RASĀYAN *J. Chem.*
Vol. 16 | No. 4 |2361-2369| October - December | 2023
ISSN: 0974-1496 | e-ISSN: 0976-0083 | CODEN: RJCABP
http://www.rasayanjournal.com
http://www.rasayanjournal.co.in

PICRIC ACID CO-CRYSTALS: STRUCTURE, DFT AND HIRSHFELD SURFACE ANALYSIS

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ABSTRACT

A comparative analysis of some crystal structures as obtained from the CSD repository has been made using crystallographic and computational approaches, for an in-depth and extensive investigation of the properties of the picric acid co-crystals. Theoretical optimization of each co-crystal structure has been performed using Density Functional Theory (DFT) at the B3LYP/6-311G(d,p) level and the geometrical parameters have been compared with their corresponding X-ray data. The optimized structure geometry, atomic Mulliken charges, molecular electrostatic potential (MEP), HOMO-LUMO, and some other relevant molecular properties have been thoroughly investigated. The Hirshfeld surface analysis has been performed to investigate and quantify the contributions of different intermolecular interactions existing in co-crystals. The analysis reveals that the maximum contribution to the Hirshfeld surface comes from the O…H/H…O contacts. The physical strength of each molecule has been ascertained by computing the void volume percentage which is, by and large, the same for all the identified molecules.

Keywords: Co-crystals, DFT, Molecular Electrostatic Potential, Hirshfeld Surfaces, Crystal Voids.

RASĀYAN *J. Chem.*, Vol. 16, No. 4, 2023

INTRODUCTION

The field of co-crystal engineering has gained significant attention in recent years due to its potential applications in the fields of drug delivery, pharmaceuticals, crystal engineering, and materials science.[1-4] The design of co-crystals is usually aimed at enhancing the solubility and bioavailability of drugs, altering their release rates, and/or improving their physical stability, besides having gained significant interest as a viable option for enhancing the properties of active pharmaceutical ingredients (APIs). The co-crystals consist of multiple molecules that are combined within the same crystal lattice, held together by non-covalent interactions, and maintain a fixed stoichiometric ratio.[5] Understanding and rationalizing crystal structures of these types is crucial as it allows utilization of computational tools for valuable predictions, based on quantitative and qualitative analysis of the intra and intermolecular interactions. Besides, hydrogen bonding plays a pivotal role in crystal engineering by ensuring the stability of molecular crystals. Picric acid has a propensity to form co-crystals with various substances, particularly aromatic compounds.[6-8] In a remarkable investigation conducted by Chen *et al*., the electron transfer properties of picric acid, a well-known co-crystal former, has highlighted the fundamental significance of van der Waals forces, hydrogen bonding, and π-π stacking interactions as key contributors to the process of co-crystallization.[9] Picric acid exhibits remarkable acidity, making it highly reactive with metals to form salts. Its lead salt is widely used as a primary explosive. X-ray crystallography plays a vital role in the field of structure-based drug design, necessitating a complete understanding of target macromolecules and their complex formation with the ligand.[10] As a result, computational quantum chemistry is progressively gaining importance in the fields of biochemistry and materials science.[11] As a part of our ongoing crystallographic research work on a variety of co-crystals, an attempt has been made to look into the theoretical aspects of picric acid–based co-crystals existing in CSD via authorized access using ConQuest (version 2022) (Fig.-1).[12,13] The crystal structures of picric acid co-crystals as identified from the CSD search are coded as AJULEW01, BODSUL, BUFCEL01, and RATBET.[13-16] The crystallographic information files (CIFs) for each structure can be accessed at https://www.ccdc.cam.ac.uk/structures. The

http://doi.org/10.31788/RJC.2023.1648656

visualization of intermolecular contacts and stacking interactions has been obtained through Hirshfeld surface (HS) analysis. Table-1 provides a detailed summary of the crystal data about each structure.

