

Elucidation of molecular crystals with one-, two- or three-dimensional geometrical models

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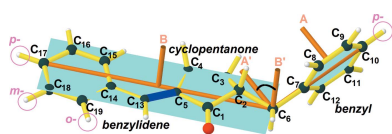
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The spatial structure of molecular crystals is a real challenge for explanation and prediction. Although the general model in which such crystals are considered as a packing of molecules seems clear and unambiguous, the devil is in the details. Since organic molecules possess an unlimited diversity of sizes, shapes and active centers of specific intermolecular interactions (hydrogen bonds, halogen–halogen interactions, *etc.*), the arrangement of a particular molecule depends on many parameters. The crucial point in the rationalization of a molecular crystal structure consists in revealing these parameters and establishing their importance for the structure formation. Thus, the invention of new structural descriptors, *i.e.* concepts or magnitudes that characterize molecular crystals, is always valuable. Among them, geometrical descriptors are the simplest and most obvious and retain their importance despite the evident progress of the high-throughput computer modeling (Oganov *et al.*, 2019).

The oldest but still relevant geometrical approach to the understanding of the architecture of molecular crystals was proposed by Kitaigorodsky (1961). This approach is based on a three-dimensional model of close packing of rigid molecules, similar to the model of the closest packing of rigid atoms in inorganic crystal chemistry. Despite differences in the shape of atoms, which are considered balls, and organic molecules, Kitaigorodsky's approach exhibited its viability and revealed similarities in the structure of atomic and molecular packings. In particular, both packings prefer to have coordination number 12 and are assembled from close-packed layers with a hexagonal structure. However, this model does not account for the details of the molecular shape and specific interactions between molecules that result in a number of deviations from the general trends in the crystal organization. In particular, Kitaigorodsky (1973) mentioned that molecular coordination numbers often differ from 12 and values 10 or 14 are also widespread. To formalize Kitaigorodsky's approach, Fischer & Koch (1979) proposed representing molecules by their Voronoi polyhedra, *i.e.* the unions of the Voronoi polyhedra of atoms, which compose the molecule. Peresypkina & Blatov (2000) implemented Fischer & Koch's model into software, analyzed molecular packings in all available organic crystals and showed that coordination number 14 is the most abundant. This conclusion does not contradict the close-packing approximation if one considers the molecules as deformable and flexible objects. Thus the three-dimensional model has exhibited its efficiency in the analysis of the molecular packing as a whole; however, to reveal the details of the crystal architecture one could need other approaches.

The paper by Thomas & Hughes (2023) proposes such approaches and provides an essential contribution to the problem under discussion. The authors supplement the three-dimensional model with two other geometrical models that treat the molecular packing at lower dimensions. The first model can be called one-dimensional since it represents a molecule as a chain of rods; each rod is directed along the longest principal axis of inertia of a selected section of the molecule. The molecules considered in the paper are represented as chains of two hinged rods, but it seems this approach can be extended to more complicated cases of chain-like molecules with many sections. Such a model is simpler than the Voronoi polyhedron representation but preserves the general shape of the molecule and enables one to clearly visualize a molecular packing. It seems however that this approach is inapplicable to discotic or polyhedral molecules, where two or even three principal axes of inertia are of equal length. The second model perceives a molecular packing as a series of two-dimensional slices. The molecules in the slices can be represented as unions of atomic van der Waals spheres, polygons built for the centers of



intermolecular voids or Dirichlet domains, *i.e.* two-dimensional analogs of Voronoi polyhedra, which are constructed for the systems of molecular centroids. Such an approach enabled the authors to explore the molecular packings in more detail than the three-dimensional model permitted and to find similarities and differences in two series of organic crystals: five sulfathiazole polymorphs and 16 substituted 2-benzyl-5-benzylidene cyclopentanones. An important advantage of the two-dimensional model is that it provides a diagram showing both the densest and the rarest places of the molecular packing as well as the low-density space where the molecular ends come together ('junction zones' in the authors' terminology). In addition to the geometrical consideration, the authors estimated the intermolecular interactions using the semi-empirical potentials given by Gavezzotti & Filippini (1994).

As a result, a number of new geometrical descriptors have been proposed that provide a detailed description of molecular packings and essentially supplement the three-dimensional model. This approach seems very efficient in the analysis of series of chemically similar molecular crystals as was demonstrated by the authors. However, it is hardly applicable for an automated analysis of big crystallographic data, where the Voronoi polyhedron model is preferable (Peresypkina & Blatov, 2000).

The paper by Thomas & Hughes (2023) is quite heavy for an initial reading due to many details that the proposed approach provides for each molecular structure. I would recommend the reader to start from the paper by Thomas (2015) where some

basic concepts of the approach were introduced. Then if the reader wants to have just a general idea of the approach the parts 'Method and Discussion' should be enough, while parts 3 and 4 are good for a deeper insight. On the other hand, I would encourage the authors to adjust this promising approach for a wide application by making their software *PROCUSTES* (Thomas, 2022, unpublished) available for downloading and usage. This is the spirit of the time: new theoretical approaches should be implemented into user-friendly software as soon as possible. Since the authors intend to develop this topic it would be interesting to read in their next paper(s) about the limitations and possible improvements of the approach. For this purpose, the variety of the analyzed molecular crystals should be essentially extended. That is what the authors actually promise at the end of the paper, so let us wait for their new contributions.

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