

## Hirshfeld surface analysis of two new amidophosphinates

Anahid Saneei<sup>1</sup>, Mehrdad Pourayoubi<sup>1</sup>, Aurelien Crochet<sup>2</sup>

<sup>1</sup>Department of Chemistry, Faculty of Sciences, Ferdowsi University of Mashhad, Mashhad, Iran

<sup>2</sup>Fribourg Centre for Nanomaterial's, FriMat, University of Fribourg, Chemin du Musée 3, CH-1700 Fribourg, Switzerland

---

### ABSTRACT

*Hirshfeld surfaces and 2D fingerprint plots are used to analysis of intermolecular interactions in two new amidophosphinates: (2-Cl-C<sub>6</sub>H<sub>4</sub>O)P(O)[X]<sub>2</sub> {X = NHC<sub>5</sub>H<sub>10</sub> (I), [X]<sub>2</sub>= NHCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>NH (II)}. The N—H...O=P hydrogen bonds are the characteristic interaction in both structures and appear as two very large red spots in the Hirshfeld surface maps. The pairs of long spikes in the corresponding fingerprint plots are related to the O...H contacts and the points around 2.2 Å correspond to the N—H...O=P hydrogen bonds in both structures.*

**Keywords:** Hirshfeld surface analysis, Finger print plot, Amidophosphinate, Crystal structure

---

### 1. INTRODUCTION

In the last few years the analysis of molecular crystal structures using tools based on Hirshfeld surfaces has rapidly gained in popularity. This approach attempts to identification of close contacts deemed to be important [1, 2]. Recently, Hirshfeld surface analyses were applied to evaluate the nature, type and percentage of intermolecular interactions in selected examples of phosphoramidate structures [3, 4]. In continuation of our previous works in this area, we used the Hirshfeld surface analyses to study of two new amidophosphinate structures.

### 2. EXPERIMENTAL

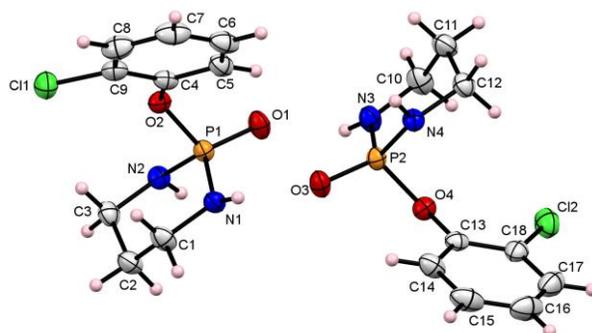
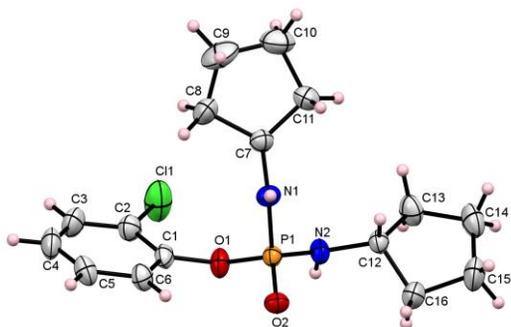
The starting material 2-Cl-C<sub>6</sub>H<sub>4</sub>P(O)Cl<sub>2</sub> (A) was commercially available.

**2.1. Synthesis of 2-chloro phenyl bis(cyclopentylamido) phosphinate (I):** a solution of 4 mmol cyclopentyl amine in CHCl<sub>3</sub> (5 mL) was added dropwise to a stirred solution of 1 mmol of (A) in the same solvent (30 mL) at 0°C. After 4 h, the solvent was removed and product was washed with distilled water. Single crystals, suitable for X-ray crystallography, were obtained at room temperature from a mixture of CH<sub>3</sub>OH/CH<sub>3</sub>CN. IR (KBr, cm<sup>-1</sup>): 3243, 2952, 2867, 1586, 1481, 1280, 1244, 1201, 1114, 1062, 987, 928, 755, 671.

**2.2. Synthesis of 2-[2-chloro phenoxy]-1,3,2λ<sup>5</sup>-diazaphosphinan-2-one (II):** Compound (II) was synthesized in a similar procedure to (I) by using 2 mmol 1,3-propane diamine instead of 4 mmol cyclopentyl amine. IR (KBr, cm<sup>-1</sup>): 3269, 1584, 1480, 1386, 1336, 1275, 1233, 1097, 1063, 996, 913, 860, 805, 759.