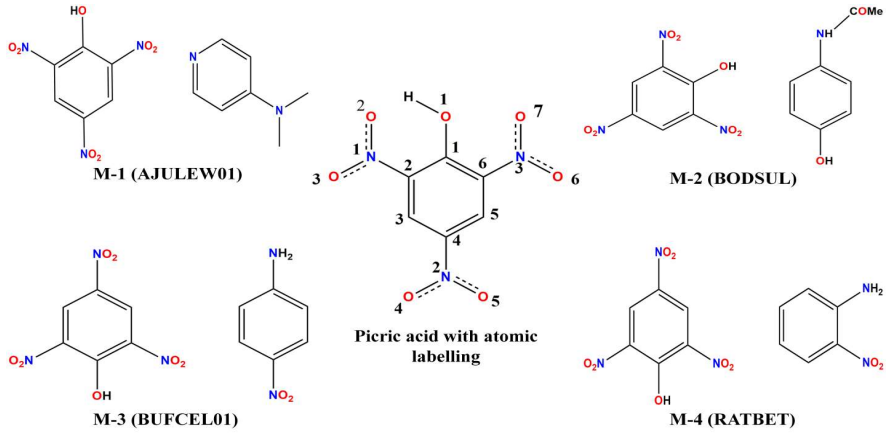


Fig.-1: Chemical Structures of Picric Acid Co-Crystals

Table-1: Precise X-ray Data of Each Co-Crystal

Parameters	M-1	M-2	M-3	M-4
CCDC code	AJULEW01	BODSUL	BUFCEL01	RATBET
Molecular Formula	$C_{26}H_{26}N_{10}O_{14}$	$C_{14}H_{12}N_4O_9$	$C_{12}H_9N_5O_9$	$C_{20}H_{17}N_5O_{11}$
Chemical Name	2,4,6-trinitrophenol N, N-dimethylpyridin - 4-amine	N-(4-hydroxyphenyl) acetamide 2,4,6-trinitrophenol	hemikis(4-nitroaniline) 2,4,6-trinitrophenol	bis(Anthranilic acid) picric acid
Crystal system	Monoclinic	Monoclinic	Orthorhombic	Monoclinic
Space group	$P2_1/n$	$P2_1/c$	Pbcn	Cc
Cell parameters	a = 15.439(1) b = 12.637(1) c = 15.987(3) α = 90.00 β = 99.62(8) γ = 90.00	a = 7.285(7) b = 14.056(1) c = 15.557(1) α = 90.00 β = 95.11(2) γ = 90.00	a = 23.498(2) b = 9.331(8) c = 10.487(8) α = 90.00 β = 90.00 γ = 90.00	a = 10.356(2) b = 15.350(3) c = 13.394(3) α = 90.00 β = 96.38(4) γ = 90.00
Cell volume	3075.2(7)	1586.9(2)	2299.7(3)	2116.0(8)
Z	4	4	8	4
R-factor (%)	5.65	4.61	7.77	5.90

EXPERIMENTAL

DFT Calculations

Density functional theory (DFT) is a computational technique used in quantum chemistry to investigate the electronic structures of complex systems by calculating the total electron densities. It helps optimize a structure by making use of Gaussian 09 software with atomic coordinates as input from the Crystallographic Information File (CIF) of a given structure.[17] In the instant case, the atomic coordinates were obtained from the CIF for each identified structure and their geometries were fully optimized using the B3LYP density functional and the 6-311G (d, p) basis set.[18,19] The optimized structures were analyzed using Gauss View 6.0.16 software and the resulting optimized parameters i.e., bond distances and bond angles were then compared with their respective experimental data.[20] The MEP map, Mulliken charges, and HOMO-LUMO energy gap were calculated based on the optimized structures of the co-crystals, and the global reactivity parameters for each structure were subsequently determined. All calculations were carried out using Gaussian 09W software.

Hirshfeld Surface Analysis

HS is a tool employed for visual analyses of intermolecular interactions in crystal structures, providing some insights into the packing stability of molecules.[21,22] Various visualization techniques, such as d_{norm}

plots, shape index plots, curvedness plots, and crystal voids, help assess quantitatively the contribution of each intermolecular contact in determining the packing characteristics. For the characterization of 2D fingerprint plots, the parameters that signify the distances between the Hirshfeld surface and the nearest atom, both inside (represented by d_i) and outside (represented by d_e), are involved. These plots employ a color gradient ranging from blue to red to depict the relative contribution of inter-contacts across the Hirshfeld surface.[23-26] The molecular characteristics, including intermolecular interactions (both the 3D-Hirshfeld surfaces and 2D-fingerprint plots) are generated using the CIF files as input in the Crystal Explorer 21.5 software.[27] The HS method employs the (0.002 atomic units) isosurface of the spherical molecular electron density to visualize voids in crystal structures.[28-31]

