European Review, Vol. 13, Supp. No. 2, 61–75 (2005) © Academia Europaea, Printed in the United Kingdom

Symmetry in chemistry

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Symmetry and chemistry have been in a fruitful interplay, initially in spectroscopy and crystallography, lately in more traditional domains of chemistry, such as reactivity and conformational analysis. A simple phenomenological approach suffices to get an idea about the symmetries of molecules whereas group theoretical approach greatly facilitates the understanding of molecular vibrations, electronic structure, and the mechanism of chemical reactions. In our discussion, the multi-level relationship between symmetry and chemistry is demonstrated by a sampler of examples, including the variations of symmetry of free molecules and molecular packing in crystals. Symmetry considerations continue to assist chemistry in systematizing and interpreting observations and also in discovering new reactions, molecules, and other materials.

Eugene P. Wigner's legacy

Eugene P. Wigner taught us that in our studies of phenomena in physics and chemistry we can rely on separating them into two parts. There are the arbitrary, complicated, and unpredictable initial conditions and there are the laws of nature, independent of initial conditions that summarize the regularities.[1] As he further pointed out, symmetry principles play a similar role with respect to the laws of nature as the laws of nature play to the physical phenomena. They 'provide a structure and coherence to the laws of nature just as the laws of nature provide a structure and coherence to a set of events.'[1] In his banquet speech following the Nobel Prize award ceremony in Stockholm in 1963,[2] Wigner quoted his teacher Michael Polanyi when he said that 'science begins when a body of phenomena

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In memoriam
Eugene P. Wigner (1902–95) and Aleksandr I. Kitaigorodskii (1914–85)

is available which shows some coherence and regularities, that science consists in assimilating these regularities in a natural way.' He stressed that this method of science was transferable among various fields of learning rather than the various concepts themselves (such as energy). Recognizing symmetry is a most efficient means to recognize regularities.[3]

We were fortunate to have been introduced to the utility of the symmetry concept by Eugene Wigner.[4] Of course, what Wigner and Gross[1] mean by physics, includes chemistry and Wigner's group theoretical arguments[5] have greatly benefited the development of the treatment of molecular vibrations, electronic structures, and chemical reactions in chemistry.[6] Wigner and Witmer[7] published the first application of symmetry considerations to chemical reactions jointly and their rules were concerned with the conservation of spin and orbital momentum in the reaction of diatomic molecules. Before, however, the symmetries and their changes can be considered in chemical events, the symmetries have to be established and understood in the analysis of molecular structure.

Molecules

Generally it is the geometry and symmetry of the system of atomic nuclei in the molecule that is considered to be the geometry and symmetry of the molecule. They are point group symmetries that have no limitations in contrast with the symmetries of extended structures, such as crystals. In considering molecular symmetries, free molecules have the advantage that they are not influenced by intermolecular interactions and their structure is solely determined by intramolecular forces. In discussing molecular structure, an extreme approach is to consider the molecule to be motionless. A completely rigid molecule is a hypothetical structure corresponding to the minimum position of the potential energy function of the molecule. Such a motionless structure has an important and well-defined physical meaning and is called the *equilibrium structure*. It is this equilibrium structure that emerges from quantum chemical calculations.

On the other hand, real molecules are never motionless, not even at the temperatures approaching 0 kelvin. In particular, large-amplitude and low-frequency vibrations may lower the molecular symmetry of the average structure from the higher symmetry of the equilibrium structure. The average structure may be a time-average during the molecular vibrations or may be the structure at an instantaneous moment, averaging over all vibrational states present, distributed according to the temperature of the sample. The various physical measurement techniques determine the structures of real molecules and the result of such determination will depend on the relationship between the lifetime of the structure and the time scale of the measurement. Figure 1 shows the models of a series of

