections.

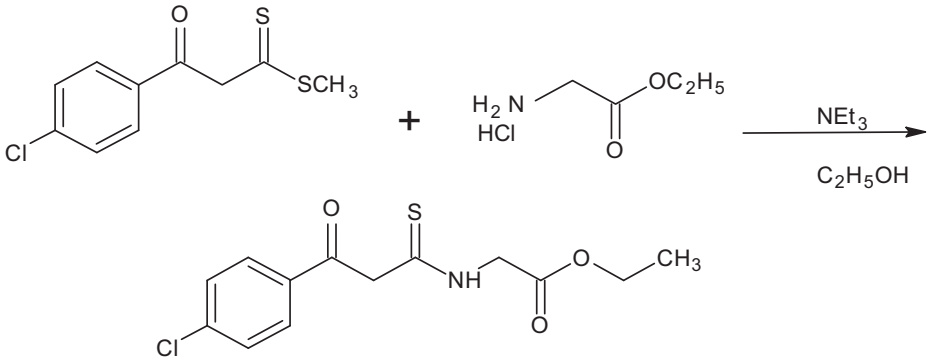

Fig. 3a. Reaction for the preparation of ethyl 2-{[(*Z*)3-(4-chlorophenyl)-3-hydroxy-2-propene-1-thione] amino} acetate.

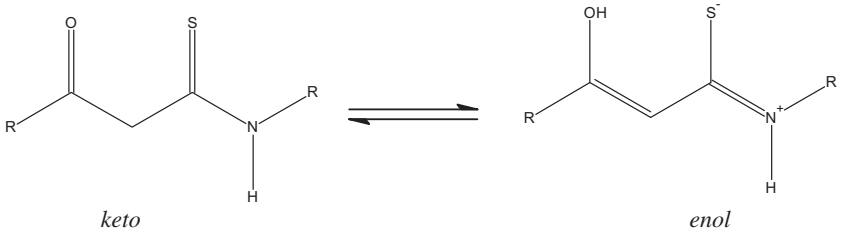

Fig. 3b. The *keto* and *enolic* forms of thioamide resulting from extended conjugation.

Structure solution and refinement

The structure was solved by direct method using the program SHELXS 97 [16]. The top 19 peaks of the E-map with $R_E = 0.261$ formed the complete structure. The structure was refined by the program SHELXL 97 [17]. The position of all H atoms were geometrically fixed and treated with riding atoms, with C—H distances of 0.93 or 0.96 Å. Their isotropic displacement parameters were defined as U*iso* = 1.5 U_{eq} of the adjacent atom for the methyl H atoms and U*iso* = 1.2 U_{eq} for all other atoms. Anisotropic refinement of non-hydrogen atoms and isotropic refinement of hydrogen atoms using 1702 reflections with $I > 2\sigma(I)$ converged the *R*-factor to 0.0462. The crystal data and the structure solution details are given in Table 1.

Table 1
X-ray crystal data and structure refinement parameters for ethyl 2-{[(*Z*)3-(4-chlorophenyl)-3-hydroxy-2-propene-1-thione] amino} acetate.

Empirical formula	$C_{13}H_{14}ClNO_3S$
Formula weight	299.76 g/mol.
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, $P2_1/c$
Unit cell dimensions	$a = 12.514(2)$ Å $\alpha = 90°$
	$b = 5.403(5)$ Å $\beta = 94.597(4)°$
	$c = 21.233(3)$ Å $\gamma = 90°$
Volume	1431.0(14) $Å^3$
Z, calculated density	4, 1.391 Mg/m^3
Absorption coefficient	0.415 mm^{-1}
F (000)	624
Crystal size	0.25 × 0.25 × 0.20 mm
Theta range for data collection	3.66–25.98°
Index ranges	$-13 \leqslant h \leqslant 14$; $-6 \leqslant k \leqslant 6$; $-26 \leqslant l \leqslant 26$
Reflections collected/unique	4141/2396
Data completeness	85.2%
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	2396/0/207
Goodness-of-fit on F^2	1.026
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0462$ $\omega R_2 = 0.1177$
R indices (all data)	$R_1 = 0.0675$ $\omega R_2 = 0.1359$
Largest diff. peak and hole	0.16 to −0.24 e $Å^{-3}$

Molecular geometry

The optimized geometry of the molecule is shown in Fig. 4. The optimized geometrical parameters such as bond lengths, bond angles and dihedral angles were calculated by RHF and DFT/B3LYP methods with 6-31G(d) as basis set and the calculated energies are −1636.493 and −1642.648 Hartree, respectively. The optimized structures were compared with the X-ray structure (Fig. 5) (the geometrical parameters are given in supplementary data). The optimized geometrical parameters calculated using DFT/B3LYP are in better agreement with the experimental values. Dipole moment is a vector in three dimensions which describes the molecular charge distribution. Direction of the dipole moment vector in a molecule depends on the centers of negative and positive charges. From the dipole moment we can get the movement of charge across the molecule [18,19]. Using HF and DFT the dipole moment was calculated, the values are 4.67 and 5.0 Debye respectively.

