New Method of Analysis of Intermolecular Contacts in the Crystal Structure: π-Complexes

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Abstract—A new method for analysis of intermolecular contacts in the crystal structure based on characteristics of the Voronoi–Dirichlet polyhedra (VDP) is considered using metal π-complexes as examples. The crystal data of the compounds were used to determine the surface area of the VDP faces corresponding to all intermolecular contacts in one π-complex, the total volume of the pyramids with VDP faces as bases and the nuclei of atoms involved in the intermolecular contacts at the vertices, and the total solid angle at which the “intermolecular” VDP faces are seen from the corresponding nuclei of the molecule. A common linear correlation between the enthalpy of sublimation of π-complexes and saturated or unsaturated hydrocarbons and the molecular VDP characteristics was elucidated. On the basis of the results, the enthalpies of sublimation were calculated for some iron π-complexes (for which data on the crystal structure were available) and C_{60} and C_{70} fullerenes.

Recently, the capabilities of the new method of analysis of intermolecular contacts (IMC) in the crystal structures were considered for saturated and unsaturated hydrocarbons [1, 2]. A specific feature of the method is that all characteristics of the IMC in the crystal structures are calculated only on the basis of fundamental crystal-structural information (the space group of symmetry, unit cell parameters, and the basis atom coordinates) without resorting to any interatomic potentials. Quantitative estimate of IMC is done using only parameters of the Voronoi–Dirichlet polyhedra (VDP) of atoms, which are determined unambiguously by the three-dimensional structure of the crystal and which can be calculated without any a priori considerations on the type of bonds between the atoms and without using the crystal chemical radii (in particular, van der Waals radii).

The key goal of the present study is to verify experimentally the applicability of the method [1, 2] to analysis of the IMC in the crystal structures of transition metal π-complexes.

It is known [3–9] that the VDP of some atom A surrounded by atoms Y is a convex polyhedron whose surface is formed by the planes that pass through the midpoints of the A–Y segments connecting the A atom with all neighboring Y atoms and are located normal to the segments. In the crystal structure, every crystallographic sort of atoms (A, Y, etc.) is described by a VDP of a definite shape, size, and symmetry whose parameters are dictated unambiguously by the mutual spatial arrangement of all atoms in the structure. The VDP adjoin one another through common faces and thus fill the whole space of the crystal and form the Voronoi–Dirichlet splitting. Each VDP face corresponds to a particular pair interatomic contact and is matched by a solid angle at which this face is “seen” from the neighboring nuclei. Therefore, the VDP underlie a three-dimensional image of a chemical bond as a bipyramid whose base is the common VDP face of two neighboring atoms, A and Y, while the apical positions are occupied by the nuclei of the proper atoms [5].

Apart from the interatomic distance r(A−Y), which is the altitude of the above-mentioned bipyramid and the only characteristics of a pair interatomic contact used in traditional crystal chemistry, three additional parameters are introduced to describe quantitatively the contact between the A and Y atoms. These include the area of the common face (Sij), the solid angle (Ωij) at which this face is “seen” from the A or Y nucleus, and the volume (Vij) of the pyramid whose base is the common face of the VDP and the vertex is occupied by the A or Y nucleus. From this standpoint, a criterion for direct contact between some atoms, A_{i} and Y_{j}, in the crystal is that the VDP of these atoms share a face. Therefore, in what follows, all Y_{j} atoms for which S_{ij}, Ω_{ij}, or V_{ij} differ from zero are regarded as the environment (or neighbors) of the A_{i} atom.