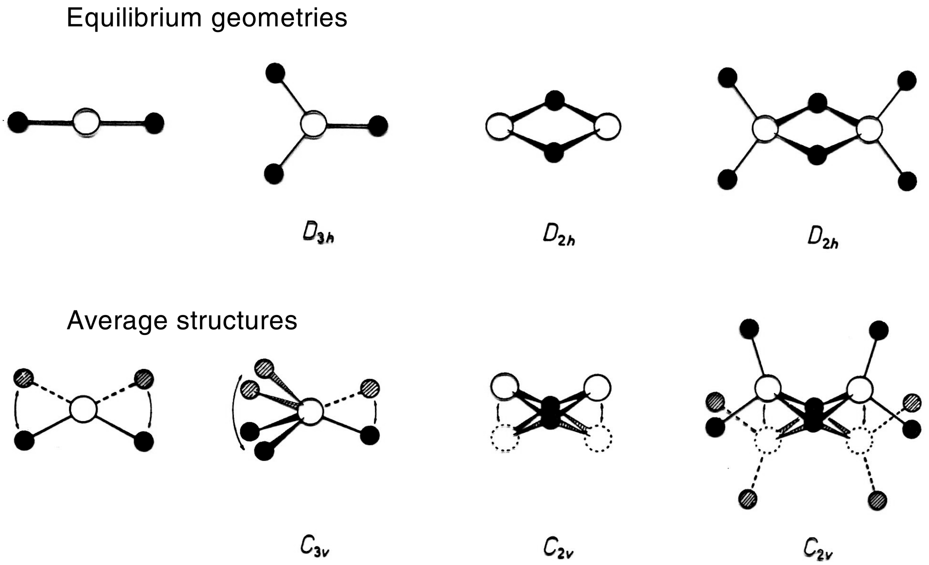

Figure 1. Symmetry changes in equilibrium and average structures of metal halide molecules as a consequence of large-amplitude, low-frequency motion.

metal halide molecules indicating the symmetry changes between their equilibrium and average structures.

A special kind of molecular motion is conformational change when one group of atoms turns around a selected bond as an axis with respect to another group of atoms. Conformational isomerism is important in biochemistry. During a complete rotation of one methyl group around the C–C bond relative to the other methyl group, the ethane molecule, $H_3C–CH_3$, appears three times in the stable staggered form and three times in the unstable eclipsed form. As all the hydrogen atoms of one methyl group are equivalent, the three energy minima are equivalent, and so are the three energy maxima.

The situation becomes more complicated when the three ligands bonded to the carbon atoms are not the same. Two important cases in rotational isomerism may be distinguished by considering the nature of the central bond. When it is a double bond, rotation of one form into another is hindered by a very high potential barrier. This barrier may be so high that the two rotational isomers will be stable enough to make their physical separation possible. An example is the *cis* and *trans* isomers of 1,2-dichloroethylene, $ClHC = CHCl$. An example of the rotational isomerism relative to a single bond, with considerably lower barrier to rotation is the *gauche* and *anti* forms of 1,2-dichloroethane, $ClH_2C–CH_2Cl$. The important observation is that the symmetrical forms of rotation always belong to extreme energies, either minima or maxima.

A special kind of isomerism is chirality. A chiral molecule and its mirror image are each other's enantiomers. Homomers are identical molecules and superimposable, enantiomers are not superimposable mirror images. The simplest case of a chiral pair is a methane derivative in which three of the four hydrogens have been substituted by three non-identical ligands; its formula can be represented as HXYZC in which the carbon atom in the central position is called an asymmetry centre. At the birth of stereochemistry, during the last decades of the 19th century, the absolute configuration could not be determined. An arbitrary assignment was introduced, which, luckily proved to be correct, when J.M. Bijvoet and his group determined experimentally the sense of molecules in the 1950s.[8] They did this for a rubidium salt of tartaric acid and for quite a while this substance served as a starting point to deduce the absolute configuration of other substances through often tedious series of chemical reactions. The absolute configuration of many simple and even of large biological molecules have now been determined.

Natural products extracted from plants and animals are purely of one enantiomer. However, when obtained by chemical synthesis equal amounts of all the enantiomers are produced. In most cases, when examined in biological reactions, one of the enantiomers is active and the other one is either inactive or of very much lower activity.

There are a few instances where the enantiomers have different effects, for instance in aspartame (Nutrasweet), one enantiomer is sweet and the other bitter. In some instances the second enantiomer is toxic as for instance in the anti-tubercular drug Ethambutol.

It is obviously highly desirable to produce enantiomerically pure drugs and in most cases drugs will not obtain a licence if not enantiomerically pure. This is normally achieved by forming a salt or complex with an enantiomerically pure substance by which the two forms can be separated by crystallization. An alternative is to attach the enantiomer of a suitable substance to a polymer and then do the separation on a chromatographic column. Less readily applicable in asymmetric synthesis is the strategy employing chiral catalysts.