The geometric parameters of this compound from X-ray analysis and calculated by theoretical methods are within the limits of the expected range of values and our discussion is mainly concentrated on X-ray results, however the relevant differences between the experimental and theoretical values are highlighted.

The central chromophore of the molecule is planar as seen from the torsion angle S(1)—C(10)—N(1)—C(11) = −7.0(4)° and adopts the *Z*-conformation about the C—N bond. The corresponding value for the torsion from HF and B3LYP are 0.2° and −0.1°, respectively. The *Z*-conformation for this bond has been observed, although rarely [20] in the crystal structures of O-Ethyl and O-methyl N-(2,3,4,6-tetra-O-acetyl-β-D-glucopyranosyl)-thiocarbamate [21] and in (4-Pyridyl) methyl N-phenylthiocarbamate [22]. Both the sulphur (S1) and the oxygen (O1) atoms become electron rich due to the delocalization of the lone pair electrons from the

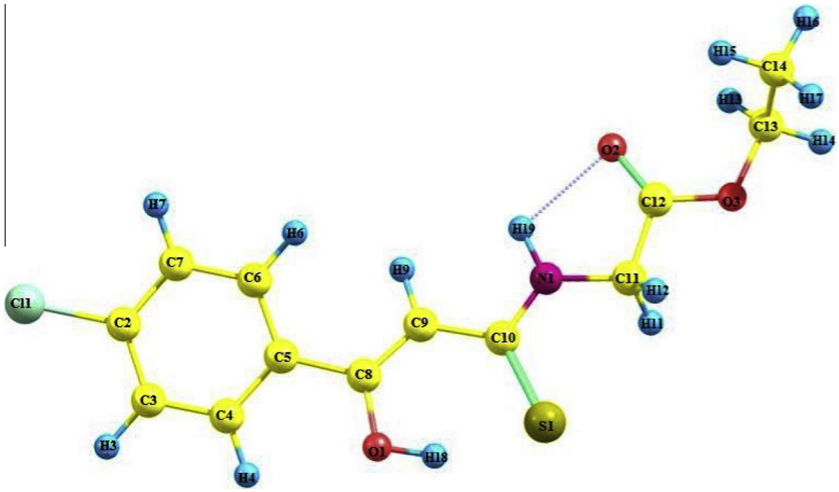

Fig. 4. Optimized structure of the compound using B3LYP method. The geometry of the molecule is almost identical to this when RHF is used.

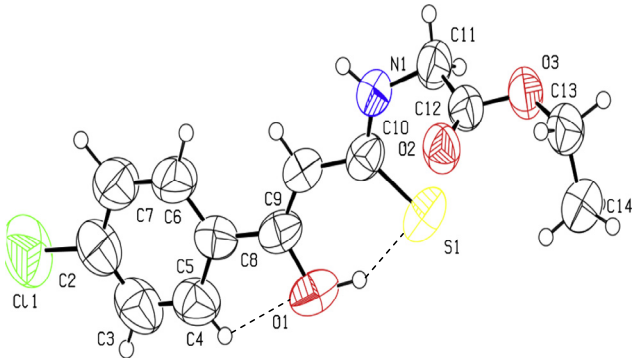

Fig. 5. Ortep plot of the compound with thermal ellipsoid at 50% probability. Intramolecular H-bonds are marked by dotted lines.

nitrogen atom or it could be due to a combination of keto-*enol* tautomerism and thioamide delocalization.

