SETSCI Conference Indexing System,
Volume 3 (2018), 698-700

ISAS 2018-Winter
2nd International Symposium on Innovative Approaches in Scientific Studies
November 30 – December 2, 2018, Samsun, Turkey

Intermolecular Interactions and Fingerprint Plots with Hirshfeld Surface Analysis

Zeynep Demircioğlu[1*+], Orhan Büyükgüngör[2] and CemCüneyt Ersanlı[1]

[1]*Department of Pyhsics/Faculty of Arts and Science,Sinop University, Sinop, Turkey*
[2]*Department of Pyhsics/Faculty of Arts and Science,OndokuzMayıs University, Samsun, Turkey*
[*]*Corresponding author: zdemircioglu@sinop.edu.tr*
[+]*Speaker: zdemircioglu@sinop.edu.tr*
Presentation/Paper Type: Oral / Tam Metin

Abstract –Hirshfeld surface (HS) analysis survey the intermolecular interactions in terms of surface contribution and generating graphical representations, plotting 2D fingerprint plots, and generating electrostatic potential. HS mapped with d_{norm}, d_i, $d_e$and 2D fingerprint plots were produced with Crystal Explorer 3.1 program. The electrostatic potential surfaces are figured with red region, which is a negative electrostatic potential (hydrogen acceptors) and blue region, which is a positive electrostatic potential (hydrogen donor). For the distance from the surface to the nearest atom interior to the surface is known as d_i, while d_e represents the distance from the surface to the nearest atom exterior to the surface. The d_{norm} (normalized contact distance) values are mapped on to the Hirshfeld surface by using three different colors (red–blue–white), where a red spots show the shortest contacts, blue shows longer contacts and White spots are assigned to the contacts that are around the Van der Walls separation. Also, the fingerprintplots can be decomposed to highlight particular atom pair close contacts and this decomposition enables separation of contributions from different interaction types, which overlap in the full fingerprint. The fingerprint plots and molecular HS are good way fo runderstanding the contributions of various intercontacts, which help to stabilized the molecular structures. These % values suggest that th emolecular arrangement is primarily driven by these strong electrostatic attractions which are the driving force of crystal packing for studied compound.

Keywords *–Hirshfeld Surface analysis, Fingerprint Plots, Intermolecularinteractions, d_{norm}, $d_i$and d_e surfaces*

I. Introduction

Hirshfeld surface (HS) analysis survey the intermolecular interactions in terms of surface contribution and generating graphical representations, plotting 2D fingerprint plots [1, 2], and generating electrostatic potential [3]. The electrostatic potential surfaces are figured with red region, which is a negative electrostatic potential (hydrogen acceptors) and blue region, which is a positive electrostatic potential (hydrogen donor). Crystallographic information file (CIF) was used as input for the analysis. Hirshfeld surface analysis is an effective tool for exploring packing modes and intermolecular interactions in molecular crystals, as they provide a visual picture of intermolecular interactions and of molecular shapes in a crystalline environment.

II. Materials and Method

The Hirshfeld surfaces (HSs) are a practical tool for designating the surface characteristics of the molecules and it is useful for understanding the nature of intermolecular interactions within the crystal structure. The spherical atom electron densities were used to calculate the electron distribution based on which the molecular HSs in the crystal structure were constructed. In a molecule, close contacts and hydrogen bond interactions are described by performing this analysis. Quantification of the various intermolecular interactions, HSs of the molecule and its fingerprint plots (FPs) were generated by using Crystal Explorer version 3.1 software [4].

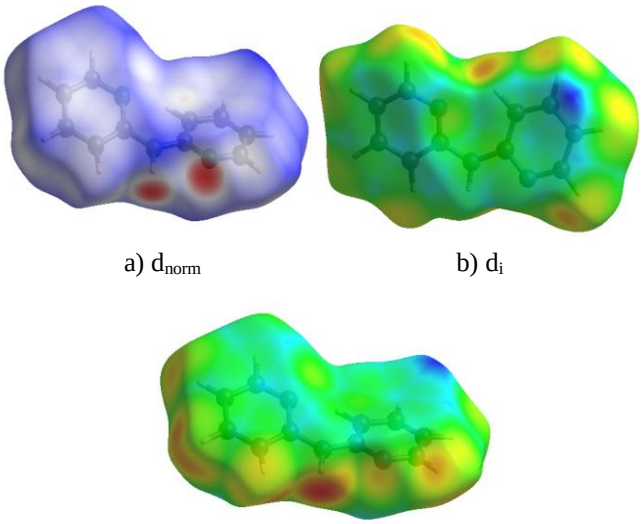
III. DISCUSSION

Hirshfeld surfaces and 2D fingerprint plots were generated using the Crystal Explorer 3.1 program using the crystallographic information files (CIF) obtained from the X-ray diffraction method computations. These surfaces are constructed based on the electron distribution calculated as the sum of spherical atom electron densities [5]. The function d_{norm} is given by the relation involving the ratio encompassing the distances of any surface point to the nearest interior (d_i) and exterior (d_e) atom and the van der Waals radii (r^{vdw}) of the atoms [6].