Molecules taking the shapes of various polyhedra have high symmetries and they come in a great variety. A simple example is in molecules of tetrahedral shape, such as tetraarsene, As_4, and methane, CH_4. Both have T_d symmetry, but there are important differences between the two structures. In As_4, all four constituent nuclei are located at the vertices of a regular tetrahedron and all edges of this tetrahedron are chemical bonds between the arsenic atoms. In the methane molecule, there is a central carbon atom and the four chemical bonds are directed from it to the four vertices of the regular tetrahedron, where the four hydrogens are located. The edges of the tetrahedron are not chemical bonds. Buckminsterfullerene, C_{60}, a relatively recent discovery[9] is a polyhedral molecule that has the shape and symmetry of a truncated icosahedron, one of the 13 Archimedean polyhedra.

Dynamic properties

Molecular properties can be of either static or dynamic nature. Looking at them from the point of view of symmetry, a static property remains unchanged by every symmetry operation carried out on the molecule. The geometry of the nuclear arrangement in the molecule is such a property: a symmetry operation transforms the nuclear arrangement into another, which will be indistinguishable from the initial one. The mass and the energy of a molecule are also static properties.

The dynamic properties, on the other hand, may change under symmetry operations. Molecular motion itself is a most common dynamic property; in fact, ‘real-life’ molecules are never motionless, not even at the absolute zero kelvin. When we talk about the point-group symmetries of molecules, strictly speaking we refer to the hypothetical, motionless, equilibrium structure. This structure can never be measured by experiments but this is the one that is found by quantum chemical calculations and is the one that can be used for comparing structures determined by different methods.

The dynamic properties of molecules are connected either with their nuclear or with their electronic motion. The nuclear motion may be translational, rotational, and vibrational whereas the electronic motion is basically the changes in the electron density distribution. While the point-group symmetry of the nuclear arrangement can be determined rather easily, the symmetry of the dynamic properties can only be meaningfully discussed by group theory. Here, only a very short account will be given about the symmetry properties of two dynamic properties, namely those of molecular vibrations (nuclear motion) and those of the electronic structure. Their common feature is a special kind of symmetry, called anti-symmetry. It is used to describe any characteristic that changes into its opposite during a particular symmetry operation.

Molecular vibrations

The atoms in the molecule are continuously changing their relative positions at all temperatures (even at absolute zero) without changing the position of the molecular centre of mass. In terms of the molecular geometry, these vibrations amount to continuously changing bond lengths and bond angles. This means that the symmetry of molecules also continuously changes during molecular vibrations; in fact, as already mentioned before in connection with the equilibrium

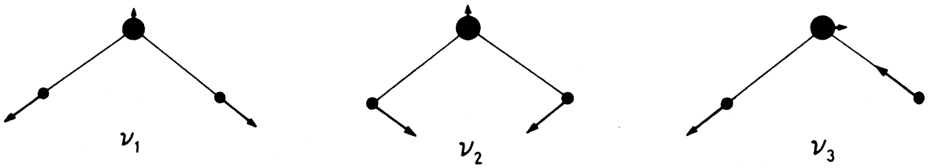

Figure 2. Normal modes of vibration of the water molecule.

versus average geometries, molecular vibrations almost always reduce the symmetry of the so-called equilibrium structure of a molecule.

The seemingly random motion of molecular vibrations can be decomposed into the sum of relatively simple components, called *normal modes of vibration*. Each of the normal modes is associated with a certain frequency. For a normal mode, every atom of the molecule moves with the same frequency and in phase. There are three characteristics of normal vibrations: their number, their symmetry, and their type. Here, we will be concerned mainly with their symmetry and refer to two classic books on other aspects of molecular vibrations.[10,11] For a nonlinear molecule consisting of N number of atoms, there are altogether $3N$-6 number of normal vibrations (the other forms of motion, translation and rotation are deducted). This number is $3N$-5 for linear molecules.

There is a close relationship between symmetry and vibrations in that for each molecule the normal vibrations must belong to one or another 'symmetry type' (the so-called irreducible representation) of the particular point group to which the molecule belongs. With group theoretical arguments it is easy to deduce what symmetries the different vibrations of a molecule will belong to but this is beyond the scope of this paper. Let us take a simple example – the water molecule, H_2O. Its point group symmetry is C_{2v} and it has three normal vibrations (three atoms and $3N-6 = 3$). Its three normal modes are shown in Figure 2. The first two of these belong to the totally symmetric vibration of the point group, a_1 and the third to b_2.