The torsion angles about the C(10)—N(1) and C(9)—C(10) bonds are *E*, {C(9)—C(10)—N(1)—C(11) [171.8(3)°] and C(8)—C(9)—C(10)—N(1) [−175.6(3)°]}, and from B3LYP the corresponding values are −179.8° and −179.1° respectively. As a result C—S and the O—H groups are oriented on the same side of the molecule, favoring an O—H···S intra molecular hydrogen bond [O···S = 2.942(3) Å, H···S = 1.97(4) Å, O—H···S = 154(3)°] forming a six-membered ring [O(1)—H···S(1)—C(10)—C(9)—C(8)]. This six membered ring is almost planar as shown by the torsion angles O(1)—C(8)—C(9)—C(10) [2.8(5)°] and C(8)—C(9)—C(10)—S(1) [5.6(4)°]. From the B3LYP method the corresponding torsion angles are −1.5° and 1.2°, respectively. The C(10)—N(1) bond [1.334(4) Å] is shorter than C(11)—N(1) bond [1.445(4) Å]. The C(10)—S(1) bond [1.685(3) Å] is elongated with respect to the corresponding bond in thiocarbamide compounds reported in the literature [23]. These values are indicative of the π-electron delocalization along these bonds. The C—N bond is shortened resulting in a high rotational barrier and was also reported by theoretical calculations in compounds containing thioamides [1]. The C—N and C—S bonds in our calculations by B3LYP are 1.334 Å and 1.6848 Å, respectively. The C—N bond is 1.355(3) Å and C—S bond is 1.679(3) Å in the crystal structure of 4-methyl-N-phenylpiperidine-1-thio-amide and are also comparable to the thioamide groups in the crystal structures of O-isopropyl-N-aryl-thiocarbamides [24], and (E)-O-Ethyl-N-(4-nitroplehyl) thiocarbamate [20]. The C(8)—C(9) bond [1.344(4) Å] is shorter than C(9)—C(10) bond [1.439(4) Å] and the C(8)—O(1) bond is 1.338(3) Å and the bond angle C(8)—C(9)—C(10) = 127.7(3)° shows that C(9) is close to the sp^2 planar conformation, all these values underline the existence of π-electron delocalization. The corresponding bond angles and bond lengths obtained from B3LYP and RHF agree well with the experimental values.

The *para* chlorophenyl ring is planar with C—C bond lengths ranging from 1.354(5) Å to 1.386(4) Å with an average of 1.373(5) Å and bond angles vary from 117.3(3)° to 121.8(3)° with an average of 120(3)°, by B3LYP method C—C bond lengths ranging from 1.353 to 1.38 Å and the bond angle varying from 117.2° to 121.8°. The planarity of the phenyl ring is evident from the endocyclic torsion angles C(2)—C(3)—C(4)—C(5) [0.3(6)°], C(3)—C(4)—C(5)—C(6) [−2.2(5)°], C(4)—C(5)—C(6)—C(7) [−2.5(6)°], C(5)—C(6)—C(7)—C(2) [1.0(6)°], C(6)—C(7)—C(2)—C(3) [−0.9(6)°] and C(7)—C(2)—C(3)—C(4) [−1.3(6)°]. The chlorine atom Cl(1) is in the plane of the phenyl ring as shown by the torsion angle Cl(1)—C(2)—C(3)—C(4) = 176.7(3)° and is at a distance of [Cl(1)—C(2)] 1.727(4) Å from the phenyl ring. Similar values for the C—Cl distance was observed in 1,7-bis(4-chlorophenyl)-4-(1,3-dithiolan 2-yilidene)-1,6-heptadine-3,5-dione [25]. The torsion angle C(5)—C(8)—C(9)—C(10) [−175.1(3)°] indicates configuration *E*, indicating that the *para* chlorophenyl substitution is also in the plane of the H-bonded ring system thereby allowing the molecule to adopt a planar conformation. The molecule is linear, except for the ethyl ester part, where the torsion C(10)—N(1)—C(11)—C(12) [−71.6(4)°] shows configuration Z, that interrupts the linear conformation of the molecule. This Z conformation is responsible for the orientation of the C(12) = O(2) group of the ester towards the sulphur atom resulting in a non-bonded interaction between C=O and C—S with S(1)···O(2) distance of 3.47 Å. The bond lengths C(12)—O(3), C(13)—O(3) and C(13)—C(14) are 1.324(3) Å, 1.457(4) Å and 1.477(5) Å, respectively.

Intermolecular interactions and packing

Dimer interactions between symmetry related molecules

The symmetry related molecules are bonded pair-wise by two intermolecular H-bonds, with N(1)H and C(9)H, respectively, acting as donors and the ester carbonyl oxygen atom O(2) from a symmetry related molecule (in the $-x$, $1/2 + y$, $1/2 - z$ position) acting as the acceptor. These intermolecular N—H···O and C—H···O hydrogen bonds between the symmetry related molecules form hydrogen-bonded dimers (Fig. 6a) and are arranged to form infinite columns connected by very weak H-bonds involving Cl atoms;

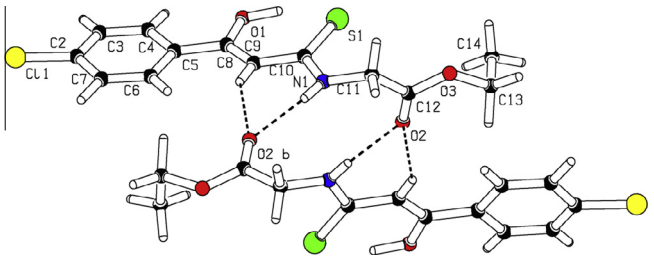

Fig. 6a. Intermolecular N—H···O and C—H···O hydrogen bonds between symmetry related molecules the atom O(2) acts as an acceptor from both the N1H and C8H groups.

