

## The twentieth year in *Structural Chemistry*

István Hargittai · Attila Kovács

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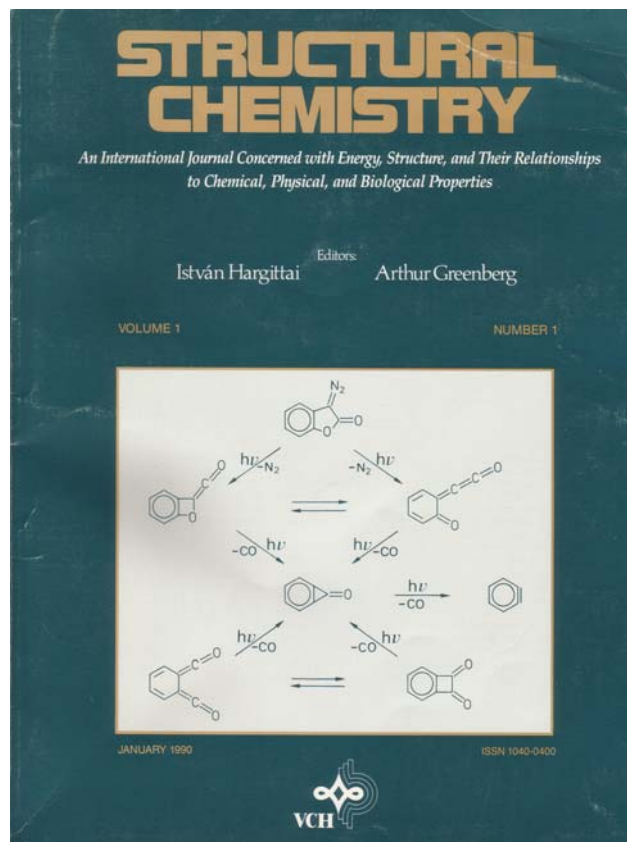
**Abstract** Twenty years ago our journal *Structural Chemistry* was founded with the primary purpose of providing a quality venue for reports that present the result of complex studies of chemical and biological systems and in the field of materials science, using diverse physical and computational techniques simultaneously and in a concerted way and that are concerned with the chemical, biological, and physical implications of the findings. A sampler of contributions witnesses the fulfillment of this goal and points justified expectations of a bright future for our publication.

**Keywords** Structural chemistry · Crystallography · Liquid-phase studies · Gas-phase studies · Spectroscopy · Theoretical studies · Modeling

Matter is much more complicated than most materialists believe, or even are capable of imagining. What is yet to be discovered about the structure of molecules will contain many surprises. Edward Teller [1]

I. Hargittai (✉) · A. Kovács  
Department of Inorganic and Analytical Chemistry  
and Materials Structure and Modeling Research Group  
of the Hungarian Academy of Sciences, Budapest University  
of Technology and Economics, P.O. Box 91,  
1521 Budapest, Hungary  
e-mail: istvan.hargittai@gmail.com

A. Kovács  
e-mail: akovacs@mail.bme.hu



Cover of the first issue of *Structural Chemistry*, Volume 1, 1990

It was some time in the spring of 1988 when one of us (IH) during his visiting professorship at the Chemistry Department of the University of Connecticut, gave a talk at the Naval Research Laboratory in Washington, DC. There, IH met Joel Liebman, and through him, got acquainted with his friend, Arthur Greenberg of New

Jersey Institute of Technology. IH and Greenberg found a lot of common interest and their discussions led to the idea of a new journal called *Structural Chemistry*. IH at the time was connected with VCH Publishers, New York, as they were then, which had published the soft cover version of the first edition of the book *Symmetry through the Eyes of a Chemist*, which had appeared a couple of years before in hardcover version by VCH Weinheim. Martin Grayson, the publisher, welcomed the idea of the new journal, and soon preparations started for the first issue. From the start, we wanted it to be a quality journal with strong reviewing; we put together a distinguished Editorial Board, which was a good mix of big names and active researchers. The name of the journal has remained the same although its subtitle has changed from “An International Journal Concerned with Energy, Structure, and Their Relationship to Chemical, Physical, and Biological Properties” to today’s “Computational and Experimental Studies of Chemical and Biological Systems.” The subtitle has become shorter, but the essence of the scope has not changed. We had 35 members of the Editorial Board initially with Joel Liebman as Consulting Editor, Magdolna Hargittai as Book Reviews Editor, and Susan Greenberg as Assistant Editor. It is noted with sorrow that Jeremy K. Burdett, Jacques-Emile Dubois, and Amatz Y. Meyer of the initial Editorial Board are no longer around; we miss them, and remember them fondly. At some point, Art Greenberg resigned from his editorship because of his administrative duties at his university, but has continued to serve as member of the Editorial Board. A new editorial structure was set up with IH as Editor-in-Chief and Jerzy Leszczynski of Jackson State University assumed the role of Editor. Sue Greenberg left the Board and Judit Szűcs of Budapest University of Technology and Economics joined it as Editorial Assistant. We have worked now for years in this composition managing the journal in the greatest harmony.

