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Hirshfeld Surface Analysis and Interaction Energy Calculations of Bis(4-chlorophenylacetate)bis(pyridine-4-carboxamide)Zinc(II)

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Abstract

Hirshfeld surface analysis has been widely used in crystallography in recent years to investigate intermolecular interactions and to determine the contribution of these interactions to the crystal lattice. Fingerprint plots, which are given as color plots, present quantitative results of the types of intermolecular interactions in a molecule. In this study, we have been investigated intermolecular interactions and energy frameworks pyridine 4-carboxamide complex of Zn(II) 4-chlorophenylacetate by using CrystalExplorer program. Intermolecular interactions of the complex were determined using Hirshfeld Surface analysis. The intermolecular interaction energies of the complex were calculated using CE-HF/3-21G, CE-HF/6-31G (d), CE-HF/6-31G (d,p), CE-MP2/3-21G, CE-MP2/6-31G (d), CE-MP2/6-31G (d,p), CE-B3LYP/3-21G, CE-B3LYP/6-31G (d), CE-B3LYP/6-31G (d,p), CE-DFT/3-21G, CE-DFT/6-31G (d) and CE-DFT/6-31G (d,p) energy models that involved in CrystalExplorer (CE) program. The estimation of the intermolecular interactions and energies of the complexes is very important for the classification and investigation of their application areas.

Keywords: 4-Chlorophenylacetatic acid, pyridine-4-carboxamide, Hirshfeld Surface analysis, Energy Calculations, CrystalExplorer program.

1. INTRODUCTION

In recent years, theoretical chemistry has get importance in researching the structural, physical and biological properties of materials. The results obtained from theoretical studies help to estimate and interpret the results that can be obtained from experimental results, and it is much cheaper and faster in obtaining theoretical results compared to experimental results. For these reasons, to avoid from squander of money and time for experimets, the making of the theoretical calculations before the experiments is very important (Kirste, 2016; Toy, Tanak ve Şenöz, 2020). CrystalExplorer program is the most used theoretical calculation program, that it has been widely used by Crystallographs, in recent years (Turner, McKinnon, Wolff, Grimwood, Spackman, Jayatilaka, Spackman, 2017). Hirshfeld Surface analysis is an analysis that can leads to determination of the interactions among molecules, and the contribution of

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these interactions to the crystal lattice, by creating graphs and two-dimensional fingerprint plots. Thanks to this analysis, by determining the surface of Hirshfeld, it is possible to separate the electron density of the crystal into molecular parts and to describe the area in which the molecule is located. In this way, it can be detemined the similarity and/or differencies among structurally investigated crystal structures. With this analysis, it is possible to define not only the contribution of intermolecular interactions to crystal packing but also the characteristics of different intermolecular interactions (Tan, Jotani and Tiekink, 2019). That, is, Hirshfeld surface analysis helps to investigate the role of non-covalent interactions such as hydrogen bonds and other intermolecular contacts and to determine the effects of these interactions on crystal lattice stability. A new feature has been added to the Crystal Explorer 17.5 Program to allow calculation of pair-wise interaction energies within a crystal. Users can apply the energy models available in the software to perform the calculation for neutral organic molecules, organic salts, solvates, coordination compounds, and radicals (Hirshfeld, 1977; McKinnon, Jayatilaka and Spackman, 2007; Spackman and Jayatilaka, 2009). Within the scope of this study, the Hirhsfeld Surface analysis and Interaction Energy Analysis of the bis(4-chlorophenylacetate)bis(pyridine-4-carboxamide)zinc(II) complex, which we previously synthesized and determined its structure, were performed using the CrystalExplorer program.

In order to interpret the interactions among the molecules of the complex, d_{norm} map, shape index, curvedness map, 2D fingerprint plots and fragment patches of the molecule were determined. For the energy frameworks analysis of the complex, electrostatic energy, polarization energy, dispersion energy, exchange-repulsion energy and total intermolecular energy were computed using twelve energy models which were notified as: CE-HF/3-21G, CE-HF/6-31G (d), CE-HF/6-31G (d,p), CE-MP2/3-21G, CE-MP2/6-31G (d), CE-MP2/6-31G (d,p), CE-B3LYP/3-21G, CE-B3LYP/6-31G (d), CE-B3LYP/6-31G (d,p), CE-DFT/3-21G, CE-DFT/6-31G (d) and CE-DFT/6-31G (d,p).