### RESULTS AND DISCUSSION

The asymmetric unit of structure (I) contains one complete molecule (Fig. 1), while it for structure (II) consists of two symmetry-independent molecules (Fig. 2). The crystallographic data and the details of X-ray analysis of (I) and (II) are given in Table 1. The P atoms are found within a distorted P[O][O][N]<sub>2</sub> tetrahedral environment and the P=O bond lengths have good agreement with previously reported amidophosphinates [5, 6].



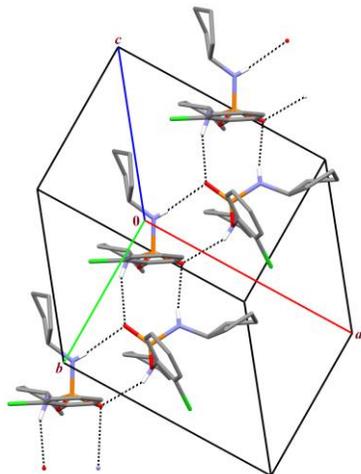
**Fig. 1.** Displacement ellipsoid plot (50% probability) is shown for (I) with atom numbering scheme

**Fig. 2.** Displacement ellipsoid plot (30% probability) is shown for (II) with atom numbering scheme

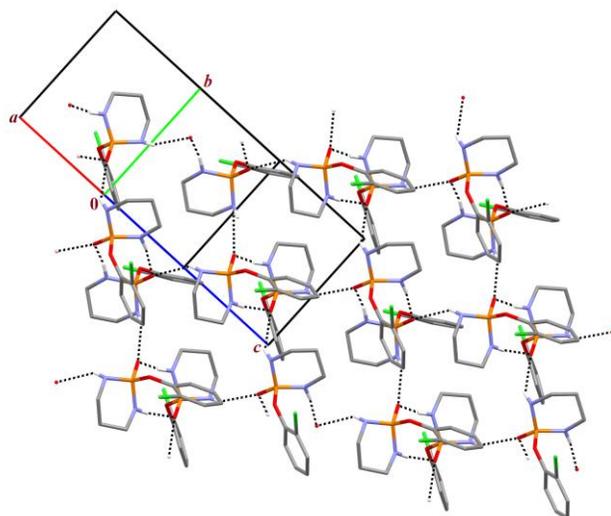
In the structure (I), the molecules are aggregated in a 1-D arrangement *via* N—H...O=P hydrogen bonds along the *b* axis. In this pattern, the oxygen atom of the 2-ClC<sub>6</sub>H<sub>4</sub>O group, doesn't take part in hydrogen bonding interaction, as the oxygen atom of P=O group is a better H-atom acceptor than the oxygen atom of the 2-ClC<sub>6</sub>H<sub>4</sub>O group. In the hydrogen bonding pattern of (II), the oxygen atom of P=O group in each of symmetry-independent molecules acts as a double hydrogen bond acceptor and interacts with two N—H units of adjacent molecules. This aggregation led to a 2-D network parallel to the *bc* plane with forming the hydrogen-bonded motifs of R<sub>2</sub><sup>2</sup>(8) (cyclic dimer motif) and R<sub>6</sub><sup>4</sup>(20) (cyclic hexamer motif) (Fig. 4). In contrast to structure (I), the oxygen atom O4 from 2-ClC<sub>6</sub>H<sub>4</sub>O groups in molecule P2 of structure (II), participates in a weak C—H...O hydrogen bonding which causes to change dimensionality from 2-D to 3-D.

The most important interactions in both structures (N—H...O=P) are monitored in the related Hirshfeld surface maps (Fig. 5), which appeared as two large red regions. In the structure (I), there is no another significant interaction with separation less than Van der Waals radii for neighbourhood atoms, whereas in (II), the highlighted C—H...O interaction (related to the interaction between O4 atom of the 2-ClC<sub>6</sub>H<sub>4</sub>O group and carbon atom of phenyl ring) is seen as small red spot (Fig. 5).