C(7)—H(7)···Cl(1) [with C···Cl = 3.954 Å, H···Cl = 2.865 Å, C—H = 1.097 Å and C—H···Cl = 171.7°], C(13)—H(13)B···Cl(1) [with C···Cl = 3.623 Å, H···Cl = 3.010 Å, C—H = 0.98 Å and C—H···Cl = 121.9°] and C(14)—H(14)B···Cl(1) [with C···Cl = 3.798 Å, H···Cl = 3.138 Å, C—H = 0.96 Å and C—H···Cl = 152.4°], [these H-bonds are marked in Fig. 6b]. These columns are further interconnected by weak hydrogen bonds involving sulphur atoms: C(14)—H(14B)···S(1) [with C(14)···S(1) = 4.031 Å, H(14B)···S(1) = 3.363 Å, C(14)—H(14B) = 0.96 Å and C(14)—H(14B)···S(1) = 128.5°] and π–π stacking interaction between the phenyl groups of symmetry related molecules [1 − *x*, 0.5 + *y*, 0.5 − *z*] with a centroid – centroid distance of 5.286(5) Å. Thus the intermolecular hydrogen bonding and weak stacking interactions together form a layer type crystal packing (Fig. 6b).

^1H NMR

The experimental and calculated chemical shifts of ethyl 2-{[(*Z*)3-(4-chlorophenyl)-3-hydroxy-2-propene-1-thione] amino} acetate are given in Table 2. ^{1}H NMR spectrum of the thioamide in $CDCl_3$ shows its existence of the compound as *keto* and *enol* forms in the ratio 3:2. The *enol* form shows distinct peaks at 4.33 (d, 0.8.H, —NCH_2), 5.98 (s, 0.4 H, vinyl), whereas *keto* form shows peaks at 4.36 (d, 1.2H, *J* = 4H, —NCH_2), 4.42 (s, 1.2H, methylene). Other peaks due to both *keto* and *enol* forms are at 1.26 (m, 3H, —CH_2CH_3), 4.21 (m, 2H, —CH_2CH$_3$) and at 7.32–7.92 (m, 4H, ArH). Full geometry optimization was performed with DFT using the hybrid B3LYP and RHF methods with 6-31G (d) as the basis set. Then, gauge-including atomic orbital (GIAO) ^{1}H NMR chemical shift calculations of the compound were made by same method using 6-31G (d) basis set [26]. The correlation between calculated and experimental chemical shifts of ethyl

Table 2
Experimental and calculated ^{1}H NMR chemical shifts (ppm) of ethyl 2-{[(*Z*)3-(4-chlorophenyl)-3-hydroxy-2-propene-1-thione] amino} acetate.

Fixed atom position	Experimental	Theoretical
18H	9.395	9.916
6H	7.928	7.956
4H	7.414	7.427
7H	7.309	7.271
3H	7.193	7.147
19H	5.977	5.591
9H	4.427	4.658
14H	4.331	4.222
17H	1.277	1.422
16H	1.018	1.243

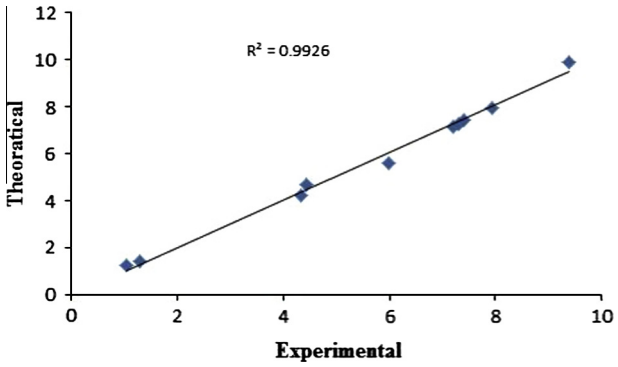

Fig. 7. Correlation between the calculated and experimental chemical shifts of ethyl 2-{[(*Z*)3-(4-chlorophenyl)-3-hydroxy-2-propene-1-thione] amino} acetate.

