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COMPREHENSIVE STRUCTURAL CHARACTERIZATION OF (3E,3'E)-3,3'-(PROPANE-1,3-DIYLBIS(AZANEYLYLIDENE))BIS(1-PHENYLBUTAN-1-ONE) THROUGH FTIR SPECTROSCOPY AND HIRSHFELD SURFACE ANALYSIS

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Abstract. The symmetric Schiff base ligand, (3E,3'E)-3,3'-(propane-1,3-diylbis(azaneylylidene))bis(1-phenylbutan-1-one), was synthesized via a condensation reaction between benzoylacetone and propane-1,3-diamine and comprehensively characterized using Fourier-transform infrared (FTIR) spectroscopy and Hirshfeld surface analysis. The FTIR spectrum exhibited a characteristic $\nu(\text{C}=\text{N})$ absorption band at 1654.9 cm^{-1} , confirming the formation of the azomethine groups and successful synthesis of the Schiff base ligand. Hirshfeld surface analysis was employed to investigate the intermolecular interactions governing the crystal packing and to elucidate the supramolecular architecture of the compound. The d_{norm} , shape index, and curvedness mappings revealed close van der Waals contacts and weak $\pi \cdots \pi$ stacking interactions within the crystal structure. The corresponding two-dimensional fingerprint plots demonstrated that $\text{H} \cdots \text{H}$ contacts make the largest contribution to the crystal packing, accounting for 55.7%, followed by $\text{C} \cdots \text{H}/\text{H} \cdots \text{C}$ (17.7%), $\text{O} \cdots \text{H}/\text{H} \cdots \text{O}$ (5.9%), $\text{N} \cdots \text{H}/\text{H} \cdots \text{N}$ (1.0%), and $\text{N} \cdots \text{C}/\text{C} \cdots \text{N}$ (0.2%) interactions.

Keywords: Schiff base ligand; Benzoylacetone; Propane-1,3-diamine; FTIR spectroscopy; Hirshfeld surface analysis; Crystal packing; Fingerprint plot; Intermolecular interactions.

Аннотация. Симметричный лиганд основания Шиффа (3E,3'E)-3,3'-(пропан-1,3-диилбис(азанейлилиден))бис(1-фенилбутан-1-он) был синтезирован реакцией конденсации бензоилацетона с пропан-1,3-диамином и всесторонне исследован методами ИК-Фурье спектроскопии и анализа поверхности Хиршфельда. Полоса валентных колебаний $\nu(\text{C}=\text{N})$ при $1654,9 \text{ см}^{-1}$ подтверждает образование азометиновой

группы и успешный синтез лиганда. Анализ поверхности Хиршфельда позволил выявить особенности межмолекулярных взаимодействий, определяющих упаковку кристалла. Карты *dnorm*, *Shape Index* и *Curvedness* показали наличие коротких ван-дер-ваальсовых контактов и слабых $\pi \cdots \pi$ -взаимодействий. Количественный анализ двумерных *fingerprint*-диаграмм показал, что основной вклад в структура кристалла вносят контакты $H \cdots H$ (55,7%), далее следуют $C \cdots H/H \cdots C$ (17,7%), $O \cdots H/H \cdots O$ (5,9%), $N \cdots H/H \cdots N$ (1,0%) и $N \cdots C/C \cdots N$ (0,2%).

Ключевые слова: основание Шиффа; бензоилацетон; пропан-1,3-диамин; ИК-Фурье спектроскопия; поверхность Хиршфельда; структура кристалла; *fingerprint*-диаграмма; межмолекулярные взаимодействия.

(3E,3'E)-3,3'-(propan-1,3-diilbis(azanililiden))bis(1-fenilbutan-1-on) Schiff asosi ligandining IQ spektroskopiyasi va Hirshfeld yuzasi tahlili yordamida keng qamrovli strukturaviy tadqiqi