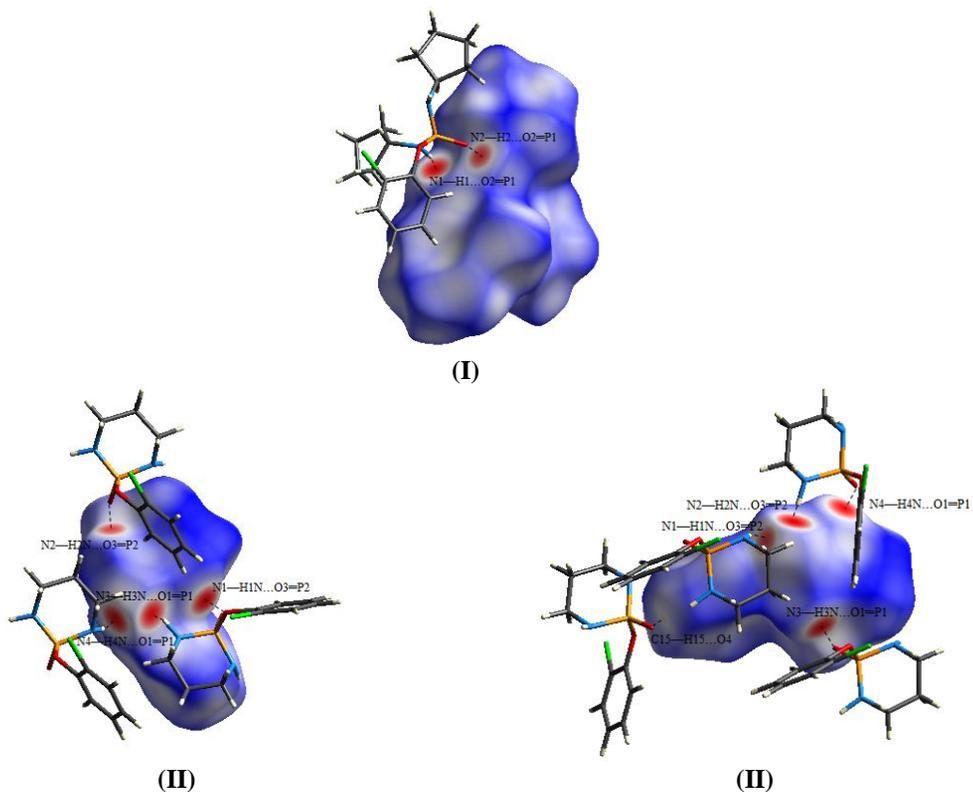
The fingerprint plots (FPs) of the Hirshfeld surfaces were illustrated in Fig. 6. The O...H interactions in two structures were recognized by two sharp spikes with the shortest distance near to the 2.2 Å for the N—H...O=P hydrogen bonds. The other interactions in (I) and (II) are as follow: for (I) H...H (67.1%), Cl...H (12.2%), O...H (11.3%) and C...H (8.7%), and for (II) H...H (47.0%), C...H (15.4%), Cl...H (15.1%) and O...H (14.8%), C...Cl (3.6%) and N...H (3.5%).



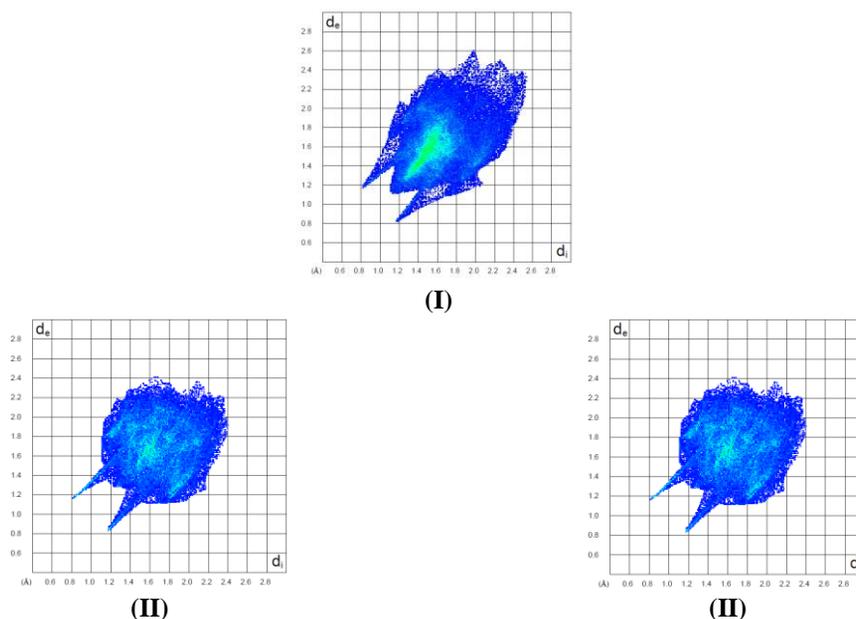
**Fig. 3.** Part of the crystal packing of (I) with the hydrogen bonds shown as dotted lines (the C bound hydrogen atoms are omitted for clarity)