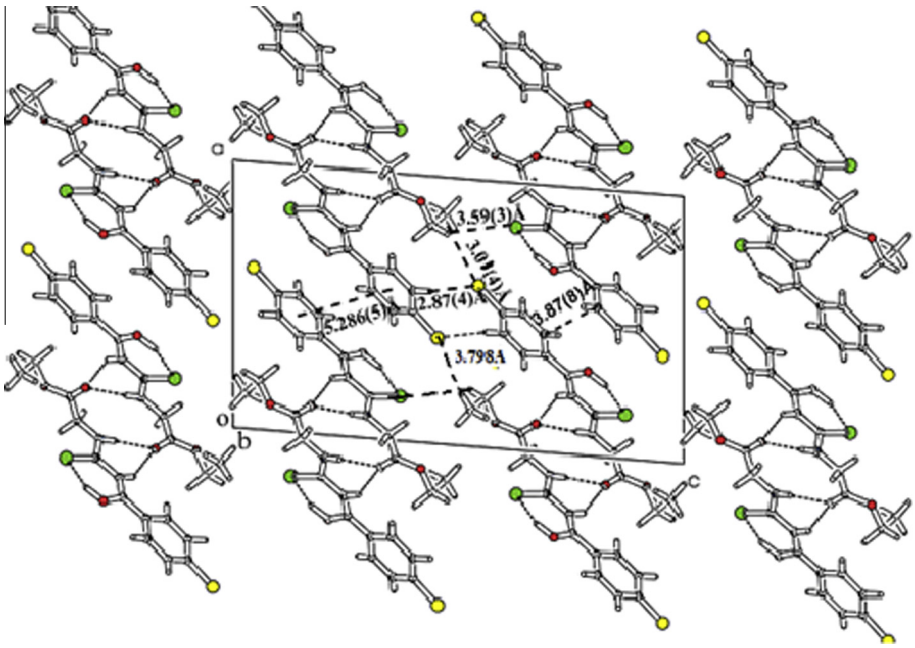

Fig. 6b. Packing of molecules of the compound down the *b*-axis. Dashed lines indicated hydrogen bonds and stacking interactions.

Table 3a
Calculated vibrational wavenumbers, measured Infrared and Raman bands position of ethyl 2-{[(*Z*)3-(4-chlorophenyl)-3-hydroxy-2-propene-1-thione] amino} acetate.

Unscaled frequency (cm^{-1}) B3LYP	Scaled frequency B3LYP	Intensity B3LYP	Frequency (cm^{-1}) experimental	Unscaled frequency (cm^{-1}) RHF	Scaled frequency (cm^{-1}) RHF	Raman activity B3LYP	Raman activity RHF	Raman frequency (cm^{-1}) experimental
206.928	199.064736	4.1649	–	211.0194	196.6700808	4.1649	0.845	230.20
310.1453	298.3597786	5.6431	–	301.4468	280.9484176	5.6431	1.8119	334.054
352.2004	338.8167848	2.5514	–	363.1963	338.4989516	2.5514	0.3313	383.8
477.8486	459.6903532	12.5829	–	459.0297	427.8156804	12.5829	0.3416	490.9
564.0348	542.6014776	27.3647	–	585.7143	545.8857276	27.3647	0.3235	596.92
646.1044	621.5524328	1.1574	–	634.7706	591.6061992	1.1574	2.0716	713.76
707.9623	681.0597326	13.022	707	704.5047	656.5983804	13.022	12.2858	
741.6128	713.4315136	5.7142	–	759.2888	707.6571616	5.7142	6.8206	801.38
752.6019	724.0030278	20.615	768	–	–	20.615	11.3164	
815.3645	784.380649	1.1452	819	822.6456	766.7056992	1.1452	12.048	
888.5047	854.7415214	15.2895	–	905.0046	843.4642872	15.2895	9.9265	983.12
964.191	927.551742	0.3537	964	960.281	894.981892	0.3537	4.194	
981.4424	944.1475888	0.7341	–	961.1198	895.7636536	0.7341	3.783	1106.44
1018.5333	979.8290346	2.9588	1019	1027.0752	957.2340864	2.9588	0.7704	
1089.402	1048.004724	27.8484	1053	1096.9793	1022.384708	27.8484	47.4944	1183
1169.2956	1124.862367	14.387	–	1161.2547	1082.28938	14.387	9.4364	1244.56
1206.9722	1161.107256	27.0565	1207	1209.445	1127.20274	27.0565	2.7689	
1274.3726	1225.946441	138.2444	1284	1281.8606	1194.694079	138.2444	473.5271	
1337.1938	1286.380436	2.1587	–	–	–	2.1587	4.8818	1434.58
1363.4907	1311.678053	174.6456	1374	1362.0525	1269.43293	174.6456	26.1181	
1486.0658	1429.5953	55.8774	–	–	–	55.8774	59.8461	1607.009
1536.0037	1477.635559	9.6704	1529	1544.4048	1439.385274	9.6704	6.8725	
1616.9179	1555.47502	60.1271	1614	1606.9425	1497.67041	60.1271	76.5473	
1651.8881	1589.116352	35.67	1653	1645.2995	1533.419134	35.67	67.6545	
1658.4542	1595.43294	413.3635	–	1660.6624	1547.737357	413.3635	1104.4951	1803
2976.8226	2863.703341	603.3231	2990	1997.6757	1861.833752	603.3231	119.4355	2901.94

2-{[(*Z*)3-(4-chlorophenyl)-3-hydroxy-2-propene-1-thione] amino} acetate is shown in Fig. 7.

