E CONF SERIES

International Conference on Multidisciplinary Sciences and Educational Practices
Hosted online from Rome, Italy
Website: econfseries.com 27th May, 2025

BIS(2-METHYL-4-NITROANILINIUM) HEXACHLORO-TIN(IV) MONOHYDRATE. HIRSHFELD SURFACE ANALYSIS

Samandarov E. Sh[1].,
Yakubov.Y. Y[2].,
C. Balakrishnan[3].
[1]Khorezm Mamun branch of Uzbekistan Academy of Sciences, Markaz-1, Khiva 220900, Uzbekistan. [2]Institute of General and Inorganic Chemistry of Uzbekistan Academy of Sciences,100170, Mirzo Ulug'bek str., 77a.
[3]Department of Chemistry, Erode Sengunthar Engineering College, Erode 638057, Tamil Nadu, India

Analysis of Hirshfeld surfaces of discrete nonlinear optical (NLO) materials.

Molecular crystalline structures can be quantitatively analyzed through the Hirshfeld surface technique. This methodology illuminates the shifts happening at every point on the Hirshfeld surface, pertaining to neighboring atoms situated on both the external and internal surfaces. These distinct attributes have been pivotal in scrutinizing the selectivity and specificity of intermolecular forces acting upon molecular arrangements.

The creation of these surfaces involves partitioning the space enclosed by the crystal using the Hirshfeld ratio, where the procrystal is effectively delineated by employing a promolecule characterized by an electron density of 0.5. The normalized contact distance, referred to as $\mathbf{d_{norm}}$, is calculated by considering perspectives from both the exterior and interior of the surface, as outlined below:

$$d_{norm} = \frac{d_i - r_i^{vdW}}{r_i^{vdW}} + \frac{d_e - r_e^{vdW}}{r_e^{vdW}}$$

The Hirshfeld surface analysis elucidates the intricate relationships between the external and internal components of a crystalline structure. The parameter denoted as $\mathbf{d_{norm}}$ represents the normalized contact distance, where $\mathbf{d_e}$ signifies the distance from the Hirshfeld surface to the nearest external nucleus, $\mathbf{d_i}$ denotes the corresponding distance to the nearest internal nucleus, and r^{vdW} designates the van der Waals radius of the atom in question.

The $\mathbf{d_{norm}}$ parameter is visually depicted on the Hirshfeld surface through a color gradient ranging from red to white to blue. The bright red regions indicate intermolecular contacts occurring within a distance shorter than the respective van der Waals radii, while the blue regions signify intermolecular contacts at distances greater than the van der Waals radii. The white regions correspond to the cumulative van der Waals radii for the associated atoms.To analyze the short-range contacts between neighboring molecules in crystal lattice structures, the researchers utilized CrystalExplorer version 17. This software was employed to examine the Hirshfeld surfaces of the crystal structures and generate the corresponding two-dimensional (2D) fingerprint plots.

The analysis of Hirschfeld surfaces is an important tool for understanding the intermolecular interactions and crystal packing in nonlinear optical (NLO) materials. Here are some key insights from the search results.

1.The Hirshfeld surface analysis can provide valuable information about the nature and strength of intermolecular interactions that stabilize the crystal structure of NLO materials [1][2]. This includes hydrogen bonding, π-π stacking, and other noncovalent interactions.

2.The Hirshfeld surface analysis can reveal the contribution of different types of intermolecular contacts (e.g., C-H•••Cl; C-H•••O; C-H•••Br) to the overall crystal packing [1]. This information is crucial for understanding the structure-property relationships in NLO crystals.

3.The Hirshfeld surface analysis can also be used to visualize the molecular shape and surface properties of NLO chromophores, which can provide insights into their nonlinear optical response [2][3]. The shape and charge distribution of the molecules can influence their second-order and third-order nonlinear optical susceptibilities.

4.In addition to Hirshfeld surface analysis, other computational techniques such as density functional theory (DFT) calculations can be employed to further investigate the electronic structure, molecular orbitals, and nonlinear optical properties of NLO materials [2][3]. These complementary analyses can help in the rational design of new NLO materials with improved performance.

5.The search results highlight several examples of NLO crystals, such as stilbazolium derivatives, Schiff base complexes, and organic-inorganic hybrid

materials, where Hirshfeld surface analysis has been used to understand the structure-property relationships [1-3].

Hirschfeld analysis.

Hirshfeld surface analysis was performed on a (NLO) compound using its CIF file. The asymmetric part of the structure was selected for the surface analysis.

During the analysis, the Hirshfeld surface was obtained from the normalized contact distance and its $\mathbf{d_i}$ and $\mathbf{d_e}$ indicators.

Quantitative analysis of the Hirschfeld surface area ($\mathbf{d_{norm}}$) revealed that the total volume is 292.86 Å^3 and the surface area is 294.76 Å^2. Generally, larger volume and surface area indicate more extensive intermolecular bonding and interactions within the crystal structure (Fig-1).

