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PII: S0022-2860(15)30117-4

DOI: 10.1016/j.molstruc.2015.07.005

Reference: MOLSTR 21660

To appear in: Journal of Molecular Structure

Received Date: 3 March 2015

Revised Date: 24 June 2015

Accepted Date: 3 July 2015

Please cite this article as: P. Rawat, R.N. Singh , Eco-friendly synthesis, spectral and computational study of Pyrrole-2-carboxaldehyde salicylhydrazone (PCSH) for its application, *Journal of Molecular Structure* (2015), doi: 10.1016/j.molstruc.2015.07.005.

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# Eco-friendly synthesis, spectral and computational study of Pyrrole-2carboxaldehyde salicylhydrazone (PCSH) for its application

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#### Abstract

In this paper we present eco-friendly synthesis of Pyrrole-2-carboxaldehyde salicylhydrazone (PCSH) and its molecular structural elucidation, spectral analysis and reactivity evaluation. Pyrrole-2-carboxaldehyde and salicyl hydrazide in water undergo condensation reaction to produce PCSH in good yield (88%). All results of quantum chemical calculation corroborate well with the experimental findings. The PCSH has been characterized by elemental analysis, FT-IR, <sup>1</sup>H-NMR, UV-Visible, and ESI-Mass spectroscopy. Density functional theory (DFT) calculations have been carried out for PCSH by performing B3LYP functional using the standard basis set 6-31+g (d, p), and additional basis sets 6D and 10F. Two most stable conformers for PCSH have been observed around the dihedral angle N1C5C6N7. The red shift observed in O-H stretching vibration in the FT-IR spectrum indicates the presence of intramolecular hydrogen bonding. The rotational barrier between *syn-syn* (closed) *syn-syn* (open) found to be 2966.9 kcal/mol. The presence of hydroxyl proton at 10.45 ppm downfield in experimental <sup>1</sup>H-NMR spectrum confirms the existence of intramolecular hydrogen bonding in PCSH. Further, topological parameters analysis at the bond critical points using 'Atoms in molecules' theory reveals intramolecular hydrogen bonding. The energy of homonuclear intramolecular hydrogen bond (O17-H28···O10) is calculated to be 14.03 kcal/mol. The ellipticity results confirm the resonance assisted nature of this intramolecular hydrogen bond. In addition to this work, the reactive sites in PCSH have been explored using DFT descriptors, predicting nucleophilic reactions at carbonyl carbon and electrophilic reactions are possible at pyrrolic NH, amidic NH and double bond C=N leading to several heterocyclic products and metal complexes.

**Keywords:** Density functional theory, AIM, intramolecular hydrogen bonding, reactivity descriptor, <sup>1</sup>H-NMR chemical shifts

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#### 1. Introduction

Compound containing heteroatoms influence various properties of materials and their applications [1-3]. Hydrazides and their derivatives are used as versatile intermediates for the syntheses of vast number of heterocyclic compounds [4-6]. Hydrazones and their metal chelates have wide applications in biological systems, catalysis, dying processes, analytical work and the spectral studies [7-13]. The structural frame –CH=NNHCO- of hydrazide-hydrazones provide basis for very effective synthons for organic synthesis as well as metal complexation [14]. The hydrazide-hydrazones of pyrrole-2-carbaldehyde, their metal and organometallic complexes possess variety of biological activity such as antimalerial [11], antimicrobial [14], anticancer [15], antituberculosis, etc. [16].

Most of the hydrazide-hydrazones synthesis methods involve the use of methanol, ethanol, tetrahydrofuran, butanol, glacial acetic acid, ethanol-glacial acetic acid as solvent without catalysts at reflux. Another route for the synthesis of hydrazones use the coupling of aryldiazonium salts with active hydrogen compounds [17]. In addition, 4-acetylphenazone isonicotinoylhydrazones was prepared by exposing an alcohol solution of 4-acetylphenazone and isoniazid to sunlight or by mixing them with a mortar in the absence of the solvent. Improvements in yields of the hydrazones synthesis have been achieved when MW irradiation at solvent free conditions were used. Few Aryl-hydrazones have been synthesized in the presence of an aqueous medium (under acid conditions) at room temperature [18, 19]. Organic synthesis in aqueous media has importance because of fact that many toxic and volatile organic solvents, contributes to pollution [20-22]. Water is the cheapest and safest solvent available offers many advantages, such as improving reactivities, selectivities, simplifying the workup procedures, enabling recycling of the catalyst, allowing mild reaction conditions and protecting-group free

synthesis, simple operation and high efficiency in many organic reactions that involve watersoluble substrates, reagents, and renewable materials, such as carbohydrates, without the necessary derivatizations. The AIM method gives the opportunity to have an insight into a region of a system [23]. AIM efficiently describes H-bonding and its concept without border. With respect to change of both the method used and the basis set the reliability and stability of values of AIM parameters have been studied and found that they were almost independent of basis set in case of used functional B3LYP in DFT [24].

The PCSH have not been synthesized in aqueous medium although the synthesis and brief spectral data of PCSH in organic solvent have been reported in literature [14]. The quantum chemical calculation and spectral analysis are powerful approaches for study of different aspects of compounds. However, literature survey revealed that till date neither complete spectroscopic nor quantum chemical calculations for PCSH have been reported. Therefore the present investigation was undertaken to taking into account the solubility of pyrrole-2-carbaldehyde and salicylhydrazide in water, increasing demand of pyrrole precursors for heterocyclic synthesis and metal complexes. In this paper we describe an efficient, rapid synthesis process for PCSH, evaluation of structure, reactivity and detailing out the spectral analysis. Information about the geometry, conformations of the molecule, rotational barriers, electrostatic potential surface, chemical reactivity, complete analysis of the FT-IR spectrum and potential energy distribution (PED) over the internal coordinates help in understanding the structural and spectral characteristics.

#### 2. Experimental Section

The entire chemicals were purchased from the commercial supplier S.D. Fine, Sigma Aldrich and used as such without further purification. The reaction was monitored by thin layer chromatography (TLC) using Silica Gel 60 F254 plates. TLC plates were visualized by exposure to them in iodine vapors. The FT-IR-spectrum of the compound was recorded in KBr on a Bruker-spectrometer. The <sup>1</sup>H-NMR spectrum was recorded in MeOD and CDCl<sub>3</sub> on Bruker DRX-300 spectrometer using TMS as an internal reference. The UV-visible absorption spectrum was recorded on ELICO SL-164 spectrophotometer in DMSO using concentration of solution as  $1 \times 10^{-5}$ M. EI-Mass spectra were recorded on a MICROMASS QUATTRO II triple quadrupole mass spectrometer. Melting points was determined using open capillary tube method and are uncorrected.

Pyrrole-2-carboxaldehyde was prepared according to the previous reported method in literature [25]. 2-Hydroxy benzohydrazide (salicylhydrazide) was prepared by reflux the equimolar reaction mixture of Ethyl-2-hydroxy benzoate (Ethylsalicylate) and Hydrazine hydrate in ethanol as solvent [26].

### 2.1 Synthesis Pyrrole-2-carboxaldehyde salicylhydrazone

Pyrrole-2-carboxaldehyde (0.100 g, 1.0522 mmol) was dissolved in 10 ml of water and 2-Hydroxy benzohydrazide (0.160 g, 1.0522 mmol) dissolved in 15 ml of water. A cold solution of 2-Hydroxy benzohydrazide was added dropwise with stirring in ice cold solution of Pyrrole-2-carboxaldehyde. The reaction was monitored by Silica Gel coated TLC plates. After 2 hours light

yellow precipitate was obtained. The precipitate was filtered off, washed with water and dried in air. Yield: 88.46%. The compound decomposes above  $215^{\circ}$ C without melting. EI-MS m/z: obs. 230.12 [M<sup>+</sup>+1] amu, Cal.: 229.08 amu. Elemental analysis for C<sub>12</sub>H<sub>11</sub>N<sub>3</sub>O<sub>2</sub> Obs. C 62.92%, H 4.78%, N 18.40%, Cal.: C 62.85%, H 4.83%, N 18.33%

#### 3. Computational methods

All calculations were performed on B3LYP [27, 28] functional and 6-31+G(d,p) basis set [29, 30]. The calculated wavenumbers were scaled down by using 0.9608 scaling factors [31]. All calculations were performed with the Gaussian 03 program package [32]. The vibrational assignments of the normal modes were proposed on the basis of the PED calculated using program GAR2PED [33] and internal coordinates was defined using Pulay's recommendations [34]. <sup>1</sup>HNMR chemical shifts of PCSH were calculated by employing the Gauge-Included Atomic Orbital (GIAO) [35]. A TD-DFT calculation was also carried out to obtain the theoretical excitation spectrum. The reaction energies  $\Delta E^0$ , standard enthalpies  $\Delta H^0$  and Gibbs free energies  $\Delta G^0$  of inter conversions between the PCSH syn and anti-conformers was derived from frequency calculations at the B3LYP/6-31G(d,p) level of theory. The reaction entropies  $(\Delta S^0)$  of rotational conversions were evaluated using a thermodynamic equation  $\Delta S^0 = (\Delta H^0)$ .  $\Delta G^0$ /T. The rate constant k(T) derived from transition state theory was computed from the Gibbs free energy of activation  $\Delta^{\ddagger}G^{0}$ , using k(T) = (k<sub>B</sub>T/hc<sup>0</sup>)exp(- $\Delta^{\ddagger}G^{0}/RT$ ) where the factor c<sup>0</sup> is assigned to unity [36]. The equilibrium constant K at 298.15 K and 1 atm is computed using the equation  $\Delta G^0$  = - RT lnK. The global and local indexes (philicity, hardness, softness, chemical potential, electronegativity and condense Fukui functions etc.) of reactivity were calculated with Koopman's approximation [37-40]. Visualization of molecules at their optimized geometries was

performed with CHEMCRAFT [41] program package, images of molecular orbital and molecular electrostatic potential surfaces (MEP) was developed with the help of Gauss View [42] program package. The AIM calculation was performed by AIM 2000 program package [43].

