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Graphical Abstract:





Experimental, quantum chemical studies and Hirshfeld surface analysis on molecular structure of two pictrate salts: 1, 4-diaza bicyclo[2,22] octane and Furan-2yl methanamine

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Abstract

Two new picrate salts, namely, 1, 4-diaza bicyclo(2,2,2)octanium picrate [DABCOP] and Furan-2yl methanaminium picrate [FMP] has been successfully crystallized by Slow Evaporation Solution growth Technique (SEST). The crystal and molecular structures have been determined by single crystal X-ray diffraction method. The crystal packings of the both the crystals feature classical N-H...O hydrogen bonds and C-H...O interactions. In DABCOP, each diaza molecule is linked to the picric acid which forms cyclic R_4^4 (19) and R_4^4 (18) motifs. In FMP, most of the *ortho* related nitro group in anion are involved in N-H...O hydrogen bonding network forming five ring R_1^2 (6), R_2^1 (4), R_2^4 (4), R_1^2 (6), and R_2^2 (5) motifs. Also, a weak C-H...O interaction forming a dimer R_2^2 (8) motif with donor-acceptor distance of 3.413(2) Å. Based on the Hartree-Fock (HF) and Density Functional Theory (DFT) method with 6-311++G (d,p) basis set, the molecular vibrational bands were interpreted. HOMO and LUMO analysis of the molecules were calculated using corresponding methods with the same basis set. In addition, Mulliken charge analysis and thermodynamic properties were calculated. Hirshfeld surface analysis and associated two dimensional fingerprint plots show intermolecular contacts and their relative contribution via colored contour approach

Introduction

The growing interest paid to heterocyclic molecules with intermolecular interactions remains a challenge for researchers around the world and understanding the crystal packing which mandates the field of crystal engineering [1-6]. Hydrogen bond is a unique feature to exhibit the properties of molecular crystals. The formation of charge transfer complex depending on the nature of the donor-acceptor system and the orientation of anionic and cationic species [7,8]. It facilitates the formation of hydrogen bonds between the cation and anion in the crystalline assembly. In the present work, two different compounds of picrate salts namely 1, 4-diazabicyclo (2, 2, 2) octane (DABCO) and Furan-2-yl methanamine (FM) were successfully crystallized and investigated. Picric acid is used in making explosives and also as an intermediate in dye manufacturing [9]. As a proton donor, it has the capability of forming stable picrate compounds with organic molecules due to the presence of active and ionic bonds [10]. The complexes of picric acid are interesting candidates due to the presence of phenolic OH and electron withdrawing nitro groups. These groups are acting as hydrogen bond donors and acceptors for the ions leading to organic salts. Crystals of 1,4-diazabicyclo (2.2.2) octane (DABCO) is widely used as catalyst [11] and the resemblance of cage like structure exhibit outstanding complex forming ability, physical and chemical properties [12]. DABCO are used in dye lasers and nontoxic base catalyst for various organic reactions with high yield [13]. The presence of nitrogen atoms shows different basic nature, facilitating the formation of monocations [14]. Numerous crystal structures of salts [15-17] and addition compounds of DABCO, such as adducts with trimethyl aluminium boron trifluoride and boranes [18] and coordination polymers with metal ions have been published [19]. Charge-transfer interactions of DABCO with bromine and carbon tetrabromide resulting in crystalline complexes have also been reported. Furthermore, cocrystallization phenomena of DABCO with phenols have successfully been employed for the separation of phenolic natural products by molecular recognition [20-22]. Substituted furan derivatives are fundamentally important heterocyclic molecules and are present in many natural and medicinal structures [23,24]. Among various furan derivatives, butenolides have appeared in the literature as interesting components for the formation of natural and pharmacological compounds [25]. The synthesis of heterocyclic molecules is in great demand due to its wide range of biological activities. Many drugs, such as antifungal drugs, nitroimidazole, azomycin and metronidazole, contain an imidazole ring as its prime importance. It was already reported

that the imidazole ring react with picric acid molecule and forms a salt of imidazolium picrate in acetone, which crystallizes in the orthorhombic system and the structural, optical, mechanical and vibrational properties of the salt were also been investigated [26-28]. Surprisingly, a new crystal has been crystallized in triclinic system with centrosymmetric space group. A literature survey done through Cambridge Structural Database (CSD) and other related scientific works reveals more work on synthesis point of view of these two molecules whereas there are few work on materials aspect for its physiochemical properties [29-33].

The two new salts, namely, 1, 4-diazabicyclo (2,2,2) octanium picrate (DABCOP) and Furan 2-yl methanammonia picrate (FMP) has been reported which predicts the hydrogen bonding patterns and motifs obtained in the ionic crystals. The structural and electronic properties of new salts have been studied using Hartree-Fock (HF) and Density Functional Theory (DFT) methods. The interaction between these molecules provide useful information for researchers to know the nature of hydrogen bonding interactions. The optimized structure and vibrational frequencies are done using the same quantum chemical methods. Further, experimental IR spectral analyses were also done for the two salts and compared with its theoretical counterparts. The HOMO-LUMO energies were also been computed with other thermodynamic parameters by the same methods.

