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Comparison of Intermolecular Interactions in Dimeric Bismuth(III) Thioamides with Hirshfeld Surface Analysis

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Research Article

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ABSTRACT

Hirshfeld surface analysis is a very useful method for examining the intermolecular interactions that form the lattice within a crystal. The percentage of intermolecular interactions can be determined with the two-dimensional fingerprint graphics obtained. In this work, four dimeric bismuth(III) halide-thioamide complexes {[$BiCl_3(\mu_2$-S-PYT)(PYT)]$_2$} (**1**), {[$BiBr_2(\mu_2$-Br)(tHPMT)$_2$.$CH_3CN]_2$} (**2**), {[$BiBr_2(\mu_2$-Br)(PYT)$_2]_2$.CH_3CN} (**3**) and {[$BiI_2(\mu_2$-I)(MBZIM)$_2]_2$} (**4**), previously synthesized and characterized, were selected (PYT: 2-mercaptopyridine, tHPMT: 2-mercapto-3,4,5,6-tetrahydro-pyrimidine and MBZIM: 2-mercaptobenzimidazole). To determine of intermolecular interactions of complexes **1**-**4** Crystal Explorer ver. 21.5 used. According to the obtained hirshfeld surfaces, it was determined that the interactions that gave the most contribution to the dimeric bismuth(III) halide complexes **1**-**4** were X···H/H···X (X: Cl, Br or I) and H···H contacts.

1. Introduction

Bismuth is a pnictogen group element that has been known since ancient times [1,2]. Bismuth attracts the attention of biological research due to its low toxic properties [3,4]. Bismuth compounds have been reported to be used in gastrointestinal diseases [5]. Bismuth compounds have been used especially in the treatment of infections caused by Helicobacter Pylori [6]. Helicobacter pylori is a type of gram-negative bacteria that infects stomach tissue [7]. It causes diseases such as ulcers and gastritis. Pepto-Bismol® (Bismuth subsalicylate), De-Nol® (Colloidal bismuth subcitrate) and Pylorid® (Ranitidine) bismuth citrate) are among the main bismuth-containing drugs used in the treatment of these diseases [8]. In recent time, the antibacterial [9], anticancer [10] and antimicrobial [11] activities of complexes of bismuth formed with ligands containing sulfur donor atoms were determined.

The complexes formed by heterocyclic thioamides with transition metals and main group elements are biochemically important compounds [12,13]. Thioamide ligands have monodentate, bidentate, bridging, tridentate and polydentate bonding types with -NH-C(=S)- ↔ -N = C(-SH)- functional groups [14–17]. Interest in thioamides is increasing day by day due to both their biochemical and coordination chemistries.

Bismuth has two oxidation states, +3 and +5, +3 state is the most stable and common form [18]. Because bismuth has various coordination numbers from 3 to 10, it can form complexes with different molecular geometries [19]. Many complexes formed by bismuth(III) halides with thioamide ligands have been obtained. Bismuth(III) halide-thioamide complexes in square pyramid geometry [BiX3L2] form dimeric

Hirshfeld surface analysis is a method that qualitatively and quantitatively determines the intermolecular and intramolecular interactions that exist within a crystal [26,27]. The coordination chemistries and biological activities of the complexes vary depending on these interactions.

In this work, the previously synthesized complexes {[$BiCl_3(\mu_2$-S-PYT)(PYT)]$_2$} (**1**), {[$BiBr_2(\mu_2$-Br)(tHPMT)$_2$.$CH_3CN]_2$} (**2**), {[$BiBr_2(\mu_2$-Br)(PYT)$_2]_2$.CH_3CN} (**3**) and {[$BiI_2(\mu_2$-I)(MBZIM)$_2]_2$} (**4**) were selected (Fig 2). The complexes **1**-**4** were characterized by various spectroscopic methods and single X-ray diffraction anaylsis [21,22,25]. The intermolecular interactions of the bismuth(III) halide-thioamide complexes

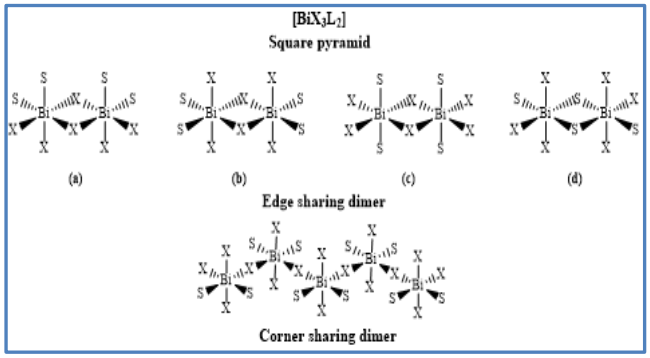

Fig 1. Bismut(III) halide-thioamide complexes in square pyramid and dimerization types.

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were determined by using Crystal Explorer version 21.5.