RESULTS AND DISCUSSION

Molecular Geometry Optimization

The geometry of all four structures has been optimized using the DFT method (with the B3LYP/6-311G (d, p) basis set). A comparison has been made between the theoretically obtained bond parameters with their respective X-ray values available in the literature.[13-16] The results indicate a fair agreement between the experimental and theoretical values, except for M-4, where the experimental data are reported to have lower quality due to poor morphology of the crystal used for intensity data collection.[16] To highlight the correspondence between the theoretical (DFT) and experimental (XRD) geometrical parameters, the correlation coefficients (R^2) have been computed and the analysis reveals that the R^2 values are highly proximal to 1 except for M-4 (bond angles), indicating a good correlation between the experimental and theoretical values. Fig.-2 and Fig.-3 show the correlation plots for the bond distances and bond angles of all four co-crystals.

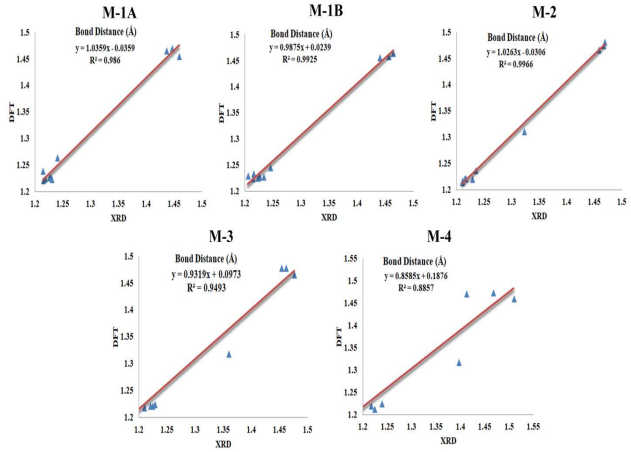


Fig.-2: XRD vs. DFT Bond Distance Correlation Plots for the Picric Acid Moiety

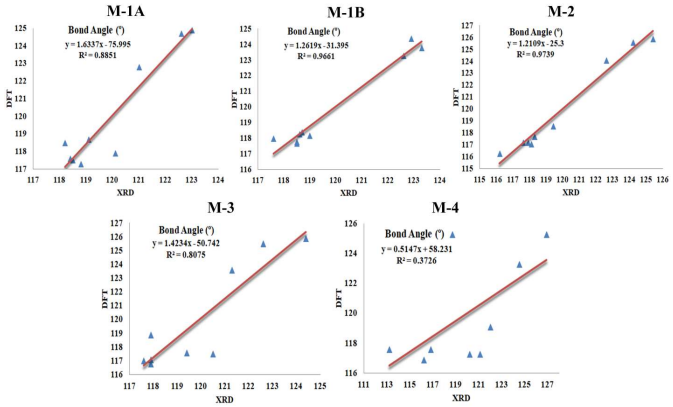


Fig.-3: XRD vs. DFT Bond Angle Correlation Plots for the Picric Acid Moiety

Frontier Molecular Orbital Analysis

The chemical properties of the molecules are observed to undergo significant influence from the HOMO-LUMO orbitals generated using the DFT/B3LYP/6311-G+(d,p) method (Fig.-4).[32] The LUMO orbitals

have been observed to be localized primarily on the picric acid of all four co-crystals whereas the HOMO orbital has been localized on the picric acid in the case of M-1. The molecules with relatively higher ΔE are assumed to be more stable.[33] In the instant case, the value of ΔE (3.22 eV) is large in the case of M-1 while it is 2.17 eV in the case of M-1. A careful analysis of ΔE in the case of all four structures reveals that these molecules are less stable and more reactive. The global reactivity parameters (Table-2) indicate that M-3 has a strong electrophilic character (with χ = 12.83 eV and η = 5.42 eV).