Experimental

1,4–Diazabicyclo[2.2.2]octane (0.112g, 0.001M) was dissolved in distilled ethanol and transferred slowly in drops to the ethanolic solution of picric acid (0.229g, 0.001M). After continuous stirring for about 1 hr, a homogeneous yellow colour solution was the final stage and the solution was kept for crystallization at room temperature under atmospheric condition by slow evaporation method. Yellow coloured, needle shaped crystals were obtained in one week. Ethanolic solution of Furan-2-yl-methanamine (0.1018g, 0.001M) was added drop wise to picric acid (0.229g, 0.001M) ethanol solution with an effective stirring. The final solution was kept for crystallization under atmospheric condition free from any disturbance. Red coloured, prismatic shaped crystals were obtained by the slow evaporation. X-ray intensity data of the grown crystals were collected at room temperature with MoK_{α} radiation (λ =0.71073 Å) using Bruker AXS KAPPA APEX-2 diffractometer equipped with graphite monochromator. The structure was solved by direct methods and refined by full-matrix least-squares calculations using

SHELXL2014 software [34]. The FTIR spectra of the grown crystals were recorded in the KBr phase in the frequency region of 4000–400 cm⁻¹ using a Jasco Spectrometer, model 410 under a resolution of 4 cm⁻¹ with a scanning speed of 2mm/sec.

Computational details

Theoretical calculations were carried out using Gaussian 09 [35] software package. The geometry optimization and vibrational modes calculation of DABCOP and FMP were carried out with both Density Functional Theory (DFT) and Hartree–Fock (HF) methods, which gives the structural and spectral characteristics. The starting geometry for both the salts were taken from single crystal X-ray studies and optimized using DFT employing the Becke-3–Lee–Yang–Parr (B3LYP) and HF methods supplemented with the standard 6-311++G(d,p) basis set. The electronic properties of the compounds have been computed, which determines the way a molecule interacts with other species [36]. HOMO-LUMO for both DABCOP and FMP were performed. Both the compounds were compared to analyze the charge interaction and activity of the compound. The thermodynamic parameters for both the salts were also calculated by HF and DFT methods.

Results and Discussion

Molecular Geometry

The molecular structures of the compounds, DABCOP and FMP, with atom labeling were shown in Fig.1 (a-b) which crystallizes in P2₁/n and P1 space group respectively. The unit cell parameters and crystallographic data are shown in Table 1. The selected geometric parameters (bond length, bond angle and torsion angle) are shown in Table S1, S2 and S3 which are slightly deviated from the experimental values. In FMP, there occurs disorder of the picric acid in the *ortho*-NO₂ group and the structure description is based on the major orientation of the disordered picric acid. Normally, in picric acid the C-C bond distance varies from 1.36 to 1.40 Å. However, the elongation in the C-C bond distance of picric acid confirms the presence of inter-molecular interaction in both the compounds. The experimental C-C bond distance varies from the theoretical values by 0.01 to 0.03 Å. The C-N bond distance agrees well with the experimental value. The two oxygen atoms O1 and O3 bridge the neighbouring diaza compound (DABCOP), where as O1 atom do the same in furan compound (FMP). The bond angles of picrate anion confirm the deprotonation of phenolic group and the geometry is similar to other picrate complexes [37]. Also, the phenolic proton transfer of anion to DABCO and FM is confirmed by the C11-O1 bond distance. The diaza cation C-N bond distances are elongated compared to a similar feature observed by Ferguson et al. [38, 39]. In both the cations, the C-N bond involving the protonated N atoms are elongated than the non-protonated N atoms. The nitro groups in DABCOP⁻ are slightly twisted around their C-N bond distances. The N-H bond distance is stronger in diaza cation than furan cation which confirms that there exhibits stronger N-H...O intermolecular interactions that stabilize the crystal structure. All the bond distances and bond angles for both the compound are slightly deviated from the theoretical value. The difference is due to the fact that in experimental measurement the molecules are in condensed phase and in theoretical measurement the molecules are in gaseous phase.