**Fig. 4.** A view of the two-dimensional array of (II) built from N—H...O=P hydrogen bonds (the C bound hydrogen atoms are omitted for clarity)



**Fig. 5.** Hirshfeld surface maps for (I) (top) and for symmetry-independent molecules of (II) (bottom)



**Fig. 6.** Fingerprint plots for (I) (top) and for symmetry-independent molecules of (II) (bottom)

**Table 1.** Crystal data and structure refinement for (I) and (II)

	(I)	(II)
Empirical formula	$C_{16}H_{24}ClN_2O_2P$	$(C_9H_{12}ClN_2O_2P)_2$
Formula weight	342.79	493.25
Temperature (K)	293(2)	300(2)
Wavelength (Å)	1.54186	0.71073
Crystal system	Orthorhombic	Monoclinic
Space group	$Pbca$	$Pc$
Unit cell dimensions	$a = 11.1452(10)$ Å $b = 7.7659(7)$ Å $c = 39.904(3)$ Å	$a = 11.8694(7)$ Å $b = 7.7092(5)$ Å $c = 12.5093(7)$ Å
$\beta$ (°)	90	104.261(4)
Volume (Å <sup>3</sup> )	3453.8(5)	1109.37(12)
Z	8	2
Density (calculated) (Mg/m <sup>3</sup> )	1.318	1.477
Absorption coefficient (mm <sup>-1</sup> )	2.902	0.470
$F(000)$	1456	512
Index ranges	$-12 \leq h \leq 13, -7 \leq k \leq 8, -47 \leq l \leq 47$	$-14 \leq h \leq 14, -9 \leq k \leq 9, -14 \leq l \leq 14$
Reflections collected	11972	13330
Independent reflections	2312 [ $R_{int} = 0.1333$ ]	3880 [ $R_{int} = 0.0469$ ]
Data/restraints/parameters	11972/0/203	13330/4/283
Goodness-of-fit on $F^2$	0.953	1.057
Final $R$ indices [ $I > 2\sigma(I)$ ]	$R_1 = 0.0665, wR_2 = 0.1923$	$R_1 = 0.0273, wR_2 = 0.0722$
$R$ indices (all data)	$R_1 = 0.0772, wR_2 = 0.2034$	$R_1 = 0.0287, wR_2 = 0.0732$
Largest diff. peak and hole (e.Å <sup>-3</sup> )	0.488 and $-0.436$	0.289 and $-0.158$

## REFERENCES

- [1] Spackman, M. A., Jayatilaka, D. (2009). *Hirshfeld surface analysis*. CrystEngComm, vol. 11, p. 19–32.
- [2] McKinnon, J. J., Spackman, M. A., Mitchell, A. S. (2004). *Novel tools for visualizing and exploring intermolecular interactions in molecular crystals*. Acta Crystallogr B, vol. 60, p. 627–668.
- [3] Alamdar, A. H., Pourayoubi, M., Saneei, A., Dušek, M., Kučeráková, M., Henriques, M. S. (2015). *Hirshfeld surface analysis of two new phosphorothioic triamide structures*. Acta Crystallogr C, vol. 71, p. 824–833.
- [4] Tarahhomi, A., Pourayoubi, M., Golen, J. A., Zargarani, P., Elahi, B., Rheingold, A. L., Leyva Ramírez, M. A., Mancilla Percino, T. (2013). *Hirshfeld surface analysis of new phosphoramidates*. Acta Crystallogr B, vol. 69, p. 260–270.
- [5] Pourayoubi, M., Karimi Ahmadabad, F., Nečas, M. (2011). *rac-Phenyl (benzylamido)(p-tolylamido)-phosphinate*. Acta Crystallogr E, vol. 67, p. o2523.
- [6] Pourayoubi, M., Rheingold, A. L., Chen, C., Karimi Ahmadabad, F., Tarahhomi, A. (2011). *o-Phenyl (tert-butylamido)(p-tolylamido)phosphinate*. Acta Crystallogr E, vol. 67, p. o3405–o3406.