Annotatsiya. (3E,3'E)-3,3'-(propan-1,3-diilbis(azanililiden))bis(1-fenilbutan-1-on) nomli simmetrik Schiff asosi ligandi benzoilatseton va propan-1,3-diaminning kondensatsiya reaksiyasi orqali sintez qilindi hamda IQ spektroskopiyasi va Hirshfeld yuzasi tahlili yordamida batafsil strukturaviy tavsiflandi. IQ spektrida $1654,9 \text{ cm}^{-1}$ da kuzatilgan $\nu(C=N)$ tebranishi azometin guruhining hosil bo‘lganligini va Schiff asosi muvaffaqiyatli sintez qilinganligini tasdiqladi. Hirshfeld yuzasi tahlili kristall panjarasini barqarorlashtiruvchi molekulalararo o‘zaro ta’sirlarni aniqlash imkonini berdi. *dnorm*, *Shape Index* va *Curvedness* xaritalari yaqin van-der-Vaals kontaktlari hamda kuchsiz $\pi \cdots \pi$ o‘zaro ta’sirlar mavjudligini ko‘rsatdi. Ikki o‘lchamli *fingerprint* diagrammalari $H \cdots H$ kontaktlari (55,7%) kristall tuzulishiga eng katta hissa qo‘shishini, undan keyin $C \cdots H/H \cdots C$ (17,7%), $O \cdots H/H \cdots O$ (5,9%), $N \cdots H/H \cdots N$ (1,0%) va $N \cdots C/C \cdots N$ (0,2%) kontaktlari kelishini ko‘rsatdi.

Kalit so'zlar: Schiff asosi; benzoilatseton; propan-1,3-diamin; IQ spektroskopiyasi; Hirshfeld yuzasi; kristall tuzulishi; ikki o‘lchovli barmoq izi diagrammasi; molekulalararo o'zaro ta'sirlar.

Introduction. Schiff bases constitute one of the most versatile classes of nitrogen-containing organic compounds and continue to attract considerable attention because of their structural diversity, facile synthesis, and broad applicability in coordination chemistry, materials science, supramolecular chemistry, and medicinal chemistry. The presence of the azomethine ($-\text{CH}=\text{N}-$) functional group provides an efficient coordination site for metal ions and plays a fundamental role in governing the electronic structure, coordination behavior, and physicochemical properties of these compounds. Consequently, Schiff base ligands readily form stable coordination complexes with transition and main-group metals, exhibiting diverse structural architectures and functional properties. These complexes have been extensively investigated for applications in homogeneous and heterogeneous catalysis, molecular sensing, crystal engineering, optoelectronic materials, corrosion inhibition, and biologically active systems owing to their tunable electronic characteristics and remarkable structural flexibility [1–4].

Among the numerous synthetic strategies available for Schiff base preparation, the condensation of β -dicarbonyl compounds with primary diamines represents one of the most effective and versatile approaches for obtaining multidentate ligands with adjustable steric and electronic properties. Benzoylacetone is a particularly attractive precursor because its reactive carbonyl groups, together with keto–enol tautomerism and conjugation with the aromatic phenyl ring, facilitate condensation reactions with diamines to produce structurally diverse azomethine derivatives. Depending on the molecular symmetry of the diamine and the reaction conditions, both symmetric and asymmetric Schiff base ligands can be obtained. Their molecular geometry, conformational flexibility, and degree of π -electron delocalization significantly influence their coordination behavior as well as their optical, electrochemical, and biological properties [5,6].

Accurate structural characterization is essential for confirming the successful formation of Schiff base ligands and for understanding the relationship between molecular structure and chemical properties. Among the available analytical techniques, Fourier-transform infrared (FTIR) spectroscopy remains one of the most reliable and informative methods for identifying functional groups and monitoring structural changes occurring during condensation reactions. The appearance of the characteristic $\nu(\text{C}=\text{N})$ stretching vibration, accompanied by the disappearance or substantial reduction of the amino and carbonyl stretching bands of the starting materials, provides direct spectroscopic evidence for the successful formation of the azomethine linkage. In addition to confirming the synthesis, FTIR spectroscopy offers valuable information regarding the electronic environment and molecular framework of the resulting ligand [3,6,7].

Beyond molecular characterization, understanding the nature of intermolecular interactions is essential for elucidating crystal packing and predicting the physicochemical behavior of molecular solids. In this context, Hirshfeld surface (HS) analysis has emerged as a powerful crystallographic approach for the qualitative visualization and quantitative evaluation of intermolecular contacts within crystal structures. The d_{norm} , d_i , d_e , Shape Index, and Curvedness surface mappings enable detailed identification of hydrogen bonds, $\text{C}-\text{H}\cdots\pi$ interactions, $\pi\cdots\pi$ stacking, and other weak non-covalent interactions responsible for crystal stabilization. Furthermore, two-dimensional fingerprint plots provide quantitative information on the relative contributions of individual intermolecular contacts, thereby offering deeper insight into crystal packing mechanisms and supramolecular organization [4,8,9].