IR and Raman spectra

Vibrational assignments

The IR and Raman spectra are recorded and the bands are assigned for the molecule ethyl 2-{[(*Z*)3-(4-chlorophenyl)-3-hydroxy-2-propene-1-thione] amino} acetate. Using RHF and B3LYP methods vibrational wave numbers are computed and their total energy distributions are given in Tables 3a and 3b. The molecule has 33 atoms and 83 normal modes of vibrations are assigned among the possible 93 normal modes. The observed and calculated IR and Raman spectra are given in Figs. 8–13. Due to the combination of electron correlation effects and the basis set deficiencies the calculated frequencies are usually greater than the corresponding experimental quantities. After applying the scaling factors, the theoretical calculations agree well with the experimental data, particularly by B3LYP.

C—H vibrations

The C—H stretching vibration of the *p*-Chlorophenol group in the compound is observed at 3054 cm^{-1} (Fig. 13). When calculated by RHF C—H stretching vibrations are at 3217, 3251, 3299, 3393, 3400, 3409 $cm^{-1}$and DFT the frequencies are at 3197, 3212, 3222, 3229, 3240 cm^{-1}. The C—H stretching vibrations are generally reported in the range 3000–2850 cm^{-1}, while in *p*-chlorophenol it is reported in the range 3096–3144 cm^{-1} [18,27]. The two observed bands in the IR spectrum at 1207 cm^{-1} and 1288 cm^{-1}, and in the Raman spectrum at 1183 cm^{-1} and 1244 cm^{-1} correspond to the C—H in plane bending vibrations. The corresponding calculated vibrations by RHF and B3LYP are in the range 1209–1317 cm^{-1} and 1217–1274 cm^{-1}, respectively, these values are in good agreement with the reported values and are generally appearing in the region between 1300 and 1150 cm^{-1} [28,29]. The observed band at 707–964 cm^{-1}in the IR and the band at 713–983 cm^{-1} in Raman are attributed to the C—H out of plane bending vibrations, the corresponding values calculated by RHF an B3LYP methods are 704–1110 cm^{-1} and 707–981 cm^{-1}, respectively [30]. Similar values between 675 and 1000 cm^{-1} are reported in *p*-N,N-dimethyl amino benzylidene malononitrile [18].

C—C vibrations

The aromatic C—C stretching vibrations are generally observed in the frequency range 1600–1585 cm^{-1} and in *p*-chlorobenzene it was reported in the range 1611–1430 cm^{-1} [31]. In ethyl 2-{[(*Z*)3-(4-chlorophenyl)-3-hydroxy-2-propene-1-thione] amino} acetate this vibration computed by RHF is at1671 cm^{-1} and by B3LYP, two vibrations at 1651 cm^{-1} and 1658 cm^{-1} are attributed and the observed band in the IR spectrum at 1653 cm^{-1} corresponds to this vibration.

N—H vibrations

The N—H stretching modes are reported in the range 3500–3300 cm^{-1} [29]. The calculated RHF and B3LYP bands at 3841 cm^{-1} and 3554 cm^{-1} respectively are assigned to N—H stretching in ethyl 2-{[(*Z*)3-(4-chlorophenyl)-3-hydroxy-2-propene-1-thione] amino} acetate. The band observed at 3288 cm^{-1} in the IR spectrum may correspond to this mode of vibration, this shows a red shift on account of the involvement of this group in hydrogen bonding as seen in the crystal structure (Fig. 6a) [31].

C—N vibrations

The C—N stretching modes are reported in the region 1100–1300 cm^{-1} [28]. In ethyl 2-{[(*Z*)3-(4-chlorophenyl)-3-hydroxy-2-propene-1-thione] amino} acetate the measured IR bands in the region 1113–1212 cm^{-1} and the calculated wavenumbers at 1161 cm^{-1} and 1169 cm^{-1} by HF and B3LYP, respectively are assigned for C—N stretching vibration [32].

C=O vibrations

The C=O stretching bands are generally reported in the range 1720–1790 cm^{-1} [33]. In ethyl 2-{[(*Z*)3-(4-chlorophenyl)-3-hydroxy-2-propene-1-thione] amino} acetate the observed IR

Table 3b
Assignments of the IR bands.

