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 PII:
 S0022-3697(16)30070-1

 DOI:
 http://dx.doi.org/10.1016/j.jpcs.2016.04.002

 Reference:
 PCS7761

To appear in: Journal of Physical and Chemistry of Solids

Received date: 28 November 2015 Revised date: 25 January 2016 Accepted date: 7 April 2016

Cite this article as: N. Moorthy, P.C. Jobe Prabakar, S. Ramalingam, M Govindarajan, S. Joshua Gnanamuthu and G.V. Pandian, Spectroscopic analysis AIM, NLO and VCD investigations of acetaldehyde thiosemicarbazone using quantum mechanical simulations, *Journal of Physical and Chemistry of Solids* http://dx.doi.org/10.1016/j.jpcs.2016.04.002

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Spectroscopic Analysis, AIM, NLO and VCD investigations of Acetaldehyde thiosemicarbazone using quantum mechanical simulations

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ABSTRACT

The prepared Acetaldehyde thiosemicarbazone (ATSC) have been investigated by both the experimental and theoretical methods; through this work, the essentiality of elucidation of molecular fragments source linear and non linear optical properties was explored. The stability of the structure and entire calculations have been performed on HF and B3LYP methods with 6-311++G(d,p) level of basis set. The Mulliken charge profile, electronic, optical and hyper polarizability analyses have been carried out in order to evaluate nonlinear optical (NLO) performance of the present compound. The exact optical location of the ATSC was determined by executing UV-Visible calculations on TDSCF method. The existence of the molecular group for the inducement and tuning of NLO properties were thoroughly investigated by performing fundamental vibrational investigation. The optical energy transformation among frontier molecular levels has been described in UV-Visible region. The Gibbs energy coefficient of thermodynamic functions was monitored in different temperature and it was found constant irrespective of temperatures. The appearance of different chemical environment of H and C was monitored from the ¹H and ¹³C NMR spectra. The vibrational optical polarization characteristics with respect to molecular composition in the compound have been studied by VCD spectrum.

The bond critical point, Laplacian of electron density, electron kinetic energy density and total electron energy density have calculated and analysed using AIM study.

Keywords: Acetaldehyde thiosemicarbazone, Mulliken charge, Gibbs energy, VCD spectrum, AIM.

1. Introduction

The organic synthesized materials usually have rich second-order nonlinear optical (NLO) susceptibilities due to the symmetrical occurrence of ligand groups with suitable base molecule [1-6]. The formation of compound has high degree of symmetry order by fusing optically inducible ligand with optically active base compound. Particularly, the enumerable structural variations are stimulated on aldehyde-amide group condensation in the chemical amalgamation of acetaldehyde (ligand) with thiosemicarbazide (base compound) which is favour for the product; acetaldehyde thiosemicarbazone compound with large second order optical nonlinearities [7-8]. In this compound, the molecular crystal symmetry depends mainly on the polarizability of the electrons in the σ -bonding orbital of aldehyde (CHO) and azine group (N-N) and the π -electron delocalization of imine (C=N) group. These group formations in present compound are speculating the optical properties with high degree which facilitate doubling and tripling of frequencies of entering light waves.

Thiosemicarbazone is fascinating compound because they form highly stable and intensely colored complexes able to manipulate photonic signals efficiently are of importance in technologies such as optical computing and second and third order harmonic generation[9-10]. Acetaldehyde is an industrially important solvent used as an intermediate for the synthesis of a wide range of compounds [11]. The literatures [12-14] revealed that, no attempt has been made to detect SHG and THG on Acetaldehyde thiosemicarbazone so far. In this work, the Acetaldehyde was fused with thiosemicarbazide and Acetaldehyde thiosemicarbazone crystal was formed and the characterization has been carried out to evaluate the NLO and optical characteristics of the compound.

2. Experimental details

2.1. Preparation of thiosemicarbazone of acetaldehyde

Thiosemicarbazone of acetaldehyde crystal was prepared by adopting general procedure [15-16].In a hot solution of thiosemicarbazide with methanol, the solution of acetaldehyde with methanol was added drop wise for thirty minutes. The mixture was stirred and refluxed for four hours. Then, it was filtered and the filtrate was concentrated to half the volume. After making slow evaporation of the concentrate at room temperature, crystals were collected by filtration, washed with cold ethanol and dried. The grown crystals were purified by repeated recrystallization.

2.2. Spectroscopic measurements of FT-IR, FT-Raman, NMR and UV-Visible spectra

- FT-IR, FT-Raman spectra were recorded in Bruker RFS 27 spectrometer with full specification.
- UV- Visible spectrum was recorded using Lambda 25 Spectrometer with latest specification.
- The ¹H and ¹³C NMR spectral data was obtained from BRUKER 300 NMR spectrometer.

3. Computational profile

The efficient quantum mechanical calculations have been carried out to optimize the molecular structure on by using Gaussian 09 (D.01) Program package [17-18] [LC/089/07500280042/1004 TIN:07500280042]. In DFT methods, Becke's three parameter exact exchange-functional (B3) combined with gradient-corrected correlational functional of Lee, Yang and Parr (LYP) provides the best predicting results for molecular geometry and vibrational wave numbers for moderately larger molecule. The minimum energy of geometrical structure is obtained by using same level of theory. All the computations have been done by adding polarization function d and diffuse function on heavy atoms and polarization function p and diffuse function on hydrogen atoms [16-19], in addition to triple split valence basis set (6-

311++G(d,p), for better treatment of polar bonds of chlorine atom, hydroxyl group, amino group. The calculations to optimize the structural parameters by HF and B3LYP methods with 6-311++G(d,p) level without looking of molecular symmetry boundary were presented in the Table 1. The VCD spectral data was calculated at B3LYP/6-311++G(d,p) level of calculation. The electronic absorption spectra represent the frontier molecular orbitals gives the band gap of the title molecular system which were calculated at B3LYP/6-311++G(d,p) level. These set of theories exposed the details of internal chemical reaction mechanism between ligand and base compound. The ¹³C and ¹H NMR chemical shift of ATSC was imitated in gas and solvent phase (DMSO and chloroform) at GIAO approach at B3LYP/6-311G++(d,p) level. The natural bond orbital (NBO) was identified by using Gauss sum program and the transitions among bonding and antibonding orbitals were analysed. Moreover the MEP view was simulated using the B3LYP/6-311++G(d,p) method and their charge levels on reactive sites was evaluated. The Gibbs energy related to thermodynamic functions (the heat capacity, entropy, and enthalpy) was calculated for the temperature region 100-1000K.

4. Results and discussion

4.1. Optimization; Energy structure scan

The monomer and dimmer molecular structure of ATSC was shown in Figure 1. In the analytical study of molecular interactions, the optimization of geometrical structure is most essential to elucidate different symmetrical structure. The scan was performed on the molecular structure and the potential energy scan curve with different conformers was shown in Figure 2. The orientation of dihedral angle C1-N7-N8-C10 was varied from 0 to 360° in steps of 10 rotations about 36° . All the optimized parameters were relaxed during the calculations in dihedral angle. There were eleven conformers obtained and out of which four conformers were having same energy. In this process, the global minimum energy was found in two angles which were at 72° and 288° named conformer 3 (0.0813 Hartree) and at 36° and 324° called conformer 2 (0.0829067 Hartree).