#### 4. Results and discussion

# 4.1 Molecular geometry, Rotational energy barrier, reaction energies and topological parameters of PCSH

The optimization of PCSH was conducted after the establishment of the structure with the help of IR, <sup>1</sup>HNMR, MASS and UV-VIS spectroscopy. A further conformational study has been conducted with help of optimized geometry without imposing any symmetry constrains on the molecule. The optimized geometry of ground state syn-syn (closed), anti-syn (closed) and synsyn (open) conformer and transition state between them are shown in Figure 1. The syn-syn (closed), anti-syn (closed) and syn-syn (open) conformer have energy -778.60369930, -778.59621905, -778.58395664 a.u., at room temperature with energy difference 4.6939 and 12.3887 kcal/mol indicating they exist in ratio 99.96 :  $0.04 : 10^{-16}$  respectively, in the gas phase as per Boltzmann distribution. The Molecular structures of all three conformers possess C<sub>1</sub> point group symmetry. The homonuclear intramolecular hydrogen bonding (O-H.....O) between hydroxyl (O-H) and carbonyl (C=O) oxygen form six membered ring. To best of our knowledge, experimental synthesis in water, X-Ray structure, detail spectral analysis and exact experimental data on the geometrical parameters of PCSH have never been reported. Therefore, the crystal data [44] of a closely related molecule is compared with that of PCSH. Some of the optimized bond lengths are slightly different from the experimental ones, because the molecular states are different during experimental and theoretical processes. One isolated molecule is

considered in gas phase in theoretical calculation; whereas many packed molecules are treated in condensed phase in the experimental measurements. The endocyclic angles of the pyrrole ring exactly add up to 540°, indicating that the hetrocycle ring is most perfectly planar.

The calculated thermodynamic quantities and their changes for the reaction of PCSH at room temperature are listed in Table 2. For overall reaction, enthalpy ( $\Delta H_{Reaction}$ ), Gibbs free energy ( $\Delta G_{Reaction}$ ) and entropy ( $\Delta S_{Reaction}$ ) changes are found to be -3.0057, -1.9044 kcal/mol and -3.6930 cal/mol-K respectively. The reaction has negative values for  $\Delta H_{\text{Reaction}}$  and  $\Delta G_{\text{Reaction}}$ indicating that the reaction is exothermic and spontaneous at room temperature. The value of  $K_{eq}$  is calculated as 24.89 ie  $K_{eq} >> 1$ . Therefore, the reaction product favored in forward direction and obtained in good yield at room temperature. The rotation about single bonds is never truly "free", and in some special cases it can be restricted by high potential energy barriers. In order to gain insight into the nature of the energetic of the rotational equilibrium between the two almost planer structure of PCSH we have performed quantum chemical calculation on both minima and the rotational transition state. The transition structures TS1 and TS2 between the (syn-syn (closed) and anti-syn (closed), and (syn-syn (closed) and syn-syn (open)) forms were confirmed by single imaginary frequency for both at -129.56, -294.89 cm<sup>-1</sup>, respectively. The rotational barrier between syn-syn (closed), anti-syn (closed) forms is 12.28 kcal/mol in the gas phase. This rotational barrier is larger than the energy difference (4.6939 kcal/mol) between the syn-syn (closed) and anti-syn (closed) conformers and thus the free rotation is quite a difficult task at room temperature. The rotational barrier between syn-syn (closed) and syn-syn (open) found to be 2966.9 kcal/mol. The energy difference between closed and open structure 12.3887 kcal/mol. Using Eyring equation, the forward  $(k_f)$  and backward  $(k_b)$  rate coefficient of equilibrium conversion evaluated from Gibbs free energies of activation according to TS1

expressed as as 7.4717 x  $10^3$ , 9.4915 x  $10^6 \sec^{-1}$  respectively. Therefore,  $k_b \gg k_f$  and favors the formation of *syn-syn* (closed) conformer at room temperature. The conversion from *syn-syn* (closed), to *anti-syn* (closed) would only be possible when energy is provided to the *syn-syn* (closed) conformer.

The calculated topological parameters of hydrazone bonding are listed in Table 2. The Bader's theory of Atoms in molecules is useful tool to characterize the strength of hydrogen bond. Bond critical point is used in the recognition of chemical bonds and strength between atoms. The  $\rho$  values and its corresponding Laplacins  $\nabla^2 \rho$  at bond critical point found within the range of 0.00782-0.016284 a.u. and 0.07983-0.02708 a.u., respectively. The bond strength is determined by accumulation of electron density in the bond region and the screening of nuclei by this density. All the values which are obtained in our calculations follow Koch and Propelier [45] criteria and satisfy Poincare-Hopf Relationship [46]. Laplacian of electron density ( $\nabla^2 \rho_{(BCP)}$ ) is related to the energy of bond interaction by the local expression of the virial theorem [47, 48] and additionally to total electron energy density  $H_{(BCP)}$  [49]  $\frac{1}{2}\nabla^2 \rho_{(BCP)} = 2G_{(BCP)} + V\rho_{(BCP)} + V\rho_{(BCP)} = 2G_{(BCP)} + 2G_{(BCP)} + V\rho_{(BCP)} = 2G_{(BCP)} + 2G_{(BCP)} = 2G_{$  $H(_{BCP})$  where,  $G(_{BCP})$  is the kinetic electron energy density,  $V(_{BCP})$  potential electron energy density and  $\rho(BCP)$  electron density at bond critical point. The molecular graph of PCSH is given in Figure 3. Two types of intramolecular interaction are seen in the molecular graph. The intramolecular H--H interaction is weaker than O-H--O interaction. The hydrogen bond energy of the O-H--O and H--H bond are found to be -14.028, -2.5705 kcal/mol, respectively. The O-H--O bonds are strongly bonded through intramolecular hydrogen bonding with carbonyl (C=O) oxygen atom. This interaction has not been only observed in AIM calculations but also observed in FT-IR spectrum of PCSH. The  $\varepsilon$  values for bonds involved six membered pseudo rings O10-C9, C9-C11, C11-O16, C16-O17 associated with the O17-H28---O10 are in the range

0.1007-0.2885. This confirms the presence of resonance assisted hydrogen bonds because both O10 and O17 atoms are interconnected by a system of  $\pi$ -conjugated double bonds. Another six membered ring (H23-N8, N8-C9, C9-C11, C11-C12, C12-H24, H24<sup>.....</sup>H23), is formed due to H-H bonding (N8-H23<sup>.....</sup>H24-C12). When syn-syn (open) conformer changes to syn-syn (closed) conformer, molecular physical ground structure change having H-H bond distance (1.97 Å), and somewhat molecule becomes planar with H<sup>...</sup>H interaction energy (1.12 kcal/mol) observed in NBO analysis, leading to further stabilization of molecule. As result of these interactions this part of molecule forms three ring fused structure leading to delocalization and higher stability and much more clear in molecular graph. The NBOs provides an accurate method for studying interaction among intra- and intermolecular bonding and an efficient basis for investigating charge transfer or conjugative interaction in various molecular systems. In order to characterize intra and intermolecular interactions quantitatively, a second order perturbation theory is applied that gives the energy lowering associated with such interactions. Second-order perturbation theory analysis of the Fock matrix in NBO basis is presented in (supplementary Table S1). The  $\pi$ (C2-C3) / (C4-C5) $\rightarrow \pi^*$ (C4-C5) / (C2-C3) interactions are responsible for conjugation of respective  $\pi$ -bonds in pyrrole ring. The electron density at the conjugated  $\pi$ bonds (1.795) and  $\pi^*$  bonds (0.4088) of pyrrole ring indicate strong  $\pi$ -electron delocalization within ring leading to a maximum stabilization of energy ~23.19 kcal/mol. The interactions  $\pi$ (C11–C16) / (C12-C13) / (C14-C15) $\rightarrow$  $\pi$ \*((C9–O10) / (C12-C13) / C14-C15)) / ((C9-O10) / (C12-C13) / (C14-C15)) / ((C11-C16) / (C14-C15)) / ((C11-C16) / (C12-C13)), respectively, are also stabilized to the molecule up to ~23.33 kcal/mol. The hyperconjugative interactions  $n_1(O10) \rightarrow \sigma^*(O17 - H28)$  is responsible for intramolecular hydrogen bonding as O10···H28-O17.

