

# Space concept in chemistry

István Hargittai

Technical University of Budapest and Hungarian Academy of Sciences,  
Szt. Gellért tér 4, H-1521 Budapest, Hungary

*Abstract* - Steric effects have been considered important in structural chemistry for a long time. Space requirements of electron-pair domains seem to be decisive for the shapes of molecules and geometrical variations in a great variety of chemical compounds. In spite of its simplicity, the Valence Shell Electron Pair Repulsion Model is widely applicable. With increasing ligand size relative to the size of the central atom, nonbonded interactions take gradually over as decisive factor in the determination of molecular shape.

## 1. INTRODUCTION

It is no mere synergy that space considerations are useful and important in chemistry. They are usually applied in simple and qualitative but remarkably successful structural models. A simple model of electron-pair domains in the valence shell accounts for and predicts the variations of molecular geometry in large classes of compounds. Nonbonded interactions, crystal packing, and enzyme action are all related to spatial properties. Increased experimental and computational accuracy as well as energy considerations facilitate a better understanding of how chemical structures work. Recognizing the importance of simple space considerations may facilitate synergic interactions of chemistry with other fields.

Buckminster Fuller [1], best known for his synergic geometry and for his stable light-weight Geodesic Dome, has recognized the fruitfulness of chemical approach in perceiving volumes as material domains rather than merely geometrical abstractions. In order to illustrate this he quoted Avogadro's law according to which equal volumes of all gases, under the same conditions, contain the same number of molecules. Chemistry, along, perhaps, with biology, has special affinity for synergy. However, geometry, volume, and space requirements are an integral part of chemistry.

Johannes Kepler [2] on the zenith of his life was wondering about the beauty, diversity, and internal structure of the snow crystals. He was stacking in his doodlings equal spheres and came to the conclusion of the importance of packing in crystal structures for the first time. His attempts to understand outer shape by internal structure and, in particular, by packing considerations came two hundred years before John Dalton's theory of atoms and three hundred years before X-ray crystallography began. Kepler can be considered to be the first crystallographer and to be the first who introduced the space concept into what chemical sciences are today.

## 2. QUALITATIVE CONCEPTS

Chemistry is a pragmatic science. It is very empirical yet theories and models have always been important to it. Chemists have always strived to rationalize their findings and to predict the results of not-yet-performed experiments. Chemical theories and models have been mostly qualitative yet very useful, and their longevity is a wonder of Science. We are still using intuitive concepts that were introduced at the end of the last century. The initial qualitative concepts have been often blended with later more rigorous foundations.

The Periodic Table is among the best to exemplify the roles of empirical chemical theories. Dmitrii I. Mendeleev and others have noticed periodicity in the element properties according to increasing atomic weights. What distinguished Mendeleev's achievements from those of others that he predicted the existence of yet unknown elements on the basis of already acquired knowledge. The soundness of the Periodic Table was proven by the eventual discovery of those elements whose existence Mendeleev had predicted.

Eventually, the Periodic Table was put onto firm bases as the electronic structure of atoms was discovered by quantum mechanics, and it was finally understood that chemical behavior and the periodicity in its variations are intimately related to electronic structure.

Possibly the most important chemical discovery of the twentieth century was the electron-pair description of the covalent bond by Gilbert N. Lewis [3]. This notion has survived all other development and is being applied virtually in its original form. Moreover, the provocatively unsophisticated Lewis dot structures for the description of electron configurations have been around whenever an easy electron count is needed to understand molecule formation.

### 3. ADDING THE THIRD DIMENSION

In the last third of the nineteenth century van't Hoff introduced the concept of the tetrahedral carbon bond configuration, thereby extending chemical thinking into the third dimension and into twentieth century science. Together with Pasteur's observation of chiral properties, they have truly initiated the understanding of the intimate correlation between chemical structure and chemical properties. Spatial structural differences between substances of the same composition, leading to isomerism (Fig. @.1), have vital consequences in chemical properties. These consequences are still being uncovered and putting to new uses.

*Enantiomers* have no distance differences and their spatial difference occurs in their being each other's mirror images without being superimposable. Due to the usual difference in their ability to rotate polarized light, the enantiomers are also called optical isomers. They are also called stereoisomers. Other isomerisms involve differences in interatomic distances.