Vibrations	Frequency (calculated) cm^{-1}		Frequency (experimental) cm^{-1}
	RHF	B3LYP	
C—H stretching vibrations	3217–3409		3054
C—H in plane bending	1209–1317	1217–1274	1207, 1288
C—H out of plane bending	704–110	707–981	707–964
C—C stretching	1671	1651, 1658	1653
N—H stretching	3841	3554	3288
C—N stretching	1161	1169	1113–1212
C═O stretching	1997	1812	1764–1788
O—H vibrations	3746	2976	2980
Methyl group vibrations			
Symmetric stretching	3217	3063	–
Asymmetric stretching	3276, 3288	3132	2900
CH2 symmetric stretching	3251	3052, 3078	–
CH2 asymmetric stretching	3276	3132	2996

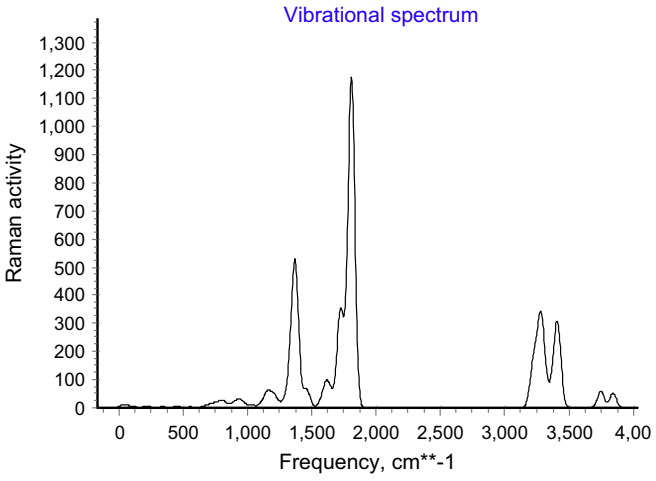

Fig. 8. Raman spectrum HF method.

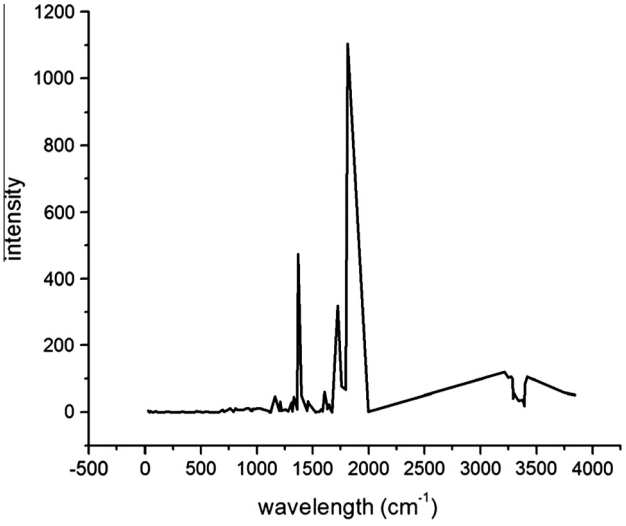

Fig. 10. Raman spectrum experimental.

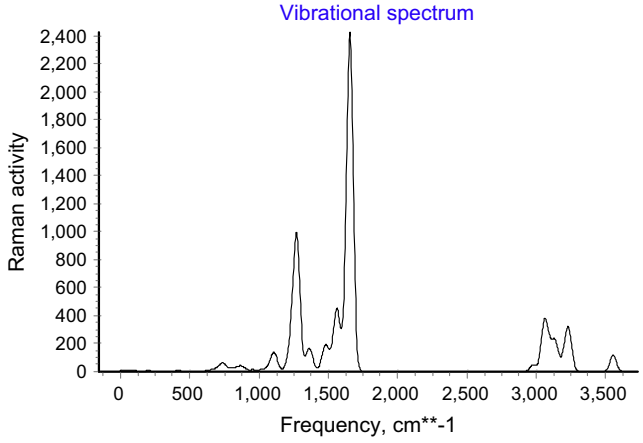

Fig. 9. Raman spectrum B3LYP method.

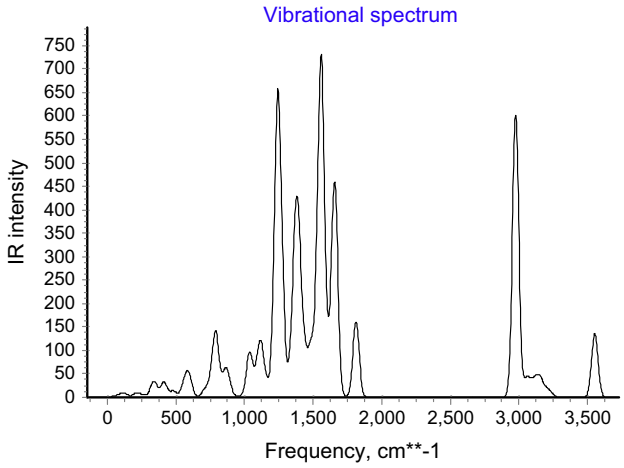

Fig. 11. IR spectrum B3LYP method.

spectrum in the range 1764–1788 cm^{-1} and in the Raman spectrum the band at 1720 cm^{-1} are assigned to the C═O stretching. The calculated frequencies by RHF and B3LYP methods are at 1997 cm^{-1} and 1812 cm^{-1}, respectively.