The scope of *Structural Chemistry* has hardly changed, but it may be instructive to quote here the description in the first issue and the one that we have displayed lately. We wrote in the first issue:

The aim of *Structural Chemistry* is to overcome the unnatural separation that exists in the current literature among structure determination, energetics, and applications and to build a bridge to other chemical disciplines. It is comprehensive, embracing the condensed and gaseous states of matter and involving the numerous techniques for the determination of structure and energetics, their results, and the conclusions derived from these studies. *Structural Chemistry* emphasizes a broad discussion of results, observation of relationships among various properties, and

description and application of structure and energy information in all domains of chemistry.

Among the topics of interest to this journal are experimental structure determination (X-ray, neutron, and electron diffraction; microwave spectroscopy, NMR, IR, and UV spectroscopies, nuclear techniques), experimental thermochemistry (enthalpies of combustion and reaction as well as gas-phase ion energetics), and other relevant techniques such as photoelectron spectroscopy. Computational studies and new structural models and bonding theories as well as new methodologies are also of interest.

Twenty years later, here it is what we have for our scope and aims:

*Structural Chemistry* is an international forum for the publication of peer-reviewed original research papers, communications, reviews, book reviews, and topical special issues. *Structural Chemistry* recognizes and encourages the strong complementarity between theoretical and experimental chemistry that forms the basis for modern structural chemistry. Indeed, structural chemistry is the foundation for understanding chemical energetics, reactivities, and physical and biological properties, and the journal views itself as building bridges to other disciplines that had not previously recognized these connections so explicitly. The journal is comprehensive, embracing all states of matter and all techniques for the determination of structure and energetics. In particular, it recognizes the growing importance of computational chemistry in structural chemistry and in linking structural chemistry with the rest of chemistry and related fields, such as molecular biology. *Structural Chemistry* emphasizes a broad discussion of results, observation of relationships among various properties, and description and applications of structural and energy information in all domains of chemistry. Among the topics of interest to *Structural Chemistry* are computational studies as well as new structural models and theories of bonding, experimental structure determinations and methodological innovations, thermochemistry, and other relevant areas.

There has been some change in emphasis, which could be summarized in two items, one, computational studies, and the other, biological systems. In the following, we are going to single out a few papers that may be characteristic for our publication and it is hoped that they in their totality convey the flavor of the journal. The choice is admittedly arbitrary and subjective, and, also, eclectic, and it does not in any way express a value judgment with respect to those

many more papers that are not being mentioned below. At the end of this note, we will try to chart the future of our journal at least for a few forthcoming years.

## Crystallography

The most widely used experimental method for determination of crystal and molecular structure is X-ray diffraction. There are several journals devoted to this field: *Acta Crystallographica (Sections A–F)*, *Journal of Applied Crystallography*. We have tried to encourage publication of such papers in *Structural Chemistry* that go beyond routine structure determination and mere presentation of structural information.

One of the main questions in bio-organic research is the identification and characterization of hydrogen bonds. Julius Rebek, Jr. [2] analyzed the structure of histidine, a molecule that is found at the active sites of several enzymes. He pointed out that this molecule is able to transfer protons in a variety of directions due to a rotation around the single bond between C5 of histidine and the main molecule. The feasibility of his proposal was demonstrated on the crystal structure of  $\alpha$ -chymotrypsin.

Infantes and Motherwell [3] developed an empirical method for predicting hydrogen-bonding motifs for pyrazoles and oximes in the crystalline phase. Analyzing related structures in the Cambridge Structural Database, they found the accessible surface (fraction of the atomic surface available for interaction) of the nitrogen atoms as a discriminator to divide structures into dimer/tetramer and trimer/catemer (infinite chain) motifs for both types of compounds.

Crystals are built up by competing intermolecular interactions. Among them the strong ones determine the primary characteristics of the crystal structures, like the charge-assisted  $-\text{NH}_3^+ \cdots ^-\text{OOC}-$  hydrogen bonds generating either one-dimensional ribbons or two-dimensional sheets in benzylammonium benzoates [4]. The effect of the weaker halogen–halogen,  $\pi$ – $\pi$ , or C–H $\cdots$ X (X = heteroatom) intermolecular interactions on the structure was found to be rather limited in this type of compounds.

Charge-assisted hydrogen bonding appears also in super-molecules like the ones formed from dialkylammonium cations and crown ethers by  $\text{N}^+-\text{H}\cdots\text{O}$  and C–H $\cdots\text{O}$  hydrogen bonds. With multiple dialkylammonium centers and/or larger crown ethers, multiply stranded or multiply encircled super-molecules could be prepared. The basic step in these non-covalent syntheses was the evaluation of the character of the charge-assisted hydrogen bonding interactions by X-ray crystallography [5].