2. MATERIALS AND METHOD

To investigated the visualization of intermolecular interactions of bis(4-chlorophenylacetate)bis(pyridine-4-carboxamide)zinc(II) complex, that we previously synthesized and characterized its structure (Figure 1) (Özbek, Sertçelik, Yüksek, Uğurlu, Tonbul, Necefoğlu and Hökelek, 2019) Hirshfeld surface analysis (Hirshfeld, 1977; Spackman and Jayatilaka, 2009) was carried out. Hirshfeld surface (Turner et.al., 2017; McKinnon et al., 2007), 2D fingerprint (Spackman and Jayatilaka, 2009) plots and intearction energy analysis were obtained using CrystalExplorer Version 17.5 program based on the input CIF (Turner et al., 2017). To get more accuracy about molecular interactions, we used Tonto quantum chemistry package for energy framework analysis (Jayatilaka and Grimwood, 2003; Mackenzie, Spackman, Jayatilaka and Spackman, 2017; Tan et al., 2019). The intermolecular interaction energies of for bis(4-chlorophenylacetate)bis(pyridine-4-carboxamide)zinc(II) complex were computed using CE-HF/3-21G, CE-HF/6-31G (d), CE-HF/6-31G (d,p), CE-MP2/3-21G, CE-MP2/6-31G (d), CE-MP2/6-31G (d,p), CE-B3LYP/3-21G, CE-B3LYP/6-31G (d), CE-B3LYP/6-31G (d,p), CE-DFT/3-21G, CE-DFT/6-31G (d) and CE-DFT/6-31G (d,p) energy models in Crystal-Explorer (CE).

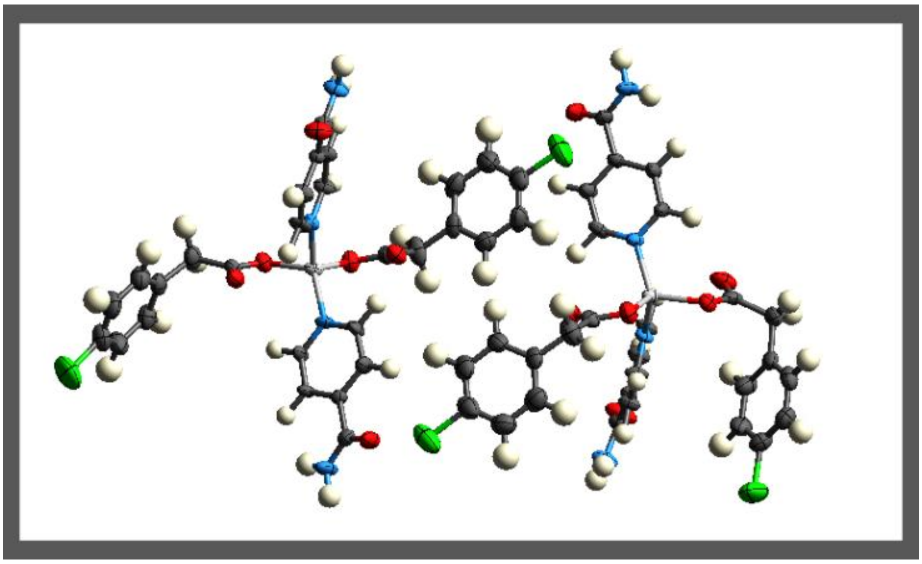

Figure 1. Crystal Structure of the complex

3. RESULTS AND DISCUSSION

3.1. Hirshfeld Surface Analysis

Hirshfeld surface analysis enables intermolecular interactions and short or long contacts to be visualized by presenting them with different colors and color intensity. The d_{norm} maps of the complex were given in Figure 2. In the d_{norm} map of the Hirshfeld Surface of complex 1, red and blue surfaces represent the contacts with distances shorter (in close contact) or longer (distinct contact) than the Van der Waals radii, respectively. In addition the white surface indicates the distance equal to the sum of Van der Waals radii. Three-dimensional Hirshfeld surfaces of the complex were plotted over d_{norm} in the range of -0.5875 to 1.6094 a.u. (Spackman, McKinnon and Jayatilaka, 2008).

