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EDITORIAL

Tribute to pioneers: introduction to the contributions on bonding and structure

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On November 1, 2021, we announced the organization of a special collection of papers under the ambitious title "Bonding and Structure," where by structure the emphasis was given to geometry. This call was issued in answer to prior interest expressed by many potential authors internationally. The publication of the issue was envisioned for the beginning of 2023 as the first issue of Volume 34 of *Structural Chemistry*.

Formally, all these plans have been fulfilled, and the collection is coming out in the first issue in 2023, but the interest in participation dwindled as compared with that prior to the announcement. At least one of the reasons was the poisoning of the atmosphere by the tragic war involving two of the countries whose scientists had planned active participation. The loss of lives, livelihoods, and conditions of work have contributed. Here, we express our unconditional solidarity with those who have suffered from this unjustifiable war following Russia's ruthless attack against Ukraine.

Even so, a valuable content has come together in this special collection. One of the purposes of this project was to remember a number of important contributors to the broad domain of structural chemistry who had some jubilees around the time of the collection and publication of this issue. Here, the names with dates are augmented with information about relevant current and earlier publications: Richard Bader (1931−2012), Lawrence L. Bartell (1923−2017) [1], Mirra E. Dyatkina (1915−1972), Jack D. Dunitz (1923−2021) [2], Ronald J. Gillespie (1924−2021) [3–5], Aleksandr I. Kitaigorodsky (1914−1985) [6][1], Kurt Mislow (1923–2017) [7], Max F. Perutz (1914−2002) [8, 9], Yakov K. Syrkin (1894−1974), and Vladimir M. Tatevsky (1914−1999).

Bader is well known, perhaps, best known, for his atoms-in-molecules model [10]. This was also the term William E. Moffitt (1925–1958) used for his approach in investigating electronic energies of molecules [11]. As Moffitt died tragically early, his teachings could not fully develop, but they still constituted a considerable body of advancement. For example, he noted the poor results obtained for chemical binding energies. These were small energies derived as the difference between two very large and not very accurately known energies: the total molecular electronic energy and the sum of the electronic energies of its constituting atoms. Instead, he treated the interaction between the atoms in the molecule as a perturbation and its effects separated from the atomic internal energies. Let us remember Moffitt with his uplifting words: "I am a scientist because I enjoy being one more than anything else. I find nothing so satisfying as trying to form convincing bridges between the elegant and elementary principles of modern physics and the much more complicated and yet empirically well characterized situations encountered in chemistry" [12].

Returning to Bader, he and Gillespie were at the same chemistry department at McMaster University, and he used to push Gillespie toward placing his qualitative VSEPR model onto quantum mechanical foundations. This was not necessarily beneficial for the VSEPR model, because its utility was in its simple applicability. Bader's relentless criticism generated a great deal of uncertainty in Gillespie's approach toward his own model. In contrast, Gillespie long resisted opening toward considerations of non-bonded interactions. This I can say from personal experience while working on our joint book, *The VSEPR Model of Molecular Geometry* [13]. Many years after the original 1991 publication of this book, in 2008, he issued a gracious apology: "I wish to express my sincere thanks to the following colleagues and friends: … Istvan Hargittai for the exchange of ideas on molecular geometry over many years, and for his collaboration on the book we wrote together. I also apologize to him not at first taking his strong conviction that ligand

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[1] Kitaigorodsky and Kitaigorodskii have both been used in the English-language literature.

repulsion plays an important role in determining molecular geometry too seriously” ([14] pp. 1326–1327).

The VSEPR model started out as a pedagogical tool and has remained so ever since its inception. It has also made great strides as a research tool, starting with two spectacular successes. One was when Gillespie sent back the spectroscopists to repeat their recording of the spectra of the new substance, $OClF_3$. By analogy with OPF_3, C_{3v} symmetry had been suggested for it, based on spectroscopic evidence. According to the VSEPR model, Gillespie expected C_s symmetry. When the spectra were rerun in a wider interval, it was fully consistent with the lower symmetry. The other conspicuous success was the geometry of XeF_6 for which Gillespie found the suggested O_h symmetry unacceptable, again, based on VSEPR predictions. Indeed, its electron diffraction study showed that its octahedral geometry was considerably distorted. XeF_6 is an AX_6E rather than an AX_6 molecule, where E stands for a lone pair of electrons. These were early successes. Subsequent studies though, many years later, introduced some doubts of the validity of the simple structure of XeF_6 just referred to. A whole series of experimental and computational studies followed, yielding less than unambiguous geometries. They culminated in computational investigations, including both relativistic and nonrelativistic approaches, to determine NMR properties. They suggested that even if XeF_6 exists as O_h or C_{3v} shapes, their energy differences should be very small. Reviewing these studies we wrote, “We might conclude that we still do not know fully the shape and symmetry of the XeF_6 molecule, but we do not know it at a much higher level of sophistication than before” [15].