X-ray diffraction played an important role in the structure determination of novel macrocyclic uracil derivatives

[6]. Semenov et al. used a combination of experimental techniques (X-ray diffraction, IR, UV, NMR spectroscopy, and dipole moment measurements), and their investigation revealed the characteristic twist of the macrocyclic ring upon solvent effects with respect to the solid-phase structure.

The huge database on crystal structures has facilitated the evaluation of general trends in the variations of intermolecular and intramolecular interactions on the basis of geometrical characteristics. A representative case was the work by Shimoni and Glusker who analyzed the propensity of C–F groups to form C–F $\cdots$ H–C interactions with C–H groups on other molecules [7]. They found the C–F $\cdots$ H–C interactions to be generally weak and less favorable than C–O $\cdots$ H–C, when a C=O/C–O group is also present. On the other hand, in the absence of other hetero-atoms, the C–F $\cdots$ H–C interactions were found dominating the resulting crystal packing.

The intriguing phenomenon of two-metal binding motifs in protein crystal structures has been elucidated by Glusker et al. upon a crystallographic structural database analysis and joint density functional theory calculations on model complexes [8]. Such metal ions assist the protein to maintain a required folding shape or aid in the chemistry of their enzymatic mechanism. The repulsion of the two metal ions being some 3–6 Å apart is compensated for by bridging small anionic moieties, like hydroxide ions in the case of the shorter (around 3 Å) distances.

An important goal of structural chemistry is to provide information on structure–chemical reactivity and structure–biological activity relationships. Related studies have yielded considerable progress in both aspects. Klebe [9] used a set of examples to demonstrate how these relationships can be evaluated by the joint analysis of crystallographic data with those from spectroscopic, kinetic, and computational techniques. Within this complex task, the ground-state structures were provided by crystallography while information on the dynamic processes (molecular transformations, intermediates, transition states, conformational interconversions, and intermolecular interactions) could be extracted from the other techniques. The examples included conformational flexibility of Ph–X–Ph (X = CH<sub>2</sub>, C=O, etc.) type molecules, nucleophilic addition of nitrogen to a carbonyl group, S<sub>N</sub>2 substitution at silicon, and topochemical interconversion pathways in penta-coordinate complexes.

Another set of joint analyses comparing solid-phase and solution-phase structures were compiled in the review by Kleinpeter [10]. He discussed the conformational behavior of numerous hydantoin derivatives, their tautomerism and acidity on the basis of NMR spectroscopic and X-ray diffraction results. Some 5,5-diphenyl-hydantoin derivatives displayed biological (anticonvulsant) activity, which could

be related to the arrangement of polar and apolar domains of their structures.

Experience gained from X-ray diffraction molecular structure studies has provided helpful input in molecular modeling for the construction of reasonable initial structures. Dubois and Cossé-Barbi [11] suggested a set of general rules for structure prediction considering mainly steric effects on the basis of crystallographic databanks augmented by spectroscopic and computational results. These qualitative rules have provided assistance in the compilation of initial structures in molecular modeling as well as at other stages in the search strategies for stable conformers.

The review of Beagley and Titloye [12] summarized attempts to model the similarities and differences between the  $\beta$ -cages in sodalite zeolites of type A and zeolites with faujansite frameworks using crystal structure data. The results of modeling provided the lists of coordinates necessary for constructing computer graphics of framework structures and their variation with framework composition and cavity contents. They also predicted the arrangements of ions and molecules within the cavities.

Simmons [13] demonstrated how X-ray diffraction could be used to study the potential energy surface of a molecule. In the example demonstrating the capabilities of his model, he determined several topological features of the adiabatic potential energy surface of pseudo-Jahn–Teller Cu(II) complexes. He also showed how Gaussian displacement parameters could be used to study stereochemically labile molecules.

Wagner et al. [14] studied the change of packing upon a solid-phase reaction. Extracting diethylether from its Lewis acid-base adduct with 2-chloro-2-boraindane in vacuo resulted in a change of the crystal packing. They showed that a complete rearrangement of the crystal occurs in the solid phase, which requires pronounced molecular motion. Accordingly, the reaction times showed strong temperature-dependence.

The phase problem has constituted a major limitation in X-ray crystallography, and Sayre reviewed the situation and provided useful approaches to facilitate the solution of this problem. Thanks to his activities and other innovations, it has become possible to provide a straightforward determination of the atomic arrangements in many systems [15]. Sayre demonstrated also two future directions: (i) more powerful crystal-growing techniques for crystalline compounds, and (ii) fine sampling from arbitrary (non-crystalline) specimens by the free-electron laser-flash technique or by the synchrotron/cryoprotection technique. A related review by Karle and Karle [16] described the work on the development of gas-phase electron diffraction, particularly the application of the non-negativity condition for the results of a diffraction experiment for gaseous

substances. Switching later to X-ray crystallography, they contributed to the solution of the phase problem in the 1950s. Some early applications to complicated structures were demonstrated as examples.