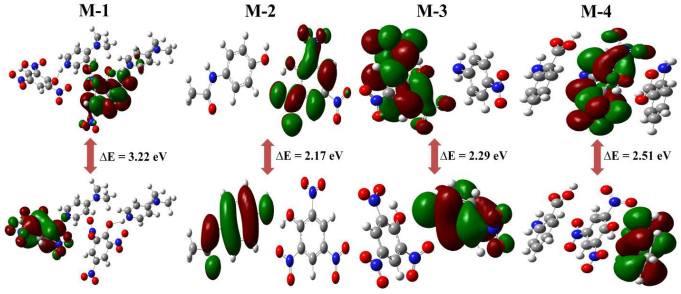


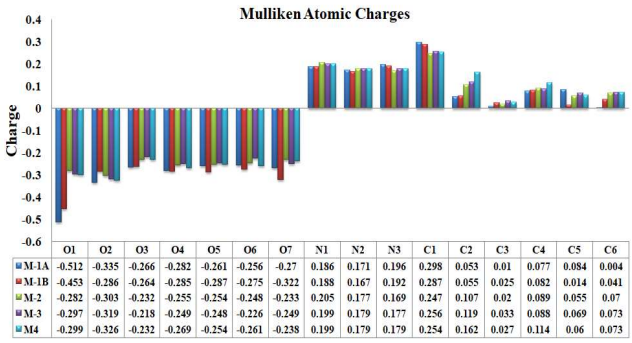
Fig.-4: HOMO-LUMO Energy Gap in the Co-Crystals

Table-2: Global Reactivity Parameters of Each Co-Crystal

Reactivity parameters	M-1	M-2	M-3	M-4
E_{HOMO} (eV)	-5.95	-5.95	-6.57	-6.12
E_{LUMO} (eV)	-2.73	-3.78	-4.28	-3.61
$\Delta E = (E_{LUMO} - E_{HOMO})$ (eV)	3.22	2.17	2.29	2.51
Chemical Hardness, $\eta = \Delta E/2$ (eV)	1.61	1.08	1.14	1.25
Softness, $\sigma = 1/2\eta$ (eV^{-1})	0.31	0.46	0.44	0.40
Chemical Potential, $(\mu = (E_{LUMO} + E_{HOMO})/2)$ (eV)	-4.34	-4.86	-5.42	-4.86
Electrophilicity Index, $\omega = \mu^2/2\eta$ (eV)	5.85	10.88	12.83	9.41
Electronegativity, $\chi = -\mu$ (eV)	4.34	4.86	5.42	4.86

Mulliken Population Analysis

Mulliken atomic charge calculation is quite useful for quantum chemical computations of molecular systems, offering valuable insights into various aspects. These calculations have wide-ranging applications, particularly in understanding the arrangement of molecules in crystals through intermolecular interactions. The Mulliken charges significantly impact important molecular properties, including dipole moments, polarizability, electronic structure, and vibrational modes. The Mulliken charge analysis results for the picric acid moiety (Fig.-5) illustrate the population distribution of charges among the atoms in the co-crystals. In all the four co-crystals of picric acid, the nitrogen and carbon atoms exhibit positive charge and its distribution arises from the positioning of these atoms between or adjacent to the electronegative atoms within the molecular structure. On the other hand, the oxygen atoms carry a negative charge and its distribution facilitates the formation of intermolecular hydrogen bond interactions with oxygen and hydrogen atoms, specifically C-H...O and O-H…O bonds.



	O1	O2	O3	O4	O5	O6	O7	N1	N2	N3	C1	C2	C3	C4	C5	C6
M-1A	-0.512	-0.335	-0.266	-0.282	-0.261	-0.256	-0.27	0.186	0.171	0.196	0.298	0.053	0.01	0.077	0.084	0.004
M-1B	-0.453	-0.286	-0.264	-0.285	-0.287	-0.275	-0.322	0.188	0.167	0.192	0.287	0.055	0.025	0.082	0.014	0.041
M-2	-0.282	-0.303	-0.232	-0.255	-0.254	-0.248	-0.233	0.205	0.177	0.169	0.247	0.107	0.02	0.089	0.055	0.07
M-3	-0.297	-0.319	-0.218	-0.249	-0.248	-0.226	-0.249	0.199	0.179	0.177	0.256	0.119	0.033	0.088	0.069	0.073
M4	-0.299	-0.326	-0.232	-0.269	-0.254	-0.261	-0.238	0.199	0.179	0.179	0.254	0.162	0.027	0.114	0.06	0.073

Fig.-5: Mulliken Charge Distribution in the Picric Acid of Each Co-Crystal

Molecular Electrostatic Potential Map Analysis

The molecular electrostatic potential (MEP) maps (Fig.-6) provide valuable insights into the nucleophilic and electrophilic regions that usually favor hydrogen bonding.[34] The different colors represent varying electrostatic potential values, with the order of intensity being: red < orange < yellow < green < blue. The nitro groups (NO_2) in all four molecules exhibit maximum negative potential, indicating their electronegativity and nucleophilic reactivity. Thus, these groups serve as nucleophilic sites for potential chemical reactions within the co-crystals. Conversely, the hydrogen atoms associated with various fragments in the co-crystals exhibit regions of maximum positive electrostatic potential, signifying their electropositivity and electrophilic reactivity. These regions represent the electrophilic sites within the co-crystals. Figure-6 provides a visual representation of the nucleophilic and electrophilic sites present in each co-crystal.