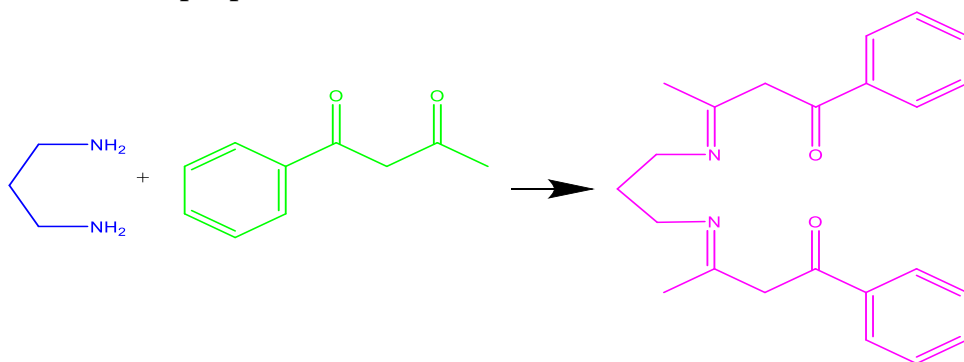
Although numerous Schiff base ligands derived from β -dicarbonyl compounds have been reported, most previous studies have primarily focused on synthetic procedures, spectroscopic characterization, or the preparation of their transition-metal complexes[9,10]. Comparatively fewer investigations have combined comprehensive spectroscopic characterization with detailed Hirshfeld surface analysis to establish correlations between molecular structure, crystal packing, and intermolecular interaction patterns. In particular, structural information concerning Schiff base ligands derived from benzoylacetone and propane-1,3-diamine remains limited, and quantitative evaluation of the intermolecular

contacts governing their crystal stabilization has not been sufficiently explored. Consequently, a detailed structural investigation integrating both spectroscopic and crystallographic analyses is required to improve the understanding of these ligands and to facilitate their future application in coordination chemistry.

In the present work, the Schiff base ligand (3E,3'E)-3,3'-(propane-1,3-diylbis(azaneylylidene))bis(1-phenylbutan-1-one) was synthesized through the condensation reaction of benzoylacetone with propane-1,3-diamine. The synthesized compound was characterized by Fourier-transform infrared spectroscopy to confirm the formation of the azomethine functionality and to investigate its principal vibrational features[10]. Furthermore, Hirshfeld surface analysis was performed to elucidate the intermolecular interactions governing crystal packing and to quantify the contributions of different intermolecular contacts to crystal stabilization. The novelty of the present study lies in the integration of spectroscopic characterization with quantitative Hirshfeld surface analysis to provide a comprehensive description of both the molecular and supramolecular structural features of this benzoylacetone-derived Schiff base ligand. The results provide valuable insight into the relationship between molecular structure and crystal packing, establish a reliable structural basis for future coordination studies involving transition-metal complexes, and contribute to the rational design of new Schiff base-based functional materials.

Experimental

Synthesis of (3E,3'E)-3,3'-(propane-1,3-diylbis(azaneylylidene))bis(1-phenylbutan-1-one) Propane-1,3-diamine (0.83 mL, 0.01 mol; density = 0.888 g mL⁻¹) was dissolved in 25 mL of absolute ethanol under continuous magnetic stirring. A solution of benzoylacetone (3.243 g, 0.02 mol) in 30 mL of absolute ethanol was then added dropwise to the diamine solution while maintaining constant stirring. The reaction mixture was stirred at room temperature for 1 h, during which a clear homogeneous pale-yellow solution was obtained, indicating the progress of the condensation reaction. After completion of the reaction, the resulting solution was left undisturbed in a dark place at room temperature for two days to allow the slow evaporation of the solvent. Gradual solvent evaporation resulted in the formation of well-defined pale-yellow (light amber) crystalline products. The crystals were collected by vacuum filtration, thoroughly washed with a small amount of cold ethanol to remove any residual impurities, and subsequently dried under ambient conditions to constant weight. The synthesis of the Schiff base ligand proceeded via a condensation reaction between benzoylacetone and propane-1,3-diamine, as illustrated in **Scheme 1**.