2. Material and Method

Hirshfeld surface analysis was performed using the Crystal Explorer programme ver. 21.5. of the CIF files of the crystal structures [28]. This analysis allows visualization of contact types according to the distance between atoms in the crystal. Molecular hirshfeld surfaces provide extensive information about the bonding between atoms. The white areas on the dnorm maps indicate contact at a distance equal to the sum of the van der Waals radii. The red and blue colors in the dnorm correspond to shorter or longer contact distances compared to van der Waals radii. di is defined as the distance from the Hirshfeld surface to the nearest atom inside, and de is defined as the distance from the Hirshfeld surface to the nearest atom outside and the equation [29–31]:

$$d_{norm} = [(di\text{-}ri^{dvW})/ ri^{dvW}] + [(de\text{-}re^{dvW})/re^{dvW}]$$

2D fingerprints are obtained by the combination of d_e and d_i. In each 2D fingerprint plot, the area of the surface corresponding to the interactions is revealed [32,33]. In the graph, the points that contribute to the surface are colored blue, green and red, respectively, from smallest to largest [34,35]

3. Results and Discussion

One of the best methods for examining intermolecular interactions within the crystal structure is Hirshfeld surface analysis. Hirshfeld surface analyzes of complexes 1-4 were examined. In Figure 3, the dnorm (normalized contact distance), di (interior distance) and de (exterior distance) surfaces of the bismuth(III) complexes 1-4 are given. dnorm ranges of the complexes 1-4 are -0.3356 Å to 1.0831 Å (1), -0.20 Å to 1.0 Å (2), -0.2 Å to 1.0 Å (3) and -0.2 Å to 1.0 Å (4).

The d_{norm} maps shown in Fig. 3 show red dots of different intensities of bismuth(III) halide complexes. Significant intermolecular interactions are shown as red dots, indicating that the intramolecular contact distance is shorter than the sum of the van der Waals radii. The most intense red dot on the d_{norm} surface of complex 1 indicate H···Cl/Cl···H type intermolecular