The normal modes of a molecule can usually be associated with a certain kind of motion of the molecule. Taking the water molecule as an example, the first vibration, shown in Figure 2, is the so-called symmetric stretching vibration; it expresses the simultaneous elongation and contraction of the two bonds in the molecule. Stretching a bond usually requires large energies and thus stretching vibrations usually have the largest frequency. The second one has the same symmetry as the first one, a_1, but it expresses a different kind of motion. It is the bending motion of the molecule, describing the closing and opening of the H–O–H bond angle. This kind of motion requires less energy than stretching a bond; therefore it has a smaller frequency. There are, of course, many other types of vibrations in larger molecules, such as out-of-plane deformation vibrations, just to mention one. Keeping with the water molecule, its third vibration is the so-called asymmetric stretching mode, which again describes the stretching of the two O–H bonds but in an asymmetrical way.

There is one more topic to be mentioned here and that is the so-called selection rules. They are again intimately related to symmetry. The considerations on the symmetries of the ground and excited states lead to the selection rule for infrared spectroscopy: *A fundamental vibration will be infrared active if the corresponding normal mode belongs to the same irreducible representation as one or more of the Cartesian coordinates*. The selection rule for Raman spectroscopy can also be derived by similar reasoning. It says: *fundamental vibration will be Raman active if the normal mode undergoing the vibration belongs to the same irreducible representation as one or more of the components of the polarizability tensor of the molecule*.

The selection rules predict for us what type of vibrations we might expect in a certain molecule, and this uniquely depends on their symmetry; in fact, vibrational spectroscopy is one of the best techniques to determine the symmetry of a molecule; depending on what type of vibrations will appear and what types will be forbidden in their spectrum.

Electronic structure

Everything that really counts in chemistry is related to the electronic structure of atoms and molecules. The formation of molecules from atoms, their behaviour and reactivity all depend on their electronic structure. What is the role of symmetry? In various aspects of the electronic structure, symmetry can tell us a good deal; why certain bonds can form and others cannot, why certain electronic transitions are allowed and others are not, and why certain chemical reactions occur and others do not. In fact, symmetry considerations are almost omnipresent in all aspects of the electronic structure.

One example is how the molecular orbitals (MOs) are built from atomic orbitals (AOs). Molecular orbitals are linear combinations of atomic orbitals (LCAO). When constructing molecular orbitals from atomic orbitals, there may be a large number of possible linear combinations. Many of them however are unnecessary. Symmetry is instrumental as a criterion in choosing among them. The following statement is attributed to Michelangelo: ‘The sculpture is already there in the raw stone; the task of a good sculptor is merely to eliminate the unnecessary parts of the stone’. In the LCAO procedure, the knowledge of symmetry eliminates the unnecessary linear combinations. All those linear combinations must be eliminated that do not belong to any irreducible representation of the molecular point group. The reverse of this statement constitutes the fundamental principle of forming the molecular orbitals: each possible molecular orbital must belong to an irreducible representation of the molecular point group. Another equally important rule for the construction of molecular orbitals is that only those atomic orbitals can form a molecular orbital that belong to the same irreducible representation of the molecular point group; that is those that have the same symmetry properties.

Another symmetry related aspect of the electronic structure is the degeneracy of atomic or molecular orbitals. We talk about degenerate orbitals if two or more orbitals have the same energy. *The greater the degree of symmetry the smaller will be the number of different energy levels and the greater will be the degeneracy of these levels.* This relationship is valid not only when increasing symmetry renders the energy levels degenerate but also when energy levels are split as molecular symmetry decreases. This is what happens in the so-called Jahn–Teller effect.

The Jahn–Teller effect

According to its original formulation, a nonlinear symmetrical molecule with a partially filled set of degenerate orbitals will be unstable with respect to distortion and thus it will distort to a lower-symmetry geometry and thereby remove the electronic degeneracy.[12]

The electronic ground state of molecules with completely filled orbitals is always totally symmetric and cannot be degenerate. Transition metals have partially filled *d* or *f* orbitals, therefore it is their compounds in which we might expect partially filled orbitals, which may then be subject to Jahn–Teller distortion.

An example of Jahn–Teller distortion is the crystal of manganese trifluoride, in which manganese has a d^4 electronic configuration. Manganese is six-coordinated by fluorine ions in its crystal and without the Jahn–Teller effect it should have a high-symmetry octahedral arrangement. However, this high-symmetry coordination is not stable and the crystals undergo a tetragonal elongation and the symmetry becomes D_{4h}.