Another weak intermolecular interaction  $\sigma(C12-H24) \rightarrow \sigma^*(N8-H23)$  confirms the presence of non-conventional interaction (C12-H24···H23) stabilized the molecule upto ~1.12 kcal/mol.

#### 4.2. Chemical reactivity

#### 4.2.1 Molecular electrostatic potential (MEP)

Molecular electrostatic potential surfaces MESP is greatly useful to explain hydrogen bonding, chemical reactivity, dipole moment, electronegativity and partial charges of the molecule [50]. The electrostatic potential V(r) is defined as:

$$V(\mathbf{r}) = \sum_{A} \frac{Z_{A}}{|\vec{R}_{A} - \vec{r}|} - \int \frac{\rho(\vec{r}')dr'}{|\vec{r}' - \vec{r}|}$$

where Z<sub>4</sub> is the charges on nucleus A located at  $\overrightarrow{R_4}$ , and  $\overrightarrow{\rho(r)}$  is the electron density at a point r for a molecule.  $\overrightarrow{V(r)}$  can assume positive as well as negative values and can provide useful information about the electron rich sites. The electrostatic potential  $\overrightarrow{V(r)}$  created in the space around a molecule by its nuclei and electrons has recently become a well–established tool to understand the chemical reactivity of the molecule [51]. The MESP regions of the PCSH syn conformer, ranges from -0.0410 to -0.0388 au. The MEP for PCSH is given in Figure 4. The red colour around carbonyl and hydroxyl group shows the negative electrostatic potential in electrostatic potential map of PCSH. The blue colour around the pyrrolic and amidic NH shows most positive electrostatic potential, whereas the rest of the region of molecule is shown by green colour having moderate electrostatic potential. The negative charge located on pyrrolic N(-0.582), amidic N(-0.271), N(-0.420), carbonyl O(-0.560), C(0.627) and O(-0.568) of hydroxy group suggested that electrophilic reaction could occur at these centers.

#### 4.2.2 Global reactivity and Local descriptors

The application of DFT descriptors in the global chemical reactivity and local site selectivity are highly successful [52-60]. Nowadays, DFT derived descriptors have been extensively used for rationalization and interpretation of diverse aspects of chemical binding and reaction mechanism. Global electronic descriptor helps in prediction of electrophilic and nucleophilic reagent whereas local electronic descriptors help in prediction site of electrophilic and nucleophilic attack as well as order of preference.

The synthesized molecule PCSH may be used as intermediate for the synthesis of new heterocyclic compounds such as thiadiazoline, thiazolidinones and azetidinones which posssess remarkably biological activities. Therefore, in this work an attempt has been made to explore the uses of DFT descriptors to investigate the reactive sites of PCSH. The global electronic descriptors (( $\varepsilon_{HOMO}$ ,  $\varepsilon_{LUMO}$ ), band gap ( $\varepsilon_{LUMO}$ - $\varepsilon_{HOMO}$ ), electronegativity ( $\chi$ ), chemical potential ( $\mu$ ), chemical hardness ( $\eta$ ), global softness (S), global electrophilicity index ( $\omega$ ) additional electronic charge ( $\Delta N_{max}$ ) have been calculated using the standard formula [52-60] and condensed Fukui Functions ( $f_k^+$ ), ( $f_k^-$ ), Local softness ( $s_k^+$ ), ( $s_k^-$ ) and electrophilicity ( $\omega_k^+$ ), ( $\omega_k^-$ ) indices of reactants Pyrrole-2-carboxaldehyde, 2-Hydroxy benzohydrazide and product PCSH have also been calculated using the standard formula [52-61] and listed in Table 4. The high value of electrophilicity index ( $\omega = 3.1082 \text{ eV}$ ) for product shows that it is a strong electrophile than the reactants. The local electronic descriptors are listed in Table 5. The PCSH molecule may be used as intermediates for the synthesis of effective heterocyclic and organic compounds like substituted 1,3,4 oxadiazolines, 2-Azetidinones, 4-Thiazolidinones can be synthesized when they are heated in the presence of acetic anhydride, trietylamine chloro acetylchloride,

thioglycolic acid/thiolactic acid [8] respectively, coupling products can be synthesized by using the active hydrogen component of –CONHN=CH- azomethine group [8]. *N*-Alkyl hydrazides can be synthesized by reduction of hydrazones with NaBH [8]. The maximum values of the local Fukui Function, softness and electrophilicity ( $f_k^+$ ,  $s_k^+$ ,  $\omega_k^+$ ) indices at C6 indicates that C6 site is more prone to nucleophilic attack. In the same way, the maximum values of local Fukui Function, softness and electrophilicity indices ( $f_k^-$ ,  $s_k^-$ ,  $\omega_k^-$ ) at N8 in comparison to N7 indicate that N8 site is more prone towards the electrophile and leads to number of new heterocyclic compounds.

## 4.3 <sup>1</sup>H-NMR Spectroscopy

Identification of carbon and hydrogen environment in the compounds has been frequently determined by NMR spectroscopy. The experimental and calculated values of <sup>1</sup>H chemical shifts of the title compound are given in Table 6 and the correlation curve between the experimental and calculated <sup>1</sup>H NMR chemical shifts is shown in Figure 4. The value of correlation coefficient found between experimental and calculated <sup>1</sup>HNMR chemical shifts found to be  $R^2 = 0.960$ . The calculated <sup>1</sup>HNMR chemical shifts corroborate well with the experimental chemical shifts. The <sup>1</sup>HNMR spectrum PCSH was recorded in MeOD and DMSO solvent. In MeOD signal of OH and amidic NH was unobserved due to proton exchange. Therefore, the spectrum of PCSH was rerecorded in DMSO– $d_6$  solvent. The <sup>1</sup>HNMR spectrum shows singlet in DMSO– $d_6$  solvent at 10.459 ppm for the pyrrolic NH. The azomethine proton (-CH=N-) appears at 7.890 and 8.758 ppm in methanol and DMSO solvent, respectively. The NH proton of the hydrazide-hydrazone (-CH=NHCO) exhibited the expected singlets at 10.28 ppm. The NH proton of the hydrazide-

hydrazone (-CH=NHCO-) resonated at downfield due to electronegativity of nitrogen atom as well as by presence of two electron withdrawing carbonyl and vinylic group near to N atom therefore the chemical shifts value seem to be high similarly, the pyrrolic NH group includes nitrogen which shows electronegativity property, so H atom contributes to the downfield resonance. Another reason for appearing these single at downfield due the formation of intermolecular hydrogen bonding with DMSO solvent also. The hydroxyl group OH resonates as singlet at 12.71 ppm. The presence of the intramolecular hydrogen bond O10–H28…O17 is also confirmed by the <sup>1</sup>H NMR spectrum where the signal of O10–H28 proton appears downfield. Signal arising from (>CH-N=N-) structures at 3.00-4.00ppm was not observed. This finding also supported that the structures of title compound might be given in hydrazide-hydrazone form.

#### 4.4 UV-Visible spectroscopy

The observed and calculated electronic transitions of high oscillatory strength are listed in Table 7 and shown in Figure 6. The theoretical findings corroborated well with the experimental results in CHCl<sub>3</sub>, MeOH and DMSO solvent. Molecular orbitals are very useful in qualitative descriptions of bonding, biological activity and reactivity. The band gap between HOMO and LUMO orbital of the most stable molecule *syn-syn* (closed) conformer is -3.986 eV. The HOMO $\rightarrow$ LUMO transition implies an electron density transfer from pyrrole ring to antibonding orbital of carbonyl group present in azomethine framework of hydrazone. The atomic orbital compositions of the frontier molecular orbitals are sketch in Figure 7. The first electronic absorption corresponds to the transition from the ground to the first excited state and is mainly described by one electron excitation from the highest occupied molecular orbital (HOMO) to the

lowest unoccupied molecular orbital (LUMO) with strong oscillatory strength and which is  $\pi$ - $\pi^*$ in nature. The second excitation originates from HOMO to LUMO+1 with oscillatory strength of moderate oscillatory strength. In HOMO→LUMO+2 transitions, electron density transfer to antibonding orbital of HC=N. The experimentally observed  $\lambda_{max}$  at 349, 358 and 362 in CHCl<sub>3</sub>, MeOH and DMSO respectively indicate that the  $\lambda_{max}$  increases with the polarity of the solvent. The bathochromic shift is observed in the spectrum due to molecule-solvent interactions through hydrogen bonding. The nature of transitions found in *syn-syn* (closed) is  $\pi$ - $\pi^*$ .