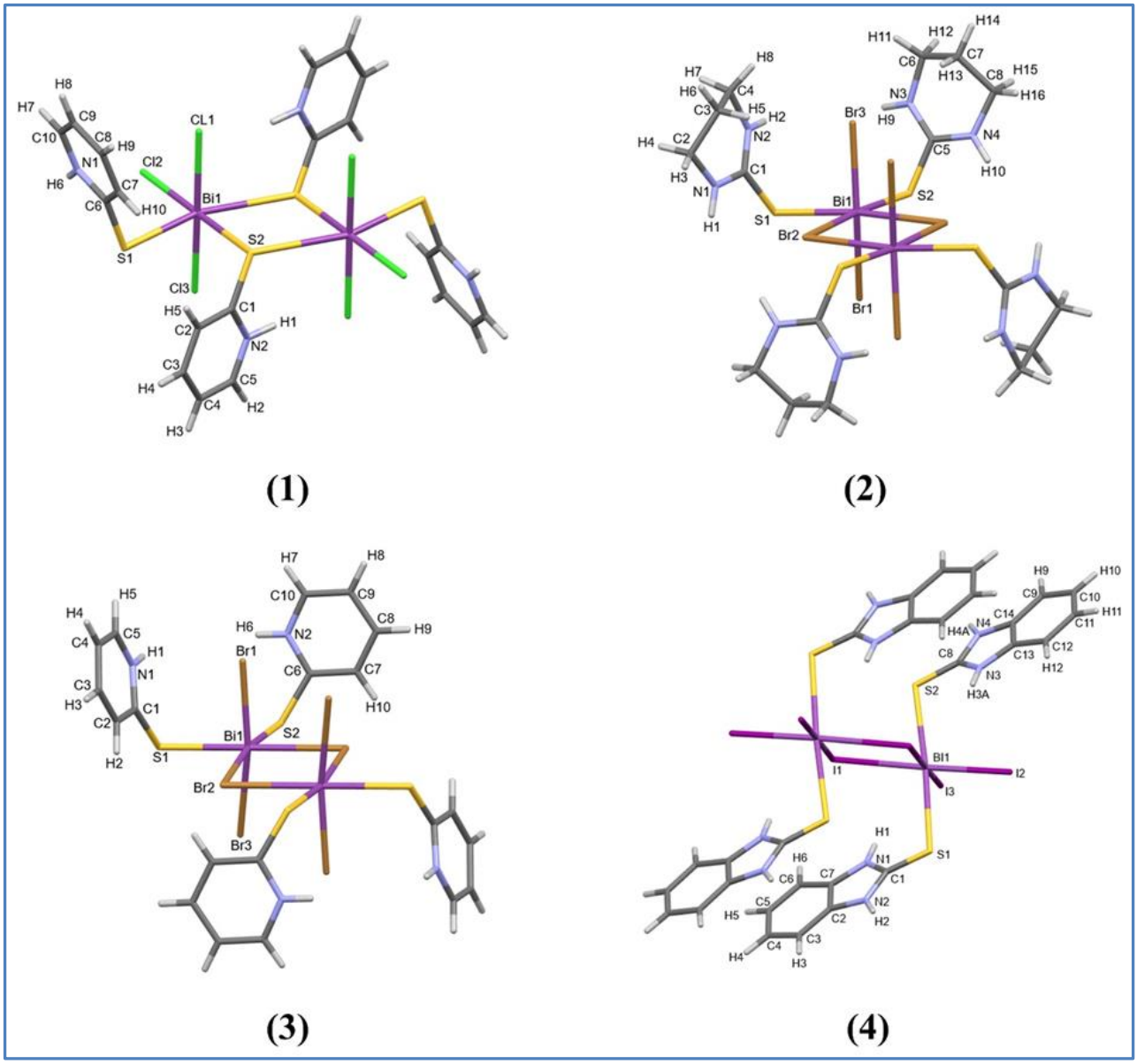

Fig 2. The crystal structures of the bismuth(III) complexes 1-4

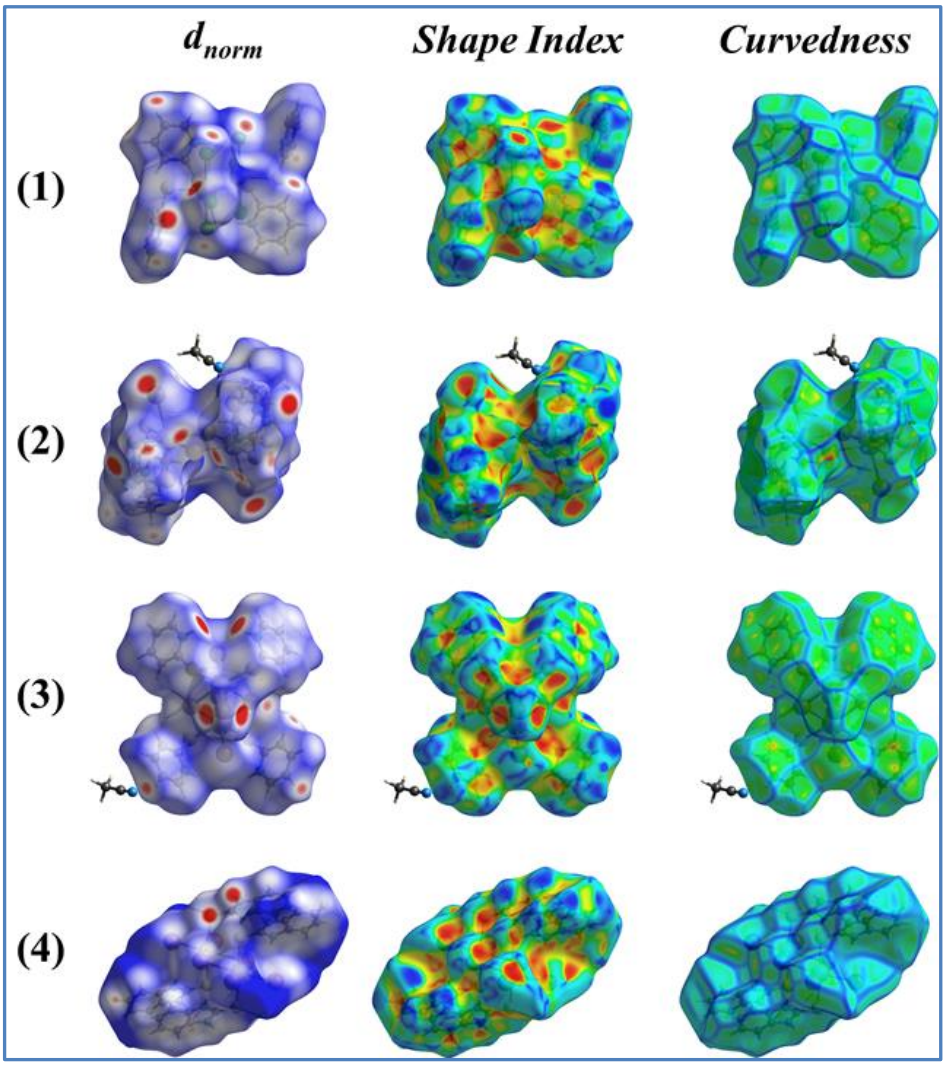

Fig 3. Hirshfeld surfaces mapped with di (interior distance), de (exterior distance) and dnorm (normalized contact distance) in bismuth(III) halide complexes **1**-**4**.

The other pale red spots on the d_{norm} surface of 1 are C···H/H···C, H···H, and S···H/H···S interaction. In complex **2**, the darkest red dots on the d_{norm} map correspond to Br···H/H···Br interactions. C···H/H···C, H···H, and S···H/H···S interactions appear as lighter red dots. On the d_{norm} mapped surface of the complex **3**, while Br···H/H···Br interactions create the most intense red dots, C···H/H···C, H···H, and S···H/H···S contacts achieve paler red points. In complex **4**, the intense red spots on the d_{norm} surface indicate S···H/H···S type intermolecular interactions and the paler red spots indicate I···H/H···I, H···H, and C···H/H···C type intermolecular contacts.

The shape index, curvedness and fragment patch Hirshfeld surfaces of the complexes **1**-**4** are given in Fig 2. The shape index is mapped in the range −1.0 to 1.0 Å, and the curvature is mapped in the range −4.0 to 0.4 Å. Shape index and curvature surfaces can be used to reveal stacking patterns. The colored regions resulting from π-π interactions can be seen in the shape index map of complex **1** shown in Fig. 4a. The C···C intermolecular interactions that pyridine rings form with each other are given in Fig. 4b. This situation is not observed in other complexes **2**-**4**.

2D fingerprint plots show the contributions of various atoms to the formation of the hirshfeld surfaces of the complexes. In these fingerprint graphs, interactions between atoms are expressed as a percentage, X···Y/Y···Z. The fingerprint plots of the bismuth(III) complexes **1**-**4** are shown in Fig. 5 and 6. In complexes **1**, **3** and **4** the X···H/H···X intermolecular interactions (X: Cl, Br or I) are strongest contacts with 45.4% (**1**), 35.5% (**3**) and 49.8% (**4**). Each of them has two spikes in the fingerprints graphs. Only for complex **2**, the main contribution to the Hirshfeld surface area comes from the H···H contacts (39.6%). The second significant interactions of crystal packing in complexes **1**, **3** and **4** are H···H contacts. The contribution percentages of these contacts are 19.6% (**1**), 23.0% (**3**) and 18.7% (**4**), respectively. The Br···H/H···Br contacts are the second highest interactions in complex **2**, with 30.6%. The next significant contributions are S···H/H···S interactions in all complexes. S…H/H…S contacts appear in two symmetrical sharp spikes in fingerprint plots. The contribution values of these contacts are 13.3% (**1**), 16.4% (**2**), 15.3% (**3**) and 13.9% (**4**). The C···H/H···C interactions in complexes **1**-**4** are the fourth largest contributing contacts to crystal packing, with 11.1% (**1**), 4.3% (**2**), 12.1% (**3**) and 7.3% (**4**). The other contributions of complexes **1**-**4** are presented in Fig 7.