4.2. Molecular geometry deformation analysis

The present accumulated molecular system posses C_S point group of symmetry and consists of 14 atoms. The compound was shaped by blending of thiosemicarbazide with acetaldehyde in which H₂O was evaporated and all the atoms conjugated in a chain making Acetaldehyde thiosemicarbazone. Here, the formation of azine and imine groups and C=S were significant since they were root cause of the optical properties. In this compound, thiosemicarbazone segment was situated in one plane whereas acetaldehyde group was placed perpendicular to that plane. This is the main reason for the existence of various orbital lobe interactions which stipulated suitable lattice formation for optical phonon momentum.

When the acetaldehyde injected to the thiosemicarbazone, N7-N8 and C1-C3 bonds become strong and it makes C=N very strong and was evidenced from shrinking of bond length C1=N7 was about 1.276 which was smaller than experimental value (1.287)[19]. The calculated bond length of N-N was 1.412Å whereas the observed value was 1.384Å. This was due to the steeving of acetaldehyde group in the chain. As the carbon was substituted on both sides by H and H₂ asymmetrically, the bond lengths N8-C10 and C10-N12 were differed by 0.005Å and also fluctuated experimentally by 0.02Å. Actually, the symmetrical placement of NH group was disturbed the bond angle about C, in this case, thio substitution was kept the bond angle at constant level. The calculated bond angle N7-N8-C10 was 123.9° while its experimental value was 119.3°, both were differed slightly. Actually, the bond angle should be 120°, but due to the substitutions with different mass and twisting of CH₃. The calculated optimized parameters along with observed values were presented in the Table 1.

4.3. Mulliken charge distribution analysis

The Mulliken charge levels were presented in the Table 2 and its diagram was depicted in Figure 3. Generally, when two separate molecules coupled one another, the Mulliken charge redistributed according to the charge levels of atoms and electron density of particular group. In this case, the CH₃CH(O) inserted with thiocarbazide, the imine group was created and the charge levels were completely disturbed and the C of methyl group become more negative than C=N group, even though the bond was heteronuclear. In addition to that, N of imine group was more negative than C of same. In azine group, one of N was neutral while another N was faded

negative. In the case of C=S, both C and S having same color of negative but N of amine group was lesser negative than C and S. This redistribution of Mulliken charge levels was swerved the weak interaction bonds in thiosemicarbazone wing whereas strong interaction bond in acetaldehyde arm. Here, the bonding of two groups was sublimed by molecular interactions. Irrespective of molecular groups, the entire substitutions of H bonds made strong interaction host atoms.

According to the dimmer form, the sulphur and H atoms were building chain with next group of molecule and both were made negative and positive respectively. The atom N8 was found to be positive when compared with N7 and N12 which was due to the N being injection point of coupling. The resultant dipole moment and reactive re-gion of the compound was depends upon the CH₃ and NH₂ group. The charge levels of the compound ensure the active electronic and optical polarizability which was subtilised NLO properties. From the charge range of the compound, the pathway of charge transportation was found as following

C1→N7→N8→C10→C12 →S11

4.4. Vibrational assignments

The vibrational fundamental of the organic compound is depends on the planes of the functional groups of whole compound. According to the molecular symmetry (C_s), the molecule was unwound in to 14 atoms and there were 36 fundamental modes of vibrations found in which IR and Raman active. The entire fundamental modes break up in to in plane and out plane vibrations which were represented by A' and A" respectively.

Γ36=Σ(25Α'+11 Α")

The calculated raw frequencies were scaled down in order to coincide with the observed wavenumber values and were depicted in the Table 3. The simulated and experimental FT-IR and FT-Raman spectra were sketched in the Figures 4 and 5 respectively. The realistic fundamental modes were assigned and verified along with the characteristics region of group frequencies. The entire observed modes were influenced by their nearby attractive vibrations.

4.4.1. N-H vibrations

Usually, the molecular interaction is very much concentrated between N and H in thio amino group derivatives which stimulate rich force constant in N-H bonds. This is the main basis upon which the vibrational motion is always on the top of the IR and Raman observed region of spectra. Here, three N-H bonds identified along with the C-N and C=N bonds in the compound. So that, there were 9 vibrational modes corresponding to the N-H bonds would be the part of the entire vibrational pattern. Regularly, hetero aromatics having an N-H group show its stretching absorption in the region 3500-3100 cm⁻¹[20]. The place of IR absorption of N-H vibration in the region depends upon the nature of hydrogen bonding and the substitutional effect [21]. In the present compound, thiosemicarbazone holds three N-H hetero bonds and the resultant stretching vibrations were found with strong to medium intensity in IR and weak intensity in Raman at 3390, 3240 and 3160 cm⁻¹. Even though, the observed N-H stretching vibrations have not affected much, one among those band was found at the lower end of the expected region. This was actually moved down by the attraction of high negativity N of imine group(C=N). Out of three vibrations, last two bands were identified as symmetric. In this compound, other than amino group, there were no dominated vibrations found. So, these stretching vibrations should not be affected anymore. This trend was true in this case.

The N-H scissoring bend vibrations usually observed in the region 1580-1640 cm⁻¹ and the rocking modes are assigned in the range 1170-1080 cm⁻¹ in thio amides which may be affected little bit by the inductive effect with high electronegative group [22-24]. Here, three in plane bending modes observed at 1470, 1380 and 1370 cm⁻¹. Here, there was no possibility that, the above vibrational modes to be the scissoring bands since; the dominating vibrational bands should not be suppressed. So, those bands were to be the rocking modes that were found moved over the expected region. This was mainly due to the thio group present in the compound which was also the root cause of the optical properties. The out of plane bending vibrations in thio amides are observed in the region 710-580 cm⁻¹[25]. Accordingly, the out of plane bending modes were identified at 995, 870 and 790 cm⁻¹. Similar to the in plane bending, all the out of plane bands were elevated and prove its leading character. The source of optical orientation of crystal lattice was thio amide group and it was active in this compound.

4.4.2. C-H vibrations of methyl and aldehyde

When the present compound shaped, the methyl group was present and their vibrational assignments ensure the place of methyl group within a molecule. Generally, the asymmetric and the symmetric C-H symmetric vibrations in methyl group observed between 2990-2920 cm⁻¹, whereas the symmetric C-H vibrations for methyl group are observed at 2900 – 2840 cm-1 [26-28]. Being in excellent agreement with the literature, in this study, the C-H vibrations were occurring at 2930, 2920 and 2910 cm⁻¹. Here all were asymmetric and these were not affected by other vibrations. In the methyl group, the bending vibrational bands are normally observed within the region with medium to weak intensity. The in plane and out of plane bending vibrations are observed in the region 1190- 940 cm⁻¹ and 870-630 cm⁻¹[29-30] respectively. The in plane and out of plane bending vibrations were observed at 1140, 1110 and 1100 cm⁻¹ and 730, 640 and 630 cm⁻¹ respectively. From these bending vibrations, it was observed that, the entire bending vibrations found within the expected region and this view ensured that all bands were pure. The methyl group in the compound also play important role in the creation of optical properties. The active modes of vibrational energy levels of methyl group ensured its energetic presence in the compound.