The Jahn–Teller effect is usually observed in crystals. It was only relatively recently that the effect was also observed by electron diffraction experiment in the gas-phase MnF_3 molecule.[13] Figure 3 shows the so-called radial distribution function, which is the probability density distribution of all atom–atom distances in a molecule. This curve shows clearly that the contribution from the non-bonded $F \cdots F$ interactions splits into two, indicating that there are two different such distances. The expected symmetrical D_{3h} arrangement is distorted into the lower C_{2v}-symmetry geometry. Gold trihalides, having a d^8 electronic configuration in gold, also show a considerable distortion from the D_{3h}-symmetry structure, indicating that they also undergo a Jahn–Teller type distortion.[14–16] Figure 4 shows

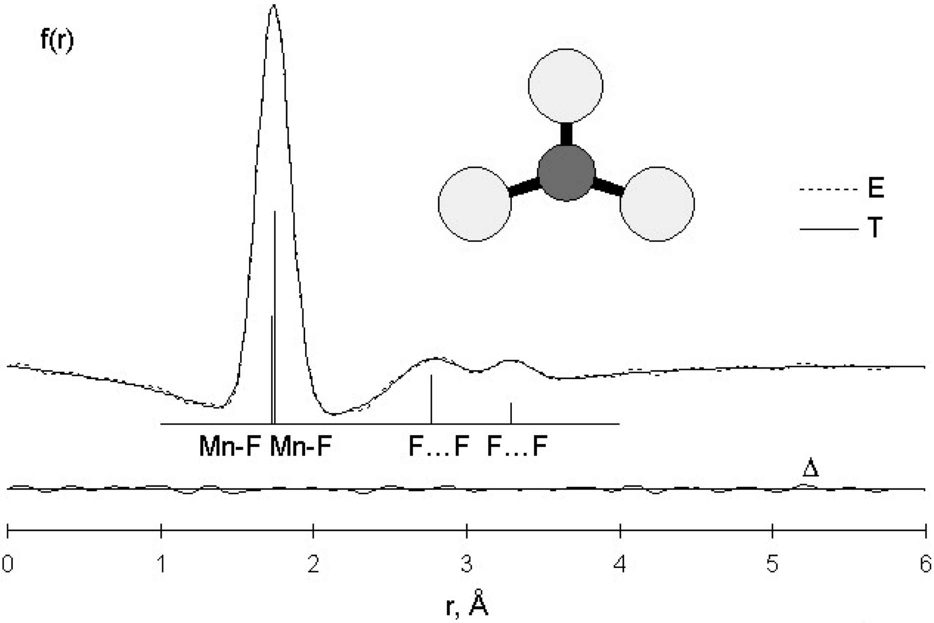

Figure 3. The radial distribution curve of MnF_3.