#### 4.5. Vibrational assignments

The experimental and calculated vibrational wavenumbers for closed and open system of PCSH using B3LYP/6-31+G(d,p) and their assignments are given in Table 8. The simulated experimental and theoretical FT-IR spectrum of PCSH is shown in Figure 8. The calculated vibrational wavenumbers are higher than the experimental values for the majority of the normal modes. Therefore, calculated wavenumbers are scaled using scaling factor to discard the anharmonicity present in real system.

In the FT-IR spectrum, the N–H stretch of pyrrole ( $v_{NH}$ ) is observed at 3300 cm<sup>-1</sup>, whereas it is calculated as 3519 cm<sup>-1</sup>. The observed  $v_{NH}$  at 3300 cm<sup>-1</sup> also correlates with the earlier reported free  $v_{NH}$  absorption band at 3465 cm<sup>-1</sup> for pyrrole-2-carboxylic acid [62]. The N-H wagging mode of pyrrole at 536 cm<sup>-1</sup> corresponds to the calculated wavenumber at 544 cm<sup>-1</sup>. The observed N–H deformation of pyrrole at 1514 cm<sup>-1</sup> agrees well with the calculated wavenumber at 1548 cm<sup>-1</sup> with 8% contribution in PED. A weak stretching vibration of hydrazide N-H is observed at 3184 cm<sup>-1</sup>, whereas it is calculated as 3406 cm<sup>-1</sup>. The observed

rocking and wagging mode of hydrazide N-H at 1191, 469 cm<sup>-1</sup> correspond to the calculated wavenumber at 1199, 475 cm<sup>-1</sup>, respectively.

The red shift is observed in O-H--O stretching vibrations. The non-hydrogen bonded or free hydroxyl group of phenols absorbs strongly in 3700-3584 cm<sup>-1</sup> region. Intramolecular hydrogen bonding is stronger when a  $\pi$ -delocalized six-membered ring is formed than a smaller ring results from bonding. In *o*-hydroxy aryl acids and esters, the vibrational wavenumber of hydrogen-bonded O-H group shifts towards lower wavenumber due to the presence of intramolecular hydrogen bonding [63]. In the FT-IR spectrum, the O-H stretching vibration (v<sub>OH</sub>) is observed at 3184 cm<sup>-1</sup>, whereas it is calculated as 3129 (closed system), 3670 (open system) cm<sup>-1</sup>. The observed v<sub>OH</sub> at 3184 cm<sup>-1</sup> confirms the presence of the hydrogen bonded O-H group in molecule. Therefore, solid state spectrum of PCSH attributes to the vibration of intramolecular hydrogen bonded O-H group. A combination band of O-H deformation and R1 ring deformations at 1371 cm<sup>-1</sup> corresponds to the calculated wavenumber at 1385 cm<sup>-1</sup>.

The observed C-H stretches in benzene ring at 2931, 2850 cm<sup>-1</sup> correlate with the calculated wavenumber at 3084, 3064 cm<sup>-1</sup>, respectively. The C-H stretching mode of schiff linkage CH=N is observed at 2702 cm<sup>-1</sup>, whereas it is calculated to be 2938 cm<sup>-1</sup>.

In experimental FT-IR spectrum, a combination band of C-C stretches and C-H-C deformations in benzene ring at 1567 cm<sup>-1</sup> agrees the calculated wavenumber at 1596 cm<sup>-1</sup>. The observed C-C stretches in pyrrole at 1514 cm<sup>-1</sup> correspond to the calculated wavenumber at 1548 cm<sup>-1</sup>.

The carbonyl group stretching ( $v_{C9=O10}$ ) is observed at 1674 cm<sup>-1</sup> agrees well with the calculated wavenumber at 1661 cm<sup>-1</sup>. The absorption band at 1674 cm<sup>-1</sup> is in good agreement with the earlier reported free  $v_{C=O}$  absorption band at 1744 cm<sup>-1</sup> for syn-pyrrole-2-carboxylic acid

[64]. An observed C-O group stretching ' $v_{C16-O17}$ ' at 1307 cm<sup>-1</sup> agrees well with the calculated wavenumber at 1309 cm<sup>-1</sup>.

The C15=N16 stretching vibration ( $v_{C=N}$ ) at 1514 cm<sup>-1</sup> agrees well with the calculated wavenumber at 1548 cm<sup>-1</sup> with 15% contribution in PED. The observed  $v_{C=N}$  at 1514 cm<sup>-1</sup> also correlates with the earlier reported C=N absorption band at 1498 cm<sup>-1</sup> for 2-formylpyrrole-<sup>4</sup>*N*-ethylthiosemicarbazone [65]. The presence of  $v_{C=N}$  in FT-IR spectrum confirms the hydrazone linkage in PCSH molecule. The observed C8-N9 stretch in hydrazide part of molecule at 1452 cm<sup>-1</sup> corresponds to the calculated wavenumber at 1511 cm<sup>-1</sup> with 17% contribution in PED. A combination band of N7H22C6 deformation and ring C-C stretches at 1325 cm<sup>-1</sup> agrees well with the calculated wavenumber at 1322 cm<sup>-1</sup>.

The observed N-N stretching vibration  $(v_{N-N})$  at 1100 cm<sup>-1</sup> agrees well with the calculated wavenumber at 1101 cm<sup>-1</sup>. The  $v_{N-N}$  at 1100 cm<sup>-1</sup> also correlates with the earlier reported N-N absorption band at 1034 cm<sup>-1</sup> [65-67].

#### 5. Conclusions

The eco-friendly synthesis, thermodynamic aspects of synthesis, molecular structure elucidation, spectral analysis and chemical reactivity evaluation of pyrrole-2-carboxaldehyde salicylhydrazone has been reported. The PCSH has been characterized by elemental analysis FT-IR, <sup>1</sup>H-NMR, UV-Visible and ESI-Mass spectroscopy. The O-H stretching vibration (v<sub>OH</sub>) observed at 3184 cm<sup>-1</sup> indicating O-H involved in intramolecular hydrogen bonding having *synsyn* (closed) form. The molecular orbital coefficients analyses suggest electronic transitions as  $\pi \rightarrow \pi^*$ . The AIM analysis confirms the existence of homonuclear intramolecular hydrogen bonding. The results of AIM confirm the existence of resonance assisted hydrogen bonds having five membered rings. The molecular electrostatic potential surfaces and local reactivity descriptors of PCSH show that molecule may be used as precursor for the synthesis of new heterocyclic compounds thiadiazoline, thiazolidinones and azetidinones and metal complexes.

#### Acknowledgement

The authors are thankful to the Directors of IIT Kanpur and CDRI Lucknow for providing spectral measurements as well as to the NCERT and CSIR funding agencies for providing the funds.

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#### Captions

#### **Figure Captions**

Figure 1 Depicted scheme for formation of the PCSH

Figure 2 The optimized geometries of ground state syn-*syn* and *syn-anti*-conformers along with open conformer and transition states

**Figure 3** Molecular graph of ground state syn-syn (closed) and syn-syn (open) conformers: bond critical points (small red spheres), ring critical points (small yellow sphere), bond paths (pink lines)

**Figure 4** Calculated molecular surface of the title compound. Colour in eV: From red 0.5 to blue 20.5 at DFT B3LYP functional and 6-31g\*\* basis set.

**Figure 5** The correlation curve between experimental and calculated <sup>1</sup>H-NMR chemical shifts using B3LYP/6-31+G(d,p)

Figure 6 Experimental and calculated UV-Visible spectrum of PCSH

Figure 7 Molecular orbitals of the PCSH

Figure 8 The experimental and theoretical FT-IR spectrum along with correlation curve

#### **Table Captions**

**Table 1** Selected optimized geometrical parameters of PCSH calculated at B3LYP/6–31G(d,p):bond length (Å), bond angle (°) and dihedral angle (°)

**Table 2** Calculated Enthalpy (*H*), Gibbs free energy (*G*) and Entropy (*S*) of reactant, product and byproduct (water) and Reaction at room temperature, using B3LYP/6-31G(d,p)

**Table 3** Geometrical parameter bond length (Å), sum of vander Wall radii ( $r_a + r_B$ ) and topological parameters for bonds of interacting atoms: electron density ( $\rho_{BCP}$ ),  $\rho_{BCP}$ , Laplacian of electron density ( ${}^{2}\rho_{BCP}$ ), electron kinetic energy density ( $G_{BCP}$ ), electron potential energy density ( $V_{BCP}$ ), total electron energy density ( $H_{BCP}$ ), estimated interaction energy ( $E_{int}$ ) at bond critical point (BCP)

**Table 4.** Calculated  $\varepsilon_{HOMO}$ ,  $\varepsilon_{LUMO}$ , Energy band gap ( $\varepsilon_L$ - $\varepsilon_H$ ), Electronegativity ( $\chi$ ), Chemical Potential ( $\mu$ ), Global Hardness ( $\eta$ ), Global Softness (S), Global Electrophilicity Index ( $\omega$ ) (in eV) for 2-Formyl-1H-pyrrole (Reactant I), salicylic acid hydrazide (Reactant II) and PCSH (Product), using B3LYP/6-31G(d,p)

**Table 5** Calculated Fukui functions (fk+, fk-) for selected atomic sites of 2-Formyl-1H-pyrrole (Reactant I), salicylic acid hydrazide (Reactant II) and PCSH (Product) using Hirshfeld population analysis at B3LYP/6-31+G(d,p) level

**Table 6** Experimental and calculated GIAO <sup>1</sup>H NMR chemical shifts of PCSH using B3LYP/6–31G(d,p) in Methanol and DMSO– $d_6$  as the solvent (25 °C)

**Table 7** Comparison between experimental and calculated electronic transitions for PCSH: *E* (eV), oscillatory strength (*f*),  $\lambda_{max}$  (nm) using TD–DFT/B3LYP/6–31G(d,p) in Chloroform, Methanol and DMSO at (25 °C)

**Table 8**. IR vibrational wavenumbers (calculated and experimental in cm<sup>-1</sup>) for dimer and their assignments.