Another paper concerned with future developments in X-ray crystallography was one by Shenoy [17] who compiled the basic characteristics and instrumentation of synchrotron radiation. Synchrotron radiation has several advantageous properties: high brightness, high collimation, broad energy spectrum, variable polarization, coherent power, and sub-nanosecond pulse width. Developments in X-ray techniques like high-resolution monochromatization and submicron focusing open new possibilities for the future.

In 2002, *Structural Chemistry* published a special issue dedicated to the 75th anniversary of Alan L. Mackay, who “has expanded the realm of crystallography, has broken out of the rigid rules of classical crystallography, did pioneering work, among others, in icosahedral packing, discovered what is known today as the Mackay polyhedron, and had predicted the existence of quasicrystals.” This special issue evolved into a collection of important papers on Generalized Crystallography, introduced by Mackay, extending the role of crystallography beyond the determination of crystal and molecular structure. In his own words: “The aim of Generalized Crystallography is to understand the properties of matter, inert and living, at our human scale, in terms of the arrangement and operation of atoms” [18]. Within this interpretation, the structures become carriers of information and are related to growth, form, morphogenesis, and life. In the following, a few representative papers are mentioned from the special issue.

An important contribution to crystallographic interpretation of structural relationships in the framework of Generalized Crystallography was demonstrated by Janner [19]. He showed using the left-handed Z-DNA form of the nucleic acid poly  $d(\text{As}^4\text{T})\cdots$ poly  $d(\text{As}^4\text{T})$  and the heptameric transmembrane pore protein  $\alpha$ -hemolysin as examples of how one can get a faithful integral six-dimensional (6-D) representation leading to a crystallographic approach to structural properties of single molecules with a sevenfold point-group symmetry. The orbifold concept for two-dimensional symmetry groups was assessed by Conway and Huson [20]. They analyzed the correspondence between properties of orbifolds and symmetries in the original surface and presented proofs of the classification of Euclidean and spherical two-dimensional symmetry groups.

The structures carry information on chemical bonding, which can be evaluated by various topological descriptions like the ball and stick model of atoms and bonds, the model of close-packed atoms, models based on linked coordination polyhedra, or those based on scalar fields such as the

electron density distribution. Important aspects of the properties of atoms and three-dimensional space were reviewed by Brown [21] who discussed the topological descriptions of scalar fields (electron density and electrostatic potential) associated with chemical structures. He showed that such topological descriptions reflect directly the localized chemical bonding in non-metallic compounds.

The brief review of Blundell et al. [22] dealt with the symmetry of signaling multi-protein systems. The authors pointed out that, unlike multi-enzyme complexes and viruses, signaling multi-protein systems do not have high point-group symmetries. The required high specificity, reversibility, and high signal-to-noise properties were invoked as the reasons and the highly dynamic abilities were pointed out as consequences.

An interesting non-chemical application of the concept of Generalized Crystallography was demonstrated in the paper of Ogawa and Ogawa [23]. The concept was applied to the seats to parties in the electoral system, which is a basis of democracy. The authors elucidated some geometric properties that, in this sense, are the reflection of democracy.

The concept of icosahedral shell structure (consisting of concentric icosahedra displaying fivefold rotational symmetry) and hierarchic icosahedral structures (caused by the presence of stacking faults) introduced by Mackay in 1962 [24] has made significant impact on research of particles, clusters, intermetallics, quasicrystals, and nanotechnology. A unified geometrical analysis of Mackay, anti-Mackay, double-Mackay, pseudo-Mackay, and related icosahedral shell clusters was presented by Kuo [25]. Icosahedral structures appear, among others, in fullerenes possessing pentagonal and heptagonal carbon rings. Such nested “chiral” icosahedral fullerenes may be obtained by transformation of polyhedral graphitic particles as their carbon atoms are reorganized under extreme conditions, e.g., by high-energy electron irradiation. Terrones et al. [26] summarized the available circumstantial experimental evidence for the possible formation of these metastable spherical structures and proposed a model interpreting how graphitic carbon atoms rearrange in order to attain sphericity. Shevchenko et al. [27] introduced a generalized model for describing the shell structures of icosahedral nanoparticles. The most important terms of the model are the spatial coherence (capability of individual fragments to combine without significant distortions at an interface), geometrical structural complexes (building blocks for more complex structures of the next level of hierarchy), and locally minimal manifolds (generalization of planar sheets). This general approach promises a wide applicability from inorganic to organometallic and to biological nanoparticles.