Since the full solid angle equals 4π steradian for any point in the three-dimensional space, then, irrespective of the mode of spatial arrangement of atoms and the distances between them, due to the requirement

\[ \sum_{j} \Omega_{ij} = 4 \pi \text{sr}, \]

the number of Y_{j} atoms surrounding an A_{i} atom taken as the central one is always a finite value equal to the number of VDP faces of this atom. Thus, with inclusion of all neighbors Y, an atom A always forms a quasi-complex AY_{f} where f is the number of VDP faces of the A atom. A systematic analysis of the VDP characteristics of different elements has shown [6–9] that f is most often greater than the traditional coordination number (C.N.) of the atom. For example, in the Fe(C_{5}H_{5})_{2} structure [10], the Fe, C(1), and H(1)
VDP (Table 1, Fig. 1) have 20, 10, and 23 faces, whereas the classical C.N.s of these atoms are only 10, 4, and 1.

Since \( f \geq \text{C.N.} \), to describe the real environment of the \( A \) atom in the crystal structure, we will transform \( AY_f \) to the form \( AX_nZ_m \), where \( f = n + m \). The formula \( AX_nZ_m \) also takes into account all neighbors \( Y \); however, unlike (1), they are divided into two types, \( X \) and \( Z \). The character \( X \) designates the atoms that form strong chemical bonds (in the general case, covalent, metallic, or ionic bonds) with the central atom and that are taken into account by the classical crystal chemistry in determining the C.N. of the \( A \) atom and in describing the shape of its coordination polyhedron. The character \( Z \) designates other atoms of the environment that do not form chemical bonds with the central atom \( A \), according to the existing views, i.e., do not belong to the first coordination sphere of \( A \). Below, all non-valence contacts are designated by \( A/Z \), the slash denoting the common VDP face of the atoms indicated on both sides of the slash.

Sorting of the VDP faces of an \( A \) atom in the structure of any compound into valence (\( A-X \)) and non-valence (\( A/Z \)) ones (in other words, the \( AY_f \rightarrow AX_nZ_m \) transformation) can be accomplished by the method of intersecting spheres [6] embodied in the TOPOS software [7]. Although the method [6] provides objective and unambiguous identification of all non-valence contacts (for example, Table 1), the question of whether a particular \( A/Z \) contact is intra- or intermolecular has been difficult to answer until recently. Answering this question unambiguously has required introduction of one more characteristic of any VDP face, namely, the rank.

According to published data [1, 2], the rank of a face (RF) indicates the smallest number of chemical bonds connecting the \( A_i \) and \( Z_j \) atoms in the structure whose VDP form this face. If such bonds are missing, RF = 0. In other words, the \( A \) and \( Z \) atoms whose VDP share a face with RF = 0 are parts of different molecules (chains or layers) and, hence, it is impossible to travel from one atom to the other along a continuous chain of chemical bonds in the crystal structure. The RF is non-zero (positive and integer) only in the case where the common VDP face is formed by the polyhedra of atoms occurring within the same molecule, chain, layer, or a framework. Naturally, for the common face of two chemically bonded \( A \) and \( X \) atoms, the RF is always equal to unity. For example, in the \( \text{Fe}(\text{C}_5\text{H}_5)_2 \) structure, these faces match only \( \text{Fe}–\text{C} \), \( \text{C}–\text{C} \), or \( \text{C}–\text{H} \) bonds (Table 1). Meanwhile, for a common face of the VDP of any hydrogen atom and the central iron atom of the same ferrocene molecule (\( \text{Fe}/\text{H} \) contacts), RF = 2.

Fig. 1. VDP of (a) \( \text{Fe} \), (b) \( \text{C}(1) \), and (c) \( \text{H}(1) \) in the ferrocene structure [10]. The hatched face of the \( \text{Fe} \) VDP corresponds to the \( \text{Fe}–\text{C}(1) \) bond. The three-dimensional image of this bond is a bipyramid whose base is the hatched face and the apical positions are occupied by the \( \text{Fe} \) and \( \text{C}(1) \) nuclei. The characteristics of all \( \text{Fe} \), \( \text{C}(1) \), and \( \text{H}(1) \) VDP in the ferrocene structure are summarized in Table 1. The atom numbering in Fig. 1 and in Table 1 is the same.