The stretching, in plane and out of plane bending of C-H bond in aldehyde group of the present compound were identified at 2850, 1000 and 580 cm⁻¹ respectively. According to the literatures [31], all these vibrations have not affected even in tiny amount and this was mainly due to the consistent position of aldehyde group in the compound.

4.4.3. Chain C-C and C=S vibrations

The carbon-carbon bond existed in between aldehyde and methyl group and usually, the related vibrations suppressed since it was acting as bridge [32]. The C-C stretching vibration was observed at 1250 cm⁻¹. The C-C in-plane bending vibration is found at 390cm⁻¹ and out-of-plane bending vibration is observed at 175 cm⁻¹. These assignments are made disagreement with the literature [33]. Normally, the thiosemicarbazone group has strong vibrational band in the region of 1570-1395 cm⁻¹ due to the C=S stretching vibration [34-35]. In this present case, the C=S stretching band was observed with strong intensity at 1507 cm⁻¹. This stretching vibration was

found at the top end of the expected region which was due to no other attack of substitutional group.

4.4.4. C=N, C-N and N-N vibrations

The heteronuclear bond named as dipole bond (C=N and C-N) which was existed along with azine and methyl groups in the compound. Generally, the C=N stretching vibration has higher energy and observed in the region 1600-1490 cm⁻¹[36]. In this case, the vibrational peak was appeared at 1600 cm⁻¹ in IR only. This strong manifestation of the imine group ensured its active presence. It's in plane bending was present at 400 cm⁻¹ which was also ensured the activity extension. Another important existence of dipole bond C-N and the resultant stretching absorption peak was observed in the region 1382–1266 cm⁻¹ for aromatic amines [37]. In benzamide the band observed at 1368 cm⁻¹ was assigned to be due to C–N stretching [38]. Hence, in this case, two strong bands were observed at 1310 and 1270 cm⁻¹ for C-N stretching vibrations. The in plane and out of plane bending vibrations are found at 530 and 500 cm⁻¹ and 240 and 180 cm⁻¹. The stretching vibrations have not affected whereas entire bending vibrations have suffered much due to the azine and thio group.

The rare homonuclear bond N-N which is important core bond of azine group since it was bridge point for NLO properties of title molecule. Generally, the azine bond N-N stretching vibration was found around 1080 cm⁻¹ [39]. The N-N stretching vibration was strongly observed at 1150 cm⁻¹ in IR only. Normally, the homonuclear bond found in Raman, but in this case, it was eluded. The consequent in plane and out of plane bending modes was observed at 300 and 150 cm⁻¹ respectively. The obtained azine group peaks were accurately coordinated with the literature and ensure its presence and explored the semiconducting properties of the compound.

4.5. NMR confinement

The chemical information of the molecular components of the compound can be extracted from the experimental chemical shift and it can be found that whether the results true or not, from the calculated data. In this case, the experimental data was collected by recording the spectra and the ¹H and ¹³C NMR spectral data was calculated at B3LYP method with 6-

311++G(d,p) level on the basis of GIAO method and the chemical shifts were reported in ppm relative to TMS. The NMR spectra were presented in Tables 4 and the corresponding spectra were shown in Figure 6.

Isotropic and anisotrophic effect is particularly important in molecules containing σ and π bonds respectively. Thus, a neighboring nucleus, which may not be directly chemically bonded to the σ and π -system, may be shielded or deshielded depending on its orientation in space with respect to the σ and π system. In this case, two double bonds and others were sigma bonds in which the isotropic and anisotrophic shifts were cal calculated. In general, the chemical shifts of carbon and hydrogen are depends upon the bonded atoms and chemical environment within the compound [40]. Usually, the isotropic chemical shifts spread out in the region of 100-160 ppm [41]. The chemical shift corresponding to the base molecule and ligand group was proportionately to the chemical properties. Usually, the chemical shift of aliphatic chain is constantly behind the aromatic compound [42-43]. On the basis of the diamagnetic shielding, one may expect that the values of the chemical shifts should follow the order sp>sp2>sp3, depending on the electronegativity of carbons to which hydrogen is attached [44].

In this compound, there were 3 carbons and 7 hydrogens in which the carbons were connected with methyl, aldehyde and sulphur group. The hydrogens have been liked with C and N. the chemical shift of C1, C3 and C10 were 140.0, 40.0 and 181.0 ppm respectively. Here, the chemical shift of C10 was higher than C1 which was greater than C3. This order was due to the high degree of breaking of proton shield of carbon by sulphur and nitrogen with different electron pulling. According to calculation, the chemical shift of C1 was 169.2 ppm which was near to the C10 (184.2ppm). The cause of such shift was formation of imine group and the chemical property of imine group was linked with azine group. Usually, the chemical shift in SP³ hybridization would be very low. In this case, this was true in the chemical shift of C3. In the case of hydrogen, the chemical shift of H2 and H9 were high when compared with rest of others since it was singly substituted. The chemical shift of H4, H5 and H6 were very low which was due to no further attraction on the same. This was also the reason for the conception of strong interactive bonds. Thus, the hydrogens and carbons in the chain were taken part in the alternation of the chemical properties of the compound.

4.6. Frontier molecular analysis - Electronic properties

The electronic reactivity in terms of frontier molecular orbitals of the compound explained the electronic exchange among the orbitals and the electronic response of the compound. From this study, it can be confirmed whether this compound active electronic property or not. The 3 Dimensional arrangements of frontier molecular orbitals in IR and UV-Visible region for present compound were displayed in Figures 7 and 8 respectively. In the case of LUMO, the empty orbitals were found S, C and methyl H. The empty σ bond orbital interaction taking place between N-N, C-H and H-N-H bonds and which were being acceptor. In the case of LUMO-1, the interaction of orbital extended as umbrella pattern among the hydrogens of NH₂, NH and N of azine group. The entire spatial of σ bond orbitals were overlapped and that space was common for their electrons. Thus, whenever the electron jumped from the HOMO orbitals to LUMO, that electron travelling over the common orbitals and their properties of such orbitals also mingled with one another. In the case of further extension of LUMO-2, the umbrella pattern was extended and touched with N.

In the case of HOMO, the spatial quantization of S was found big when compared with the other orbitals. So, it was able to provide the electron density to other related orbitals. The σ orbital interaction appeared in N-H, C-N and N-N bonds. Here, there was no π bonding interaction lobes found. From this observation, it can be inferred that, the interaction taking place in sigma instead of pi bond. In the case of HOMO+1, the σ -bond interaction appeared on C=S bond and its space was extended in big size. In addition to that, the δ bonding interaction found among N-H and N=C-H orbitals and available spatial orientation of electron density extended up to four bonds. The σ and π orbital interaction identified and that interaction was further extended up to N=C-H bonds. From this observation, it was found all the σ and π bond interactions involved among the bonds of the compound and the transitions taking place entire pathway of interaction lobes.