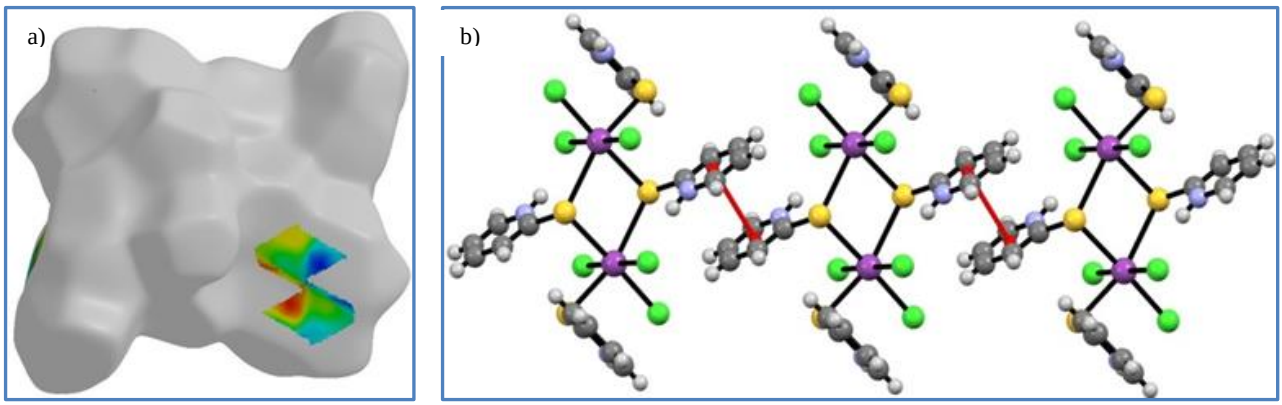

Figure 4. π-π interactions shown in the shape index map in the bismuth(III) complex 1 (a), fingerprint graph of the bismuth(III) complex 1 showing contributing from C···C contact.