The *ortho* nitro group of picrate anion is twisted from the plane of the ring while the *para* nitro nitro group is nearly co-planar. The angle between the rings of picrate anion and the FMP / DABCOP cation are 24.2(1) / 20.3(1)°, respectively. In DABCOP compound, the back bone conformation angles of cation ψ^1 (C27-N20-C24-C21, C33-N20-C24-C21) and ψ^2 (C14-C15-C16-N8) are cis- and trans-oriented respectively. The side-chain conformation of anion in DABCOP χ^1 (O3-N2-C12-C11) is 13.7° and the calculated values by HF/DFT are -26.887°/-25.182° respectively. There is a disorder in picrate anion when crystallize with furan-2yl methanamine. In FMP compound, the back bone conformation angles of picrate anion $\psi^{1}(O10-$ N8-C16-C11) and ψ^2 (C12-C13-C14-N5) are *cis*- and *trans*- oriented respectively. In solid crystalline state, the side-chain conformation angles of anion and cation χ^1 (O3-N2-C12-C11, O9-N8-C16-C15) and χ^2 (N30-C26-C25-C23, N30-C26-C25-O29) are -28.1°, 48.5°, -92.8°, 89.2° respectively whereas they differ from the calculated values. In the anion and cation, the formation of charge transfer complex depends on the nature of the donor-acceptor system and the orientation of anionic and cationic species which facilitates the formation of expected N-H…O hydrogen bonds between amino hydrogen and phenolic oxygen. The protonation on the N site of the cation is confirmed from C-N bond distances and C-N-C bond angles.

Hydrogen bonding features

The intermolecular and intramolecular hydrogen bonds usually involve a hydrogen atom that normally bound to an electronegative atom such as N, O and interacts by electrostatic forces to another electronegative atom and this kind of interactions can enhance the packing arrangement and stability of crystal. It is also responsible for large modifications of the nonlinear polarizabilities [40]. The crystal structure of DABCOP and FMP displays a three dimensional hydrogen bonding network shown in Table 2 and 3. Different crystal packing is observed in DABCOP and FMP compound (Fig.2 (a-b)). In FMP, most of the ortho related nitro group of picrate are involved in the N-H...O hydrogen bonding interactions thereby forming five ring $R_1^2(6)$, $R_2^1(4)$, $R_2^4(4)$, $R_1^2(6)$, and $R_2^2(5)$ motifs. Also, a weaker C-H...O interaction is formed with H atom in the cation forming a dimer $R_2^2(8)$ motif with donor-acceptor distances of 3.41 Å. From Fig.3a, when viewed along a axis, the face to face molecules [41], anion-anion and cationcation, is almost parallel with a dihedral angle of 2.8 and 2.2° respectively. But in DABCOP when viewed along a axis no face to face molecule is observed (Fig.3b). The two bifurcated ring $R_1^2(6)$ motifs are formed by same phenol H atom but different *ortho* nitro group of picric acid. The ring $R_2^4(4)$ motif is formed by the same N-H..O hydrogen bond formed between the H atom of the amine group in furan compound and O atom in nitro group of anion. The crystal packing of FMP consists of dimer and ring as shown in Fig. 2 (a) with a sheet like structure when viewed along crystallographic c axis and they form an infinite one-dimensional chain and are separated by a distance of 6.84 Å. The ortho nitro group of picric acid and side-amine chain of furan compound are twisted from the plane of the ring of about 0.73 and 1.03 respectively. But in DABCOP, the nitro group of picric acid is twisted from the plane of the ring of about 0.97 Å. Hence, the anion is slightly twisted in FMP than DABCOP compound. The disorder in the nitro group of anion affects the chain formation and packing arrangement of the atoms. In the asymmetric unit (Fig.1 (b)), the diaza and picrate ions are linked by the intermolecular N-H...O hydrogen bond and C-H...O, C-H...N intermolecular interactions, where the cation acts as a hydrogen donor in this bifurcated system. Each diaza molecule is linked to the picric acid which forms cyclic $R_4^{4}(19)$ and $R_4^{4}(18)$ motifs (Fig.2 (b)) which are packed into molecular ribbons [42] forms corrugated layer structure parallel to each other in (0) and (202) planes and are separated by a distance of 9.37 Å. The adjacent cyclic motifs are bridged by C-H...N interaction (Fig. 2 (b)). From the result, it is clear that four N-H...O hydrogen bonding network with the donor-acceptor distances of about 2.73, 2.93, 2.83 and 2.96 Å respectively stabilizes the FMP crystal structure where in DABCOP crystal structure is stabilized by a single N-H...O hydrogen formed the phenol H atom of the anion. Fig. 4 shows the showing (a) face to face molecule in FMP (b) no face to face molecule when viewed along a axis

Mulliken Population Analysis

The total atomic charges of DABCOP and FMP obtained by Mulliken population analysis with HF and DFT by 6-311++G (d,p) basis set are listed in Table. 4, 5 and as a bar diagram in Fig 5. From the result, it is clear that the substitution of proton in the N atom of both the compound have redistributed the electron density over the molecule. In FMP, the N8 atom is positive in DFT whereas negative in HF this is due to the high electronegative character of O atom in DFT whereas in DABCOP, N20 atom is positive may be due to the formation of C-H...N interaction. Among the carbon atoms, C23 is more positive charged. The C25 atom is connected to highly electro negativity atom O29, hence the adjacent atom C23 loses electrons and this is reason for the high positive nature. In DABCOP, the carbon atoms C11 and C12 are highly positive may be they losses their electrons to N atom that take part in N-H...O hydrogen bonding. Carbon atoms have both positive and negative charges, which show that carbon atoms are highly influenced by their substituent. All the H atoms in anion as well as in cation are positive as they lose their electrons to the nearby carbon atoms. The presence of large negative charge on O and N atom and net positive charge on H atom may suggest the formation of intermolecular interaction in solid forms [43]. When magnitudes of the charge of each atom predicted by the two methods are compared, the magnitude predicted by B3LYP is relevant than predicted by HF method even though the basis set is same.