4.7. Optical properties analysis

The optoelectronic character was clarified from the transition data of the electronic energy levels of present compound which was acknowledged that, whether the compound optically

dynamic or not. The electronic energy calculations of the present molecule were carried out by B3LYP/6-311++G(d,p) level adopted with TD-DFT approach in gas phase and with the solvent of DMSO and Chloroform. The calculated excitation energies, oscillator strength (*f*) and wavelength (λ) and spectral assignments are given in Table 5. The supportive HOMO-LUMO diagram was presented in the Figure 8. The simulated and experimental UV-Visible spectra of the title compound were displayed in the Figure 9.

In UV-Visible spectra, the quarts ultraviolet energy was observed region of 200-380 nm. If the entire absorption of the compound lies in this region, the compound will be active for quarts optics [45]. The consistent peak was observed at 300 nm in both experimental and calculated spectrum which was due to the presence of two π conjugated system of bonds in the compound.

The opto-electronic transitions were observed at 313 nm with 3.95 eV band gap which has been assigned to $n\rightarrow\sigma^*$. Another two peaks were found at 286 and 274 nm with 4.33 and 4.52 eV which was assigned to $n\rightarrow\pi^*$. These transitions happened only by the chromophores; imine and thio groups. From this observation, it was seen that, the entire transitions were belong to quartz ultraviolet crystal region. This view ensured that, the present compound is able to produce the optical waves with second and third order harmonic generation. When it was going from gas to solvent phase, it was determined that, the wavelength region was decreased and simultaneously the energy of the absorption was increased. This was the important evidence of frequency doubling in the present compound.

4.8. Molecular electrostatic potential (MEP) maps

The MEP is highly informative concerning the protonic and electronic charge loving regions of organic and inorganic compounds. It is mainly used for dimmer and molecular cluster formation and optical phonon interactions analysis. It is also used for analyzing charge morphology of the compound and molecular reactivity domain of the composite materials.

Molecular electrostatic potential view was drawn at B3LYP/6-311++G(d,p) level using which the entire molecular interactive sectors was observed and was displayed in the Figure 10. The electrostatic potential energy interaction between proton and electron fields is distinguished from high wavenumber (blue) region to lower wavenumber (red) region. These two charge dislocation designated as between electrophilic and nucleophilic boundaries. In a molecule, the

charged atoms are usually reoriented rigorously with respect to negative and positive terminals and making strong dipole moment. When two separate atoms coupled with one another, the charge levels are redistributed and this is the main reason for the optical activity. In this case, Acetaldehyde thiosemicarbazone was created by the fusing of thiosemicarbazone with acetaldehyde compound. After the formation of the compound, the electron density was reoriented and two separate charged domains were produced. The highly positive region was found around NH_2 segment of thiosemicarbazone and highly negative region was originated around C=S in same group. The neutral charge was generated about the acetaldehyde group. This outlook of the compound constructs the strong dipole moment and intensive polarization.

4.9. NLO activity analysis

The optical parameters such as polarizabilities and hyperpolarizabilities are very important in nonlinear optical materials and devices [46]. The organic compounds with wide band gap having an experiential connection between molecular structure and nonlinear response. Generally, the technique was used such that, making asymmetric polarization induced by electron donor and electron acceptor groups on either side of the molecule at suitable sites in the molecular systems for designing of efficient nonlinear optical organic materials [47]. The substitutions with π -conjugated system which is able to increase the donor acceptor capability usually develop the nonlinear optical activity of the molecular system, is associated with intramolecular charge transfer resulting from an electron cloud movement through a π -conjugated framework from electron donor to electron acceptor groups.

The first order polarizability and hyperpolarizability were calculated using standard formula [48] and using suitable method; B3LYP/6-311++G(2d,p). The calculated parameters were presented in the Table 6. The calculated average and exact polarizability of the compound were 134.77 $\times 10^{-24}$ esu and 101.12 $\times 10^{-24}$ esu. The dipole moment was the representation of the magnitude of the donor and acceptor stabilization level. In this case, the dipole moment was found to be 4.83 Debye which was very high and reflect the stabilized level of donor and acceptor. In the present case, two separate segments were fused in order to achieve rich optical properties. The optical properties are governed by the increasing of both conjugation length and

strength of donor and acceptor groups. Here, due to the addition of those two groups, two special π -conjugated groups such as C=N and C=S were produced. In addition to that, one azine group (N-N) and one torsional angle (CH₃) was formed. These groups formation was a root cause of the existence of strong acceptor donor group which generates first static hyperpolarizabilities. If the hyperpolarizability (β) is found to be high in the compound, in the crystal form is able to produce second and third order harmonic generation with two folds frequency [49]. The hyperpolarizability of this compound was 252.77 and it was active for SHG. This general mechanism of the compound helped to develop the NLO materials. The comparative polarizability and hyperpolarizability of Acetaldehyde, thiosemicarbazide and Acetaldehyde thiosemicarbazone compounds presented in the table 7. The Polarizability and hyperpolarizability of Acetaldehyde thiosemicarbazone were found higher than those functional compounds which showed the optical property was tuned up in this compound.

4.10. NBO profile

The natural bond orbital (NBO) calculations were carried out using Gaussian NBO 6.0 program [43] with B3LYP/6-311++G(d,p) method in order to determine electronic transitions from the filled orbital of one bond system and unfilled antibonding orbital of another system. It was mainly used for measuring type of delocalization of electron density and kind of hyper conjugation of electronic orbitals. The NBO analysis granted the information regarding electronic orientations inside the molecule due to the reconstruction of molecular orbitals after the optimized structure was formed.

The NBO calculations were performed to evaluate the donor–acceptor interactions among various bonds of the molecule. The interactions results the loss of occupancy from the localized NBO of the idealized Lewis structure into an empty non- Lewis orbital. This was also the evidence of stabilization of donor and acceptor energy levels causing the NLO properties. Here some of the NBO transitions were presented in the Table 8. The first transition was found from donor bond C1-H2 and acceptor N7-N8 which was assigned to σ - σ * transition by transferring the energy 41.51KJ/mol. The second transition was found from C1-C3 to C1-N7 which was also represented as σ - σ * by dislocating the energy 6.9KJ/mol. Reversibly, the transition between C1-

C7 and C3-H4&H6 (π - σ *) by shifting the energy of 9.08 and 5.15KJ/mol respectively. From this transition, it was determined that, the energy from acetaldehyde to imine point was high.

The transition between N7-N8 and C10-N12 and C1-N7 assigned to σ - σ^* and by taking the energy 9.04 and 10.8 KJ/mol. The bond C10-N12 and antibonds N7-N8 under σ - σ^* transition has taken the energy of 13.97 KJ/mol. The thio bond C10-S11 has made energy transition with N8-C10 and N12-H14 by absorbing 22.9 &10.9 KJ/mol, the difference of energy 1.1 au. The by n - π^* and n - σ^* transitions were appeared between lone pair orbital of N7, S11 and N12 atoms to non bonding orbital space of N-H, C-N and N-C bonds. From these observations, it was concluded that, there were lot of donor and acceptor orbitals interacted among base and ligand groups and constructing stabilized inter and intra molecular lobes attraction, thereby it was favor for inducing NLO properties in the compound.