During the last period of his career, Gillespie became a forceful advocate of the importance of ligand–ligand interactions in shaping molecular geometry, even at the expense of the importance of electron pair interactions. Of course, it is a question of relative sizes: When ligand size is small relative to the central atom, electron pair interactions dominate. This shifts gradually toward the domination of ligand–ligand interactions as the ligand size relative to the central atom increases. Some authors like to distinguish between the predominance of the interactions among valence shell electron pairs and the ligand–ligand interactions as electronic and steric, respectively. However, the ligand–ligand interactions are also interactions between the electron clouds of the respective ligands.

Bartell [1] pioneered the considerations of non-bonded repulsions in shaping molecular geometry. His classic example was an effect on the lengthening of the C–C single bond upon its changing environment [16]. This is consistent with the structural information communicated recently from state-of-the-art computations by Vermeeren et al. [17]. When, some fifty years ago, Bartell visited us in Budapest, he titled one of his lectures “Pauli Mechanics,” an apt choice considering the electrons elbowing for accommodation in a limited space. At the time, and for a long time subsequently, empirical observations called attention to the importance of non-bonded interactions in molecular structure. Such observations facilitated the determination of more complete structures, whether by the analysis of diffraction or spectroscopic experimental data. Such an observation was the constancy of the O…O non-bonded distances in a large series of sulfone molecules at 2.48 ångströms [18]. There were also several other instances where observations of the constancy of non-bonded distances in related molecular structures enhanced the possibilities and reliability of new structural information [19].

In discussing molecular geometry, the interpretation of experimental measurements calls for a caveat as different techniques may produce different geometries for the same structure. The reason is the difference in the relationship between the interaction time for the measurement and the time scale of the given geometry. This becomes increasingly critical when moving from relatively rigid structures toward fluxional ones, as manifested, for example, by Berry pseudorotation (see, e.g., [20]).

Three of the Russian contributors mentioned above, Dyatkina and Syrkin on the one hand and Tatevsky, on the other, are connected in a quirky way through the theory of resonance. Syrkin and his associate, Dyatkina, were pioneers of structural chemistry in the Soviet Union. The original Russian edition of their monograph, *Structure of Molecules and the Chemical Bond*, was followed by its English translation and publication [21]. During the anti-science campaign (combined with an anti-Semitic campaign) in the late 1940s and early 1950s, both Syrkin and Dyatkina lost their jobs. Only in 1957 could they resume full time their research activities at the Kurnakov Institute of General and Inorganic Chemistry of the Soviet Academy of Sciences. On the surface, the anti-science campaign in chemistry was the fierce criticism of the theory of resonance. However, its true meaning was the fear of western ideas of free thinking (see also [22]). Tatevsky was a vocal participant in renouncing the theory of resonance as a product of idealistic views and thus enemy of communist ideology. The official view and actions were to purge science of such enemy teachings and the scientists who cultivated them.

Tatevsky was a “purist” in structural chemistry who throughout his long career disliked everything that was not hard core data. Many in the West also did not like and avoided the application of resonance representations in describing molecular structures. However, what Tatevsky and others did was turning a disagreement in research approach into political controversy and into one that was life-threatening for those who disagreed with them. This sounds extreme and it was, but this was the general state of affairs in science during the Soviet dictator Iosif Stalin’s last years. Tatevsky’s later career, during a more consolidated period of Soviet power, was more ordinary. He was a respected Faculty member, and feared critic, at the Department of Chemistry, Moscow State University, with a good deal of what might be described as a cult of personality in his immediate environment. There was hardly a Master's thesis or a doctoral dissertation that would not have a sentence or two of his praise in its introduction. His insistence on facts and measurements earned him respect both at home and internationally, so did his books, among them, his advanced text on molecular structure, which, however, reached only a Russian-speaking readership [23].