Scheme 1.

Synthesis of (3E,3'E)-3,3'-(propane-1,3-diylbis(azaneylylidene))bis(1-phenylbutan-1-one) via the condensation reaction between benzoylacetone and propane-1,3-diamine.

The synthesized Schiff base ligand was characterized by Fourier-transform infrared (FTIR) spectroscopy to confirm the formation of the azomethine functionality and to identify the characteristic functional groups present in the molecular structure. The FTIR spectrum of the synthesized compound (sample: **2BA + PDA**) was analyzed by assigning the observed absorption bands to their corresponding vibrational modes. The positions and intensities of the characteristic absorption bands provide valuable information regarding the successful formation of the Schiff base and the structural features of the synthesized ligand. The detailed interpretation of the principal absorption bands is discussed below.

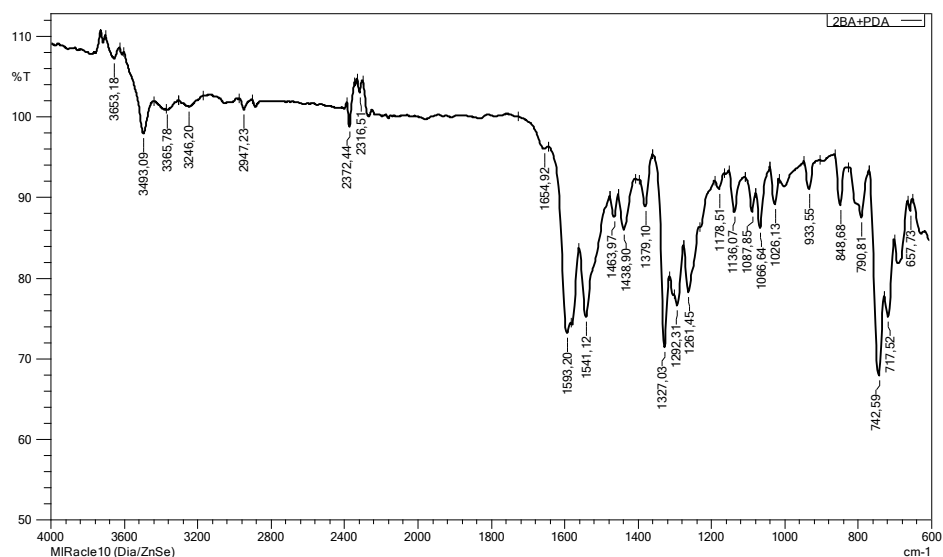


Figure 1.

*FTIR spectrum of the synthesized Schiff base ligand **L1** (2BA + PDA).*

The FTIR spectrum of the synthesized ligand provides clear spectroscopic evidence for the successful formation of the Schiff base through the condensation reaction between benzoylacetone and propane-1,3-diamine. The most significant feature of the spectrum is the strong absorption band observed at **1654.9 cm⁻¹**, which is assigned to the stretching vibration of the azomethine group, $\nu(\text{C}=\text{N})$. The appearance of this characteristic band confirms the formation of the imine linkage and serves as the principal spectroscopic indicator of Schiff base formation. The absorption bands located at **1593** and **1541 cm⁻¹** are attributed to the stretching vibrations of the aromatic $\text{C}=\text{C}$ bonds and the conjugated π -electron system, indicating that the aromatic framework and extended conjugation are preserved in the synthesized ligand. Several absorption bands observed within the **1327–1026 cm⁻¹** region are assigned to $\text{C}-\text{N}$ stretching vibrations, providing additional evidence for the formation of the azomethine framework during the condensation reaction. Furthermore, the absorption bands at **742** and **717 cm⁻¹** correspond to the out-of-plane bending vibrations of aromatic $\text{C}-\text{H}$ bonds, confirming the presence of monosubstituted phenyl rings in the molecular structure. Overall, the FTIR data demonstrate the successful synthesis of the Schiff base ligand derived from benzoylacetone and propane-1,3-diamine. The appearance of the characteristic $\nu(\text{C}=\text{N})$ absorption band, together with the characteristic $\text{C}-\text{N}$ stretching vibrations and the retention of the aromatic ring vibrations, confirms the

successful formation of the azomethine-containing ligand and is fully consistent with the proposed molecular structure.