## Liquid-phase studies

Finney [28] presented a paper, which could be considered a continuation of the previous section as it demonstrated that the science of crystallography was not restricted to crystals. He reviewed advances in the past 35 years in radiation sources, instrumentation, and computing, which facilitated obtaining detailed structural information on relatively complex liquids by X-ray and neutron diffraction. The method and selected results on aqueous solutions of tertiary butanol were summarized. Results included information about molecular interactions in solution and about the structural perturbations in the solvent under the impact of the solute.

Structure–activity relationships are determined by a variety of factors. Among them, the importance of lipophilicity has been known for a long time as this property is responsible for *in vivo* and through-membrane transport. Scholl et al. [29] determined the lipophilicity of a representative number of hydantion derivatives using reversed-phase HPLC, where the stationary phase modeled the effects of membranes. These experimental data correlated well with theoretically estimated lipophilicities based on the structures under study as well as with the parameters of hydantion derivatives with known anticonvulsant properties.

## Gas-phase structure studies

The two most important experimental techniques for the determination of the structures of gas-phase species are gas-phase electron diffraction (GED) and microwave spectroscopy (MW). While the latter method is restricted to small and preferably low-symmetry molecules, for electron diffraction high symmetry is advantageous and its applicability extends to somewhat larger systems. The development of gas-phase electron diffraction was reviewed by Hedberg [30] in 2005 on the 75th anniversary of the GED technique, mainly from his personal perspective. We can learn from this paper about the early days at the California Institute of Technology (Caltech) in Linus Pauling’s group and about the development of modern GED including the application of the first fast computers for data processing in the middle of the 1950s. From that time, the possibilities of the technique has been characterized by a precision of a few thousandths of an angstrom for bond lengths and a few tenths of a degree for bond angles in the best cases. The enhancement of precision was to a great extent due to a nearly automatic data analysis, and this facilitated the extension of the applicability of the technique toward larger molecules.

Another paper contributing to commemorating the 75th anniversary of the gas-phase electron diffraction technique, again, with a personal touch was a paper by Bartell [31]. He presented a selection of “stories” from the time of the development of instrumentation and theory, as well as some demonstrative examples from his chemical repertoire. Further interesting personalities Bartell worked with in GED and related fields, appeared in his narrative.

Above we mentioned the improvement of precision in GED structure determinations. As far as accuracy in GED is concerned, it could be improved by combined analysis with spectroscopic data on molecular vibrations as well as geometrical information from microwave spectroscopy. Joint analyses facilitated the determination of equilibrium geometries for simple polyatomic molecules, like those presented for SO<sub>2</sub>, SF<sub>6</sub>, PbCl<sub>2</sub>, and PbBr<sub>2</sub> from the school of the late Spiridonov [32]. Various joint analysis procedures, including high-resolution spectroscopy, conventional vibrational spectroscopy, and quantum chemical calculations, the latter especially fast gaining importance recently, have been reviewed somewhat later by Spiridonov et al. [33]. The paper compiled the geometrical parameters of XY<sub>2</sub>, XY<sub>3</sub>, XY<sub>4</sub>, and XY<sub>6</sub>-type molecules obtained by various methods and different models. The comparison revealed that no absolute model existed at the time (the paper was published, in 2001) and the future of the determination of highly accurate geometries needed a most careful combination of experimental and computational techniques.

The potentials of high-temperature gas-phase electron diffraction in the structure analysis of metal halides and oxides of low-volatility were reviewed by Hargittai [34]. The paper called attention to the complex composition of the vapors of these compounds (often neglected until recently) and focused on the structures of the dimers in addition to the monomers. The dimers were present in relatively low abundance and due to their floppy nature and having similar bond distances with respect to those of the monomers; their structure elucidation presented a real challenge. Additional information from high-level quantum chemical calculations as well as from mass spectrometry and vibrational spectroscopy facilitated this work. The main contributions from calculations concerned the details of the potential energy surface of the dimers pointing to the possibility of several feasible models, the differences between dimer and monomer bond distances (that could be applied as constraints in the analysis), and computed vibrational force fields for the estimation of vibrational amplitudes.

The determination of equilibrium geometrical parameters was also the topic of the paper by Berry and Harmony [35] using empirical scaling of moments of inertia obtained from microwave spectra. They introduced

this method for polyatomic molecules up to the size of cyclopropene, and obtained heavy-atom bond distances with accuracies generally in the range of  $\pm 0.001$  to  $\pm 0.002$  Å (and falling very close to the hypothetical  $r_e$  values). In another paper, Rudolph [36] clarified the fundamental aspects of the  $r_0$ -structure and some of its recent extensions. In the focus were the  $r_0$ -structure and the  $r_0$ -derived “pseudo-Kraitchman” structures as well as their inequality relationships.