#### **Supplementary Table**

**S Table 1.** Second–order perturbation theory analysis of the Fock matrix in NBO basis for dimer: Donar (*i*), Acceptor (*j*), Occupancy (O), Percentage electron density over bonded atoms  $(ED_{X}, \%)$ , Stabilization energy of charge delocalization interactions ( $E^{(2)}$ ) in (kcal/mol) and NBO hybrid orbitals of bonded atoms.

	510(u,p).				
Bond len	gth (Å)	Bond angle (°)		Dihedral an	gle (°)
R(1,2)	1.3654	A(2,1,5)	109.8294	D(5,1,2,19)	179.9686
R(1,5)	1.3778	A(2,1,18)	127.4276	D(18,1,5,6)	-0.1434
R(1,18)	1.0094	A(1,2,3)	108.1262	D(1,2,3,4)	0.0205
R(2,3)	1.385	A(2,3,4)	107.2666	D(2,3,4,5)	-0.0142
R(2,19)	1.0799	A(3,4,5)	107.4875	D(1,5,6,7)	-0.3005
R(3,4)	1.4154	A(1,5,4)	107.2903	D(5,6,7,8)	-179.695
R(3,20)	1.0804	A(1,5,6)	121.6869	D(6,7,8,9)	-175.774
R(4,5)	1.3918	A(4,5,6)	131.0228	D(7,8,9,10)	2.2144
R(4,21)	1.0812	A(5,6,7)	120.4048	D(10,9,11,16)	11.1355
R(5,6)	1.4379	A(5,6,22)	116.8636	D(16,11,12,24)	-175.828
R(6,7)	1.2893	A(6,7,8)	116.947	D(12,11,16,17)	177.4191
R(6,22)	1.0974	A(7,8,9)	120.7556	D(24,12,13,25)	-1.6936
R(7,8)	1.3628	A(7,8,23)	119.2343	D(26,14,15,27)	0.2768
R(8,9)	1.3743	A(8,9,10)	121.0197	D(27,15,16,17)	0.7161
R(8,23)	1.0147	A(8,9,11)	116.8098	D(11,16,17,28)	-4.0927
R(9,10)	1.2406	A(10,9,11)	122.1636		
R(9,11)	1.4835	A(9,11,12)	123.9911		
R(11,12)	1.4092	A(9,11,16)	117.5885		
R(11,16)	1.4224	A(12,11,16)	118.4199		
R(12,13)	1.3864	A(11,12,13)	121.6398		
R(12,24)	1.0866	A(11,12,24)	120.0493		
R(13,14)	1.4027	A(12,13,14)	119.2249		
R(13,25)	1.0848	A(13,14,15)	120.6539		
R(14,15)	1.3855	A(14,15,16)	120.5107		
R(14,26)	1.0862	A(11,16,15)	119.4985		

**Table 1** Selected optimized geometrical parameters of PCSH calculated at B3LYP/6-31G(d,p): bond length (Å), bond angle (°) and dihedral angle (°)

R(15,16)	1.4062	A(11,16,17)	122.5944
R(16,17)	1.3392	A(15,16,17)	117.907
R(17,28)	0.9951	A(16,17,28)	106.1208

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**Table 2** Calculated Enthalpy (*H*), Gibbs free energy (*G*) and Entropy (*S*) of reactant, product and byproduct (water) and Reaction at room temperature, using B3LYP/6–31G(d,p)

parameters	Pyrrole-2-	2-Hydroxy	product	Byproduct	Reaction
	carboxaldehyde	benzohydrazide	PCSH	water	
<i>H</i> (a.u.)	-323.411999	-531.349086	-778.371287	-76.394588	-0.00479
<i>G</i> (a.u.)	-323.448078	-531.394368	-778.429457	-76.416024	-0.003035
S (kcal/mol-K)	75.936	95.303	122.43	45.116	-3.693

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**Table 3** Geometrical parameter bond length (Å), sum of vander Wall radii ( $r_a + r_B$ ) and topological parameters for bonds of interacting atoms: electron density ( $\rho_{BCP}$ ),  $\rho_{BCP}$ , Laplacian of electron density ( ${}^2\rho_{BCP}$ ), electron kinetic energy density ( $G_{BCP}$ ), electron potential energy density ( $V_{BCP}$ ), total electron energy density ( $H_{BCP}$ ), estimated interaction energy ( $E_{int}$ ) at bond critical point (BCP)

Interactions	Bond	$(r_a + r_B)$	$ ho_{ m BCP}$	$\nabla^2 \rho_{\rm BCP}$	$G_{ m BCP}$	$V_{\rm BCP}$	$H_{\rm BCP}$	$E_{ m int}$	Sp	ectral
A••••B	length					S				
	(Å)	(Å)	(a.u.)	(a.u.)	(a.u.)	(a.u.)	(a.u.)	(kcal/mol)	ν(O-H) ν (C=O	intensity
C9-O10•••H28-O17	1.64983	2.55552	0.053756	0.152523	0.04142	-0.04471	-0.00329	-14.0288	s 3129 1661	616 199.2
N23-H23•••H24-C12	1.97666	2.61619	0.012817	0.054092	0.01086	-0.00819	0.002665	-2.57053		

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**Table 4.** Calculated  $\varepsilon_{HOMO}$ ,  $\varepsilon_{LUMO}$ , Energy band gap ( $\varepsilon_L$ - $\varepsilon_H$ ), Electronegativity ( $\chi$ ), Chemical Potential ( $\mu$ ), Global Hardness ( $\eta$ ), Global Softness (S), Global Electrophilicity Index ( $\omega$ ) (in eV) for 2-Formyl-1H-pyrrole (Reactant I), salicylic acid hydrazide (Reactant II) and PCSH (Product), using B3LYP/6-31G(d,p)

Molecules	$\mathcal{E}_{\mathrm{H}}$	$\mathcal{E}_{\mathrm{L}}$	$\mathcal{E}_{L}$ - $\mathcal{E}_{H}$	χ	μ	η	S	ω
Reactant I	-6.2641	-1.2585	5.0055	3.7613	-3.7613	2.5027	0.1997	2.8263
Reactant II	-6.1334	-1.3203	4.8131	3.7269	-3.7269	2.4065	0.2077	2.8857
PCSH	-5.5136	-1.5268	3.9867	3.5202	-3.5202	1.9933	0.2508	3.1082
				O Mr				
		6						
		V						

**Table 5** Calculated Fukui functions  $(f_k^+, f_k^-)$  for selected atomic sites of 2-Formyl-1H-pyrrole (Reactant I), salicylic acid hydrazide (Reactant II) and PCSH (Product) using Hirshfeld population analysis at B3LYP/6-31+G(d,p) level

Compound		I	Hirshfeld at	Fukui	functions		
		Atom	q <sub>N</sub>	<b>q</b> <sub>N+1</sub>	<b>q</b> <sub>N-1</sub>	$f_k^{\ +}$	$f_k$
	ſ	C6	0.2542	0.089	0.3039	0.1646	0.0497
Reactant I	$\left\{ \right.$	N1	-0.5187	-0.550	-0.4846	0.0314	0.0341
Reactant II	ſ	N9	0.06672	-0.00972	0.12383	0.0764	0.0571
	ĺ	N10	0.06548	-0.01928	0.14730	0.0848	0.0818
	ſ	1N	0.09379	0.05856	0.13448	0.0352	0.0407
	J	6 C	0.06595	-0.05293	0.12369	0.1189	0.0577
Product		7 N 8 N	-0.11175 0.08490	-0.15751 0.05629	-0.05568 0.15665	0.0458 0.0286	0.0561 0.0718