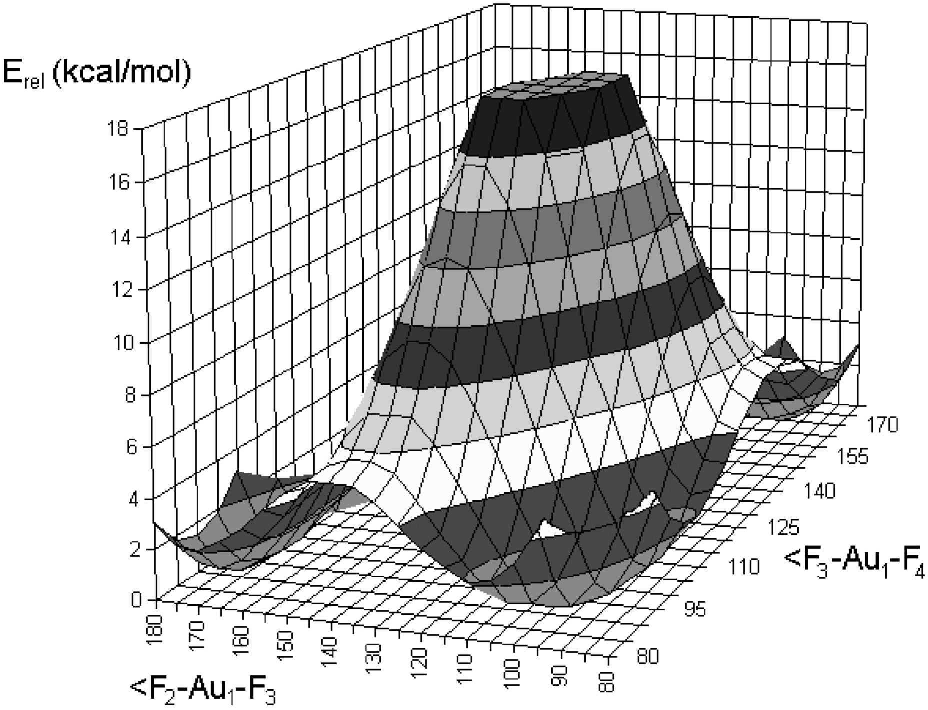

Figure 4. The Mexican-hat type potential energy surface of AuF_3.

the potential energy surface (PES) for gold trifluoride. This is a typical Mexican-hat type PES. The undistorted D_{3h}-symmetry structure has a very high energy at the centre. Around the 'brim of the hat' there are three equivalent minima positions, corresponding to the ground-state structure of the molecule and three higher energy positions between them at the saddle points, these latter are the so-called transition-state structures. As the energy of these transition structures is relatively large, the molecules can 'freeze' into the minima positions and experimental techniques can detect them there. These are the so-called static Jahn–Teller systems. Many molecules show only the dynamic Jahn–Teller effect.

Chemical reactions

The first application of symmetry considerations to chemical reactions can be attributed to Wigner and Witmer[7] but the real breakthrough in recognizing the role of symmetry in determining the course of chemical reactions happened through the work of Woodward and Hoffmann,[17,18] Fukui,[19,20] Pearson,[21,22] and others.

Their work shows that symmetry phenomena may play as important a role in chemical reactions as they do in the construction of molecular orbitals or in molecular spectroscopy. It is even possible to make certain symmetry-based 'selection rules' for the 'allowedness' and 'forbiddenness' of a chemical reaction, just as in spectroscopic transitions. There are limitations in the application of the symmetry rules to chemical reactions. It is only the relatively simple, so-called *concerted reactions*, to which they can be applied. In these reactions all relevant changes occur simultaneously; the transformation of reactants into products happens in one step with no intermediates.

The statement: a chemical reaction is 'symmetry allowed' or 'symmetry forbidden', should not be taken literally. When a reaction is symmetry allowed, it means that it has a low activation energy. This makes it possible for the given reaction to occur, although it does not mean that it always will. There are other factors that can impose a substantial activation barrier. Such factors may be steric repulsions, difficulties in approach, and unfavourable relative energies of orbitals. Similarly, 'symmetry forbidden' means that the reaction, as a concerted one, would have a high activation barrier. However, various factors may make the reaction still possible; for example, it may happen as a stepwise reaction through intermediates. In this case, of course, it is no longer a concerted reaction.

Most of the symmetry rules explaining and predicting chemical reactions deal with changes in the electronic structure. However, a chemical reaction is more than just that. Breakage of bonds and formation of new ones are also accompanied by nuclear rearrangements and changes in the vibrational behaviour of the molecule. As mentioned above, both the vibrational motion and the electronic structure of the molecules strongly depend on symmetry. This dependence can be fully utilized when discussing chemical reactions. Of course, describing the structures of both reactant and product molecules with the help of symmetry is not what we are concerned about here; it is that certain symmetry rules can be applied to the transition state in between the reactants and products.

A chemical reaction is a consequence of interaction between molecules. The electronic aspects of these interactions can be discussed in much the same way as the interaction of atomic electron distributions forming molecules. The difference is that while MOs are constructed from the AOs of the constituent atoms, in describing a chemical reaction, the MOs of the product(s) are constructed from the MOs of the reactants. Before a reaction takes place (i.e. while the reacting molecules are still far apart), their electron distribution is unperturbed. When they approach each other, their orbitals begin to overlap, and distortion of the original electron distribution takes place. There are two requirements for a constructive interaction between molecules: symmetry matching and energy matching. These two factors can be treated in different ways. The approaches of Woodward and Hoffmann[17,18] and those of Fukui[19,20] differ somewhat. Woodward and Hoffmann drew so-called correlation diagrams to see if a chemical reaction is allowed or forbidden, while Fukui looked at the symmetry and energy of the so-called 'frontier orbitals,' that is, the highest occupied MO of one molecule and the lowest unoccupied MO of the other molecule.[6]