I would like to pay a special tribute to Kitaigorodsky (Kitaigorodskii) for he had a vision of crystallography, looking for regularities and he found them. His observations regarding the relative frequency of crystal structures of various symmetries have withstood the test of time. He lived and worked under arduous conditions in an environment that punished him for his independence of thought by denying him proper recognition. His pupils and their pupils have become renowned scientists all over the world [6].

References

1. Hargittai I (2003) Candid science III: more conversations with famous chemists. Edited by M Hargittai, Imperial College Press, London. Chapter 5, ‘‘Lawrence S. Bartell,” 58–79
2. Hargittai I (2022) Jack D. Dunitz (1923–2021): a chemists' crystallographer. Struct Chem 33:291–297
3. Hargittai I (2009) Ronald J. Gillespie; the VSEPR model; and molecular symmetry. Struct Chem 20:155–159
4. Hargittai I (2003) Candid science III: more conversations with famous chemists. Edited by M Hargittai, Imperial College Press, London. Chapter 4, ‘‘Ronald J. Gillespie,” pp 48–57
5. Hargittai I (2023) Reminiscing about Ron Gillespie. Struct Chem 34 in this issue. https://doi.org/10.1007/s11224-022-02039-2
6. Hargittai I (2013) Buried glory: portraits of Soviet scientists. Oxford University Press. Chapter 11, ‘‘Aleksandr Kitaigorodskii: Soviet maverick,” pp 250–266
7. Hargittai B, Hargittai I (2023) Kurt Mislow centennial – he changed the way people think about stereochemistry. Struct Chem 34, in this issue.https://doi.org/10.1007/s11224-022-02010-1
8. Hargittai I (2002) Candid science II: conversations with famous biomedical scientists. Edited by M Hargittai, Imperial College Press, London. Chapter 18, ‘‘Max F. Perutz,” pp 280–295
9. Hargittai I (2022) On the origins of isomorphic replacement in protein crystallography. Struct Chem 33:635–639
10. Bader RFW, Nguyen-Dang TT (1981) Quantum theory of atoms in molecules – Dalton revisited. Adv Quantum Chem 14:63–124
11. Wilson EB (1959) Prof. William Moffitt. Nature Vol 184, No 4679 pp 21–22
12. Doty P, Van Vleck JH, Wilson EB Jr, Woodward RB (1959) William Eduard Moffitt (Obituary) as received as a copy of manuscript from Roald Hoffmann via e-mail, August 6, 2022
13. Gillespie RJ, Hargittai I (2012) The VSEPR model of molecular geometry. Dover. Original edition: 1991, Allyn and Bacon
14. Gillespie RJ (2008) Fifty years of the VSEPR model. Coord Chem Rev 252:1315–1327
15. Hargittai I, Menyhárd DK (2010) Further VSEPRing about molecular geometries. J Mol Struct 978:136–140
16. Bartell LS (1968) Molecular geometry: bonded versus nonbonded interactions. J Chem Educ 1968(45):754
17. Vermeeren P, van Zeist W-J, Hamlin TA, Fonseca Guerra C, Bickelhaupt FM (2021) Not carbon s–p hybridization, but coordination number determines C-H and C–C bond length. Chem Eur J 27:7074–7079
18. Hargittai M, Hargittai I (1987) Gas-solid molecular structure differences. Phys Chem Minerals 14:413–425
19. Hargittai I (1985) The structure of volatile sulphur compounds. Akadémiai, Budapest and Reidel, Dordrecht, Boston, Lancaster
20. Hargittai I, Hargittai B (2023) R. Stephen Berry and the Berry pseudorotation. Struct Chem 34 in this issue. https://doi.org/10.1007/s11224-022-02009-8
21. Syrkin YK, Dyatkina ME (1950) Structure of molecules and the chemical bond. Dover edition (1964). Original Russian edition: Сыркин ЯК, Дяткина МЕ (1946) Химическая связь и строение молекул. Учебное пособие. Госхимиздат, Москва
22. Hargittai I (2013) Buried glory: portraits of Soviet scientists. Oxford University Press. Chapter 12, ‘‘Aleksandr Nesmeyanov: brilliant administrator and Soviet courtier,” pp 268–287, see, in particular, pp 280–284
23. Татевский ВМ (1977) Строение молекул. Химия, Москва