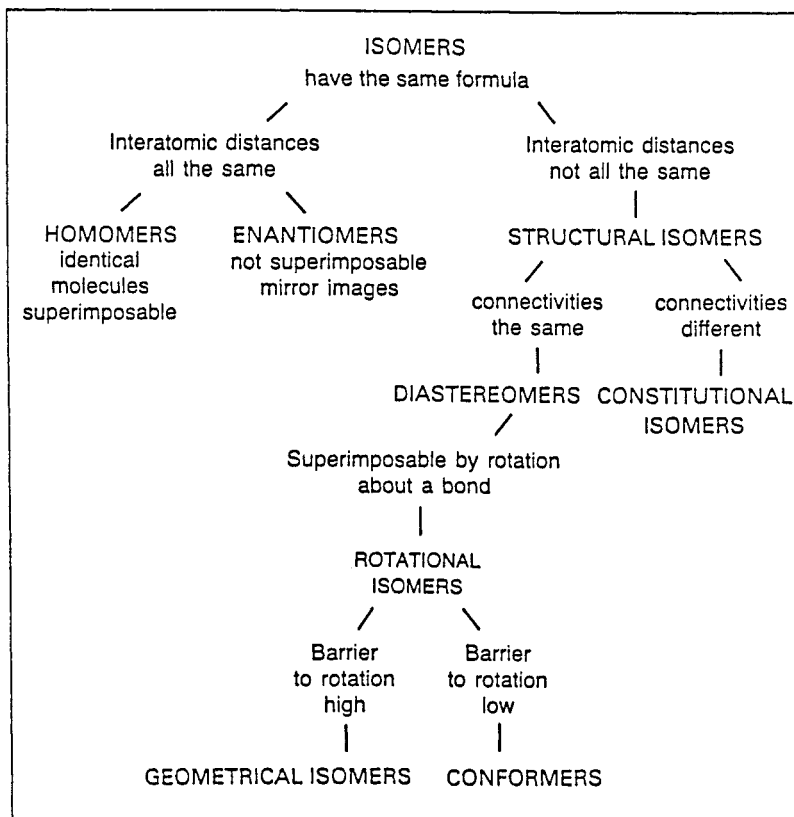


Fig.1 - Isomerisms (after Gillespie and Hargittai [7])

*Constitutional* isomers differ in atomic connectivity and thus they are truly different substances. *Rotational* isomers differ in the amount of torsion about a selected bond. If the rotational isomers are separable by their physical properties (the rotational axis is a double bond and there is a relatively high barrier to torsion), they are called *geometrical* isomers (for example, cis and trans dichloroethene). If the rotational isomers are not separable by their physical properties (the torsional axis is a single bond and the barrier to torsion is relatively low), they are called *conformers* (for example, anti and gauche 1,2-dichloroethane).

All isomerisms involve differences in chemical reactivity and other properties. The differing biological activity of enantiomers of certain substances is especially striking.

#### 4. MOLECULAR GEOMETRY

Molecular geometry may be characterized by the relative positions of the atoms in the molecule, or by bond lengths, bond angles, and angles of torsion around bonds. Relative positions of atoms and atomic nuclei are used interchangeably. However, in modern science the distinction is important, and we always mean nuclear positions in the molecule regardless whether atomic or nuclear is stated. Molecular geometry is one of the three characteristics of molecular structure. The other two are intramolecular motion, meaning nuclear displacements only, and the electron density distribution. The terms molecular geometry and molecular structure are often used interchangeably.

It is a great achievement of the ever improving physical techniques [4], both diffraction and spectroscopic, that the molecular geometries of large series of substances have been elucidated. Quantum chemical calculations are joining into this work with increasing intensity and efficiency.

Accumulated information has facilitated systematization of structural properties and the empirical observation of conspicuous trends in the variations of molecular structure. It has been again qualitative models that best capture the dominating effects determining this or that kind of structural feature and can be used not only to account for but to predict structural variations. A qualitative model usually works very well in a certain family of substances where the effect, that it stresses, prevails while other effects, that it ignores, are of much lesser importance.

Considerations of electron-pair repulsions and of ligand/ligand nonbonded interactions have served as good qualitative models for some time. These two models are complementary. The former works well with relatively large central atom and small ligands, and the applicability of the latter is enhanced with increasing relative ligand size. Thus, for example, to the question, what is the shape of the water molecule, and why is it bent, and highly bent at that (the oxygen bond angle is  $104.6^\circ$ ), the electron-pair repulsions have to be considered. With increasing ligand sizes, however, ligand/ligand interactions enter the picture as is seen on the oxygen bond angle of  $\text{Cl}_2\text{O}$ ,  $111^\circ$ , and  $\text{H}_3\text{SiOSiH}_3$ ,  $144^\circ$ .