Hirshfeld Surface Analysis. To gain a comprehensive understanding of the intermolecular interactions governing the crystal packing of the synthesized benzoylacetone–propane-1,3-diamine Schiff base ligand, Hirshfeld surface (HS) analysis was performed. This crystallographic approach enables the visualization and quantitative evaluation of intermolecular contacts within the crystal lattice, thereby providing valuable insight into the supramolecular organization and packing characteristics of the compound. The Hirshfeld surface was generated to identify the nature and distribution of intermolecular interactions responsible for crystal stabilization and to assess their relative contributions to the overall crystal packing.

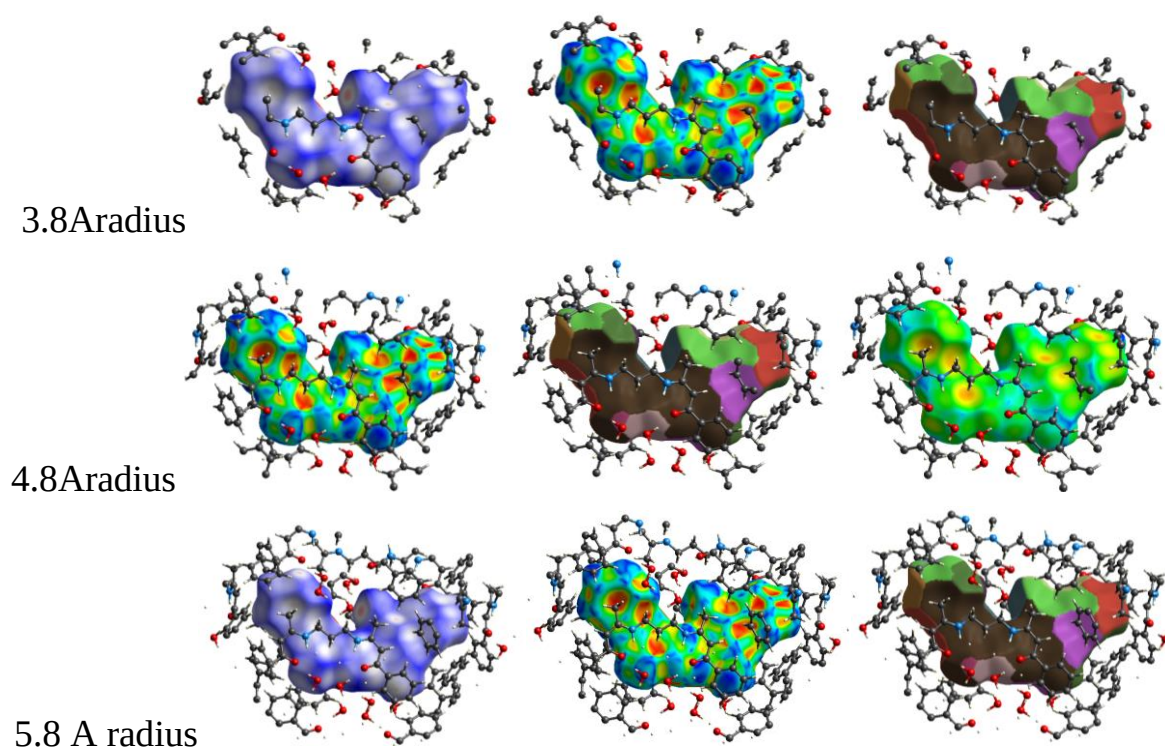


Figure 2

Figure 2. Hirshfeld surface maps of the synthesized Schiff base ligand L1 generated over d_{norm} , Shape Index, and Curvedness using surface radii of 3.8, 4.8, and 5.8 Å.

Results and Discussion

The Hirshfeld surface (HS) analysis was performed to investigate the intermolecular interactions governing the crystal packing of the synthesized Schiff base ligand L1. The Hirshfeld surface representations mapped over d_{norm} , Shape Index, and Curvedness are presented in Figure 2. To visualize intermolecular contacts at different distances from the reference molecule, the surfaces were generated using radii of 3.8, 4.8, and 5.8 Å. The d_{norm} surface provides a qualitative representation of intermolecular contacts relative to the van der Waals radii. Red regions indicate intermolecular contacts shorter than the sum of the corresponding van der Waals radii and therefore represent significant close contacts within the crystal lattice. White regions correspond to contacts approximately equal to the van der Waals distances, whereas blue regions indicate intermolecular separations longer than the corresponding van der Waals radii. The presence of several localized red patches