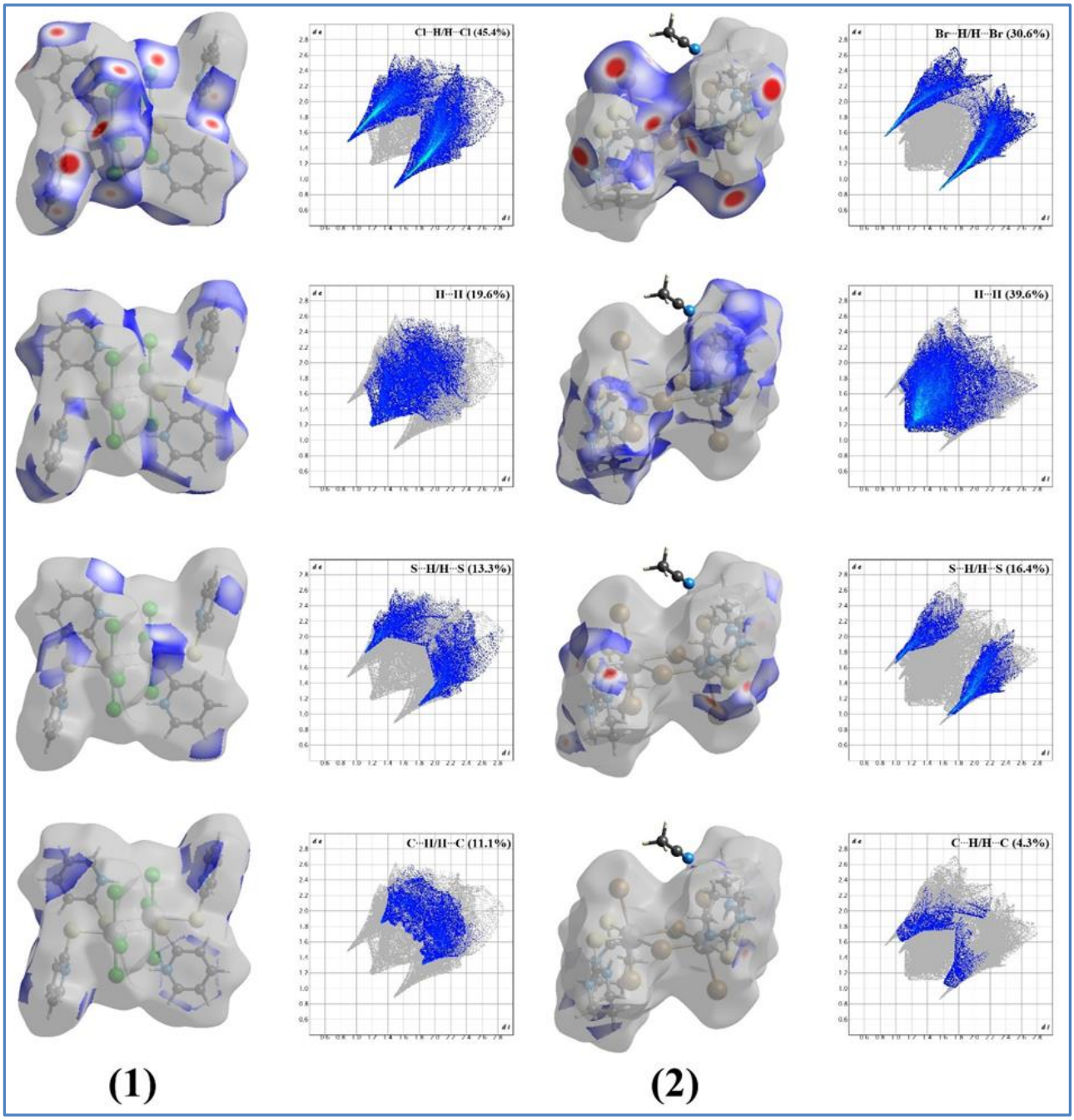

Fig 5. The intermolecular nteractions that contribute most to crystal packing in complexes 1 and 2.

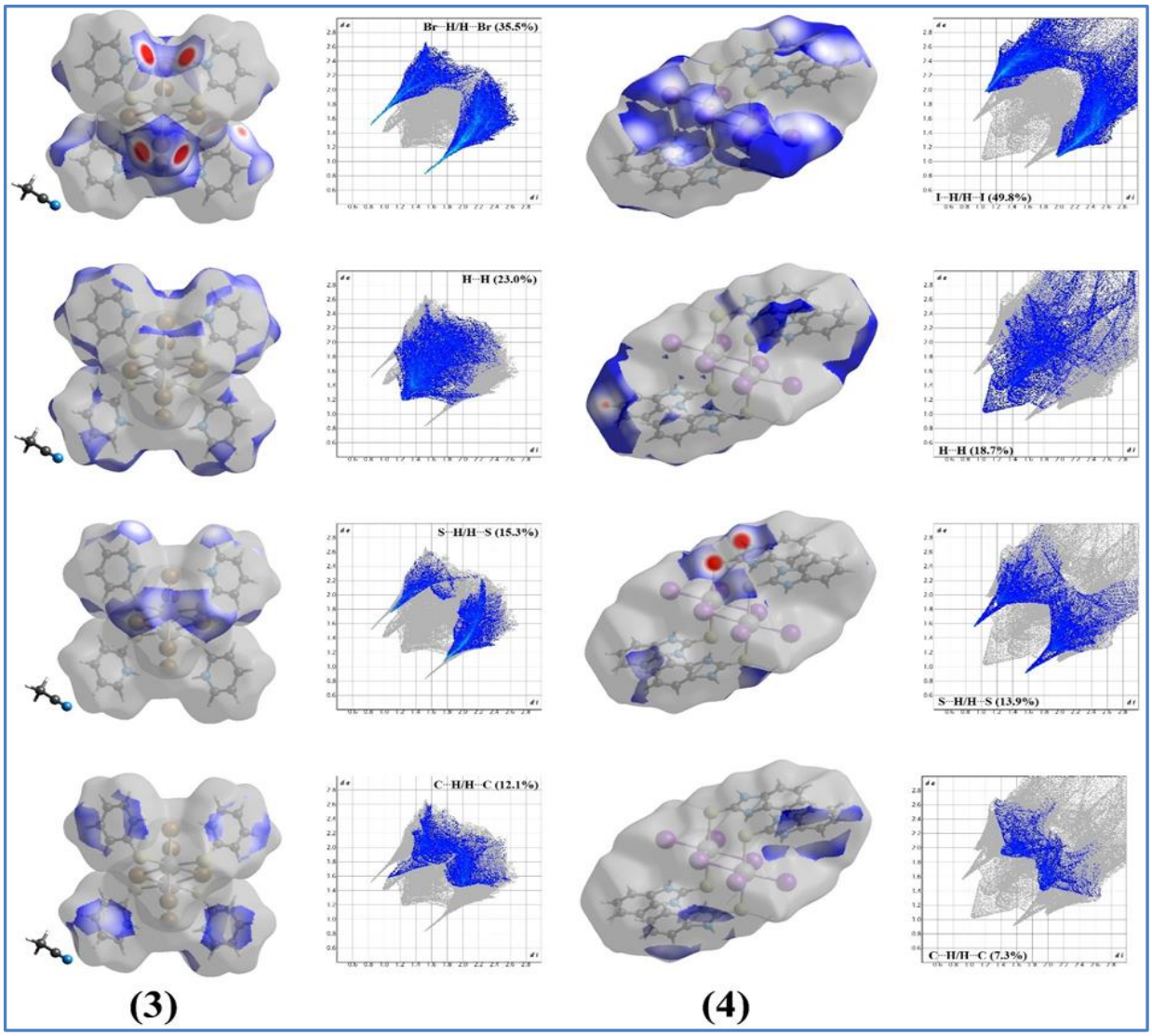

Fig 6. The intermolecular nteractions that contribute most to crystal packing in complexes 3 and 4.