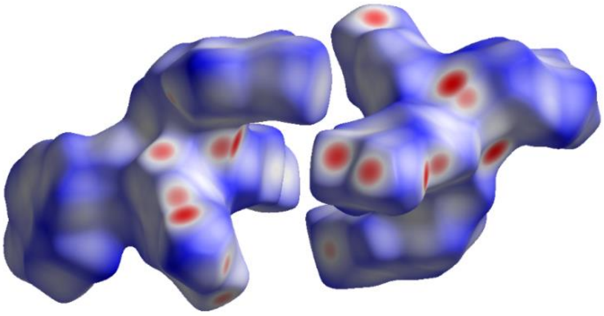

Figure 2. View of the three-dimensional Hirshfeld surface of the complex which were plotted over d_{norm} in the range -0.5875 to 1.6094 a.u.

On the shape-index for the complex, blue and red regions represent donor and acceptor groups, respectively (Figure 3). As can be seen from the Figure 3, adjacent red and blue triangles confirm the presence of π-π stacking interactions among the aromatic rings in the crystal structure of the complex (Spackman et al., 2008).

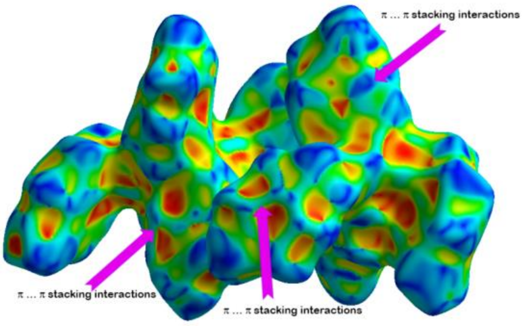

Figure 3. Shape-index plot in Hirshfeld surface of the complex.

There are showed relatively large green planes in where the benzene and pyridine rings ligands are placed. The curvedness mapping gives an idea of the planarity of complexes and that give rise to the π···π interactions between the benzene and pyridine rings in a monoclinic crystal system (Figure 4) (Spackman et al., 2008).

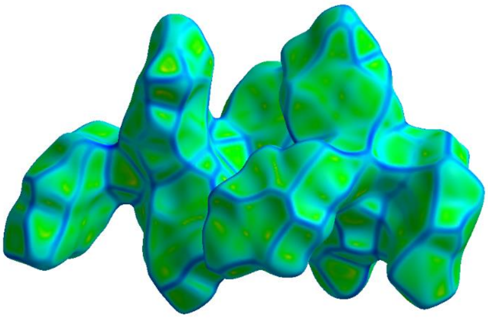

Figure 4. Curvedness mapping of the complex

2D fingerprint plots and fragment patches for all interactions and individual for each interaction are given in Figure 5. The most significant interactions are H···H (33%) interactions due to the abundance of hydrogen on the molecular surface. The second largest contribution (22.8%) was estimated as H···O/O···H interactions, which was consisted of the appearance of deep-red color and relationship with the N—H···O and C—H···O hydrogen bonds. In addition, H···C/C···H (16.9%), H···Cl/Cl···H (12.2%), C···Cl/Cl···C (4.3%), C···C (4.1%), H···N/N···H (2.5%), O···Cl/Cl···O (1.5%) and C…O/O…C (1.2%) interactions were also observed, with other contact types making a negligible contribution (Cl···Cl (0.8%) N···Cl/Cl···N (0.3%) and N···C/C···N (0.3%) (Figure 6).