FT-IR spectral analysis

The FT-IR spectrum and theoretical IR spectra of the title compounds are shown in Fig.6a,6b. The bands are calculated in the measured region 4000-450cm⁻¹ and the assignments of some important bands are given in Table 6 and 7. The formation of complex salts of picrate is strongly evident by the presence of characteristic infrared bands of the donor and acceptor in the spectrum of DABCOP and FMP salt with slight changes in frequencies. The differences between the experimental and theoretical vibrational modes are observed. This discrepancy may be due to the formation of intermolecular hydrogen bonding. Also some vibrations identified in the solid phase experimental spectra could not be identified in the simulated counterpart and therefore, have been omitted. The differences between calculated and experimental frequencies are due to anharmonicity, intermolecular interaction, an approximation treatment of electron correlation effects and the limited basis sets [44].

N-H vibrations

Normally the N-H stretching vibrations occur in the region of 3500-3000 cm⁻¹[45]. In FMP, the calculated N-H symmetric stretching vibrations by HF / DFT methods are 3694 /3476respectively, and experimentally a strong band is observed at 3435 cm⁻¹. The calculated N-H asymmetric stretching vibrations by HF / DFT methods are 3761/3537 respectively. Both the N-H symmetric and asymmetric stretching vibrations occur in the imidazole ring where the intermolecular interactions take place. The N-H in-plane bending is observed as a strong band at 1561 cm⁻¹ and calculated at 1723/ 1574 cm⁻¹ by HF/DFT methods respectively. There is a overlapping of N-H, C-H and C-N in-plane bending vibrations which are calculated by HF/DFT methods. In DABCOP, the N-H stretching vibration is observed in the region 1557 cm⁻¹ and the calculated vibrations by HF/DFT methods are 1721/1554 cm⁻¹. The scissoring vibration is predicted in HF/DFT method and experimentally it has been observed as a weak band in the region 2066 cm⁻¹.

C-H, C-N, C=C and C=O vibrations

The C-H stretching vibrations are expected to occur in the region 3000-3100 cm⁻¹ [46]. Generally this region is not affected by the nature of the substituent. But in FMP and DABCOP, the calculated values of C-H stretching vibration by HF/DFT methods differ by ~300/~100 cm⁻¹ respectively. The deviation may due to the formation C-H...O intermolecular interaction in both the compound which connects the cation and anion. In FMP, in imidazole ring the C-H symmetric stretching vibrations is observed as a strong band at 3086 cm⁻¹ and the calculated values by HF/DFT methods are 3236/3076 cm⁻¹ respectively. The C-H asymmetric stretching vibrations calculated by HF/DFT methods occur in the region 3314/3145 cm⁻¹, 3410/3245 cm⁻¹ respectively. In DABCOP, the C-H symmetric stretching vibrations are observed as strong band at 2962 cm⁻¹ and 3087 cm⁻¹. In the theoretical calculations the HF values are more deviated from DFT values which may be due to the delocalization of electron in the aromatic ring.

In pyrimidine, the C-N and C=C stretching vibrations occur in the region 1600-1500 cm⁻¹. In FMP the C-N in-plane bending vibration is not observed experimentally but the calculated values by HF/DFT methods are 1784/1628 cm⁻¹ respectively. The C=C stretching vibrations are calculated by HF/DFT methods are 1680, 1686/1513, 1527 cm⁻¹ respectively. The C=O stretching vibrations are expected to occur in the region 1710-1712 cm⁻¹ as strong band. The carbonyl absorption in DFT/HF at 1707/1834 cm⁻¹ confirms the COO-groups of the compound. In FMP, the C=O stretching band calculated by HF/DFT are1723/1574 cm⁻¹ respectively. The presence of this

band confirms the formation of picrate salts of DABCOP and FMP. The assignment is in very close agreement with data of the complex salts reported already [47, 48].

N-H...O hydrogen bond interaction

The N-H...O stretching vibration has been expected to occur in the region 3000-3500 cm⁻¹. In the present picrate salt of FMP/DABCOP, the N-H...O vibrations occur as a strong band in the region 3086 /2962cm⁻¹ respectively. The HF value agrees well with the experimental value but in DFT the downshift may be due to the increase in N-H bond distance.