O—H vibrations

In the present compound calculated O—H vibrations are at 3746 cm^{-1} and 2976 cm^{-1} by RHF and B3LYP methods, respectively. The observed IR band is at 2980 cm^{-1}, this value is closer to that calculated by B3LYP method and similar situations are also reported [34–36].

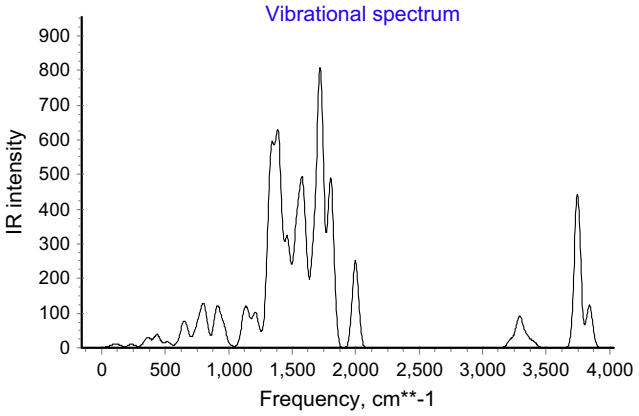

Fig. 12. IR spectrum HF method.

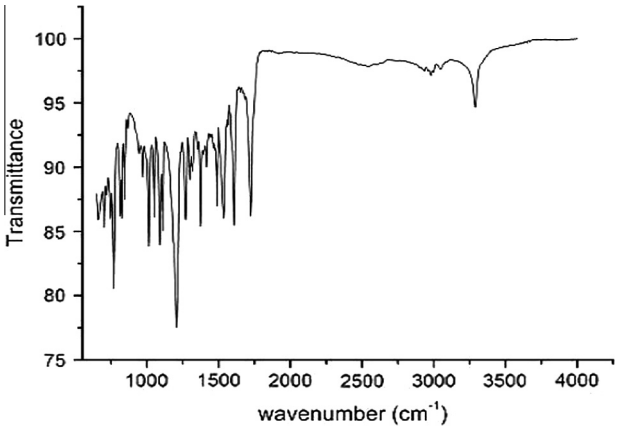

Fig. 13. IR spectrum experimental.

Methyl group vibrations

In ethyl 2-{[(*Z*)3-(4-chlorophenyl)-3-hydroxy-2-propene-1-thione] amino} acetate the symmetric stretching vibrations are calculated at 3217 cm^{-1} and 3063 cm^{-1} by RHF and B3LYP, respectively. The asymmetric vibrations are calculated at 3276 cm^{-1} and 3288 cm^{-1} by RHF and at 3132 cm^{-1} by B3LYP. The symmetric stretching mode in the title compound is observed at 2900 cm^{-1} both in the IR and Raman spectra.

The CH_2 symmetric and antisymmetric stretches calculated by RHF are at 3251 cm^{-1} and 3276 cm^{-1} respectively and from DFT the corresponding values are 3052 cm^{-1}, 3078 cm^{-1} and 3132 cm^{-1}, respectively. In the IR spectrum the symmetric stretching mode is observed at 2996 cm^{-1}.

Conclusion

Crystal structure of the molecule, ethyl 2-{[(*Z*)3-(4-chlorophenyl)-3-hydroxy-2-propene-1-thione] amino} acetate was determined and its geometry was optimized by RHF and B3LYP methods with 6-31G (d) basis set. The vibrational frequencies were assigned using the potential energy distribution analysis. ^{1}H NMR, IR and Raman spectra of the compound were experimentally measured and compared with their corresponding calculated values. The NMR spectrum in $CDCl_3$ solution showed the presence of both the *keto* and *enol* forms of the compound in the ratio 3:2, whereas the *enol* form is found in the crystal structure. The thioamide part of the molecule adopts the *Z*-conformation and the thioamide C—N bond shows a high rotational barrier. The conjugation observed in the molecule is the aftereffect of both the thioamide delocalization and the *keto-enol* tautomerism. The X-ray geometry of the molecule is in good agreement with that calculated by B3LYP. The molecules show a layer type crystal packing mediated primarily by N—H···O and C—H···O intermolecular hydrogen bonds.

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Appendix A. Supplementary material

Crystallographic data for this compound are deposited in the Cambridge Crystallographic Data Centre (CCDC No: 1015077). Geometrical parameters such as bond lengths, bond angles, torsion angles and the ^{1}H NMR spectra were given in supplementary material.

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.molstruc.2014.10.037.

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