It is more convenient to emphasize the space-occupying properties of electron pairs rather than simply consider their repulsions. Dealing with the sizes and shapes of the electron-pair domains together with the sizes and shapes of ligands (atoms and atomic groups) have the added advantage of forming a more consistent picture of the interactions governing molecular geometry. Of course it should not be forgotten that we are dealing with qualitative models which tend to stress some effects while ignoring others. Attempts to provide more rigorous physical bases for these models which work so well and can be handled so conveniently, will also be illustrated.

#### 5. ELECTRON-PAIR ARRANGEMENTS

Mention has been made above of the Periodic Table which reflects the electronic structure of atoms and of the electron-pair chemical bond which cements the atoms into molecules. The next question is the determination of the configuration of these electron-pair bonds, ie, the arrangements of the electron pairs around an atom when it is part of a molecule. For simplicity, we shall consider molecules with the general formula of  $\text{AX}_n$  where A and X are atoms and the bond configuration of atom A gives at once the molecular geometry of the whole molecule.

N.V. Sidgwick and H.M. Powell [5] recognized that the number of electron pairs in the valence shell of atom A will determine the bond configuration of an  $\text{AX}_n$  molecule. If the valence shell contains unshared electron pairs, or lone pairs, as well, they also have to be considered. A formula such as  $\text{AX}_n\text{E}_m$  describes a molecule with a central atom A,  $n$  is the number of X ligands, meaning also that there are  $n$  number of A-X bonds, and  $m$  is the number of lone pairs in the valence shell of A. The arrangements of the electron pairs will always be such as to minimize their distances apart.

For two, three, four, five, and six electron pairs, ie, when  $n + m = 2, 3, 4, 5,$  and  $6$ , the arrangements of the electron pairs will be linear, trigonal planar, tetrahedral, trigonal bipyramidal, and octahedral. It is supposed here that the core beneath the valence shell has spherical symmetry, and the distribution of the electron pairs in the valence shell is the same as when mutually repelling points are distributed along the surface of a sphere. The power exponent in the expression of the potential energy of such repulsions is not known in our case of electron pairs in the valence shell. The beauty of this model is in the invariance of the solutions on the power exponent. Incidentally, it is the five-electron-pair, ie, five-points-on-the-sphere case where the solution is somewhat sensitive to the choice of the power exponent. Considerations of mutually repelling electron pairs led to the popular name of this model, VSEPR = Valence Shell Electron Pair Repulsion Model [6].

If all the electron pairs are bonds, the bond configuration will be the same as the arrangement of the electron pairs (Fig. 2). If one or more bonding pairs (bp) are replaced by lone pairs (lp), the bond configuration will be what corresponds to the original electron pair arrangement being a part thereof. Thus, for example, carbon has four electron pairs in its valence shell in the methane molecule,  $\text{CH}_4 = \text{AX}_4$ , both the electron pair arrangement and the bond configuration will be tetrahedral. Nitrogen has also four electron pairs, three bp and one lp, in its valence shell in ammonia,  $\text{NH}_3 = \text{AX}_3\text{E}_1$ , the arrangement of the electron pairs will again be tetrahedral, but the bond configuration will be only part of it, it will be trigonal pyramidal. Oxygen has four electron pairs in its valence shell, two bp and two lp, in the water molecule,  $\text{H}_2\text{O} = \text{AX}_2\text{E}_2$ . The tetrahedral electron-pair arrangement is accompanied