demonstrates that weak intermolecular interactions contribute to the stabilization of the crystal structure. The Shape Index surface exhibits complementary red and blue patches on neighboring aromatic rings, which are characteristic features of $\pi \cdots \pi$ stacking interactions. These interactions originate from the overlap of adjacent aromatic π -electron systems and play an important role in promoting an ordered crystal packing arrangement. The Curvedness surface displays extended flat green regions, indicating relatively planar molecular fragments that facilitate aromatic stacking interactions. Such planar regions are generally associated with efficient molecular packing and enhanced crystal stability.

Overall, the Hirshfeld surface analysis demonstrates that the crystal packing of ligand L1 is governed predominantly by weak non-covalent interactions, including close van der Waals contacts and $\pi \cdots \pi$ stacking interactions. These intermolecular contacts collectively contribute to the supramolecular organization and stabilization of the crystal structure.

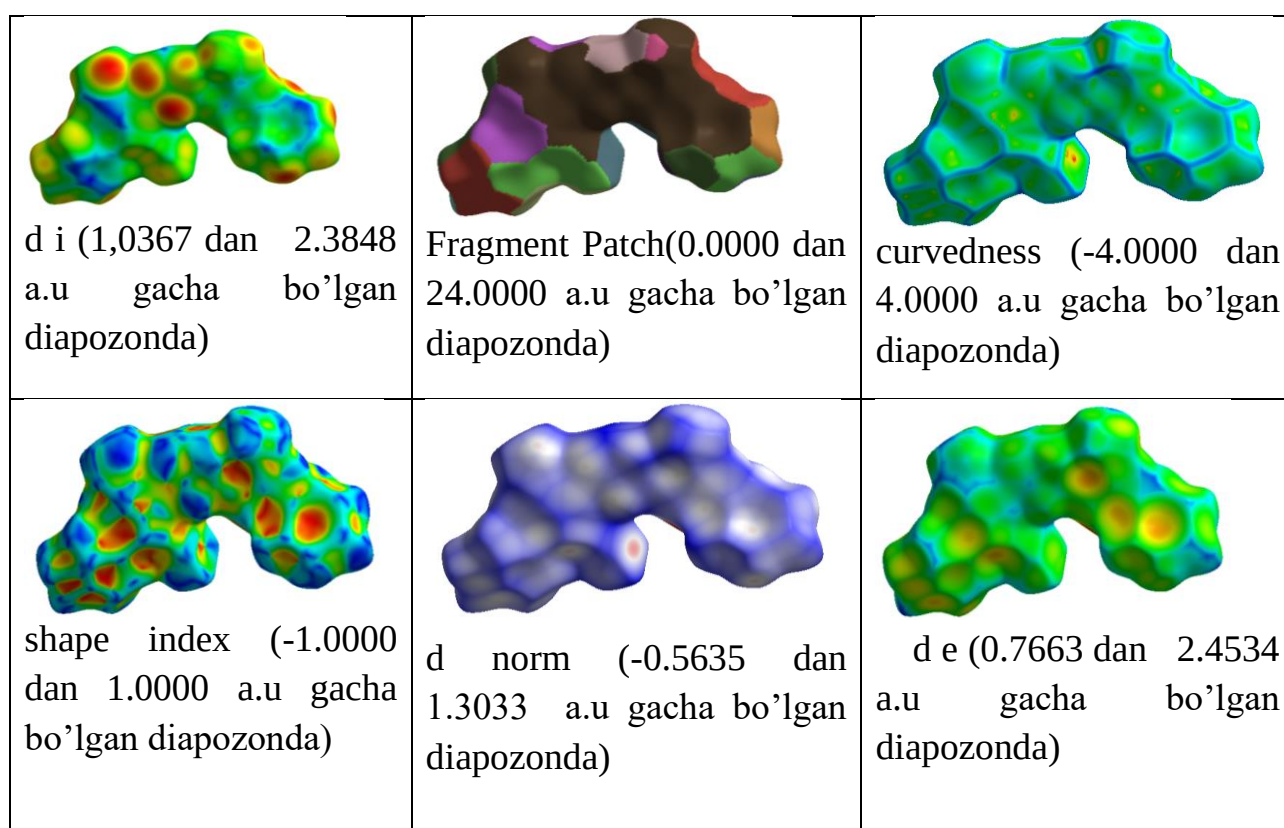


Figure 3.