### Highlights from spectroscopy

The abilities of vibrational spectroscopy to determine various molecular properties were presented by Durig and Phan [37] in the full spectroscopic analysis of chloroacetyl bromide. The properties in focus were the molecular vibrations and the potential energy function governing internal rotation. The potential function provides important data for determining the conformational equilibrium: enthalpy differences between the conformers and barriers to internal rotation. The characteristics of the fundamentals were obtained by classical normal coordinate analyses. This was but one example of similar comprehensive studies emerging from the Durig School.

Butler et al. [38] demonstrated how UV spectra can be used as an experimental technique to identify low-barrier hydrogen bonds. These short and strong interactions appear in many enzyme-catalyzed biochemical pathways between the enzyme and the substrate. Simulation of the UV spectra using time-dependent quantum mechanics revealed distinctive features in the photodissociation, photoabsorption, and emission spectra of systems containing low-barrier hydrogen bonds.

Mössbauer spectroscopy has proved to be a powerful technique in structural research of solid-phase materials, though its application is limited to about 20 isotopes, and has been applied primarily for <sup>57</sup>Fe. Morrish [39] reviewed the use of this technique in the identification of sites and phases, in particular the distribution of cations and vacancies over various crystallographic positions and phase changes in crystalline and in amorphous structures. The examples presented provided a panoramic view of the versatility and capability of Mössbauer spectroscopy.

The potentials of the angular correlation technique of positron annihilation in studies of laminar structures were demonstrated in the paper of the late Goldanskii and his associates [40]. This technique yields information about the structures of laminar samples, the material of the layers, their thickness, electronic state, and their structures. Altogether, this non-destructive approach seems to be appropriate for control and study of lamina structures in the micron and submicron ranges.

## Theoretical studies

Quantum chemical calculations represent an increasingly important source of structural information and they also augment the experimental studies on various systems in a most useful way. One of the first papers in *Structural Chemistry* reporting a combined approach utilizing both experimental and computational information was by Yeo and Ford [41]. They trapped the water dimer and ammonia dimer in cryogenic nitrogen and argon matrices and recorded the IR spectra. From two possible dimer structures, the linear ones could be identified in the matrices on the basis of comparison of the measured and computed IR spectra.

The review of Binning Jr. and Ishikawa [42] compiled the advantages of computations for metal, semimetal, and molecular clusters. The most important theoretical results used in such studies were the structures of polyatomic clusters, the energy barriers to interconversion, binding energies, and electronic structures.

Some of the theoretical papers could be viewed as important benchmark studies, showing the performance of different theoretical levels on various molecular properties. Alkorta and Elguero computed absolute nuclear shieldings for several representative compounds containing  $^1(2)\text{H}$ ,  $^6(7)\text{Li}$ ,  $^{11}\text{B}$ ,  $^{13}\text{C}$ ,  $^{14(15)}\text{N}$ ,  $^{17}\text{O}$ ,  $^{19}\text{F}$ ,  $^{29}\text{Si}$ ,  $^{31}\text{P}$ ,  $^{33}\text{S}$ , and  $^{35}\text{Cl}$  nuclei [43]. They found good agreement between the computed B3LYP/6-311++G\*\* and experimental data for most model compounds. Another type of benchmark study was reported by Freeman et al. [44] on the conformations of 4-substituted tetrahydro-2*H*-thiopyran-1,1-dioxides. The best agreement with available experimental conformation free energy values (for the 4-Cl-, 4-Br-, and 4-acetoxy derivatives) was obtained for the HF calculations using polarized 6-31G basis sets. This, however, may be due to fortunate cancellation of errors at this not very high level of sophistication. Nevertheless, the results at all the levels (HF, MP2, DFT) showed agreement as regards conformational preferences of the model molecules, with only very small (1–2 kcal/mol) energy differences between the conformers.

Beside its methodological benchmark character, the paper of Bartczak and Stawowska [45] reported interesting results on the activation of  $\text{H}_2$  on various metal clusters modeling catalytic hydrogenization. They evaluated the dissociation paths and computed the dissociation energies and activation barriers of  $\text{H}_2$  on planar  $\text{Pd}_5$ ,  $\text{Ni}_5$ ,  $\text{Ag}_4\text{Pd}$ ,  $\text{AgPd}_4$ ,  $\text{NiCu}_4$ , and  $\text{NiPd}_4$  clusters. Another example on reaction mechanism studies is the paper by Siegbahn [46]. He investigated selected crucial steps of the Wacker process (oxidization of ethylene to acetaldehyde on Pd catalyst) using a gas-phase model. This early study provided adequate description of the steps not affected by the

solvent while called for the necessity of a sophisticated solvent model that would take explicit account of the solvent molecules for a more complete description of the reaction.

