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Editorial

Special Issue Editorial: Chemical Bonding in Crystals and Their Properties

Anna V. Vologzhanina * and Yulia V. Nelyubina

A. N. Nesmeyanov Institute of Organoelement Compounds, RAS. 28 Vavilova str., 119991 Moscow, Russia; unelya@ineos.ac.ru

* Correspondence: vologzhanina@mail.ru

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Relations between physicochemical properties of chemical compounds exploited in many modern applications (including optical, magnetic, electrical, mechanical, and others) and interatomic interactions that operate in their crystals are the key to the successful design of new crystalline materials, in which X-ray crystallography has proved to be an invaluable tool. In addition to the advanced approaches in charge-density analysis that provide insights into the nature of chemical bonding, the information collected over the years by this technique and stored in huge databases has a tremendous use in drug design and other areas of material science.

This Special Issue covers a diverse range of 'structure–property' and 'composition–structure' relations identified through X-ray diffraction. Two reviews [1,2] and five articles [3–7] were submitted and published.

In reference [1], possible interconnections between crystal properties and molecular and crystal structures were summarized. This paper clearly demonstrates how the knowledge of molecular geometry and intermolecular interactions, of bonding preferences for some motifs, synthons and tectons extracted from the Cambridge Structural Database can be used for material chemistry, crystal engineering, pharmaceutical, and agrochemical research. Numerous examples of polymorphism rationalization, co-crystal design, control over crystal morphology, rationalization of mechanical and sorption properties, and studies of hydration/dehydration mechanisms were described.

The review [2] on chemical bonding in crystals of low-melting organoelement compounds allowed for the identification of a linear relation between the molecular volume or a Hirshfeld surface area and the energy of the crystal lattice for compounds with similar types of predominant intermolecular interactions. It was demonstrated that these compounds are typically involved in weak- and medium-strength interactions while strong bonding, if any, is responsible for the formation of isolated molecular associates.

As the analysis of weak intermolecular interactions requires highly accurate experimental or computational data, the authors of [3,5] used periodic density functional theory (DFT) calculations to study the role of F...F interactions in fluorinated tosylates and of halogen and chalcogen bonding in thiazolo[2,3–b][1,3]thiazinium triiodides, respectively. Such an approach when combined with the quantum theory of "Atoms-in-Molecules", electron localization function, noncovalent interactions method, or other partitioning schemes provides insight into weak interatomic interactions and even quantifies their strength. In particular, in reference [3], an almost linear dependence was uncovered between the contribution of interactions involving fluorine atoms to the lattice energy and the amount of fluorine atoms, although its increase does not lead to crystal packing stabilization. On the other hand, numerous noncovalent interactions of triiodides were attributed to a stronger I–I bond within the triiodide anion, acting as a stabilizing factor and providing a comparatively higher thermal stability and iodine retention in the melt [5].

Among other experimental techniques, Raman spectroscopy was found to be useful for understanding the bonding features of the triiodide anion [5]; however, weak intermolecular interactions can also be identified by other spectroscopic tools. For example, a study [4] of a series of salts of boron cluster anions with protonated organic bases demonstrated that dihydrogen bonds have characteristic absorption bands in the FT-IR spectra of solids, which can therefore be used to recognize these bonds even in the absence of crystallographic data [4].

Unlike the other papers in this Issue, reference [6] focuses on intermolecular interactions and supramolecular associates found in crystals of RNA. An analysis of H-bond connected sextuples of RNA bases collected in the Protein Data Bank and relative occurrences of the sextuples allowed the authors of [6] to classify some of them as a novel RNA tertiary motif.

In a comparative study of strong hydrogen bonds and weak interactions in racemic and enantiopure thiophosphorylated thioureas [7], a new synthetic pathway was suggested to control the chirality of their Ni(II) complexes at both the molecular and supramolecular levels.

In summary, this Special Issue covers very different aspects of structure–property relations identified by X-ray diffraction and complementary techniques (from conventional IR and Raman spectroscopies to cutting-edge quantum chemical calculations) and their application in crystal engineering and material science.

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References

1. Vologzhanina, A.V. Intermolecular Interaction in Functional Crystalline Materials: From Data to Knowledge. *Crystals* **2019**, *9*, 478. [CrossRef]
2. Volodin, A.D.; Korlyukov, A.A.; Smol'yakov, A.F. Organoelement Compounds Crystallized in Situ: Weak Intermolecular Interactions and Lattice Energies. *Crystals* **2020**, *10*, 15. [CrossRef]
3. Arkhipov, D.E.; Lyubeshkin, A.V.; Volodin, A.D.; Korlyukov, A.A. Molecular Structures Polymorphism the Role of F...F Interactions in Crystal Packing of Fluorinated Tosylates. *Crystals* **2019**, *9*, 242. [CrossRef]
4. Avdeeva, V.V.; Vologzhanina, A.V.; Malinina, E.A.; Kuznetsov, N.T. Dihydrogen Bonds in Salts of Boron Cluster Anions $[B_nH_n]^{2-}$ with Protonated Heterocyclic Organic Bases. *Crystals* **2019**, *9*, 330. [CrossRef]
5. Yushina, I.; Tarasova, N.; Kim, D.; Sharutin, V.; Bartashevich, E. Noncovalent Bonds, Spectral and Thermal Properties of Substituted Thiazolo[2,3-b][1,3]thiazinium Triiodides. *Crystals* **2019**, *9*, 506. [CrossRef]
6. Hamdani, H.Y.; Firdaus-Raih, M. Identification of Structural Motifs Using Networks of Hydrogen-Bonded Base Interactions in RNA Crystallographic Structures. *Crystals* **2019**, *9*, 550. [CrossRef]
7. Kataeva, O.; Metlushka, K.; Yamaleeva, Z.; Ivshin, K.; Zinnatullin, R.; Nikitina, K.; Sadkova, D.; Badeeva, E.; Sinyashin, O.; Alfonsov, V. Chirality Control in Crystalline Ni(II) Complexes of Thiophosphorylated Thioureas. *Crystals* **2019**, *9*, 606. [CrossRef]