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Synthesis, structural, hirshfeld surface, spectroscopic studies and quantum chemical calculation of the proton transfer complex between 2-amino-4-hydroxy-6-methylpyrimidine and salicylic acid

Ziya Afroz [a], Mohd Faizan [b], Mohammad Jane Alam [b], Vítor Hugo Nunes Rodrigues [c], Shabbir Ahmad [b], Afaq Ahmad [a, *]

[a] Department of Chemistry, Aligarh Muslim University, Aligarh, 202002, UP, India
[b] Department of Physics, Aligarh Muslim University, Aligarh, 202002, UP, India
[c] CFisUC, Department of Physics, Universidade de Coimbra, Rua Larga, 3004-516, Coimbra, Portugal

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ABSTRACT

The proton transfer (PT) complex of 2-amino-4-hydroxy-6-methylpyrimidine (AHMP) with salicylic acid (SA) has been synthesized and their crystal has been grown by slow evaporation technique. Further, the crystal has been investigated by single crystal X-ray diffraction (SCXRD). The complex crystallizes in the orthorhombic centrosymmetric space group *Pbca*. The vibrational spectra of PT complex and its constituents have been analysed in the solid phase. UV–Vis and ^{1}HNMR spectra of PT complex and its constituents (SA and AHMP have been studied in solution phase. Thermal stability of PT complex has been examined by thermal gravimetric and differential thermal analysis (TG/DTA). The intermolecular interactions and their contribution to the crystal formation have been analysed with the help of 3D Hirshfeld surface and 2D fingerprint plot. The theoretical calculations of the PT complex have been carried out using DFT/TD-DFT methods to support the experimental results as well as to explore various molecular properties such as frontier molecular orbitals, natural atomic charges, chemical reactivity and molecular electrostatic potential mapping (MEP).

1. Introduction

PT complexes are gaining considerable interest in the research from last decade, due to their wide potential applications in the field of pharmaceutical science [1], material science [2], bio-electrochemical energy transfer process [3], biological science [4], optoelectronic, optical communication [5,6], organic semi-conductor [7], and DNA binding, antibacterial and antifungal activity [8]. Pyrimidine and its derivatives are known for their biological and pharmaceuticals importance. These are nitrogen-containing heterocyclic compound and belong to nucleic acid family [9,10]. Pyrimidine derivatives have exhibited antibacterial, antifungal and anti-HIV activity [11,12]. While, SA is widely used in organic synthesis, plant growth regulator, as a preservative in food products, antiseptic, anti-fungal agents [13,14] and in the many skin care product for acne treatment, psoriasis, calluses, corns, keratosis pilaris and warts [15,16]. These wide range importances of AHMP and SA have motivated to synthesize their PT complex. Their single crystal has been grown by slow evaporation technique and it was investigated by SCXRD analysis. The PT complex was further investigated by quantum chemical calculations (DFT/TD-DFT) and various experimental techniques (FTIR, UV–Vis, ^{1}H NMR, TG/DTA). The characteristic absorption bands appeared in the FTIR of PT complex have been assigned with great accuracy using animated modes and simulated IR spectrum. SCXRD technique and FTIR, ^{1}H NMR and UV–Vis spectra are used to confirm the present PT complex formation. Hirshfeld surface analysis is utilized to study the contribution of the intermolecular interactions and void field space in the crystal. Thermal behaviour of the studied crystal is analysed by TG/DTA. Moreover, frontier molecular orbital energies, electrostatic potential, natural atomic charge and reactivity parameter have been discussed.

* Corresponding author.
E-mail addresses: afaqahmad3@gmail.com, zia19a@gmail.com (A. Ahmad).

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2. Experimental details

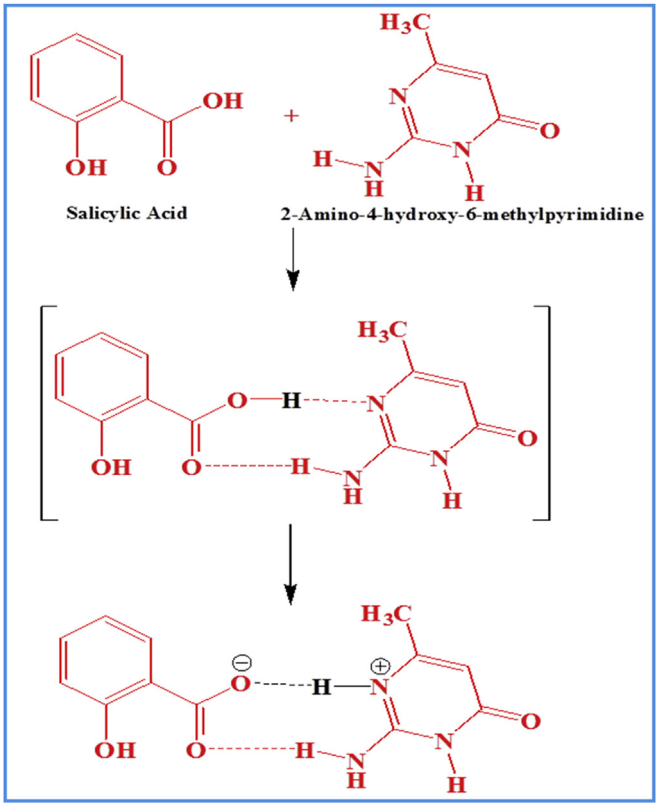
2.1. Chemical preparation

The SA and AHMP were purchased from Sigma-Aldrich Chemical Co., USA where as ethanol obtained from Merck and used without any further purification for the experiments. The 1:1 of AHMP and SA compounds were dissolved in 15 mL ethanol separately. Both solutions were stirred at 40 °C till the appearance of the transparent solution. After that, both solutions were mixed and stirred continuously for 3 h at same temp. Then, the solution was placed for slow evaporation at room temperature in the dust and vibration free atmosphere, leading to formation of crystal as per Scheme 1.