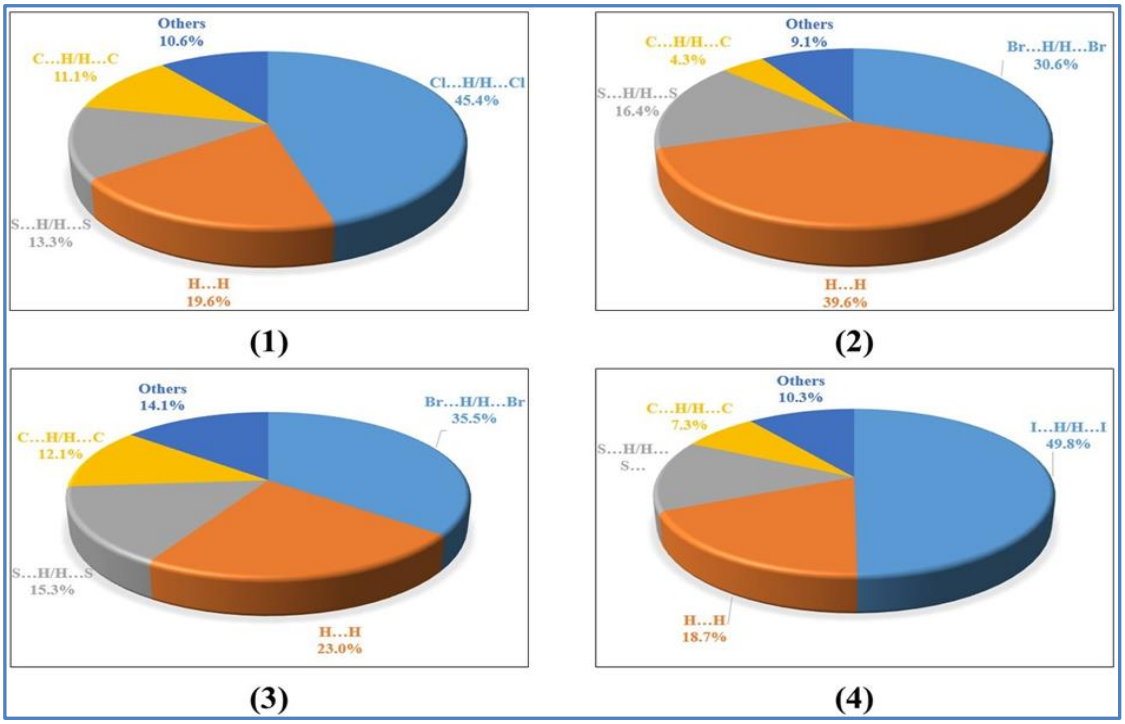

Fig 7. The contact contributions to the Hirshfeld surfaces in the bismuth(III) halide complexes 1-4.

4. Conclusion

In previously studies, bismuth(III) halide complexes with thioamide derived ligands (PYT, tHPMT, MBZIM) were synthesized and their chemical structures were characterized. Their crystal structures were determined by single crystal X-ray diffraction method in literature. The monomeric units of the complexes 1-4 have square pyramidal geometry with [BiX3L2] formulae. These are dinuclear bismuth(III) halide complexes with secondary Bi···(μ2-X) and Bi···(μ2-S) bonding interactions in 1, 2, 3 and 4 lead to octahedral arrangement (Oh). Hirshfeld surface analysis revealed that X···H/H···X, H···H, S···H/H···S, and H···H interactions were the dominant contacts in crystal packing in all complexes. The presence of π-π interactions in the crystal packing of complex 1 was observed in the shape index map.

Declaration

Author Contribution: Conceive-O.U.; Design-O.U.; Supervision-O.U.; Experimental Performance, Data Collection and/or Processing-O.U.; Analysis and/or Interpretation-O.U.; Literature Review-O.U.; Writers-O.U.; Critical Reviews–O.U.

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References

[1] I.I. Ozturk, O. Uçar, "The Hirshfeld Surface Analysis of Antimony(III) and Bismuth(III) Complexes with Dithiocarbamate Ligands," *Tekirdag Namik Kemal Univ. Inst. Nat. Appl. Sci.* vol. 1, pp. 87–95, 2022, doi: 10.55848/jbst.2022.12.

[2] O. Ucar, A.M. Grześkiewicz, C. Banti, S.K. Hadjikakou, I.I. Ozturk, "Structural characterization and biological evaluation of antimony(III) and bismuth(III) complexes with imidazolidine-2-thione," *J. Mol. Struct.* vol. 1235, pp. 1-14, 2021, doi: 10.1016/j.molstruc.2021.130270.

[3] I.I. Ozturk, M.G. Eser, "Synthesis, Characterization, Anti-bacterial and Anti-inflammatory Activities of Bismuth(III) Complexes Based on 5-chloro-2-mercaptobenzothiazole," *Hittite J Sci Eng.* vol. 9(3), pp. 225-233, 2022, doi: 10.17350/HJSE19030000275.

[4] I.I. Ozturk, C.N. Banti, S.K. Hadjikakou, N. Panagiotou, A.J. Tasiopoulos, " Bismuth(III) halide complexes of aromatic thiosemicarbazones: Synthesis, structural characterization and biological evaluation," *Polyhedron*, vol. 208, pp. 115388, 2021, doi: 10.1016/j.poly.2021.115388.

[5] K. Turk, A.M. Grześkiewicz, C.N. Banti, S.K. Hadjikakou, M. Kubicki, I.I. Ozturk, "Synthesis, characterization, and biological properties of mono-, di- and poly-nuclear bismuth(III) halide complexes containing thiophene-2-carbaldehyde thiosemicarbazones," *J. Inorg. Biochem.* vol. 237, pp. 111987, 2022, doi: 10.1016/j.jinorgbio.2022.111987.

[6] G.G. Briand, N. Burford, "Bismuth Compounds and Preparations with Biological or Medicinal Relevance," *Chem. Rev.* vol. 99, pp. 2601–2658, 1999, doi: /10.1021/cr980425s.