Extended structures

Molecules are characterized by point group symmetries and when there is periodicity in a structure then space group symmetries are applicable to them. Polymeric molecules that have periodicity in one direction only are characterized by one-dimensional space groups, layer structures by two-dimensional space groups, and crystal structures by three-dimensional space groups.[6] The 'infinite' carbon-chain carbide molecules present one-dimensional space group patterns, such as … = C = C = C = C = … and the carbon chain with alternating single and triple bonds. A screw axis is a characteristic symmetry element in extended structures. The chain of beryllium dichloride in the crystal has a fourth-order screw axis, 4_2 in which translation from unit to unit is accompanied by a 90° rotation around the translation axis. The extended polyethylene chain, $–(CH_2)_n–$, is another example of a one-dimensional space group due to its translational symmetry.

Biological molecules are often distinguished by a helical structure to which one-dimensional space groups are applicable. In the polypeptide chain of the alpha-helix[23,24] the repeating unit is a –C(O)-N(H)-C(H)(R)- moiety with a planar peptide bond configuration. The linear rod-like structure of the alpha-helix is accomplished by hydrogen bonds. The double helix structure of DNA has two helical chains, each coiling around the same axis but having opposite direction and complementing each other as a consequence of twofold symmetry of the double helix. The axis of twofold rotation is perpendicular to the axis of the double helix. The two chains are held together by purine and pyrimidine bases, joined in pairs providing the basis for symmetry and complementarity.[25,26]

There is a feature of certain chemical reactions far from equilibrium that also has the attributes of one-dimensional space group symmetry. They are the so-called oscillating reactions or Belousov–Zhabotinsky reactions, which may have temporal or spatial periodic changes in product concentrations.[27] It was hard to get oscillating reactions accepted because, unless it is stressed that the periodic changes appear far from equilibrium, they might be deemed thermodynamically impossible.

Of the extended structures, the external shapes of crystals are characterized by point group symmetries and their internal structures by three-dimensional space group symmetries. Of the many aspects of crystal symmetries[28] here we single out one characteristic feature, the importance of symmetry considerations in understanding the packing in molecular crystals. As early as 1940, Pauling and Delbrück[29] in a discussion of the nature of intermolecular forces in biological processes, suggested precedence for interaction between complementary parts rather than between identical parts. Considerations of complementarity in molecular packing culminated in the works of Kitaigorodskii.[30] He predicted that three-dimensional space groups of lower symmetry should be much more frequent than those of higher symmetry among crystal structures. This was a prediction at a time when few crystal structures had been determined experimentally. Today, with hundreds of thousands of crystal structures, Kitaigorodskii's predictions have withstood the test of time. He based his predictions on painstaking empirical investigation rather than on intuition. He used a so-called structure-finder – a simple instrument – to probe into the best possible arrangements of arbitrary but identical shapes. He established the symmetry of two-dimensional layers that allow a coordination number of six at an arbitrary tilt angle of the molecules with respect to the tilt axes of the layer unit cell. He found that such an arrangement will always be among those that have the densest packing. In the general case for molecules of arbitrary shape, there are only two kinds of such layers. One has inversion centres and is associated with a non-orthogonal lattice. The other has a rectangular net, from which the associated lattice is formed by translations, plus a second-order screw axis parallel to the translation. The next task was to select the space groups for which such layers are possible. This answered the question of why there is a high occurrence of a few space groups among the crystals while many of the 230 groups hardly ever occur.

Beyond classical crystallography, symmetry considerations helped in the discovery of the so-called quasi-crystals, linking crystal structures and quasi-periodic long-range translational order. In the traditional crystal structure, there is only one unit cell, whereas in a quasi-periodic structure there is more than just one. The repetition of the unit cell is regular in the traditional crystal whereas it is not regular, nor is it random, in the quasi-periodic structure. We use the label 'traditional' because by now it has been universally accepted that the term *crystal* includes what used to be called quasi-crystals. The first experimental observation of quasi-crystals happened in 1982 in an electron diffraction experiment on alloys produced by very rapid cooling of molten metals. The diffraction pattern showed ten-fold symmetry,[31] which should have been impossible according to the then-accepted strict dogmas of classical crystallography. The discovery opened a new chapter in solid state chemistry and materials science. It also demonstrated that symmetry considerations may assist research even in discovering new materials.

Acknowledgement

Our research is supported by grants from the Hungarian National Research Fund (OTKA T 037978 and OTKA T 046183).

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