Thermodynamic properties

The thermodynamic properties of materials are closely related to their vibrational properties, yielding not only a guidance for insights about their atomic lattice behavior, but also providing essential information for technological applications [49]. The values of some thermodynamic parameters (such as thermal energy, heat capacity, entropy, zero-point vibrational energies (ZPVE), rotational constants and dipole moment) of the title compound calculated at HF and B3LYP/6-311++G(d, p) levels without experimental determination are shown in table 8. Dipole moment reflects the molecular charge distribution and is given as a vector in three dimensions. It is used to depict the charge movement across the molecule and strictly obeys for a neutral molecule which depends on positive and negative charges. From table 8, the ZPE for FMP/DABCOP was obtained to be 156.419, 143.624 K cal mol⁻¹ and /201.897, 186.413 K cal mol⁻¹ respectively. The entropy for both the compounds is quite significant. The results of the energies, dipole moment, entropy, and ZPE can be used to the new synthesis of some hydrazine - hydrazones compounds [50].

Frontier Molecular Orbitals

Energies of HOMO and LUMO are popular quantum mechanical descriptors. It has been shown that these orbital play a major role in governing many chemical reactions, and are also responsible for charge transfer complexes [51]. The frontier orbital (HOMO and LUMO) of the chemical species are very important in defining its reactivity [52]. The difference in energy values are tabulated in Table. 9 and are shown in Fig. S1 (a-b). The value of the energy separation between the HOMO and LUMO was found as 8.704/3.889 eV (HF/DFT) for FMP and 8.432/3.753 eV (HF/DFT) for DABCOP. This large energy gap indicates that FMP is quite stable. Lower value in the HOMO and LUMO energy gap explains the eventual charge transfer interactions taking place within the molecule. The larger the HOMO-LUMO orbital energy gap,

the harder the molecule. The hardness has been associated with the stability of the chemical system [53]. In the present work, the DABCOP compound is found to softer molecule and they are highly polarizable than FMP compound. The energy gap between HOMO and LUMO has been used to prove the bioactivity from intermolecular charge transfer [54-57].

Hirshfeld surface analysis

Hirshfeld surface analysis is a novel tool for the graphical representation of intermolecular contacts in the crystal environment via colored contouring approach. It's associated two dimensional fingerprint plots provide information about the unique distribution of closer contacts involved in the molecular structure [58-62]. Hirshfeld surface analysis and their associated two dimensional fingerprint plots of the title compounds were mapped using Crystal Explorer V3.1software [63]. The Hirshfeld surfaces of the compounds FMP and DABCOP is shown in Fig. 7 and the surfaces were mapped over the d_{norm} range of -0.674 to 1.326 (FMP) and -0.689 to 1.292 (DABCOP). In the compound FMP the surfaces are dominantly highlighted by N-H...O hydrogen bond interactions through O...H contact, which are clearly exhibited by dark red color regions in the Hirshfeld surface. The ortho related nitro group in the anion is involved in bifurcation of hydrogen bonding with adjacent hydrogen atoms of the amine (NH) group was also evident from the analysis [64-65]. The light red regions on the Hirshfeld surface features to C-H...O weak hydrogen bonding interactions. Consequently in the compound 2, the Hirshfeld surfaces are mainly covered by strong N-H...O (bifurcated) hydrogen bonding interactions. Further the 2D fingerprint plots retrieved from the Hirshfeld surfaces of the compounds FMP and DABCOP is shown in Fig. S2. As discussed above the 2D fingerprint plots reveals the majority proportion of interactions are due to O...H contacts (~ 55%) involved in the strong and weak N-H...O and C-H...O hydrogen bonding interactions in both the compounds. The other highest contribution is made with H...H contacts (~ 25%) due to substituent groups. In addition relatively weak contacts such as O...C, O...O, C...H and H...C are also observed. The overall proportion of all the contacts involved in the compounds FMP and DABCOP is shown via pie chart (Fig. 8).

Conclusion

The present work of FMP and DABCOP has been thoroughly analyzed by theoretical and experimental X-ray studies. The optimized geometrical parameters have been calculated at

B3LYP/6-311+++G (d,p) basis set using HF/DFT method, which shows a slight variation from experimental values. Crystal packing of the title compound is formed by intermolecular interactions. The donor-acceptor distance agrees well making stronger N-H...O intermolecular hydrogen bonding that stabilizes the crystal structure. Mulliken population analysis gives a clear knowledge that the substitution of proton form the anion, both the compound has redistributed the electron density over the molecule. The shifting of vibrational bands as well as theoretical peaks of the infrared (IR) due to the intermolecular hydrogen bonds was also analyzed and assigned. The thermodynamic properties of both the compound were calculated. HOMO-LUMO energy gaps explain the charge transfer interactions taking place within the molecule. The occurrence of closer molecular in the crystal packing of FMP and DABCOP was visualized via Hirshfeld surface and fingerprint plot analyses.

Supplementary information:

Crystallographic data of the structure reported in this article have been deposited in the Cambridge Crystallographic data centre. The deposition numbers are CCDC-1508506 (DABCOP) and CCDC-1508507 (FMP). Copy of the data can be downloaded at free charge from CCDC website (<u>www.ccdc.cam.ac.uk</u>).