Atom No.	Magnetic shelding	$\delta$ calc. (ppm) in gas phase	δexp. (ppm) MeOD	$\delta$ exp. (ppm) DMSO- $d_6$	Assignment
H18	22.9741	8.1759	8.73	10.459	pyrrole–NH (s)
H19	24.9498	6.2002	C 100 S C002	< 122 <b>-</b> 000-	
H20	25.4904	5.6596	6.108- 0.6893	6.433-7.2807	pyrrole–CH (m)
H21	25.3963	5.7537			
H22	24.4514	6.6986	7.890	8.758	CH=N (s)
H23	23.6558	7.4942	unobserved	δ10.280	hydrazide–NH (s)
H24	24.5636	6.5864	7 20 7 41	7 702 0 246	
H25	25.0571	6.0929	/.38-/.41	7.793–8.346	Ar–H (m)
H26	24.3854	6.7646		$\sim$	
H27	24.8003	6.3497			
H28	18.7192	12.4308	unobserved	12.71	Ar–OH (s)

**Table 6** Experimental and calculated GIAO  $^{1}$ H NMR chemical shifts of PCSH usingB3LYP/6–31G(d,p) in Methanol and DMSO– $d_6$  as the solvent (25 °C)

**Table 7** Comparison between experimental and calculated electronic transitions for PCSH: *E* (eV), oscillatory strength (*f*),  $\lambda_{max}$  (nm) using TD–DFT/B3LYP/6–31G(d,p) in Chloroform, Methanol and DMSO at (25 °C)

	Gas phase Chloroform								Met	hanol			]	DMSO		Assignment
Transiti	]	Theoretica	al	Exp.	]	Theoretica	ıl	Exp.	]	Theoretica	al	Exp.	,	Theoretica	al	-
0115	$\begin{array}{c} Calculat\\ ed\\ (\lambda_{max}) \end{array}$	Oscillat ory strength (f)	E (eV)	$(\lambda_{max})$	$\begin{array}{c} Calculat\\ ed\\ (\lambda_{max}) \end{array}$	Oscillat ory strength (f)	E (eV)	$(\lambda_{max})$	$\begin{array}{c} Calculat\\ ed\\ (\lambda_{max}) \end{array}$	Oscillat ory strength (f)	E (eV)	(λ <sub>max</sub> )	$\begin{array}{c} Calculat\\ ed\\ (\lambda_{max}) \end{array}$	Oscillat ory strength (f)	E (eV)	-
H→L	337.30	0.7172	3.6758	350	350.07	0.8509	3.5417	358	350.88	0.8318	3.5335	362	353.47	0.8652	3.5076	$\pi \rightarrow \pi^*$
$H \rightarrow L + 2$	269.50	0.1872	4.6006	252	273.38	0.2742	4.5352	273	272.78	0.2865	4.5453	275	273.66	0.2821	4.5306	n→π*
							2									

Mode	unscaled	scaled	Int.	scaled	Int.	Exp.	Assignment
no.	Cl	osed syste	em	Open	system	_	
78	3662	3519	65.76	3517	52.77	3300	v(N1H18)(99)
77	3545	3406	10.49	3376	67.07		v(N8H23)(100)
76	3282	3153	1.89	3151	9.46		v(C3C4)(65)+v(C4C5)(31)
75	3265	3137	3.93	3135	2.78		v(C4C5)(40)-v(C3C4)(31)+v(C4H21)(28)
74	3257	3129	616.09	3670	6.04	3184	v(O17H28)(100)
73	3252	3125	4.06	3124	4.62		v(C4H21)(68)- v(C3H20)(28)
72	3218	3092	8.63	3087	17.35	3016	v(C15H27)(73)+v(C14H26)(15)+v(C13H25)(11)
71	3210	3084	17.8	3070	18.89	2931	v(C13H25)(70)-v(C15H27)(20)+v(C12H24)(5)
70	3189	3064	15.67	3061	2	2850	v(C14H26)(78)-v(C13H25)(9)-v(C15H27)(7)-v(C12H24)(6)
69	3176	3051	10.11	3042	16.12		v(C12H24)(87)-v(C13H25)(10)
68	3058	2938	39.91	2937	43.74	2702	v(C6H22)(99)
67	1728	1661	199.21	1731	307.1	1674	ν(C9O10)(41)-δ(O17C11C16)(11)-(ω-C9C11)(6)-δ(C12C9C11)(6)
66	1688	1622	133.87	1623	90.2	1614	ν(C6N7)(50)-ν(C5C6)(16)-(δ-N7H22C6)(11)-(ρ-
							C6C5)(6)+v(C4C5)(5)
65	1661	1596	163.88	1594	45.79	1567	$v(C12C13)(19) + v(C15C16)(13) + v(C9O10)(12) + \delta(O17C11C16)(12)$
						$\langle \rangle$	$+(\delta as-R1)(9)-v(C14C15)(7)+\delta(C13H24C12)(5)-v(C11C12)(5)$
64	1638	1574	72.04	1581	18.74		ν(C14C15)(17)-ν(C13C14)(16)-δ(C16H28O17)(15)-(δas-R1)(14)-
							v(C11C16)(13)+δ(C13H26C14)(9)+v(C11C12)(5)
63	1611	1548	101.41	1547	35.78	1514	ν(C4C5)(20)-ν(C6N7)(15)-ν(C2C3)(10)-(ρ-
							N8H23)(10)+δ(C2H18N1)(8)+δ(C3H21C4)(8)-ν(C5C6)(7)
62	1573	1511	438.58	1487	190	1452	(p-N8H23)(46)+v(N8C9)(17)-v(C2C3)(5)-v(C9C11)
61	1538	1478	135.8	1483	210.9		δ(C16H28O17)(15)-δ(C13H24C12)(15)-v(C13C14)(14)-
							δ(C16H27C15)(13)-δ(C12H25C13)(13)+v(C11C12)(8)-
							v(C16O17)(5)
60	1500	1441	32.92	1437	12.25		δ(O17C11C16)(20)+δ(C12H25C13)(11)-
							ν(C16O17)(11)+δ(C13H26C14)(11)-
							v(C12C13)(9)+v(C15C16)(7)+v(C9O10)(6)+v(C11C16)(5)
59	1497	1439	3.77	1433	56.95		$\delta(C3H19C2)(24) + \nu(N1C2)(21) - \nu(C2C3)(21) - \nu(C4C5)(9)$
58	1471	1413	17.4	1411	26.97		$v(C3C4)(18)-v(N1C2)(15)+\delta(C2H18N1)(13)+\delta(C2H20C3)(11)-$

Table 8. IR vibrational wavenumbers (calculated and experimental in cm<sup>-1</sup>) and their assignments.

							v(C2C3)(9)-v(C4C5)(9)-(\delta-R)(8)
57	1468	1410	34.05	1409	21.83		v(N1C5)(34)+v(C2C3)(10)-(δ-R)(9)-v(C4C5)(9)-
							δ(C2H20C3)(8)+δ(C2H18N1)(8)-v(C5C6)(5)
56	1441	1385	112.97	1320	32.64	1371	$(C16H28O17)(36) + \delta(C13H24C12)(13) + \nu(C14C15)(11) + \nu(C12C13)$
							$(7)+\delta(C13H26C14)(6)-\nu(C11C12)(5)$
55	1376	1322	21.79	1311	34.75	1325	(δ-N7H22C6)(13)-v(C11C16)(13)-v(C12C13)(9)-v(C14C15)(9)-
							v(C3C4)(5)+v(C15C16)(5)
54	1363	1309	50.44	1284	86.28	1307	(δ-N7H22C6)(15)-v(C16O17)(12)+v(C11C16)(7)+v(C14C15)(6)-
							v(C3C4)(6)+δ(O17C11C16)(5)+δ(C16H27C15)(5)
53	1338	1286	93.67	1269	28.07	1277	δ(O17C11C16)(17)-ν(C16O17)(14)+(δtrigonal-
							R1)(12)+ν(C9C11)(7)+(ρ-N8H23)(7)-ν(C11C16)(6)-
							δ(C13H26C14)(5)
52	1324	1272	29.2	1257	13.41		δ(C2H18N1)(16)-(δ-N7H22C6)(14)-ν(C3C4)(13)-(ρ-
							C6C5)(12)+v(C5C6)(10)-\delta(C2H20C3)(9)-
							v(N1C5)(8)+δ(C3H19C2)(7)
51	1294	1243	276.42	1226	39.52	1227	v(C11C12)(25)+δ(C13H24C12)(21)-v(C9C11)(16)-
							v(C16O17)(10)+v(N8C9)(5)
50	1276	1226	11.45	1211	295.8		$\delta$ (C3H21C4)(28)-( $\delta$ -N7H22C6)(15)-v(C3C4)(9)+ $\delta$ (C2H20C3)(9)-
							ν(N1C2)(7)-δ(C3H19C2)(6)-δ(C2H18N1)(6)-ν(C4C5)(6)
49	1248	1199	316.71	1156	108	1191	ν(C15C16)(19)+δ(C16H27C15)(12)+ν(N8C9)(11)-
						$\mathbf{\nabla}$	δ(C13H24C12)(9)-(ρ-N8H23)(8)+δ(C16H28O17)(8)-ν(C9C11)(7)-
							v(C11C16)(5)
48	1199	1152	91.43	1142	14.51	1157	$\delta(C12H25C13)(36) + \nu(C12C13)(14) + \nu(N7N8)(11) - \nu(N8C9)(6) - \nu(N8C9$
							δ(C13H24C12)(5)-δ(C13H26C14)(5)-δ(O17C11C16)(5)
47	1177	1130	10.51	1132	186.6		δ(C13H26C14)(22)+δ(C16H27C15)(19)+v(N7N8)(17)-
					)		v(C9C11)(5)+v(C13C14)(5)
46	1147	1102	35.43	1102	34.65		δ(C3H19C2)(40)-δ(C2H18N1)(16)+v(C2C3)(15)-
							$v(N1C2)(11) + \delta(C2H20C3)(5) + v(N1C5)(5)$
45	1146	1101	36.47	1088	64.8	1100	v(N7N8)(25)-δ(C13H26C14)(12)-(δtrigonal-R1)(12)-
				Y			v(C12C13)(10)+v(C14C15)(5)
44	1118	1074	43.64	1073	45.53	1030	$v(N1C2)(26) + v(C2C3)(19) + \delta(C2H18N1)(16) + \delta(C2H20C3)(11) + \delta(C2H20)(11) + \delta(C2H2$
							C3H21C4)(9)
43	1084	1041	2.65	1034	13.83		$(\delta trigonal-R1)(22) + v(N7N8)(16) + v(N8C9)(15) - (\delta - C6N7N8)(8) - (\delta - C6N7N8)(8$