[7] Y. Yang, R. Ouyang, L. Xu, N. Guo, W. Li, K. Feng, L. Ouyang, Z. Yang, S. Zhou, Y. Miao, "Review: Bismuth complexes: Synthesis and applications in biomedicine," *J. Coord. Chem.* vol. 68, pp. 379–397, 2015, doi: 10.1080/00958972.2014.999672.

[8] M. Arda, I.I. Ozturk, C.N. Banti, N. Kourkoumelis, M. Manoli, A.J. Tasiopoulosd, S.K. Hadjikakou, "Novel bismuth compounds: Synthesis, characterization and biological activity against human adenocarcinoma cells," *RSC Adv.* vol. 6, pp. 29026–29044, 2016, doi: 10.1039/c6ra01181k.

[9] M. Li, Y. Lu, M. Yang, Y. Li, L. Zhang, S. Xie, "One dodecahedral bismuth(iii) complex derived from 2-acetylpyridine N(4)-pyridylthiosemicarbazone: Synthesis, crystal structure and biological evaluation," *Dalt. Trans.* vol. 41, pp. 12882–12887, 2012, doi: 10.1039/c2dt31256e.

[10] I.I. Ozturk, C.N. Banti, N. Kourkoumelis, M.J. Manos, A.J. Tasiopoulos, A.M. Owczarzak, M. Kubicki, S.K. Hadjikakou, "Synthesis, characterization and biological activity of antimony(III) or bismuth(III) chloride complexes with dithiocarbamate ligands derived from thiuram degradation," *Polyhedron*, vol. 67, pp. 89–103, 2014, doi: 10.1016/j.poly.2013.08.052.

[11] J.C.L. Almeida, R.S. Amim, C. Pessoa, M.C.S. Lourenço, I.C. Mendes, J.A. Lessa, "Bismuth(III) complexes with pyrazineformamide thiosemicarbazones: Investigation on the antimicrobial and cytotoxic effects," *Polyhedron*, vol. 189, pp. 114709, 2020, doi: 10.1016/j.poly.2020.114709.

[12] D. Li, W.J. Shi, L. Hou, "Coordination polymers of copper(I) halides and neutral heterocyclic thiones with new coordination modes," *Inorg. Chem.* vol. 44, pp. 3907–3913, 2005, doi: 10.1021/ic050209j.

[13] B. Krebs, G. Henkel, "Transition-Metal Thiolates: From Molecular Fragments of Sulfidic Solids to Models for Active Centers in Biomolecules," *Angew. Chemie Int. Ed. English.* vol. 30, pp. 769–788, 1991, doi: 10.1002/anie.199107691.

[14] T.S. Lobana, R. Sultana, R.J. Butcher, J.P. Jasinski, J.A. Golen, A. Castineiras, K. Pröpper, F.J. Fernandez, M.C. Vega, "Heterocyclic-2-thione derivatives of silver(I): Synthesis, spectroscopy and structures of mono- and di-nuclear silver(I) halide complexes," *J. Organomet. Chem.* vol. 745–746, pp. 460–469, 2013, doi: 10.1016/j.jorganchem.2013.08.020.

[15] R. Sultana, T.S. Lobana, R. Sharma, A. Castineiras, T. Akitsu, K. Yahagi, Y. Aritake, "Heterocyclic thioamide derivatives of coinage metals (Cu, Ag): Synthesis, structures and spectroscopy," *Inorganica Chim. Acta.* vol. 363, pp. 3432–3441, 2010, doi: 10.1016/j.ica.2010.06.051.

[16] T.S. Lobana, A.K. Sandhu, A.K. Jassal, G. Hundal, R.K. Mahajan, J.P. Jasinski, R.J. Butcher, "Metal derivatives of N-substituted imidazolidine-2-thiones with d 10 metal ions (Zn – Hg): Synthesis , spectroscopy , ESI-mass and structures," *Polyhedron*, vol. 87, pp. 17–27, 2015, doi: 10.1016/j.poly.2014.10.016.

[17] T.S. Lobana, R. Sultana, A. Castineiras, R.J. Butcher, "Synthesis of CuI polymers Cu8(μ3-SN2C3H 6)4(μ-SN2C3H6) 4(η1-Cl)8," *Inorganica Chim. Acta*, vol. 362, pp. 5265–5270, 2009, doi: 10.1016/j.ica.2009.09.038.

[18] S.A. Shetu, L.M. Sanchez-Palestino, G. Rivera, D. Bandyopadhyay, "Medicinal bismuth: Bismuth-organic frameworks as pharmaceutically privileged compounds," *Tetrahedron*, vol. 129, pp. 133117, 2022, doi: 10.1016/j.tet.2022.133117.

[19] I.I. Ozturk, E.T. Sirinkaya, M. Cakmak, M. Gürgan, D. Ceyhan, N. Panagiotou, A.J. Tasiopoulos, "Structural and biological features of bismuth(III) halide complexes with heterocyclic thioamides," *J. Mol. Struct.* vol. 1227, pp. 129730, 2021, doi: 10.1016/j.molstruc.2020.129730.

[20] O. Aygun, A.M. Grześkiewicz, C.N. Banti, S.K. Hadjikakou, M. Kubicki, I.I. Ozturk, "Monomeric octahedral bismuth(III) benzaldehyde-N1-alkyl thiosemicarbazones: Synthesis, characterization and biological properties," *Polyhedron*, vol. 215, pp. 22–25, 2022, doi: 10.1016/j.poly.2022.115683.

