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HIRSHFELD SURFACE ANALYSIS COMPLEX PIRACETAM.

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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[1].

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[2].

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. 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 . This information is crucial for understanding the structure-property relationships in NLO crystals.

In the analysis of the Hirshfeld surface for the newly obtained complex compound involving 2HBA, pirocetam and copper metal, we utilized the asymmetric unit (excluding a single water molecule in the outer sphere). Figure 6 illustrates the d_{norm} Hirschfeld surface of the Cu-complex, mapped across atomic sizes ranging from -0.7024 to 1.1652 Å, with an average value of 0.3426 Å. The Hirshfeld surface occupied an area of 402.8 Å² and had a volume of 413.78Å³.

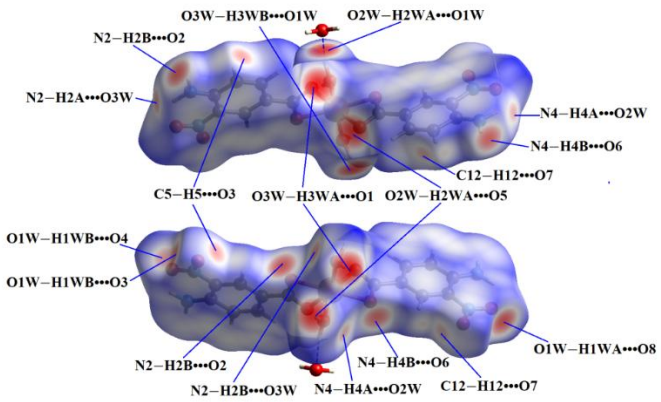

Figure 1. The Hirschfeld surface of the Cu-complex mapped in d_{norm}, the donor atom and the oxygen atoms acting as acceptors were depicted.

The shape index of the Hirshfeld surface for the copper complex (as shown in image A of Fig. 6) was presented within the atomic size range of -0.998 to 0.998, with an average value of 0.234. The shape index provides insights into the surface's depths and roundness. Based on the figure index, it was evident that there was no p-p overlap with neighbouring fragments.

In the 2D fingerprint plots of the surface, Hirshfeld revealed itself as two distinct spikes, each nearly equal in length, as depicted in Figure 5. These 2D fingerprint plots are represented in blue, with d_i and d_e values ranging from 0.4 to 2.6 Å, capturing a range of interatomic distances.

The contributions of various interatomic interactions to the formation of the surface differ significantly. The primary contribution arises from O•••H/H•••O interactions, accounting for 44.1% of the overall surface interactions. H•••H interactions contribute significantly as well, with a contribution of 23.1%. In contrast, H•••C/C•••H interactions play a lesser role, contributing 13.5%. C•••C interactions have a minor impact, representing 4.2% of the interactions, while O•••O interactions contribute 4%. Additionally, O•••C/C•••O interactions make up 3.8% of the total, N•••C/C•••N interactions contribute 2.9%, and O•••N/N•••O interactions contribute 2.2%.

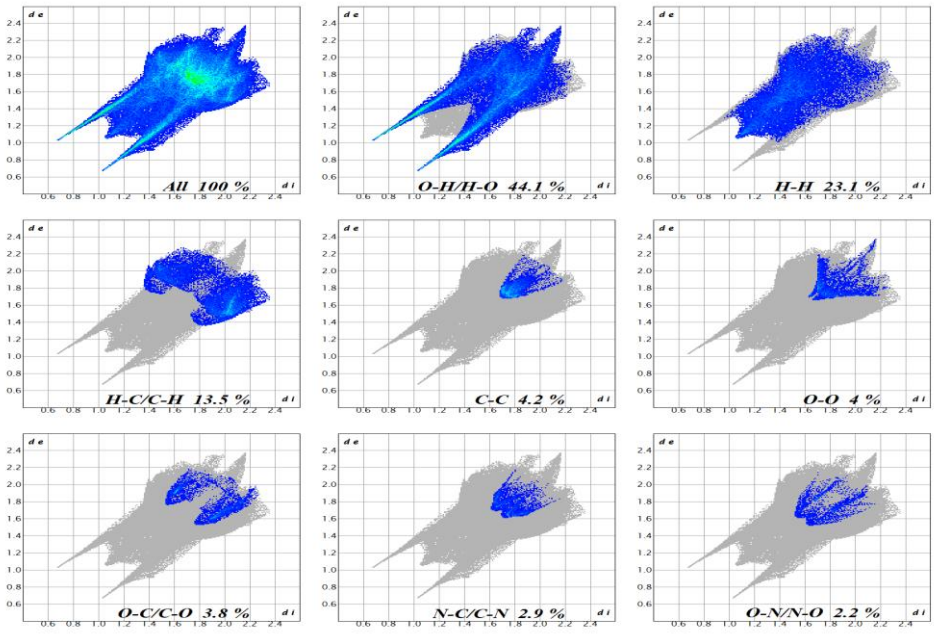

Figure 2. 2D representation of the Hirschfeld surface of the Cu-complex

References

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