							N7N8C9)(6)
42	1065	1024	17.01	1029	9.6		$v(C13C14)(20)-v(C3C4)(19)-\delta(C3H21C4)(18)+\delta(C2H20C3)(17)-$
	1000	1021	17101	102)	210		δ(C16H27C15)(6)
41	1063	1022	47.71	1020	33.63	936	$v(C13C14)(23)+v(C3C4)(13)+\delta(C3H21C4)(12)-$
							$\delta(C2H20C3)(11) + v(C14C15)(8) - (\delta trigonal-R1)(6) -$
							δ(C16H27C15)(6)
40	996	957	30.44	956	36.05	920	v(N1C5)(25)-(\delta-R)(19)-\delta(C3H19C2)(13)+v(C4C5)(9)-
							δ(C2H20C3)(8)+v(C5C6)(6)
39	987	948	0.29	939	0.3		$(\omega-C14H26)(53)+(\omega-C15H27)(20)-(\omega-C13H25)(12)-(R1-$
							puckering)(9)
38	952	915	9.88	912	2.37		$(\omega - C6C5)(67) - (\tau - C6N7)(22)$
37	934	897	0.92	911	9.27		$(\omega-C12H24)(41)-(\omega-C13H25)(32)-(\omega-C15H27)(13)+(\tau-R1)(8)$
36	920	884	20.41	881	41.28	837	(δtrigonal-R1)(38)-(δ-O10C9N8)(17)+δ(O17C11C16)(9)+(δ-
							N7N8C9)(7)-(δ-R)(5)
35	897	862	13.59	861	12.86		$(\delta - R)(58) + (\delta - R)(30)$
34	878	843	0.02	839	0.04		$(\omega$ -C3H20)(46)- $(\omega$ -C4H21)(25)+ $(\tau$ -R)(14)+ $(\omega$ -C2H19)(13)
33	869	835	7.93	824	1.46		(ω-C15H27)(36)+(ω-C12H24)(18)-(τ-C16O17)(15)-(ω-
							C14H26)(9)-(R1-puckering)(7)+(ω-C16C11)(6)
32	853	820	92.52	807	19.03	769	$(\tau - C16O17)(54) + (\omega - C15H27)(9) + (\omega - C16C11)(7) + (\omega - C12H24)(6) - (\omega - C12H$
							(R1-puckering)(6)
31	844	811	15.11	773	24		(δtrigonal-R1)(29)-(δas-
							R1)(12)+v(C16O17)(11)+v(C11C16)(9)+v(C15C16)(9)-( $\tau$ -
						7	C16O17)(5)-(\deltaas-R1)(5)
30	809	777	20.84	762	8.94		$(\omega - C4H21)(54) + (\omega - C2H19)(21) - (\tau - R)(9) + (\omega - C3H20)(7)$
29	795	764	12.19	744	6.44		$(\delta - R)(21) + (\rho - C6C5)(18) - (\delta - R)(15) + (\delta - C6N7N8)(8) - \nu(C5C6)(6) - (\delta - R)(21) + (\delta - C6N7N8)(8) - \nu(C5C6)(6) - (\delta - R)(21) + (\delta - C6N7N8)(8) - \nu(C5C6)(6) - (\delta - R)(21) + (\delta - C6N7N8)(8) - \nu(C5C6)(6) - (\delta - R)(21) + (\delta - C6N7N8)(8) - \nu(C5C6)(6) - (\delta - R)(21) + (\delta - C6N7N8)(8) - \nu(C5C6)(6) - (\delta - R)(21) + (\delta - C6N7N8)(8) - \nu(C5C6)(6) - (\delta - R)(21) + (\delta - C6N7N8)(8) - \nu(C5C6)(6) - (\delta - R)(21) + (\delta - C6N7N8)(8) - \nu(C5C6)(6) - (\delta - R)(21) + (\delta - C6N7N8)(8) - \nu(C5C6)(6) - (\delta - R)(21) + (\delta - C6N7N8)(8) - \nu(C5C6)(6) - (\delta - R)(21) + (\delta - C6N7N8)(8) - \nu(C5C6)(6) - (\delta - R)(21) + (\delta - C6N7N8)(8) - \nu(C5C6)(6) - (\delta - R)(21) + (\delta - C6N7N8)(8) - \nu(C5C6)(6) - (\delta - R)(21) + (\delta - C6N7N8)(8) - \nu(C5C6)(6) - (\delta - R)(21) + (\delta - C6N7N8)(8) - \nu(C5C6)(6) - (\delta - R)(21) + (\delta - $
							v(N1C5)(5)
28	771	741	26.55	735	50.5	747	(\omega-C9C11)(22)-(\omega-C14H26)(13)-(\omega-C11C9)(12)+(R1-
							puckering)(12)-( $\omega$ -C13H25)(10)-( $\omega$ -C12H24)(10)+( $\tau$ -
							$C9C11)(9)+(\omega-C15H27)(5)$
27	754	725	28.88	706	67.61		(R1-puckering)(26)-(ω-C16C11)(22)+(ω-C13H25)(19)+(ω-
							C9C11)(11)-( $\omega$ -C11C9)(8)+( $\omega$ -C12H24)(6)
26	740	711	67.66	687	4.09	666	(ω-C2H19)(62)-(ω-C3H20)(26)-(τ-R)(6)
25	695	668	4.55	657	4.91		(R1-puckering)(50)-(ω-C9C11)(17)-(ω-C16C11)(13)-(ω-

							C14H26)(5)-(\omega-C12H24)(5)
24	684	657	21.57	647	25.64	627	$(\delta as-R1)(26)+(\tau-R)(25)+(\omega-C5C6)(11)-(\delta as-R1)(9)+(\tau-R)(6)$
23	682	655	16.15	610	3.09		$(\tau - R)(32) - (\delta as - R1)(15) + (\omega - C5C6)(14) + (\tau - R)(7) + (R1 - C5C6)(14) + (\Gamma - R)(7) + ($
							puckering)(7)+( $\delta as-R1$ )(5)
22	633	608	2.64	559	5.97		$(\tau - R)(69) + (\omega - C3H20)(13) + (\omega - N1H18)(9)$
21	571	548	1.36	545	52.84		$(\delta as-R1)(44)+\delta(O17C11C16)(40)+\delta(C12C9C11)(5)$
20	566	544	52.49	542	0.43	536	$(\omega - N1H18)(57) + (\tau - R)(25) - (\tau - R)(11).$
19	557	535	21.67	513	2.63		$(\omega-C9C11)(20)+\nu(C5C6)(6)-(\delta-N7N8C9)(6)+\delta(C12C9C11)(6)-(\delta as-$
							$R1)(6)+(\delta-R)(5)+(\rho-C6C5)(5)+\delta(C4C6C5)(5)$
18	536	515	6.38	489	50.38		$(\omega - C16C11)(29) - (\tau - R1)(20) + (R1 - puckering)(16) - (\tau - R1)(14) + (\omega - C16C11)(29) - (\tau - R1)(20) + (R1 - puckering)(16) - (\tau - R1)(20) + (\omega - C16C11)(20) - (\tau - R1)(20) + (R1 - puckering)(16) - (\tau - R1)(20) + (\omega - C16C11)(20) + (R1 - puckering)(16) - (\tau - R1)(14) + (\omega - C16C11)(20) + (R1 - puckering)(16) - (\tau - R1)(14) + (\omega - C16C11)(20) + (R1 - puckering)(16) - (\tau - R1)(14) + (\omega - C16C11)(20) + (R1 - puckering)(16) - (\tau - R1)(14) + (\omega - C16C11)(14) + (\omega -$
							C13H25)(10)-( $\omega$ -C15H27)(5)
17	494	475	61.38	462	0.64	469	$(\omega - N8H23)(29) - (\tau - N8C9)(25) + (\tau - N7N8)(15) + (\tau - R1)(7)$
16	474	456	2.44	429	25.46		δ(017C11C16)(13)+(δ-010C9N8)(13)-
							$\delta(C4C6C5)(11) + \delta(C12C9C11)(9) + (\tau - R1)(8)$
15	456	438	1.69		12.86		δ(017C11C16)(45)-(ω-C9C11)(15)-(δ-C6N7N8)(6)
14	430	413	9.19		2.63		$(\tau-R1)(39)-(\tau-R1)(15)-(\omega-C11C9)(15)-(\omega-N8H23)(5)$
13	414	398	2.53		50.38		$(\delta as-R1)(28)+\delta(O17C11C16)(11)-v(C9C11)(10)+(\delta-O10C9N8)(8)$