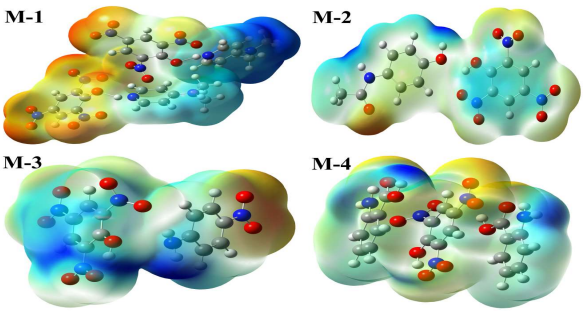


Fig.-6: MEP Maps of Each Picric Acid Co-Crystal

Hirshfeld Surface Analysis and 2D Fingerprint Plots

The 3D Hirshfeld surface formalism has been employed to visually analyze the intermolecular contacts within the crystal packing of each molecule. The d_{norm} plots, as shown in Fig.-7, depict red regions, representing different intermolecular short contacts present in each structure. The size of these spots indicates the strength of the contacts involved.[22,35] It is interesting to see in Fig.-7 the presence of X – H…O type of interactions (X = C, N, O) in Fig.-7, besides the existence of blue and red triangles indicating π...π stacking interactions. However, the planar stacking of molecules is visually represented by flat patches on the curvedness plots (Fig.-7). The primary distinction among the co-crystals M-1, M-2, M-3, and M-4 arises from the occupancy of voids within their respective crystal packings. The Crystal Explorer 21.5 program has been employed, utilizing a pro crystal electron density isosurface (0.002 au) to compute the number of voids present in each crystal (Fig.-8).[27,28] The void volume percentage for M-1 (10.5%), M-2 (10.9%), M-3(9.2%), and M-4 (8.6%) is, by and large, the same indicating that all the co-crystals exhibit good physical strength.

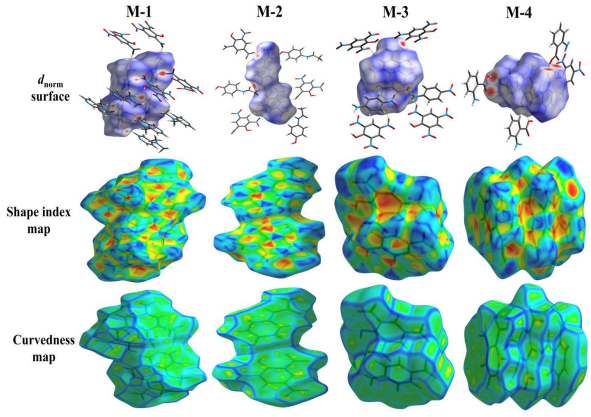


Fig.-7: Comparison of d_{norm} Surfaces, Shape Index, and Curvedness Plots of the Co-Crystals

The distinctive attributes of inter-contacts as observed on the Hirshfeld surface are effectively depicted through 2D fingerprint plots (Fig.-9) in which the hydrogen-bonded interactions are represented as spikes, and the sharpness of the peak and $d_i + d_e$ value indicate their strength. Besides, the planar stacking, arising from π... π interactions, could be identified as a prominent reddish-yellowish region in the plot. The

depiction of these features on the fingerprint plots provides valuable insights into the nature and characteristics of the intermolecular interactions.[36,37] The sharp spikes in the fingerprint plots as drawn for all the picric acid co-crystals correspond to the O…H/H…O contacts while the H...H interactions are observed at the center of the dispersed spots (Fig.-9). The presence of "butterflies" in the fingerprint plots confirms the existence of C…H contacts.