Hirshfeld surface of ligand L1 mapped over d_{norm} .

The Hirshfeld surface mapped over d_{norm} provides valuable information regarding the close intermolecular contacts present in the crystal structure of ligand L1. As shown in **Figure 3**, several localized red regions are observed on the molecular surface. These red patches correspond to intermolecular

contacts that are shorter than the sum of the corresponding van der Waals radii, indicating the presence of significant close contacts that contribute to the stabilization of the crystal packing. The d_{norm} values range from **-0.5653 to 1.3033 Å**. Negative values, represented by red regions on the surface, denote intermolecular contacts shorter than the corresponding van der Waals separations and therefore indicate relatively strong close interactions. In contrast, white regions represent contacts approximately equal to the van der Waals distances, whereas blue regions correspond to intermolecular separations longer than

the van der Waals radii. The observed distribution of the d_{norm} values suggests that weak non-covalent interactions play an important role in stabilizing the crystal lattice of the synthesized Schiff base ligand. The most intense red regions, corresponding to a minimum d_{norm} value of $-0.5653 \text{ \AA}$, indicate the shortest intermolecular contacts within the crystal structure. These contacts are consistent with close intermolecular interactions and contribute significantly to the supramolecular organization of the crystal. However, the specific nature of these interactions (e.g., hydrogen bonding or other short contacts) should be confirmed through analysis of the corresponding intermolecular contact distances and fingerprint plots.