2.2. Characterization techniques

The SCXRD analysis was performed on the BRUKER APEX-II diffractometer equipped with CCD detector using Mo-Kα radiation (λ = 0.71073 Å). The SAINT program was used for the data reduction and cell refinement [17]. The crystal structure was solved by the direct method using SHELXS- 97 [18] and refinements were performed on F^2 by the full matrix least square fitting of data with SHELXL-97 [19]. All non-hydrogen atoms were refined anisotropically and fixed their position. The crystal structure was examined with the help of PLATON [20,21] which showed no solvent-accessible voids in the crystal lattice. The molecular pictorial representation of the present crystal is illustrated using Mercury [22] and Olex-2 program [23].

FTIR spectra of SA, AHMP and their crystalline PT complex were recorded on Bruker (Tensor 37) spectrometer in the range of 4000–400 cm^{-1} at 2 cm^{-1} resolution using KBr pellet technique. UV–Vis spectral data of SA, AHMP and $SA^-.AHMP^+$ in ethanol solvent were collected using Lambda-950 UV–Vis–NIR Spectrophotometer (Perkin-Elmer). The ^1H NMR spectrum of PT complex and SA was measured on the BRUKER ADVANCE II 400 NMR spectrometer (9.4T) using DMSO-d_6 as a solvent and tetramethylsilane (TMS) as a standard reference. Sample of 10–15 mg was dissolved in 0.75 mL of DMSO-d_6 solvent for the NMR measurements. TG/DTA analysis of $SA^-.AHMP^+$ complex was carried out at DTG-60H, Shimadzu in nitrogen gas atmosphere from 40 °C to 650 °C.



Scheme 1. Depiction of formation of PT complex from its constituents, salicylic acid and 2-amino-4-hydroxy-6-methylpyrimidine and its intermediate state.

3. Computational details

All quantum chemical calculations on the present molecules in their ground electronic state were performed by DFT and TD-DFT methods implemented in Gaussian 09 software [24]. The hybrid functional, Becke three parameters exchange functional along with the Lee-Yang-Par (LYP) correlation functional, was employed in the present theoretical calculations [25]. Initial coordinates of the molecular compounds were taken from the asymmetric unit of the crystal structure. The geometry optimization and harmonic frequencies calculations were performed at B3LYP/6-311++G(d,p) level of theory. DFT/B3LYP method was chosen due to low computational cost and reasonable accuracy. Some important vibrational bands occurred in the FTIR were assigned using simulated IR spectrum and animated modes with the help of GaussView 5 program [26]. TD-DFT method was used to simulate electronic spectra in the gaseous and solvent phase using same functional and basis set. The integrated integral equation formalism for the polarizable continuum model (IEF-PCM) was applied to consider solvent effect in calculation. Furthermore, important molecular properties such as frontier molecular orbital energies (HOMO-LUMO energy and associated band gap), Natural atomic charges, reactivity parameter and molecular electrostatic potential were estimated at optimized geometry at same level of theory. Apart from this, the 3D hirshfeld surfaces and 2D finger plots are generated using CrystalExplorer 3.1 software [27].

4. Results and discussions

4.1. Crystal structure analysis

The crystal structure of the $SA^-.AHMP^+$ single crystal has been investigated by SCXRD. It is observed that the $SA^-.AHMP^+$ complex crystallizes in orthorhombic crystal system and containing Z = 8 formula unit (where Z = no. of molecules in the unit cell). The acquired unit cell parameters are a = 12.1124 (3) Å, b = 13.7787 (4) Å, c = 14.4981 (4) Å and volume of the unit cell is 2419.63 (11) $Å^3$. The goodness of fit and other refinement parameters of the $SA^-.AHMP^+$ crystal are listed in Table 1. Further, it is found that the proton of the –COOH of SA is transferred to the adjacent AHMP molecule to make protonated pyridinium cation ($AHMP^+$) and Salicylate anion (SA^-). The thermal ellipsoid plot (at 50% probability) for asymmetric unit of the crystal, comprises of the anionic SA^- and cationic $AHMP^+$, is shown by ORTEP view in Fig. 1. The packing picture of the molecular complex in the crystal is presented in Fig. 2. The OH, COO^- and NH^+, NH_2 and NH groups are involved in the hydrogen bonding interactions, result in the formation of O–H···O, N–H···O and N–H···N type hydrogen bonding interactions. In the complex, SA^- has been linked with $AHMP^+$ via strong intermolecular interaction $N8^+$–H8···$O1^-$ whose bond distance and bond angle are 2.608 Å and ∠172.96°, respectively. Whereas the proton of the hydroxyl acid group forms intramolecular hydrogen bond, i.e. O4–H4···O2, with the oxygen of COO^- (bond distance = 2.55 Å and bond