Intermolecular Interactions and Fingerprint Plots with Hirshfeld Surface Analysis

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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 \( d_{\text{norm}}, d_i \) 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 \( d_{\text{norm}} \) (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 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. The fingerprint plots and molecular HS are good way to understanding the contributions of various intercontacts, which help to stabilized 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 studied compound.

Keywords –Hirshfeld Surface analysis, Fingerprint Plots, Intermolecular interactions, \( d_{\text{norm}}, d_i \) 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 \( d_{\text{norm}} \) 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 \( (r_{\text{vdw}}) \) of the atoms [6].

\[
d_{\text{norm}} = \frac{d_i - r_{\text{vdw}}}{d_i} + \frac{d_e - r_{\text{vdw}}}{d_e}
\]  

The red regions in the Hirshfeld surfaces have negative \( d_{\text{norm}} \) 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 \( d_{\text{norm}} \) equal to zero. The blue surfaces refer to contacts longer than the sum of van der Waals radii with positive \( d_{\text{norm}} \) 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].

![Image](image1.png)

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

The \(d_{\text{norm}}\), \(d_i\) and \(d_e\) shape indices are -0.4600 to 1.2773, 0.8254 to 2.6438 and 0.8253 to 2.5717Å, respectively. The maps of \(d_{\text{norm}}\), \(d_i\) 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 crystal packing diagram was shown in Fig. 2. The red dashed lines show the N-H...N and C-H...N intermolecular hydrogen bonds.

![Image](image2.png)

Fig. 2. Crystal packing diagram and Hirshfeld surface mapped with \(d_{\text{norm}}\). 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 acts 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 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.

![Image](image3.png)

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, \(d_{\text{norm}}\), \(d_i\) and \(d_e\) surfaces by Hirshfeld surface analysis. The red spots on \(d_{\text{norm}}\) surface refer to N-H...N and C-H...N intermolecular hydrogen bonds. The fingerprint plots 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 dominant 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