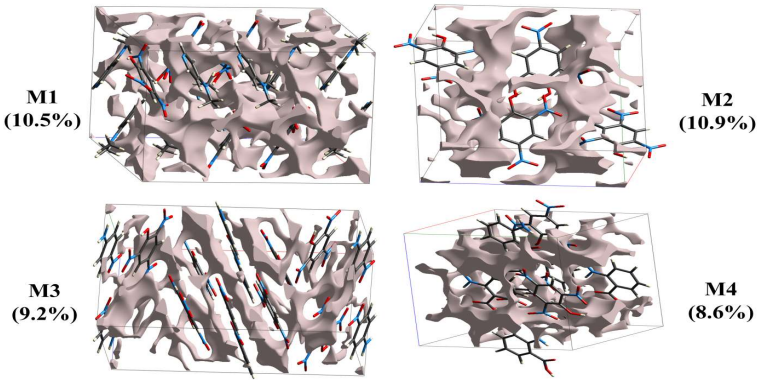


Fig.-8: Crystal Voids of Each Co-Crystal at (0.002 au)-Isosurface

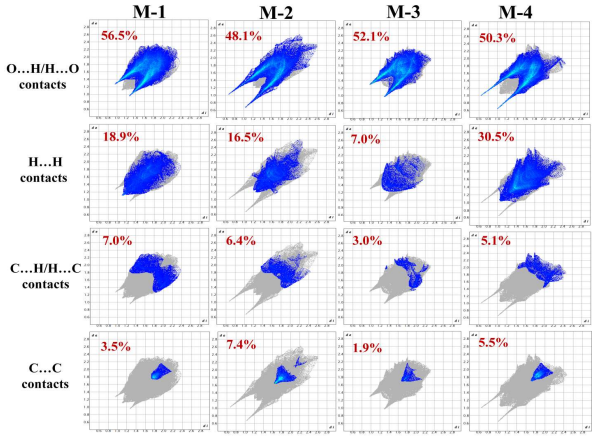


Fig.-9: Comparison of 2D-Fingerprint Plots of Each Co-Crystal (M-1 to M-4)

The population of O...H interactions (Table-3) is significantly higher as compared to that of picric acid as an independent moiety. It is followed by the existence of H…H interactions. It also highlights the significant role of hydrogen bonding and van der Waals' forces in the formation of co-crystals and also the reason why picric acid is useful in the synthesis of co-crystals. This observation is in agreement with the literature.[38] It is pertinent to note that the picric acid as such does not exhibit any C...C interactions but these interactions are present in all four co-crystals. This indicates the presence of π-π stacking in the co-crystals.[39] Hence, we can deduce that π-π stacking serves as an additional factor influencing the formation of co-crystals.

Table-3: Various Contact Contributions to the Hirshfeld Surface Area in Each Co-Crystal

Interaction	Picric Acid	M-1	M-2	M-3	M-4
O…O	25.4	5.6	9.4	17.6	7.4
O…H	34.7	56.5	48.1	52.1	50.3
O…C	26.2	1.6	5.0	10.6	0.3
O…N	11.3	1.9	2.8	6.1	0.1
N…H	1.1	2.3	1.0	0.8	0.5
H…H	0.9	18.9	16.5	7.0	30.5
C…H	0.1	7.0	6.4	3.0	5.1
C…N	0.3	2.1	3.4	0.5	0.3
C…C	0	3.5	7.4	1.9	5.5

CONCLUSION

An inclusive analysis has been reported on the X-ray and optimized structure of a series of picric acid-based co-crystals. The atomic Mulliken charges, molecular electrostatic potential, HOMO-LUMO energy gaps, and other molecular properties of these structures have been calculated by using the Density Functional Theory (DFT). The optimized molecular geometry of each co-crystal shows a good correlation with its corresponding X-ray structure, except for M-4, where some deviation has been observed. The HOMO-LUMO energy analysis reveals that the molecule M-1 exhibits relatively high chemical stability. Further, a critical examination of MEP and Mulliken charge analysis helps identify the location of electrophilic and nucleophilic reactive sites in the co-crystals, thereby confirming the existence of intermolecular interactions in their crystal structures. The HS analysis unveils some significant intermolecular contacts resulting in offset π-π stacking in all the co-crystals.

ACKNOWLEDGMENTS

Rajni Kant acknowledges the financial support provided by the University of Jammu, enabling access to the licensed version of CSD (Cambridge Structural Database).

CONFLICT OF INTERESTS

The authors declare that there is no conflict of interest.

AUTHOR CONTRIBUTIONS

All the authors contributed significantly to this manuscript, participated in reviewing/editing, and approved the final draft for publication. The research profile of the authors can be verified from their ORCID IDs, given below:

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[RJC-8656/2023]