4.11. Thermodynamical functions analysis

The entropy, specific heat capacity and enthalpy of the crystal compound since they play a important role in physical as well as chemical properties [50]. In this case, the efficient calculation method; B3LYP/6-311++G(d,p) was used to calculate the thermodynamic functions and were depicted in the Table 9. The coefficients of entropy, specific heat capacity and enthalpy were varied with respect to temperature in positive mode. When the temperature increased from 100K to 1000K, the thermodynamical functions found to vary as linear curve and sustained up to the maximum temperature. This linear variation shows the chemical stability of the present compound was consistent.

Similarly, the Gibbs free energy also has positive temperature coefficient. This positive temperature coefficient of the compound proved to be the semiconductor. Normally, the chemical reaction is feasibly occurring when the Gibbs free energy of the molecular system decreases. If ΔG is negative or less than zero, the chemical reaction will be constant. In this case, the Gibbs energy was found be varied negatively up to 1000K and it was inferred that, the present compound was chemically strong and active.

4.12. Chemical properties

The physical property of the organic compound is another important factor to study the chemical property. Thus the physical parameters are very significant to explain the chemical behavior of the compound. Accordingly, the chemical hardness and potential, electronegativity and Electrophilicity index were calculated and presented in Table 10.

In this case, the dipole moment reflects electronic property of the chemical compound which is the ability of electrical and optical polarization of a compound. The large dipole moment leads the compound; very strong intermolecular interactions. The calculated dipole moment value for the present compound was 4.83 Debye. It was comparatively very high and the present molecule which induces the strong intermolecular interactions.

The chemical hardness is a significant factor which was used to estimate the crystal hardness and thermodynamic stability of the chemical organic compound. The chemical hardness of the present compound was found to be 1.78 which was noticeable magnitude in which the present compound has definite hardness. Here, when the base molecule; thiosemicarbazone was added with acetaldehyde group, the hardness character was enriched. The Electronegativity is a chemical property which explains the tendency of a molecule or a functional group that interact the electron clouds towards it [51]. Usually, the electronegativity is associated with different functional groups of the compound. Here, the compound composed by group and the calculated electronegativity was found to be 6.43, it was high and the property of chemical bonds of title molecule to be the ionic. This was due to the addition of thiosemicarbazone and acetaldehyde.

Electrophilicity index is a factor which is used to measure the energy lowering due to maximal electron flow between ionization potential and electron affinity. As in the Table 10, the Electrophilicity index was found to be 11.6, was high and ensured the energy transition between donor (HOMO) and acceptor (LUMO). This view clearly showed that, the band gap of the present compound was within the limit. The electrophilicity based charge transfer (ECT) is another important physico chemical function which ensured the charges exchanged from base to functional group of vice versa [52]. If ECT is greater than zero, the charges will be moved from base to functional group. If ECT is less than zero, the charges will be tending to move from

functional group to base compound. In this case, the base was thiosemicarbazone and functional group was acetaldehyde. The ECT value of the present compound was -0.42 which was less than zero. So, here, the charges moved from thiosemicarbazone to acetaldehyde in order to sustain NLO property.

4.13. VCD analysis

Vibrational circular dichroism (VCD) is similar to the Zeeman Effect directly related to IR form of vibrational optical activity which detects differences in attenuation of left and right circularly polarized light passing through the compound. It is the extension of circular dichroism spectroscopy into the IR and near infrared region [53]. The VCD provides two-dimensional structural information since VCD is sensitive to the mutual orientation of distinct ligand groups in a molecule. It is also used for the identification of absolute configurations of the organic compounds [54]. The VCD spectrum is the vibrational difference with respect to left and right circularly polarized light radiations. The result of a VCD measurement is the combination of emission and absorption spectra, figure out the elucidation of biologically and optically significant molecules.

The VCD spectrum and (Mirror reflection) enantiomers of the present compound was portrayed in Figure 11. In this present case, even though, the spectrum was originated from zero, the intensive peaks were started at 400 cm⁻¹ and the intensity of the absorption and emission were elevated in positive and negative phase due to the left and right circular polarization. The absorption intensity is usually unequal on both sides (up and down) of the VCD spectrum, in this case, the probability of amalgamation was found to be high in absorption side. Both the linear and circular vibrational polarization bands belong to mid IR region which related to the C=N, C=S, C-C, N-N, N-H, C-H and C-N stretching vibrations. All such vibrational modes were extracted from both functional and base group of molecule. These circumstances encouraged the enticement of the NLO properties.

4.14. AIM analysis

Atoms in molecules technique (AIM theory) is one of the most useful tool to characterize atomic and molecular interactions, particularly, hydrogen bonding. The theory of AIM efficiently

described hydrogen bonding and its concept without border. One of the advantages of the AIM theory is that one can obtain information on changes in the electron density distribution as result of either bond formation or complex formation. According to AIM theory, any chemical bond including hydrogen bonding is characterized by the existence of bond critical point (BCP). After the BCPs have been localized, several properties can be calculated at their position in space. Amongst these, the charge density ρ_{BCP} and the Laplacian of the charge density $\nabla^2 \rho_{BCP}$ at BCP are of chief importance. According to Koch and Popelier criteria [55] based on AIM theory,

- (i) the presence of BCP between theproton (H) and acceptor (Y) is a confirmation of the existence of hydrogen bonding interaction
- (ii) The value of the charge density ρ_{BCP} should be within the range 0.0020–0.0400 a.u.
- (iii) The corresponding Laplacian $\nabla^2 \rho_{BCP}$ at BCP should be within the range 0.0240–0.1390 a.u.

In addition, the electron density value calculated at the BCPs of the intermolecular hydrogen bonds may be treated as a measure of the hydrogen bond strength. The AIM theory was applied here to analyze the nature of the bonding interaction in the ATSC. The AIM molecular graphs showing the different bond and ring critical points of the ATSC species were depicted in Figure 12. The topological parameters at BCPs for the ATSC were given in Table 11. The value of charge density for the C10-N12, C10-S11, C10-N8, N7-N8, C1-N7, C1-C3, C3-H4 bond critical points were relatively high and the $\nabla^2 \rho_{BCP}$ was negative. These results revealed that the charge density has been concentrated in the internuclear region. Moreover, the AIM analysis indicated the presence of BCP between the sulfur S11 and H4 atoms. At this BCP, the values of the charge density and the Laplacian of density are 0.0086 and 0.0292 a.u., respectively. Moreover, this BCP was calculated using relationship E_{int} = V_{BCP}/2 as described by Espinosa et al. [56]. From these topological parameters, it was concluded that the hydrogen bond S11...H4 was very weak.

5. Conclusion

In order to evaluate the NLO properties of the present compound; Acetaldehyde was investigated using spectroscopic and suitable theoretical tools. To explore the tuned optical property, two distinct functional molecular groups were added and new product was obtained. Different analyses were carried out towards electronic and optical properties, in which, the suitable evidences have been given for obtaining NLO properties in large extent. The optical activity of the compound was compared with our earlier work. The activeness of the different elements to be the motivation for the inducement of optical properties in the compound was identified from the vibrational analysis. The supportive information provided by the thermodynamical and chemical studies has been extensively described. The VCD investigated the purpose of the construction of the amalgamated compound and the source of rich optical activity. The AIM theory was applied in this compound to analyze the nature of the bonding .v interaction and their results revealed that, the charge density has been concentrated in the internuclear region.