[21] M. Cakmak, I.I. Ozturk, C.N. Banti, M. Manoli, E. Moushi, A.J. Tasiopoulos, A.M. Grzeskiewicz, M. Kubicki, S.K. Hadjikakou, "Bismuth(III) bromide-thioamide complexes: Synthesis, characterization and cytotoxic properties," *Main Gr. Met. Chem*, vol. 41, pp. 143–154, 2018, doi: 10.1515/mgmc-2018-0035.

[22] I.I. Ozturk, C.N. Banti, S.K. Hadjikakou, N. Panagiotou, A.J. Tasiopoulos, "Structural architectures and biological properties of main group bismuth(III) iodide complexes with heterocyclic thioamides," *Inorganica Chim. Acta.* vol. 497, pp. 119094, 2019, doi: 10.1016/j.ica.2019.119094.

[23] A.M. Grześkiewicz, G. Dutkiewicz, O. Aygun, I.I. Ozturk, M. Kubicki, "Solid-to-solid polymorphic phase transitions in two isostructural Bi(III) complexes with 1-phenylethyl-N-ethylthiosemicarbazide and halogens," *Sci. Rep*, vol. 13, pp. 1–11, 2023, doi: 10.1038/s41598-023-38561-4.

[24] I.I. Ozturk, K. Turk, A.M. Grześkiewicz, M. Kubicki, C.N. Banti, S.K. Hadjikakou, "Heteroleptic six-coordinate bismuth(<scp>iii</scp>) complexes with 2-acetylthiophene thiosemicarbazones: synthesis, characterization, and biological properties," *New J. Chem.* vol. 47, pp. 12779–12789, 2023, doi: 10.1039/D3NJ01411H.

[25] S. Yarar, I.I. Ozturk, C.N. Banti, N. Panagiotou, C. Papatriantafyllopoulou, M. Manoli, M.J. Manos, A.J. Tasiopoulos, S.K. Hadjikakou, "Synthesis, characterization and cytotoxic properties of bismuth(III) chloride complexes with heterocyclic thioamides," *Inorganica Chim. Acta*, vol. 471, pp. 23–33, 2018, doi: 10.1016/j.ica.2017.10.026.

[26] I.I. Ozturk, "Hirshfeld Surface Analysis of Antimony (III) Chloride Complexes with Thioamides," *Tekirdag Namik Kemal Univ. Inst. Nat. Appl. Sci.* vol. 1, pp. 7–13, 2022, doi: 10.55848/jbst.2022.2.

[27] I.I. Ozturk, "Synthesis, Characterization and Hirshfeld Surface Analysis of Some Thiosemicarbazones Containing a Five-Membered Ring," *J. Struct. Chem*. vol. 64, pp. 743–756, 2023, doi: 10.1134/S0022476623050013.

[28] M. Mhiri, O. Kammoun, S. Auguste, J. Lhoste, H. Ammar, M. Boujelbene, "Synthesis, crystal structure, Hirshfeld surface analysis, vibrational and photoluminescence properties of a supramolecular hybrid of 2-amino, 3-nitropyridinium perchlorate (C5H6N3O2)ClO4," *J. Mol. Struct.* vol. 1295, pp. 136625, 2023, doi: 10.1016/j.molstruc.2023.136625.

[29] C.G. Topkaya, S. Aslan, T. Göktürk, S. Kıncal, T. Hökelek, R. Güp, "A new 1,2,4-triazine-n-oxide compound: Synthesis, crystal structure, Hirshfeld surface analysis and supercapacitor applications," *J. Mol. Struct.* vol. 1295, pp. 2–11, 2024, doi: 10.1016/j.molstruc.2023.136689.

[30] N. Chaithra, H.A. Swarup, S. Chandrasekhar, B.K. Jayanna, K. Kumara, K. Mantelingu, N.K. Lokanath, "Regioselective benzylation of imidazo[1,5-a]pyridines and indoles via iodine catalyzed reaction using alcohols - An approach to crystal structure prediction, DFT studies and Hirshfeld surface analysis," *J. Mol. Struct.* vol. 1295, pp. 136591, 2024, doi: 10.1016/j.molstruc.2023.136591.

[31] K. Preetha, E.B. Seena, P.K. Maniyampara, E. Manoj, M.R.P. Kurup, "Synthesis, crystal structure, Hirshfeld surface analysis, DFT, molecular docking and in vitro antitumor studies of (2E)-2-[4-(diethylamino)benzylidene]-N-ethylhydrazinecarbothioamide," *J. Mol. Struct.* vol. 1295, pp. 136700. 2024, doi: 10.1016/j.molstruc.2023.136700.

[32] J.J. McKinnon, D. Jayatilaka, M.A. Spackman, "Towards quantitative analysis of intermolecular interactions with Hirshfeld surfaces," *Chem. Commun.* pp. 3814–3816, 2007, doi: 10.1039/b704980c.

[33] M.A. Spackman, D. Jayatilaka, "Hirshfeld surface analysis," *CrystEngComm*. vol. 11, pp. 19–32, 2009, doi: 10.1039/B818330A.

[34] M.A. Spackman, J.J. McKinnon, "Fingerprinting intermolecular interactions in molecular crystals," *CrystEngComm*. vol. 4, pp. 378–392, 2002, doi: 10.1039/B203191B.

[35] J.J. McKinnon, M.A. Spackman, A.S. Mitchell, "Novel tools for visualizing and exploring intermolecular interactions in molecular crystals," vol. B60, pp. 627-668, 2004, doi: 10.1107/S0108768104020300.