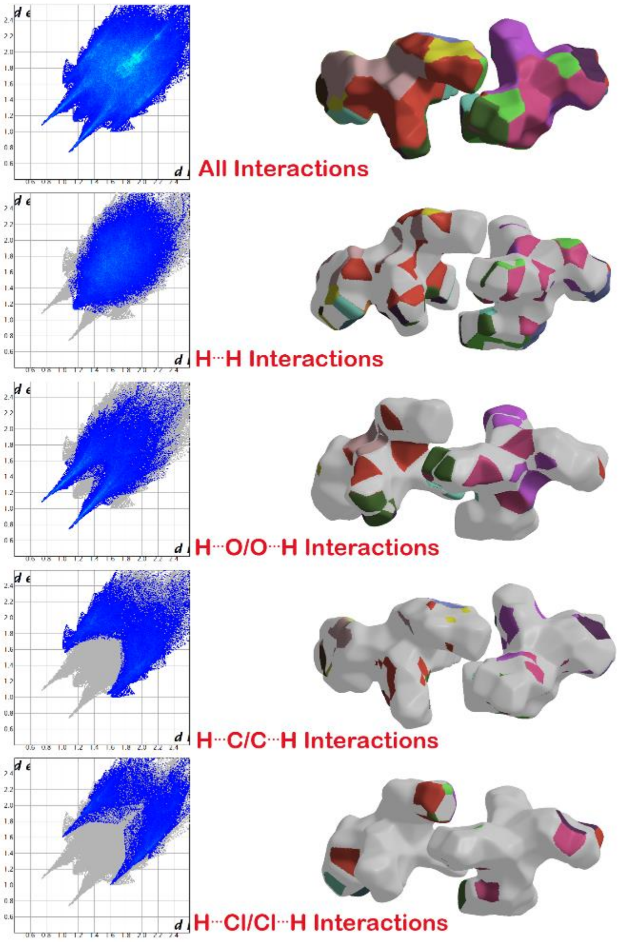

Figure 5. The Hirshfeld surface representations with the function dnorm which were plotted onto the surface.

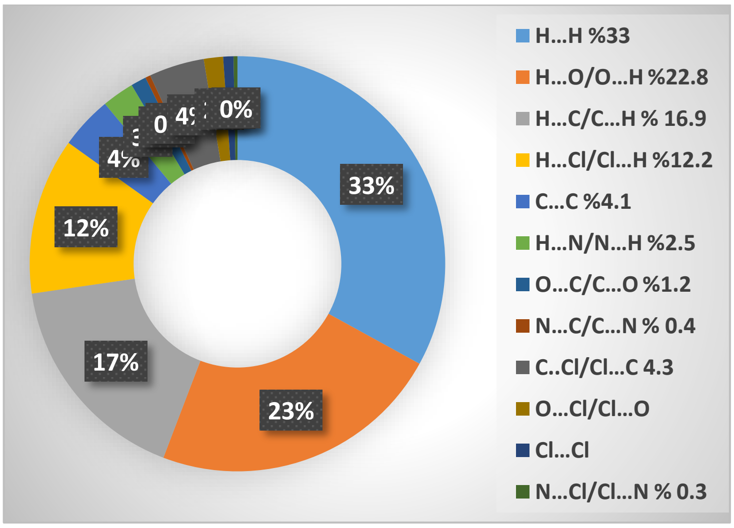

Figure 6. The percentages of the intermolecular interactions which were obtained from Hirshfeld Surface analysis of the complex.

3.2. Interactions Energy Analysis

The total intermolecular energy, E_$_{tot}$ (kJ/mol), which correlative to the reference molecule is the sum of four main energy components comprising electrostatic (E_$_{ele}$), polarization (E_$_{pol}$), dispersion (E_$_{dis}$) and exchange-repulsion (E_$_{rep}$) with scale factors (Tan et al. 2019) are given in Table 1. The energy calculation results which were taken in the Table 2, were done by using CE-HF/3-21G, CE-HF/6-31G (d), CE-HF/6-31G (d, p), CE-MP2/3-21G, CE-MP2/6-31G (d), CE-MP2/6-31G (d, p), CE-B3LYP/3-21G, CE-B3LYP/6-31G (d), CE-B3LYP/6-31G (d, p), CE-DFT/3-21G, CE-DFT/6-31G (d) and CE-DFT/6-31G (d, p) models of the program. Twelve different model of the CrystalExplorer (CE) program were used to increase the accuracy of the estimation of the energy values. Each energy model has showed very similar results in itself (Table 2). It was clearly seen from the Table that the dispersion (E_dis), polarization (E_pol) and exchange-repulsion (E_rep) energy values were obtained same for all of the models. This situation can be attributed to the stability of used reference molecule. On the other hand, the electrostatic energy (E_ele) values were generally found different and they affected the values of the total energies. In previous studies, it has been reported that hydrogen bond interactions contribute to electrostatic energy. Therefore, hydrogen bond interactions in crystal structure of the complex form as: N—H···O and C—H···O and the contributions to the electrostatic energies cause mainly from these interactions. The fact that the doesn’t change of the dispersion energy is an indicator of the stability of the molecule Especially H…H interactions, which were found to have a large contribution among the layers by Hirshfeld surface analysis of the complex, are thought to significantly increase the stability of the structure (Caracelli, Zukerman-Schpector, Schwab, Silva, Jotani and Tiekink, 2019; Etse, Lamela, Zaragoza and Pirotte, 2020; Mackenzie et al., 2017; Madan-Kumar, 2019).