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Figure captions

Figure 1: monomer and dimmer form of acetaldehyde thiosemicarbazone.

Figure 2: All the conformers of acetaldehyde thiosemicarbazone

Figure 3: Mulliken charge level diagram of acetaldehyde thiosemicarbazone.

Figure 4: Experimental and calculated FT-IR spectra of acetaldehyde thiosemicarbazone.

Figure 5: Experimental and calculated FT-Raman spectra of acetaldehyde thiosemicarbazone.

Figure 6: Experimental and simulated ¹³C and ¹H NMR spectra of acetaldehyde thiosemicarbazone.

Figure 7: Frontier molecular orbital in IR region.

Figure 8: Frontier molecular orbital in UV-Visible region.

Figure 9: Experimental and calculated UV-Visible spectra of acetaldehyde thiosemicarbazone

Figure 10: MEP and ESP display of acetaldehyde thiosemicarbazone.

Figure 11: VCD spectra of acetaldehyde thiosemicarbazone.

Figure 12: AIM diagram of acetaldehyde thiosemicarbazone

	thiosemicarb		
Parameters	HF B3LY 6-311++G(d.p) 6-311++G		Experimental
Bond lengths (Å)			
С1-Н2	1.080	1.090	-
C1-C3	1.496	1.493	-
C1-N7	1.255	1.276	1.287
С3-Н4	1.085	1.094	-
С3-Н5	1.080	1.090	-
С3-Н6	1.086	1.094	-
N7-N8	1.402	1.412	1.384
N8-H9	0.997	1.013	-

 Table 1: The calculated and experimental optimized parameters of Acetaldehyde thiosemicarbazone

N8-C10	1.356	1.380	1.346
C10-S11	1.667	1.665	1.669
C10-N12	1.350	1.375	1.326
N12-H13	0.993	1.008	-
N12-H14	0.995	1.011	-
Bond Angles (°)			
H2-C1-C3	116.2	117.0	-
H2-C1-N7	113.1	112.6	-
C3-C1-N7	130.6	130.4	-
С1-С3-Н4	109.1	109.9	-
С1-С3-Н5	112.6	111.9	-
С1-С3-Н6	108.6	109.2	
Н4-С3-Н5	108.7	107.9	- 0
Н4-С3-Н6	108.1	108.0	-
Н5-С3-Н6	109.7	109.8	-
C1-N7-N8	116.9	117.1	115.1
N7-N8-H9	108.7	108.0	-
N7-N8-C10	122.8	123.9	119.3
H9-N8-C10	113.9	113.1	-
N8-C10-S11	125.8	126.3	119.5
N8-C10-N12	113.0	111.8	117.5
S11-C10-N12	121.2	121.9	122.9
C10-N12-H13	116.6	115.0	-
C10-N12-H14	120.7	119.3	-
H13-N12-H14	117.5	115.9	-
Dihedral Angles (°)			
Н2-С1-С3-Н4	71.0	78.2	-
Н2-С1-С3-Н5	-168.3	-162.0	-
H2-C1-C3-H6	-46.5	-40.1	-
N7-C1-C3-H4	-109.8	-104.1	-
N7-C1-C3-H5	10.9	15.7	-
N7-C1-C3-H6	132.6	137.6	-
H2-C1-N7-N8	180.0	-179.4	-
C3-C1-N7-N8	0.8	2.9	-
C1-N7-N8-H9	-139.9	-149.9	-
C1-N7-N8-C10	83.4	74.4	-
N7-N8-C10-H13	-19.9	-15.0	-
N7-N8-C10-H12	160.4	163.2	-
H9-N8-C10-S11	-154.6	-148.7	-

H9-N8-C10-N12	25.8	29.4	-
N8-C10-N12-H13	170.4	171.7	-
N8-C10-N12-H14	16.5	27.2	-
S11-C10-N12H13	-9.2	-10.0	-
S11-C10-N12H14	-163.1	-154.5	_

 Table 2: The Mulliken atomic charge levels of Acetaldehyde thiosemicarbazone

Atoms	HF/6-311++G(d,p)	B3LYP/6-311++G(d,p)
C1	-0.0662	-0.0456
H2	0.2108	0.1935
C3	-0.4508	-0.4844
H4	0.1167	0.1663
H5	0.1645	0.1657
H6	0.1558	0.1378
N7	-0.1595	-0.1910
N8	-0.0062	0.0645
H9	0.3252	0.2922
C10	-0.3827	-0.2936
S11	-0.1694	-0.3303
N12	-0.2910	-0.1771
H13	0.2921	0.2658
	0.2606	0 2363

S. <u>frequencies(cm⁻¹)</u> 1) Vibrational No. <u>FT-IR</u> FT- HF/6- B3LYP/6- FT-IR Raman $311++G(d,p)$ $311++G(d,p)$ With TED	in %
No. FT-IR FT- HF/6- B3LYP/6- Species assignments Raman 311++G(d.p) 311++G(d.p) With TED	in %
FI-IK Raman $311++G(d,p) = 311++G(d,p)$ With IED	III 70
1 3390vs - 3370 3397 A' (N-H)v (100)	
2 3240s 3240w 3265 3243 A' (N-H)v (100)	
3 3160m 3160w 3174 3159 A' (N-H)v (100)	
4 2930s - 2953 2930 A' (C-H)υ (87)	
5 2920s - 2937 2914 Α' (C-H)υ (95)	
6 2910s 2910w 2896 2910 A' (C-H)υ (99)	
7 2850m - 2842 2835 Α' (C-H)υ (100)	
8 1600vs - 1602 1606 A' (C=N)v(78)	
9 1510s - 1529 1507 A' (C=S)v (82)	
10 1470s 1470w A' (N-H) $\delta(82)$ +	(C-H)
1470 1470 δ(10)	
11 1380m - Α' (N-H) δ(68)+	(C-H)
1370 1382 δ(10)	
12 1370w - A' (N-H) δ(69)+	(C-H)
1357 1369 δ(24)	
13 1310w - A' (C-N)v(52)+(N-H)
1313 1313 δ(38)	
14 1270m 1270m A' (C-N)v(60)+	(N-H)
1262 1267 δ(13)	
15 1250w - 1251 1251 A' (C-C)v(78)	
16 1150w - 1150 1150 A' (N-N)v(60)	
17 1140w - A' (C-H) δ(62)+	(C-
1135 1137 C)v(18)	
18 1110s - Α' (C-H) δ(60)+	(N-
1103 1113 N)v(29)	
19 1100s - A' (C-H) $\delta(52)$ +	(C-H)
1096 1100 τ(38)	
20 - 1000m A' (C-H) $\delta(48)$ +	(N-
1000 1000 N)υ(25)	
21 - 995m A" (N-H) γ (56)+	(C-
1004 995 C)v(24)	
22 870s - 875 870 A" (N-H) $\gamma(60)$	
23 790s 790w A" (N-H) $\gamma(64)$ +	(C-N)
791 789 $\delta(24)$	
24 730w - Α'' (C-H) γ(48)+	(C-
730 740 S)v(13)	
25 640w - A'' (C-H) γ (47)+	(C-
<u>641</u> 656 S)γ(13)	