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Fig.1 (b). Optimized Structure of DABCOP with atomic numbering scheme (a) ORTEP diagram drawn at 30 % probability level (a) HF method (b) DFT/B3LYP

Fig.2 (a) Ring motifs $R_1^2(6)$, $R_2^1(4)$, $R_2^4(4)$, $R_1^2(6)$, and $R_2^2(5)$ diagram for FMP

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Fig.3(a) .The packing diagram of FMP viewed down c axis. Dashed line indicate Hydrogen bond

Fig.3(b) .The packing diagram of DABCOP viewed down c axis. Dashed line indicate Hydrogen bond

Fig. 4 Diagram showing (a) face to face molecule in FMP (b) no face to face molecule when viewed along a axis

Fig.5. Mulliken charge distribution of (a) FMP and (b) DABCOP

Fig.6a Experimental FTIR spectrum of (a) FMP (b) DABCOP

Fig. 6b Theoretical FTIR spectrum of (a) FMP and (b) DABCOP using HF and DFT/B3LYP method

Fig.7 Hirshfeld surface analysis of (a) FMP and (b) DABCOP showing possible interaction with adjacent molecules

Fig. 8 Pie chart showing the relative contribution of all contacts in (a) FMP and (b) DABCOP

Empirical formula	C12 H15 N5 O7 [DABCOP]	C11H10N4O8 [FMP]
Formula weight	341.29	326.23
Temperature	293(2) K	293(2) K
Wavelength	0.71073 Å	0.71073 Å
Crystal system, space group	Monoclinic, $P 2_1/n$	Triclinic, P1
Unit cell dimensions	$a = 11.8306(6) \text{ Å} alpha = 90^{\circ}$	a=7.8382(3) Å alpha=107.844(2)°
	$b = 7.1718(4) \text{ Å} beta = 93.842(3)^{\circ}$	b=9.3042(6) Å beta=110.246(2)°
	$c = 17.8342(10) \text{ Å} gamma = 90^{\circ}$	c=10.8074(4) Å gamma=92.809(2)°
Volume	1509.77(14) $Å^3$	693.21(6) Å ³
Z, Calculated density	4, 1.501 Mg/m ³	2, 1.563 Mg/m ³
Absorption coefficient	0.125 mm ⁻¹	0.136 mm ⁻¹
F(000)	712	336
Crystal size	0.25 x 0.27 x 0.29 mm	0.22 x 0.24 x 0.26 mm
Theta range for data	2 133 to 25 081°	2 140 to 32 079°
collection	2.155 to 25.001	2.110 to 52.077
Limiting indices	$-13 \leq h \leq 14, -8 \leq k \leq 8, -21 \leq l \leq 21$	$-11 \le h \le 11, -13 \le k \le 12, -14 \le l \le 16$
Reflections collected / unique	14677 / 2681 [R(int) = 0.0305]	18793 / 4829 [R(int) = 0.0246]
Completeness to theta $= 25.242$	97.70%	100.00%
Refinement method	Full-matrix least-squares on F ²	Full-matrix least-squares on F ²
Data / restraints / parameters	2681 / 0 / 221	4829 / 3 / 239
Goodness-of-fit on F ²	1.06	1.043
Final R indices [I>2sigma(I)]	R1 = 0.0567, wR2 = 0.1578	R1 = 0.0595, wR2 = 0.1734
R indices (all data)	R1 = 0.0755, $wR2 = 0.1732$	R1 = 0.0905, wR2 = 0.1994
Largest diff. peak and hole	$0.402 \text{ and } -0.319 \text{ e.A}^{-3}$	$0.420 \text{ and } -0.586 \text{ e. A}^{-3}$
CCDC No.	1508506	1508507

Table 1 Crystallographic data and Structure refinement Parameters for grown crystals

D-HA (Å)	D-H (Å)	HA (Å)	(DA) (Å)	D-HA (°)
N19-H39O1	0.81(3)	1.90(3)	2.674(3)	158(3)
C15-H13N20 ⁽ⁱ⁾	0.93	2.4	3.326(3)	171.6
C21-H23O3 ⁽ⁱⁱ⁾	0.97	2.57	3.509(5)	163.7
C33-H34O6 ⁽ⁱⁱⁱ⁾	0.97	2.53	3.485(5)	169.1
C36-H37O7 ^(iv)	0.97	2.55	3.495(5)	164.2

 Table 2 Hydrogen bonding geometry of DABCOP

Symmetry transformations used to generate equivalent atoms: (i) x+1/2,-y+3/2,z-1/2 (ii) x,y+1,z (iii) x-1/2,-y+1/2,z+1/2 (iv) -x+3/2,y+1/2,-z+1/2