Proposed assignment and potential energy distribution (PED) for vibrational modes: Types of vibrations: v-stretching,  $\delta_{sc}$ -scissoring,  $\rho$ -rocking,  $\omega$ -wagging, t-twisting,  $\delta$  and  $\delta'$ -deformation,  $\delta'_{as}$ -asymmetric deformation,  $\tau$ -torsion

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Figure 1 Depicts scheme for preparation of the PCSH



Figure 2 The optimized geometries of ground state *syn-syn* and *anti-syn* conformers along with transition states.



**Figure 3** Molecular graph of ground state *syn-syn* (closed) and *syn-syn* (*open*) conformers: bond critical points (small red spheres), ring critical points (small yellow sphere), bond paths (pink lines)



**Figure 4** Calculated molecular surface of the title compound. Colour in eV: from red 0.5 to blue 20.5 at DFT B3LYP functional and 6-31g\*\* basis set.





**Figure 5** The correlation curve between experimental and calculated <sup>1</sup>H-NMR chemical shifts using B3LYP/6-31+G(d,p)



Figure 6 Experimental and calculated UV-Visible spectrum of PCSH in different solvents

CHR HIN



Figure 7 Molecular orbitals of the PCSH representing electronic transition states



Figure 8 (a) The experimental and theoretical FT-IR spectrum of PCSH. (b) correlation curve

## Highlights

- ▶ PCSH was synthesized in water with good yield (88%).
- ► The rotational barrier between syn-syn (closed), syn-anti forms is 12.28 kcal/mole.

▶ Conformer *syn-syn* (closed), *syn-anti* and *syn-syn* (open) exist in ratio 99.96: 0.04:  $10^{-16}$  respectively, in the gas phase.

► The reactivity parameters indicate its further utility in organic synthesis.

**S Table 1.** Second–order perturbation theory analysis of the Fock matrix in NBO basis for dimer: Donar (*i*), Acceptor (*j*), Occupancy (O), Percentage electron density over bonded atoms (ED<sub>X</sub>, %), Stabilization energy of charge delocalization interactions ( $E^{(2)}$ ) in (kcal/mol) and NBO hybrid orbitals of bonded atoms.

	Donor		Acceptor			
(i) / O (i)	ED <sub>A</sub> ED <sub>B</sub> (%)	NBO Hybrid Orbitals	(j) / O (j)	$\begin{array}{c} ED_{A}(\%)\\ ED_{B}(\%) \end{array}$	NBO Hybrid orbitals	
π(C2-C3)	48.33	$0.6952(sp^{1})_{C} +$	$\pi^{*}(C4-C5)$	51.39	0.7168(sp <sup>1</sup> ) <sub>C</sub> .0.6972 (sp <sup>1</sup> ) <sub>C</sub>	19.40
(1.79553)	51.67	$0.7188(sp^{-1})_{C}$	(0.40884)	48.61		
πC4-C5	48.61	$0.6972(sp^{-1})_{C} +$	$\pi * (C2 - C3)$	51.67	$0.7188(sp^1)_{\rm C}$ - $0.6952(sp^1)_{\rm C}$	18.89
(1.75664)	51.39	$0.7168(sp^{1})_{C}$	(0.34650)	48.33		
			$\pi * (C6 - N7)$	57.44	$0.7579(sp^1)_{\rm C}$ -0.6523(sp^1)_{\rm N}	23.19
			(0.23989)	42.56		
π(C11-C16)	59.01	$0.7682(sp^{1})_{C} +$	π *( <i>C</i> 9- <i>O</i> 10)	71.88	$0.8478(sp^1)_{\rm C} - 0.5303(sp^1)_{\rm O}$	27.92
(1.60382)	40.99	$0.6402(sp^{1})_{C}$	(0.35931)	28.12		
			π(C12-C13)	51.97	$0.7209(sp^1)_C - 0.6930(sp^1)_C$	23.87
			(0.32182)	48.03		
			π(C14-C15)	52.88	$0.7272(sp^1)_{\rm C}$ -0.6865 $(sp^1)_{\rm C}$	14.07
			(0.29978)	47.12		
π(C12-C13)	48.03	$0.6930(sp^{1})_{C} +$	π(C11-C16)	40.99	$0.6402(sp^{1})_{C}$ -0.7682(sp^{1})_{C}	14.62
(1.71710)	51.97	$0.7209(sp^{1})_{C}$	(0.43882)	59.01		
			π(C14-C15)	52.88	$0.7272(sp^1)_{\rm C}$ -0.6865(sp^1)_{\rm C}	20.98
			(0.29978)	47.12		
$\pi$ (C14-C15)	47.12	$0.6865(sp^1)_{\rm C} +$	π(C11-C16)	40.99	$0.6402(sp^1)_{\rm C}$ -0.7682(sp^1)_{\rm C}	23.33
(1.70539)	52.88	$0.7272(sp^{1})_{C}$	(0.43882)	59.01		
			$\pi$ (C12-C13)	51.97	$0.7209(sp^1)_{\rm C}$ -0.6930(sp^1)_{\rm C}	16.71
			(0.32182)	48.03		
σ(C12-H24)	61.32	$0.7831(sp^{2.48})_{\rm C} +$	σ(N8-H23)	28.77	$0.5364(sp^{2.30})_{\rm N}$ -0.8440 $(sp^{0.0})_{\rm H}$	1.12
(1.9792)	38.68	$0.6220(sp^{0.0})_{\rm H}$	(0.03775)	71.23		
$n_1 N1$		sp <sup>1.00</sup>	$\pi^{*}(C2-C3)$	51.67	$0.7188(sp^{1})_{C} - 0.6952(sp^{1})_{C}$	39.47
(1.57327)		*	(0.34650)	48.33		
. /			$\pi^{*}(C4-C5)$	51.39	$0.7168(sp^{1})_{C} . 0.6972 (sp^{1})_{C}$	38.35
			(0.40884)	48.61		

n1N7		*(C6-H22)	39.38	$0.6275(sp^{2.15})$ - 0.7786(sp^{0.00}) <sub>H</sub>	10.82
(1.91935)		(0.03421)	60.62		
		(N8-H23)	28.77	$0.5364(sp^{2.30})_{\rm N}$ -0.8440 $(sp^{0.00})_{\rm H}$	8.37
		(0.03775)	71.23		
$n_1 N8$	sp <sup>99.99</sup>	$\pi * (C6 - N7)$	57.44	$0.7579(sp^1)_{\rm C}$ -0.6523(sp^1)_{\rm N}	26.76
(1.66293)		(0.23989)	42.56		
		π *(C9-O10)	71.88	$0.8478(sp^{2.20})_{\rm C}$ -0.5303(sp^0) <sub>O</sub>	58.64
		(0.35931)	28.12	-	
$n_I O 10$	$sp^{0.78}$	*(N8-C9)	37.31	$0.6108(sp^{1.60})_{N}$ -0.7918 $(sp^{2.27})_{C}$	24.59
(1.96528)		(0.06956)	27.15		
		*(C9-C11)	51.58	$0.7182(sp^{1.65})_{C}$ -0.6958 $(sp^{2.24})_{C}$	11.26
		(0.05390)	48.42		
		*(O17-H28)	20.86	$0.4567(sp^{2.84})_{O}$ - $0.8896(sp^{0})_{H}$	25.57
		(0.07171)	79.14		
$n_2O17$	sp <sup>99.99</sup>	*(C11-C16)	39.64	$0.6296 (sp^{2.23})_{\rm C} - 0.7769 (sp^0)_{\rm C}$	40.58
(1.80855)		0.03449	60.36		