 Table 3: FT-IR and FT-Raman experimental and calculated (scaled) vibrational frequencies of Acetaldehyde thiosemicarbazone

26	630w	-			A ″	(C-H) γ(56)+ (C-
			637	630		S)γ(28)
27	580s	-			A ″	(C-H) γ(62)+ (C-C)
			580	568		τ(23)
28	530w	-			A'	$(C-N) \delta(65)+(C-N)$
			532	512		τ(24)
29	500w	500m			A'	$(C-N) \delta(47)+(C-S)$
			471	500		δ(38)
30	-	400w			A'	(C=N) δ(77)+ (S-C-
			399	412		N) δ(20)
31	-	390w			A'	$(C-C) \delta(78)+(C-N)$
			390	390		τ(18)
32	-	300w			A'	$(N-N) \delta(63) + (C-N-$
			300	305		N) δ(28)
33	-	240w			A″	$(C-N) \gamma(52) + (N-C-$
			240	240		N)δ(16)
34	-	180s			A″	$(C-N) \gamma(49) + (C-N)$
			173	181		τ(18)
35	-	175s			A″	(C-C) γ (48)+ τ (C-N)
			175	175		τ(38)
36	-	150s			A″	(N-N) $\gamma(72)$ + (C-N-
			150	150		N) δ (10)

Vs-very strong; s-strong; m-medium; w-weak; υ-stretching; δ-in plane bending; γ-out plane bending; τ-twisting

Table 4: Experimental and calculated ¹H and ¹³C NMR spectral data of Acetaldehyde thiosemicarbazone

Atom	¹ HNMR						¹³ CNMR calculated (B3LYP)		
Atom	Experimental calculated (B3LYP)					Experimental			
		Gas	DMSO	Chloroform			Gas	DMSO	Chloroform
H2	8.62	7.4	7.5	7.5	C1	140.0	169.2	172.8	171.7
H4	-	1.5	1.4	1.5	C3	40.0	16.9	17.38	17.2
H5	2.50	1.8	1.8	1.8	C10	181.0	184.2	185.6	185.4
H6	2.48	1.1	1.4	1.3	-	-	-	-	-
H14	4.48	3.8	4.6	4.4	-	-	-	-	-
H13	3.41	4.6	4.9	4.8	-	-	-	-	-
H9	7.54	6.5	7.0	6.8	-	-	-	-	-

λ (nm)	E (eV)	(f)	Major contribution	Assign ment	Region	Bands		
Gas								
313.6	3.95	0.00 06	H→L+1 (78%)	n→σ*		R-band		
286.0	4.33	0.00 49	H→L (80%)	n→π*	Quartz UV	radikalartig)		
274.1	4.52	0.00 90	H-1→L (57%), H- 1→L+1 (22%)	n→π*		0		
DMSO								
287.0	4.32	$\begin{array}{c} 0.00\\ 08 \end{array}$	H→L (82%)	n→π*	G			
260.7	4.76	0.03 01	H→L+1 (38%), H-1→L (31%)	n→π*	UV	K-band (German,		
254.6	4.87	0.01 86	H→L+1 (43%), H- 1→L+1 (21%)	n→π*		radikalartig)		
Chloro	form			0				
295.5	4.20	0.00 06	H→L (76%), H→L+1 (19%)	n→σ*	0			
266.4	4.65	0.01 16	H→L+1 (58%)	n→π*	UV UV	(German,		
261.2	4.75	0.02 81	H-1→L (40%), H- 1→L+1 (25%)	n→π*		radikalartig)		
IOMO; L: LUMO								
		S						

H:

Table 5: Theoretical electronic absorption spectra of Acetaldehyde thiosemicarbazone(absorption wavelength λ (nm), excitation energies E (eV) and oscillator strengths (f)) usingTD-DFT/B3LYP/6-311++G(d,p) method

Parameters	B3LYP/6-311++G(d,p)
μ _x	0.3025
μ _y	-2.739
μ _z	2.908
μ	4.00 (Debye)
Δα	101.12
α _{Total}	134.77
β_{xxx}	0.331
β_{xxy}	-3.3575
β_{xyy}	-4.665
β_{yyy}	-18.70
β_{xxz}	12.63
β_{xyz}	2.07
β_{yyz}	4.46
β_{xzz}	-3.65
β_{yzz}	-2.279
β _{zzz}	7.170
β _{total}	252.77×10^{-33} (esu)

Table 6: Calculated electric dipole moments μ (Debye), dipole moment components, α and
 β_{tot} components of Acetaldehyde thiosemicarbazone

Table 7: The molecular electric dipole moments μ (Debye), Polarizability (α_0) and hyperpolarizability (β_0)values of Acetaldehyde thiosemicarbazone

Parameters	Acetaldehyde	Thiosemicarbazide	Acetaldehyde thiosemicarbazone
Dipole moment(μ)	3.3187	4.0548	4.8373
(Debye) Average	24.187	59.652	134.762
Polarizabilities(a ₀)			
Exact polarizability (28.884	63.016	101.120
$\Delta \alpha$)x10 ⁻³³ esu			
Hyperpolarizability (β_0) x10 ⁻³³ esu	62.335	42.517	252.77

Standard value for urea (μ =1.3732 Debye, β_0 =0.3728x10⁻³⁰esu): esu-electrostatic unit.

Typ e	Donor (i)	Occupan cy ED/e	Acceptor (j)	ED/ e	E KJ/m ol	Energy difference E(j)-E(i) a.u.	Polarized energy F(i,j) a.u.
		1.0.67.6	C3 - H5	0.00 8	9.29	0.95	0.041
σ-	C1 - H2	1.9676	N7 - N8	0.03 3	41.51	0.85	0.082
σ*	C1 - C3	1.9909	C1 - N7	0.01 4	6.9	1.32	0.042
	C1 - N7	1.9915	C1 - C3	0.02 8	5.31	1.35	0.037
π-		1.0700	C3 - H4	0.00 7	9.08	0.76	0.036
σ*	c^{+} C1 - N7	1.9708	C3 - H6	0.00 8	5.15	0.75	0.027
σ-	~~ ~~	1067	C1 - N7	0.01 4	5.98	1.17	0.037
σ*	С3 - Н4	1.9071	C1 - N7	0.07 8	25.94	0.54	0.052
σ- σ*	C3 - H5	1.9872	C1 - H2	0.02 5	13.05	0.94	0.048
σ-	С2 Ц6	1 07/8	C1 - N7	0.01 4	13.89	1.17	0.056
σ*	С3 - По	C3-110 1.77+0	C1 - N7	0.07 8	14.81	0.54	0.039
σ-	NI7 NIQ	1 9802	C1 - H2	0.02 5	10.63	1.24	0.050
σ*	197 - 190	8 1.9802	C10 - N12	0.04 9	9.04	1.27	0.047
			C1 - N7	0.01 4	10.08	1.33	0.051
σ- σ* N8 - H9	1.9723	C1 - N7	0.07 8	5.06	0.70	0.026	
			C10 - S11	0.02 0	23.6	0.97	0.066
σ-	N8 - C10	1.9876	N12 - H13	0.00	8.49	1.31	0.046