D-HA (Å)	D-Н (Å)	HA (Å)	(D A) (Å)	(D A) (Å)
N30-H31O1	0.93(2)	1.82(2)	2.735(2)	169(2)
N30-H31O3	0.93(2)	2.46(2)	2.935(2)	112(2)
N30-H32O1(i)	0.92(3)	1.95(3)	2.838(2)	160(2)
N30-H32O10(i)	0.92(3)	2.38(2)	2.960(4)	120(2)
N30-H33O3(ii)	0.84(3)	2.23(3)	3.072(2)	176(2)
N30-H33O4(ii)	0.84(3)	2.69(3)	3.250(2)	126(2)
C23-H24O7(iii)	0.93	2.66	3.413(2)	139(1)
C26-H28O6(iv)	0.97	2.48	3.414(3)	162

Table 3 Hydrogen bonding geometry of FMP

Symmetry transformations used to generate equivalent atoms: (i) -x,-y+1,-z+1 (ii) -x+1,-y+1,-z+1 (iii) -x-1,-y,-z (iv) -x,-y,-z



Table 4 Mulliken charge analysis for optimized geometry of DABCOP

	•	HF/6-	DFT6-
	Atoms	311++G(d,p)	311++G(d,p)
	01	-0.471	-0.307
	O2	-0.038	0.014
	03	0.015	0.05
	O4	-0.052	-0.001
	05	-0.053	-0.003
	06	-0.038	0.018
	O7	-0.01	0.039
	N8	-0.282	-0.364
	N9	-0.166	-0.233
	N10	-0.171	-0.282
	C11	0.827	0.268
	C12	0.8	0.808
	C13	-0.594	-0.468
	H14	0.355	0.301
	C15	-0.458	-0.555
	C16	-0.479	-0.243
	H17	0.347	0.291
	C18	-0.517	-0.243
	N19	-0.032	-0.18
	N20	0.057	0.076
	C21	-0.174	-0.158
	H22	0.267	0.252
	H23	0.23	0.22
	C24	-0.746	-0.624
	H25	0.207	0.203
	H26	0.203	0.192
	C27	-0.632	-0.524
	H28	0.202	0.198
	H29	0.203	0.19
	C30	-0.209	-0.213
	H31	0.195	0.192
Y I	H32	0.231	0.227
	C33	-0.623	-0.519
	H34	0.202	0.199
	H35	0.206	0.192
	C36	-0.3	-0.279
	H37	0.211	0.204
	H38	0.261	0.25
	H39	1.023	0.812

Atoma	HF/6-	DFT/6-			
Atoms	311++G(d,p)	311++G(d,p)			
01	-0.541	-0.492			
N2	-0.255	0.186			
O3	-0.064	-0.343			
O4	-0.006	-0.265			
N5	-0.262	0.16			
O6	-0.036	-0.278			
O7	-0.03	-0.277			
N8	-0.231	0.171			
O9	-0.013	-0.279			
O10	0.086	-0.25			
C11	0.598	0.289			
C12	0.033	0.023			
C13	-0.481	0.111			
C14	0.259	0.059			
C15	-0.399	0.183			
C16	-0.094	0.005			
H17	0.266	0.093			
H18	0.219	0.048			
C19	0.363	0.119			
H20	0.181	0.101			
C21	-0.682	-0.141			
H22	0.15	0.098			
C23	0.952	-0.045			
H24	0.163	0.095			
C25	-0.364	0.034			
C26	-0.983	-0.075			
H27	0.231	0.162			
H28	0.219	0.178			
O29	-0.134	-0.263			
N30	-0.355	-0.222			
H31	0.566	0.294			
H32	0.316	0.263			
H33	0.327	0.258			

5

Table 5 Mulliken charge analysis for optimized geometry of FMP

Experimental	HF/6-311	++G(d,p)	B3LYP/6-311++G(d,p)		
FT-IR	ν_{cal}	^a I ^{IR}	v_{cal}	${}^{a}I^{IR}$	Assignment
1503(m)	1638.49	13.004	1508.11	25.213	ф С-Н
	1639.61	8.031	1511.68	22.73	ф С-Н
	1642.52	9.18	1513.15	16.026	ф С-Н
	1665.85	49.237	1533.88	12.038	ф С-Н
	1667.89	4.902	1540.37	95.766	γ Ν-Η
	1672.63	25.579	1542.97	63.737	v NO ₂
1557(s)	1721.74	173.728	1554.21	33.025	v N-H
	1748.78	151.587	1576.33	225.914	v _{as} NO ₂
	1768.55	41.333	1598.01	313.28	β C-H
1630(m)	1801.36	927.562	1632.53	423.071	β (C-H) +v(C-C)(pyrimidine ring)
2618(s)	1834.85	1977.16	1707.15	896.174	v (C-C+C=O)
2962(s)	3209.84	27.702	2671.55	3110.374	v N-HO
	3210.67	30.059	3057.45	27.469	v _s C-H
	3217.63	57.714	3058.35	23.046	v _s C-H
	3238.25	14.056	3061.09	29.711	v _s C-H
	3239.58	12.865	3082.15	9.599	v _s C-H
	3244.31	17.548	3085.78	11.613	v _s C-H
3087(s)	3249.36	3.613	3087.62	10.822	v _s C-H
	3255.48	25.961	3097.33	0.674	v _{as} C-H
	3256.33	26.365	3100.26	14.807	v _{as} C-H
	3294.74	0.101	3100.95	14.447	v _{as} C-H
	3301.72	18.896	3137.75	3.094	v _{as} C-H
	3302.78	13.365	3142.55	8.429	v _{as} C-H
	3313.85	1926.61	3144.13	11.253	v _{as} C-H
	3403.78	13.74	3222.85	38.936	v C-H (pyrimidine ring)
3427(s)	3409.98	16.801	3230.91	19.712	v C-H (pyrimidine ring)
	C C				