Hydrogen bonding is a popular field in chemical research, as this weak bond appears in many systems either as intramolecular or intermolecular interaction providing essential contribution to both chemical and biological properties of the systems. Quantum chemical calculations can be used to characterize hydrogen bonds in many ways beyond the experimental possibilities. A comprehensive work published in *Structural Chemistry* involving theoretical investigation of hydrogen bonding was reported by Pak et al. [47]. Their review included numerous chemical systems showing normal to strong hydrogen bonds: water clusters, interaction of water with polar molecules and  $\pi$ -systems, interactions in organic nanotubes, enzyme catalysis, and host–guest interactions. Utilizing considerations of cooperative versus competitive effects of hydrogen bonding, the design of various hydrogen-bonded ionophores, receptors, supramolecules, nanomaterials, and nanodevices were shown to be possible.

Pacios [48] evaluated the variations of topological properties of hydrogen bonds in small dimers in the proximity of the equilibrium inter-dimer distances ( $0.6 \leq R_e \leq 0.4 \text{ \AA}$ ) by MP2/6-311++G\*\* calculations. He showed that the characteristic features of hydrogen bonding can readily be recognized in compressed systems, while dramatic changes occur only at very strong compression.

The effects of halogen substituents on the strength of hydrogen bonding in Watson–Crick base pairs was the subject of the theoretical study of Guerra et al. [49]. The consequences of such weak effects were close to or within the experimental errors of experimental studies, hence the computations were proved to be a reliable tool for their assessment. The conclusion from the study was that halogens in general reduce the acceptor abilities of hydrogen while they tend to enhance the donating abilities of the DNA bases.

We conclude the enumeration of examples of studies of hydrogen bonding with mentioning a detailed DFT study of  $\alpha$ -maltose: Momany et al. [50] performed a survey of the conformational space of this monosaccharide, and determined and characterized its most important structures. They found trends in the variations in the geometry and correlated them with the hydroxyl rotamer directions.

It has been known that the reactivity of double bonds is affected substantially by substituents. To understand these substituent effects Rattanakin et al. [51] performed a theoretical study of 12 push-pull ethylene derivatives, which included electron donating and withdrawing groups coupled through the C=C double bond. On the basis of

elongation of the C=C bond and the reduced barriers to internal rotation, the authors determined the most effective push–pull substituents. Some push–pull chromophores have promising non-linear optical (NLO) properties that have special importance in information technology. Quantum chemical computations can assist to assess these properties, as recent codes are able to calculate the first hyperpolarizabilities. Benková et al. [52] determined these properties for 24 benzothiazole-based push–pull systems and suggested the best NLO candidates on the basis of the computed data.

Manufacturing thin layers and points with precise sizes are required in semiconducting industry, and theoretical calculations can help to understand the nature of these reactions. Agacino et al. [53] identified and characterized the surface states of different diamond surfaces using density of surface (DOS) curves obtained by DFT calculations. The surface states could qualitatively be related to the reactivity of these surfaces during the process of diamond growth. They found evidence that monohydrogenation tends to saturate the valences of the surface carbon atoms, hence the observed decrease in reactivity.

Understanding structure–property and structure–activity relationships is very important for biologically active molecules. The aminoindazole derivatives belong to such systems and they show tautomeric properties depending on the type and position of substituents. The thermodynamic properties of these forms and the  $pK_a$  values referring to their aqueous solutions were computed by Ögretir and Tay [54]. The authors tested the performance of different semi-empirical levels of theory and the applicability of soft–hard base and soft nucleophile–electrophile models on protonation reactions.

### Various models

Molecular modeling has proved to greatly facilitate the structure elucidation of novel low-abundance isomers by GC/MS [55], where the mass spectra generally do not provide enough data to determine unambiguously the structure of the unknown isomers. The key parameter here is the Henry constant, related to both the molecular geometry and the retention properties of the molecule on graphitized thermal carbon black sorbent applied in gas chromatography. Modeling in this approach helped predicting the molecular structures utilized in the calculation of the Henry constant, as was applied successfully by Kulikov and Bobyleva [55].

The late Burdett [56] used the method of moments to investigate the topological aspects of electrophilic aromatic substitution. His results showed the advantage of the

moments approach to gain a wider perspective of the problem, namely, the relationship between the fundamental electronic driving force for selectivity via this approach and the rules enunciated by Walsh and by Woodward and Hoffmann.

The valence shell electron pair repulsion (VSEPR) model was first proposed in 1957 and has been found to be successful in rationalizing and predicting the geometrical characteristics of numerous molecules of main group elements [57]. Gillespie's [58] discussion of the physical basis of the model contributed to the understanding of the underlying interactions that make the model so widely applicable. His paper was especially concerned with the Pauli exclusion principle in describing the correlation of same-spin electrons.