Table 8: Calculated NBO transition data of Acetaldehyde thiosemicarbazone

σ*				7			
σ-	C10 -	1.9834	C10 - S11	0.47	22.07	0.22	0.025
σ*	S11			8	22.97	0.22	0.035
			N8 - H9	0.02	10.67	1 10	0.047
				3	10.67	1.10	0.047
π-	C10 -	1.0766	N8 - C10	0.06			
σ*	S11	1.9/66		8	4.39	1.15	0.031
			N12 - H14	0.01			
				7	12.64	1.11	0.052
-	C10 -	1.9900	N7 - N8	0.03			
σ*	N12			3	13.97	1.19	0.057
	N12 -	1.9875	N8 - C10	0.06			
σ*	H13			8	17.2	1.13	0.062
с.	N12 -	1.9841	C10 - S11	0.02			
σ- π*	H14			0	20.21	0.99	0.062
			C1 - H2	0.02			
				5	17.15	0.81	0.052
			C1 - C3	0.02			
n -		1.000		8	47.2	0.80	0.086
σ*	LP - N7	1.9206	N8 - H9	0.02			
				3	5.06	0.79	0.028
			N8 - C10	0.06		0.04	
			0	8	11.05	0.84	0.042
			C1 - N7	0.07	• 1 • • •		
n -		1 7 4 1 7		8	21.06	0.34	0.039
π^*	LP - N8	1./41/	C10 - S11	0.47	017.5	0.04	0.110
		0		8	217.5	0.26	0.110
			N8 - C10	0.06	14.00	1 1 4	0.056
n -		1 00 40		8	14.23	1.14	0.056
σ*	LP -S11	1.9848	C10 - N12	0.04	10.05	1 1 5	0.054
				9	13.35	1.15	0.054
			N8 - C10	0.06	5 4 10	0.64	0.002
n -	ID 014	1 0020		8	54.18	0.04	0.082
σ*	LP - S11	1.0000	C10 - N12	0.04	45.00	0.65	0.076
				9	45.02	0.65	0.076
n -	LP - N12	1.7641	C10 - S11	0.47	0.47.0	0.22	0 111
σ*				8	247.8	0.23	0.111

		S_m^0 (cal mol ⁻¹ K ⁻¹)	C^0 (cal mol ⁻¹ K ⁻¹)	Gibbs free
Temperature	ΔH_m^0 (kcal mol ⁻¹)			energy
remperature			c _{p,m} (curnor iv)	$\Delta G = \Delta H - T \Delta S$
				KJmol ⁻¹
100	1.074	1.074 13.312 64.295		-1330.13
150	1.889	1.889 17.171 70.176		-2573.76
200	3.241	21.452	76.498	-4287.16
250	4.477	24.844	81.591	-6206.52
300	5.730	28.841	88.34	-8646.57
350	7.550	32.329	92.230	-11307.6
400	9.430	35.176 97.70		-14061.0
450	11.107	37.862	102.093	-17026.8
500	13.187	41.114	107.125	-20543.8
550	15.149	43.208	111.180	-23749.3
600	17.558	45.797	115.810	-27460.6
650	19.676	47.779	119.491	-31036.7
700	22.703	49.572	123.061	-34677.7
750	24.687	51.774	127.027	-38805.8
800	27.624	53.317	130.811	-42626.0
850	30.183	54.594	133.787	-46374.7
900	33.385	55.914	137.147	-50289.2
950	36.163	56.838	139.771	-53959.9
1000	39.503	57.848	142.954	-57808.5
	Accel			

Table 9: Thermodynamic parameters of Acetaldehyde thiosemicarbazone

Parameters	Values							
НОМО	-8.21742 eV							
LUMO	-4.65291 eV							
Energy gap	3.56451 eV							
Ionization potential (IP)	-8.21742 eV							
Electron affinity (EA)	-4.65291 eV							
Electrophilicity Index (ω)) 11.617							
Chemical Potential (µ)	6.435							
Electronegativity (χ)	-6.435 eV							
Hardness (η)	-1.7823							
Softness (S)	0.2805							
Dipole moment (Debye)	4.8373 Debye							
			Electrophilicity charge transfer					
Parameters	Thiosemicarbazide (A)	Acetaldehyde (B)	(ECT)					
			$(\Delta N_{max})_A$ - $(\Delta N_{max})_B$					
Chemical Potential (µ)	6.012	7.832						
Chemical Hardness (η)	-3.438	-3.608	-0.42					
$\Delta N_{max} = - \mu / \eta$	1.75	2.17						

Table 10: Chemical parameters of Acetaldehyde thiosemicarbazone

Table 11: AIM analysis for ATSC; electron density ρ_{BCP} , Laplacian of electron density $\Delta^2 \rho_{BCP}$, electron kinetic energy density G_{BCP} , total electron energy density H_{BCP} and interaction energy E_{int} at bond critical points (BCPs)

ВСР	ρ _{BCP} (a.u)	$\Delta^2 \rho_{BCP}$ (a.u)	GBCP (a.u)	H _{BCP (a.u)}	V _{BCP (a.u)}	$E_{int \ (kcal/mol)}$
C10-N12	0.3156	-0.2391	0.1743	-0.4134	-0.5877	-184.4
C10-S11	0.2142	-0.0222	0.2324	-0.2546	-0.4870	-152.8
C10-N8	0.3102	-0.9137	0.1753	-0.4037	-0.5791	-181.7
N7-N8	0.3156	-0.5126	0.1433	-0.2715	-0.4148	-130.1
C1-N7	0.3795	-0.8040	0.4009	-0.6019	-1.0028	-314.6
C1-C3	0.2576	-0.6271	0.0636	-0.2204	-0.2840	-89.1
С3-Н4	0.2720	-0.8995	0.0410	-0.2658	-0.3068	-96.3
S11H4	0.0086	-0.0292	0.0060	-0.0013	-0.0046	-1.4

Highlights

- The electro-optical impact on the structure of Acetaldehyde-thiosemicarbazone analyzed. •
- The active electronic and NLO properties found in the compound. •
- The VCD analysis confirm NL optical path in the compound.
- The electrophilicity charge transfer characteristics studied. •

Accepted manuscript











Fig. 3

















Fig. 8











Graphical Abstract

The VCD provides two-dimensional structural information since VCD is sensitive to the mutual orientation of distinct ligand groups in a molecule. It is also used for the identification of absolute configurations of the organic compounds. The VCD spectrum is the vibrational difference with respect to left and right circularly polarized light radiations. In this present case, even though, the spectrum was originated from zero, the intensive peaks were started at 400 cm⁻¹ and the intensity of the absorption and emission were elevated in positive and negative phase due to the left and right circular polarization. The absorption intensity is usually unequal on both sides (up and down) of the VCD spectrum, in this case, the probability of amalgamation was found to be high in absorption side. Both the linear and circular vibrational polarization bands belong to mid IR region which related to the C=N, C=S, C-C, N-N, N-H, C-H and C-N stretching vibrations. All such vibrational modes were extracted from both functional and base group of molecule. These circumstances encouraged the enticement of the NLO properties.