$$d_{norm} = \frac{d_i - d_i^{rdw}}{d_i^{rdw}} + \frac{d_e - d_e^{rdw}}{d_e^{rdw}} \quad (1)$$

The red regions in the Hirshfeld surfaces have negative d_{norm} values, which indicate that the sum of d_i and d_e is shorter than the sum of the relevant van der Waals radii, which is considered to be a closest contact. The white color denotes intermolecular distances close to van der Waals contacts with d_{norm} equal to zero. The blue surfaces refer to contacts longer than the sum of van der Waals radii with positive d_{norm} values. A plot of d_i versus d_e is a 2D fingerprint plot that recognizes the existence and the amount of different types of inter-molecular interactions. The combination of d_e and d_i in the

form of a 2D fingerprint plot [7] provides a summary of the intermolecular contacts in the crystal [8].



a) d_{norm} b) d_i

c) d_e

Fig. 1 Hirshfeld surface mapped with a) d_{norm}, b) d_i and c) d_e for I.

The d_{norm}, d_i and d_e shape indeces are -0.4600 to 1.2773, 0.8254 to 2.6438 and 0.8253 to 2.5717Å, respectively. The maps of d_{norm}, d_i and d_e on molecular Hirshfeld surfaces are shown in Fig. 1. The red spots over the surface indicate the inter-contacts involved in strong hydrogen bonds and interatomic contacts.The red concave region on shape index is the acceptor and the blue region is the donor atoms. The dark-red spots on the d_{norm} surface arise as a result of the inter-atomic contacts such as strong hydrogen bonds.The crystal packing diagram was shown in Fig. 2. The dashed lines were indicated the N-H…N and C-H…N intermolecular hydrogen bonds. The N-H…N intermolecular hydrogen bonds indicated the $R_2^2(8)$ ring.

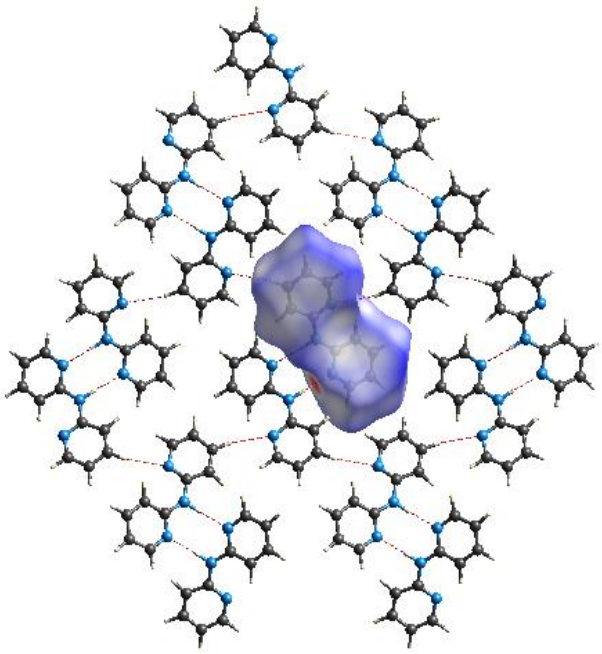


Fig. 2. CrystalpackingdiagramandHirshfeld surface mapped with d_{norm}. The red dashed lines show the N-H…N and C-H…N intermolecular hydrogen bonds.

The dominant interactions are visible on the Hirshfeld surfaces as well as in the fingerprint plots (Fig. 3), where one molecule act as donor (d_e>d_i) and the other as an acceptor (d_i>d_e). The fingerprint plots can be decomposed to highlight particular atom pair close contacts and this decomposition enables separation of contributions from different interaction types, which overlap in the full fingerprint. Reciprocal H…H/H…H,C…H/H…C and N…H/H…N intermolecular interactions are the most abundant in title compound with 55.35%, 15.7% and 15.2%, respectively. The other dominant forces are C…C/C…C (9.4%) and C…N/N…C (3.2%) contacts for I (Fig. 3). The fingerprint plots and molecular HSs are good way for understanding the contributions of various inter contacts, which help to stabilize the molecular structures. These % values suggest that the molecular arrangement is primarily driven by these strong electrostatic attractions which are the driving force of crystal packing for compound I.