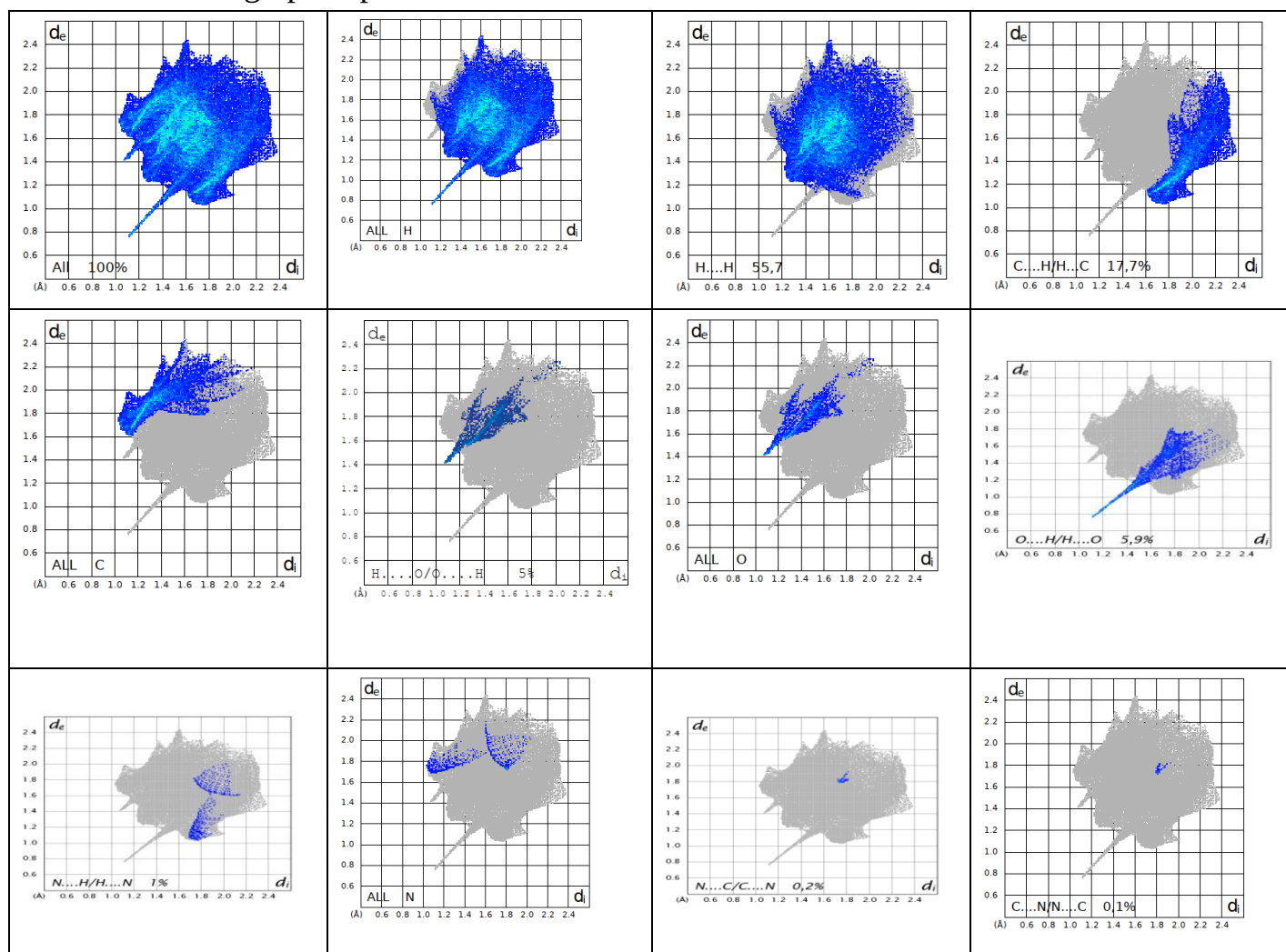


Figure 4.

Hirshfeld Surface Analysis and Two-Dimensional Fingerprint Plot Analysis

The intermolecular interactions responsible for the crystal packing of the synthesized Schiff base ligand **L1** were investigated using Hirshfeld surface analysis combined with two-dimensional (2D) fingerprint plots (**Figure 4**). This approach provides quantitative information regarding the contribution of individual intermolecular contacts to the overall crystal packing arrangement and allows a detailed evaluation of the supramolecular interactions present within the crystal lattice. The overall fingerprint plot represents the cumulative contribution of all intermolecular contacts occurring in the crystal structure. The dense central region of the plot indicates the presence of multiple short intermolecular contacts, demonstrating that different types of weak interactions collectively participate in

the stabilization of the crystal packing. The largest contribution to the Hirshfeld surface arises from **H···H contacts**, accounting for **55.7%** of the total surface. These contacts appear as a broad and diffuse region in the central part of the fingerprint plot and mainly originate from van der Waals interactions between hydrogen atoms. Although individually weak, the high percentage contribution of H···H contacts indicates their significant role in determining the overall packing efficiency and molecular arrangement within the crystal lattice. The second most significant contribution corresponds to **C···H/H···C contacts**, which account for **17.7%** of the total Hirshfeld surface. These interactions appear as characteristic wing-shaped regions in the fingerprint plot and are associated with close contacts between carbon and hydrogen atoms. The observed distribution of C···H/H···C contacts is consistent with weak aromatic C–H··· π interactions, which may contribute to the stabilization and organization of molecules within the crystal framework. The **O···H/H···O contacts** contribute **5.9%** to the Hirshfeld surface. In the fingerprint plot, these contacts appear as sharp spike-like features, indicating the presence of relatively short and directional intermolecular interactions involving oxygen atoms. These interactions, although smaller in percentage contribution, can play an important role in reinforcing the crystal lattice through hydrogen-bond-type contacts. The contribution of **N···H/H···N contacts** is relatively low (**1.0%**). These contacts appear as narrow spike features in the fingerprint plot and are attributed to close intermolecular contacts involving azomethine nitrogen atoms. Despite their limited contribution, such interactions may influence the preferred molecular orientation and supramolecular arrangement within the crystal structure. The **N···C/C···N contacts** contribute only **0.2%** of the total surface area, indicating that these interactions have a negligible influence on the overall crystal packing. Their presence represents minor secondary contacts within the molecular environment. Overall, the fingerprint plot analysis demonstrates that the crystal packing of ligand **L1** is predominantly governed by **H···H van der Waals contacts (55.7%)**, followed by **C···H/H···C interactions (17.7%)**. The presence of **O···H/H···O contacts (5.9%)** provides additional stabilization through more directional intermolecular interactions. The remaining contacts, including **N···H/H···N** and **N···C/C···N**, contribute only marginally to the crystal packing. Therefore, the Hirshfeld surface analysis confirms that both non-directional van der Waals interactions and weak directional intermolecular contacts cooperatively determine the supramolecular organization and stability of the crystal structure of the synthesized Schiff base ligand.

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