Table 6 Experimental and computed FT-IR vibrational frequencies (cm⁻¹) of DABCOP

Experiment	HF/6-		B3LYP/6-		
al	311+	+G(d,p)	311	++G(d,p)	Assignment
FT-IR	ν_{cal}	${}^{a}I^{IR}$	v_{cal}	${}^{a}I^{IR}$	
	1676	26.922	1513	298.816	β Ν-Η
	1680	41.705	1527	31.724	v C=C (imidazole ring)
	1686	203.902	1551	33.031	v C=C (pyrimidine ring)
1561(s)	1723	262.348	1574	132.889	β N-H +v C=O
	1748	208.407	1591	300.199	β (N-H+C-H+C-N)
	1770	62.14	1597	99.69	β Ν-Η
	1784	182.786	1628	361.256	β C-N
1632(s)	1801	706.68	1638	52.208	ϕ (N-H)+ β (C-H)
	1807	220.091	1645	201.575	φ N-H
	1815	885.099	1660	857.281	φ N-H
2066(w)	1846	878.076	1689	39.79	φ N-H
3086(s)	3052	1968.2	2151	3028.148	N-HO interaction
	3236	10.797	3076	12.953	v _s C-H (imidazole ring)
	3314	1.083	3145	1.637	v _{as} C-H (imidazole ring)
	3403	1.807	3232	14.014	v C-H (pyrimidine ring)
	3403	14.171	3239	18.581	v C-H (pyrimidine ring)
	3410	18.432	3245	15.433	v_{as} C-H (imidazole ring)
	3414	10.093	3255	11.575	v_{as} C-H (imidazole ring)
	3439	0.466	3280	0.248	v _s C-H (imidazole ring)
3435(s)	3694	66.366	3467	30.605	v_s N-H (side chain of imidazole ring)
	3761	87.365	3537	38.476	v_{as} N-H (side chain of imidazole ring)

Table 7 Experimental and computed FT-IR vibrational frequencies (cm⁻¹) of FMP

	DAB	СОР	FMP		
Parameters	HF/6-	DFT/6-	HF/6-	DFT/6-	
	311++G(d,p)	311++G(d,p)	311++G(d,p)	311++G(d,p)	
SCF energy (a.u.)	-1259.364	-1266.681	-1238.986	-1246	
Total thermal energy (KCal/Mol)	214.511	199.219	168.879	156.639	
Vibrational energy (KCal/Mol)	212.733	197.442	167.101	154.861	
Zero point vibrational energy (ZPE) (K Cal/Mol)	201.897	186.413	156.419	143.624	
Heat Capacity C _v (Cal/Mol/Kelvin)	72.171	76.087	69.572	74.355	
Entropy S (Cal/Mol-kelvin)	158.731	155.927	156.560	159.691	
Dipole moment					
μ_{x}	14.246	14.501	-11.672	-13.661	
μ_{y}	-1.198	-0.909	3.946	4.539	
μz	-0.854	-0.794	-1.707	-1.353	
μ total	14.322	14.551	12.439	11.021	
Rotational Constant (GHZ)					
X	0.454	0.448	0.467	0.363	
Y	0.128	0.125	0.135	0.157	
Ζ	0.106	0.104	0.108	0.135	

Table 8 The calculated thermodynamical parameters of DABCOP and FMP

Table 9 Calculated energy values of FMP and DBCOP

Molecular parameters	DAB	COP	FMP		
(eV)	HF / 6- 311++G (d,p)	DFT / 6- 311++G (d,p)	HF / 6- 311++G(d,p)	DFT / 6- 311++G(d,p)	
НОМО	-8.894	-6.772	-9.084	-6.745	
LUMO	0.462	-3.019	0.3808	-2.856	
$\Delta(E_{HOMO}-E_{LUMO})$	8.432	3.753	8.704	3.889	
Electronegativity (χ)	4.216	4.896	4.352	4.787	
Chemical potential (µ)	-4.216	-4.896	-4.352	-4.787	
Chemical hardness (h)	4.678	3.753	4.732	4.800	
Chemical softness (s)	0.106	0.133	0.105	0.2553	

Fig.1 (a).











Fig.3(b).















Fig. 6b







Highlights:

- Crystal structure analysis of the DABCOP and FMP salts were examined.
- HF/DFT-B3LYP calculations were performed for the two salts.
- A Hirshfeld surface analysis was presented.