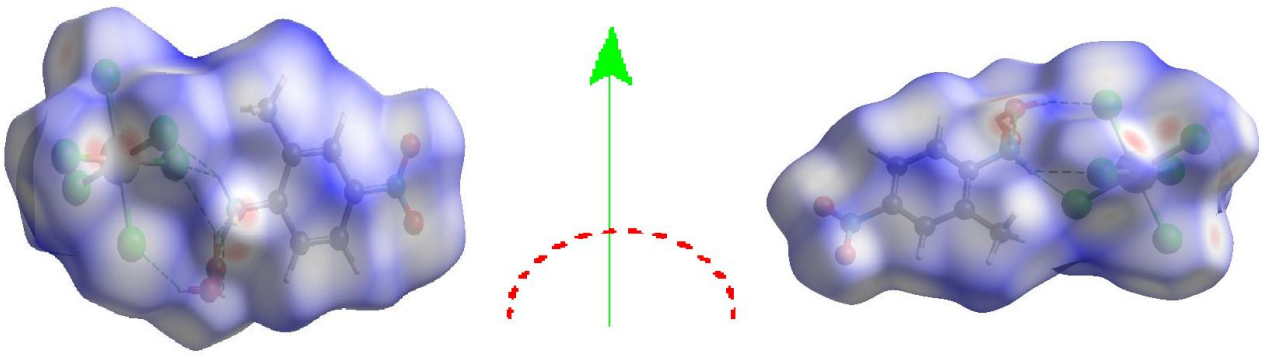

Fig-1. Hirschfeld surface of dnorma nonlinear optical (NLO) materials, interactions inside and outside the surface.

The 2D fingerprints of the Hirshfeld surface of the coordination polymer compound are shown in Fig-5. Analysis of these fingerprint patterns revealed seven different homo- and heteroatomic contact interactions within and between molecules that contribute to the overall crystal packing.

The most prominent intermolecular interactions are H-O/O-H contacts, which account for 55.1% of the Hirshfeld surface. This indicates the important role of hydrogen bonding in stabilizing the crystal structure.

The second largest contribution is H---H contacts, accounting for 11.9% of the surface area. These close hydrogen-hydrogen interactions also play an important role in intermolecular packing.

Other significant contributions include C---C contacts (1.5%). These reflect the various van der Waals and dipole-dipole interactions present in the crystal.

In slightly smaller proportions, there are All contacts (100%), All---H/H---All contacts (56.9%), O---H/H---O contacts (8.5%), Cl---O/O---Cl (2.6%) and C---H/H---C (2%) and N---O/O---N (0.5%) contacts, all of which also contribute to the Hirshfeld surface. This indicates a variety of intermolecular interactions that stabilize the crystal structure.

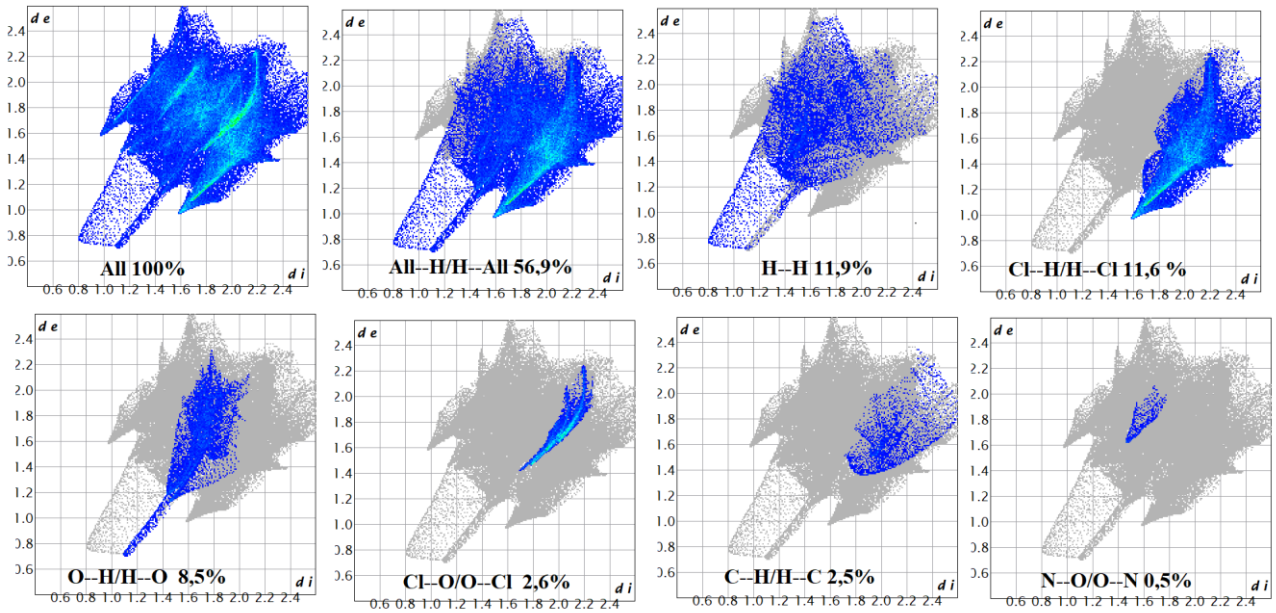

Fig-2. Fingerprint representation of a nonlinear optical (NLO) materials Hirschfeld surface, contribution of interatomic interactions to surface formation

Hydrogen contributes 51.3% to the inner part of the surface and 55.2% to the outer part. Oxygen contributes 36.3% to the inner part and 32.5% to the outer part. Carbon and the tin metal each contribute 0.5% and 0.8% respectively, with the same percentages for both the inner and outer parts of the surface.

This indicates that the contributions of the various elements to the Hirshfeld surface formation are comparable between the inner and outer parts of the molecular surface.

REFERENCES.

[1]. Jamroz, M. K.; Jamro'z, M. H.; Dobrowolski, J. Cz.; Glinski, J. A.; Davey, M. H.; Wawer, I. Spectrochim. Acta A 2011, 78, 107−112.

[2]. Arpita Poddar, Debdutta Chakraborty, in Atomic Clusters with Unusual Structure, Bonding and Reactivity, 2023.

[3]. R.C. Eckardt, in Encyclopedia of Modern Optics, 2020.

[4]. R.W. Boyd, G.L. Fischer, in Encyclopedia of Materials: Science and Technology, 2022.