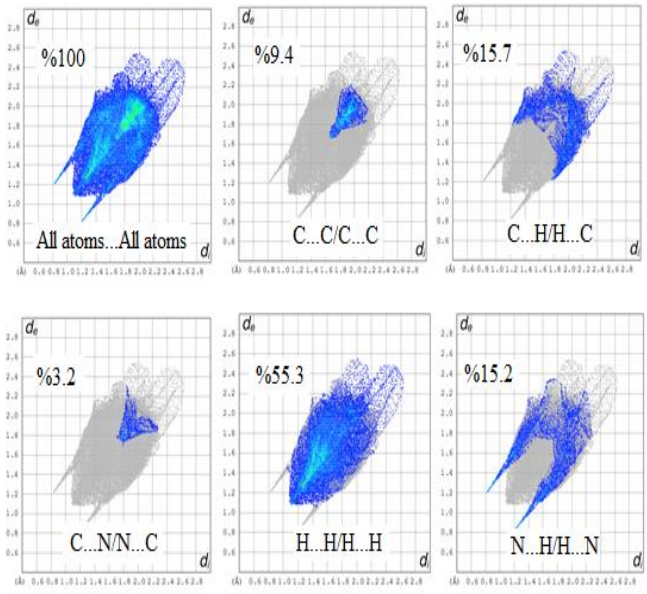


Fig. 3. Fingerprint plots of the compound I showing interactions (d_i is the closest internal distance from a given point on the HS and d_e is the closest external contacts).

IV. CONCLUSION

In this study, we have investigated the intermolecular contacts, d_{norm}, d_i and d_e surfaces by Hirshfeld surface anaysis.The red spots on d_{norm} surface refered to N-H…N and C-H…Nintermolecular hydrogen bonds. The fingerprint plots were revealed particular atom pair close contacts and this decomposition enables separation of contributions from different interaction types, which overlap in the full fingerprint. The most dominat interactions were observed with 55.35%, 15.7% and 15.2% for H…H/H…H,C…H/H…C and N…H/H…N, respectively.

REFERENCES

[1] S.K. Wolff, D.J. Grimwood, J.J. McKinnon, M.J. Turner, D. Jayatilaka , M.A. Spackman, Crystal Explorer (Version 3.0), University of Western Australia, 2012 .

[2] S.K. Seth, '' Tuning the formation of MOFs by pH influence: X-ray structural variations and Hirshfeld surface analyses of with cadmium chlorid,*'' Cryst. Eng. Comm.,* vol. 15, pp. 1772, 2013.

[3] S.K. Seth,'' Structural elucidation and contribution of intermolecular interactions in O-hydroxy acyl aromatics: Insights from X-ray and Hirshfeld surface analysis,'' *J. Mol. Struct.*, vol. 70, pp. 1064, 2014.

[4] S.K. Wolff, D.J. Grimwood, J.J. McKinnon, D. Jayatilaka, M.A. Spackman, Crystal Explorer 3.1, University of Western Australia, Perth, Australia, 2012.

[5] F.L. Hirshfeld, '' Bonded-atom fragments for describing molecular charge densities,'' *Theor. Chim.Acta*, vol. 44, pp. 129, 1977.

[6] S.M. Soliman, J. Albering, and M.A.M. Abu-Youssef, '' Structural Analyses of Two New Highly Distorted Octahedral Copper(II) Complexes with Quinoline: Type Ligands; Hirshfeld, AIM and NBO studies,'' *Polyhedron*, vol. 127, pp. 36-50,2017.

[7] M.A. Spackman, P.G. Byrom, '' A novel definition of a molecule in a crystal, ''*Chem. Phys. Lett.,vol.* 267, pp. 215, 1997.

[8] A. Parkin, G. Barr, W. Dong, C.J. Gilmore, D. Jayatilaka, J.J. Mckinnon, M.A. Spackman, and C.C. Wilson, '' Comparing entire crystal structures: structural genetic fingerprinting,''*Cryst. Eng. Comm.*, vol. 9 pp. 648, 2007.