The size of a molecule has been primarily described in two distinct ways in chemistry: (i) the volume established by a mathematically defined surface using empirical radii that are generally van der Waals or reduced molecular radii; and (ii) the average volume per molecule as measured in a condensed phase. The late Meyer [59] performed a comparative compilation of size and shape of aromatic organic molecules on the basis of existing concepts of these two properties: molecular volumes, surface areas, cross-sectional areas, average free volumes in the bulk, and packing densities. There is a similar question: "Is it possible to specify how large an atom or a molecule is?" which was raised 15 years later by Bauer [60]. He examined this problem in a critical review of the methods providing external dimensions of atoms and molecules and the diverse data derived by these methods. The conclusion of the paper was that while intermolecular distances could be determined to high precision, the external dimensions of molecules remain intrinsically fuzzy.

The concept of shape that may be difficult to determine rigorously for molecules appears to be more straightforward for the human body, but both are related to the domain of chemistry, which has been called chemical morphology, discussed in a recent paper of Scott [61]. He described "shape modules," which he defined as protein fibril modules held together by elastic carbohydrate strings. They together form the extracellular matrices of the connective tissues. The first and second laws of chemical morphology developed by Scott, and their success with respect to several physiological conditions, like osteoarthritis and aging, have begun providing a coherent picture about the human and animal bodies in their evolution.

Symmetry is a property appearing at both the macroscopic and molecular levels in chemistry. Glaser [62] called attention to the similarities in the symmetries of apple halves and the repeat units in some helical multiplexes of parallel-chain polymers exhibiting  $2n_n$ -helical axes. Another interesting symmetry-related paper with



historic character was written by the late Burckhardt [63] referring back to the discovery of crystallographic space groups. As is well known, the 230 three-dimensional space groups were discovered independently by Barlow, Fedorov, and Schoenflies. Regarding the groups Pm, Pc, Cm, and Cc there have been some differences in interpretation, and Burckhardt clarified the reason of these differences on the basis of the correspondence between two of these pioneer scientists, Fedorov and Schoenflies.

Molecular structure and thermochemistry are strongly correlated as the formation of the molecule from atoms or from other molecules has decisive energy components and consequences. Similarly, the change of phase and morphology, solvation, the transformation processes between isomers, all are related to energy variations of the systems involved. This relationship has been extensively studied by Joel L. Liebman and his associates, first in his series of book chapters in *Advances in Molecular Structure Research* [64], then, from 2003 in a series of review articles in *Structural Chemistry*. In these papers Liebman and associates have reviewed the journal volumes one by one and examined most articles in an explicitly thermochemical perspective [65–69]. Depending on the topic of the paper reviewed, the author(s) discussed thermochemical properties like enthalpy of combustion, enthalpy of formation, enthalpy of reaction, heat, phase change enthalpies, and molecular energetics, using reference data from thermochemical archives. The unique idea behind these useful reviews was to inform, raise questions, and suggest possible further research topics.

The experimental binding energies of 1s core-electrons of 31 small molecules (altogether 59 core-electrons including B1s, C1s, N1s, O1s and F1s) were correlated with calculated and atom-type descriptors from the literature by Kiralj and Takahata [70]. The partial least squares regression analyses using electronegativity, polarizability, energy, charge, density, and steric descriptors revealed the three-dimensional character of the core-electron binding energies determined by the element type, electronegativity of its chemical environment, and intramolecular stereo-electronic effects.

Originating from the fundamental properties of molecules to occupy a finite volume in three-dimensional space, relationships exist between several bulk characteristics of substances and their molecular shape. Trends observed in the melting and boiling temperatures of selected organic compounds could be rationalized by the concept of “van der Waals symmetry” [71] suggested previously by Slovokhotov et al. [72] for characterizing quantitatively the shapes of molecules.

The paper of Gavezzotti [73] demonstrated the advantages of a new semiempirical scheme, the PIXEL method [74], for the description of intermolecular potentials and

forces determining crystal packing. He presented results for three different types of compounds, viz., naphthalene as a pure hydrocarbon, naphthoquinone as a polar substituted derivative, and 2-naphthoic acid as a hydrogen-bonded derivative. The study modeled successfully the fine balance of attractive and repulsive forces in the respective crystals.

Shevchenko and Krivovichev [75] used a newly developed concept of universal optimum and the general principles of inorganic gene to construct structures of inorganic materials. They successfully reproduced the crystal structure of paulingite-related zeolites and other minerals, and predicted the structure of a new zeolite. According to their results, it seems that universal optimum contains all necessary information for its material realization and for construction of materials with certain type of interaction potential.

In conclusion, we note that in addition to a plethora of research topics and research papers and occasional reviews, *Structural Chemistry* has housed an active Book Reviews section, which included reviews and notices of over 450 volumes and has gone beyond a narrowly interpreted circle of structural chemistry publications.

The Editors and all members of the Editorial Board are convinced that the journal is on the right track of further progress. Rather than aiming at a quick expansion *Structural Chemistry* continues to be dedicated to maintaining and further enhancing the high level of our publication, and expanding our coverage toward all vital areas of current research relevant to structural chemistry. This is the principal message of this note.

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