Table 1. Scale factors for benchmarked energy models (Mackenzie et al., 2017)

Energy Model	k_ele	k_pol	k_disp	k_rep
CE-HF ... HF/3-21G electron densities	1.019	0.651	0.901	0.811
CE-B3LYP ... B3LYP/6-31G(d,p) electron densities	1.057	0.740	0.871	0.618

Table 2. Interactions energy analysis results

N	Symop	R	Electron Density	E_ele	E_pol	E_dis	E_rep	E_tot
1	-	12.03	HF/3-21G	3.4	-0.2	-3.2	0.0	0
1	-	12.03	HF/6-31G(d)	3.1	-0.2	-3.2	0.0	-0.3
0			HF/6-31G(d,p)	3.1	-0.2	-3.2	0.0	-0.3
1	-	12.03	MP2/3-21G	3.4	-0.2	-3.2	0.0	0
0			MP2/6-31G(d)	3.1	-0.2	-3.2	0.0	-0.3
0			MP2/6-31G(d,p)	3.1	-0.2	-3.2	0.0	-0.3
1	-	12.03	B3LYP/3-21G	2.5	-0.2	-3.2	0.0	-0.9
0			B3LYP/6-31G(d)	2.4	-0.2	-3.2	0.0	-1.0
1	-	12.03	B3LYP/6-31G(d,p)	2.4	-0.2	-3.2	0.0	-1.0
1	-	12.03	DFT/3-21G	2.3	-0.2	-3.2	0.0	-1.1
0			DFT/6-31G(d)	2.2	-0.2	-3.2	0.0	-1.2
1	-	12.03	DFT/6-31G(d,p)	2.2	-0.2	-3.2	0.0	-1.2

E:interaction energies components, Symop: rotational symmetry operations with respect to the reference molecule, R: the centroid-to-centroid distance between the reference molecule N: interacting molecules as well as the number of pair(s) of interacting molecules with respect to the reference molecule (Mackenzie et al., 2017).

4. CONCLUSION

In this study, Hirshfeld surfaces and the relationship 2D fingerprint plots of complex were investigated. According to Hirshfeld Surface Analysis results, H...H, H...C/C…H, H···Cl/Cl···H, C···Cl/Cl···C, C···C, H···N/N···H, O···Cl/Cl···O, C···O/O···C, Cl···Cl and N···Cl/Cl···N interactions are found. H···H interactions provide the most contribute to crystal packaging. H···O/O···H interactions also provide the second most important contribution, support the presence of hydrogen bonds in the crystal structure. In addition to, this confirms the contribution of N—H···O and C—H···O hydrogen bonds to the stability of three-dimensional networks in the crystal package, previously obtained by single crystal X-ray diffraction. On the shape-index of the complex, presences of adjacent red and blue triangles were supported the π-π stacking interactions between the benzene and pyridine rings in complex's crystal structure. As a result, it can be said that the results obtained from single crystal X-ray analysis and Hishfeld surface analysis are supportive of each other. The polarization (E_pol), dispersion (E_dis) and exchange-repulsion (E_rep) energies, which were obtained from 12 different models of the CrystalExplorer (CE) program, of the reference molecule of the complex was found as -0.2 kJ/mol, -3.2 kJ/mol and 0, respectively. On the other hand, the electrostatic (E_ele) energies of the molecule were obtained among 3.4 kJ/mol and 2.2 kJ/mol by using 12 different model of the program.

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