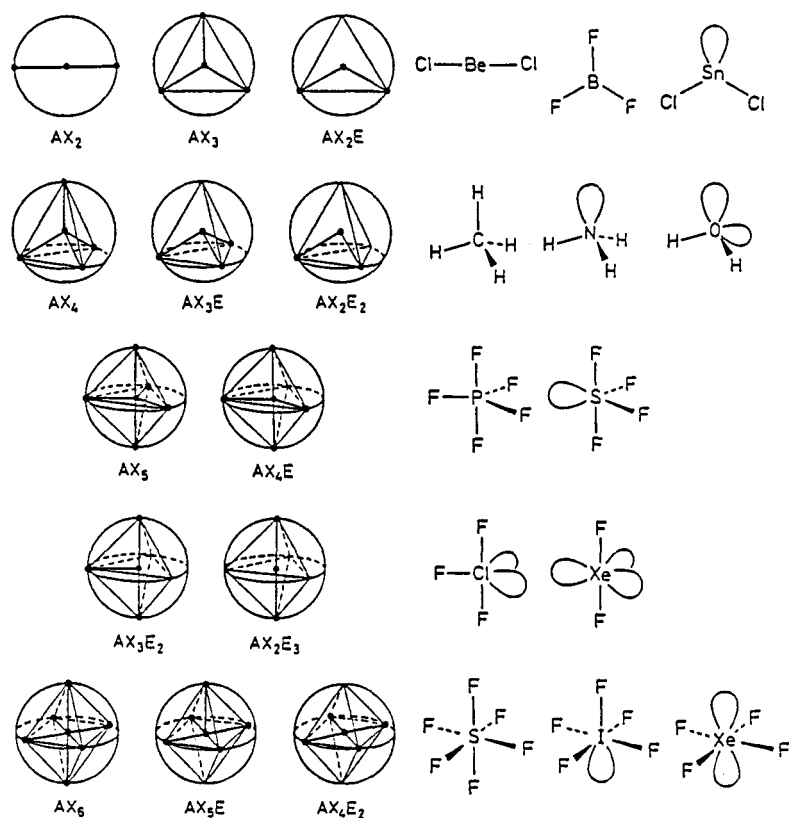


Fig. 2 - Molecular shapes based on the arrangements of two to six valence-shell electron pairs (after Gillespie and Hargittai [7])

here by a bent molecular geometry, as the H-O-H bond configuration is part of the tetrahedral electron-pair arrangement.

This simple picture, already instrumental in establishing a large number of molecular geometries, was expanded by R.J. Gillespie and R.S. Nyholm [6] who noted that the space requirement of a lone pair is greater in the vicinity of the central atom than the space requirement of a bond. Hence the lone pair will be pushing the other electron pairs further away from the central atom. Similarly, a central atom, more electronegative than its ligand, will be drawing a larger part of the bonding pair towards itself than in a bond between a less electronegative central atom and a more electronegative ligand. Due to the smaller repulsions, ie, smaller electron-pair domains, in the valence shell of the central atom, the bonds to the more electronegative ligands will get closer to each other, and, accordingly, the bond angles between bonds to more electronegative ligands will be smaller than between bonds to less electronegative ligands. Thus, for example, the bond angle of  $SF_2$  will be smaller than the bond angle of  $SCl_2$  (Fig. 3a). In an  $AX_nE_m$  description it is not specified whether the AX bonds are single bonds or multiple bonds. Each counts for one bond in forming the general picture and in establishing the general arrangement of electron pairs and bond configuration. In order to determine finer details, a multiple bond is expected to repel neighboring bonds more strongly than a single bond, ie, to have larger electron-pair domains. Accordingly, the bond angles involving multiple bonds are usually greater than the bond angles between single bonds.

The phosgene molecule,  $O=CCl_2$ , for example, has a trigonal planar configuration, as expected for an  $AX_3$  molecule. However, the three bond angles are not equivalent. Those involving the O=C double bond are greater than the bond angle involving the two single bonds (Fig. 3b). Finally, very weak bonds will be repelling less neighboring electron pairs, ie, will have smaller electron-pair domains, than stronger bonds. Thus, eg, bond angles involving three-center bonds will be smaller than analogous angles involving single bonds. Diborane,  $B_2H_6$ , has a two hydrogen-bridge structure with three different HBH bonding situations. The corresponding three kinds of bond angle involve two single bonds, one single bond and a (weaker) three-center bond, and two three-center bonds, respectively, and the bond angles decrease in this order (Fig. 3c). A recent book gives an up-to-date, comprehensive account of the model and its broad applications illustrated with a massive collection of numerical structural data [7].

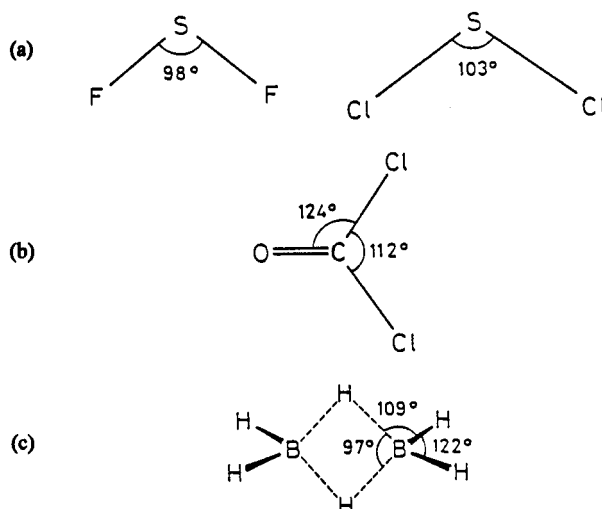


Fig. 3 - Bond angle variations  
 (a) Electronegativity difference  
 (b) Single bond versus double bond  
 (c) Single bond versus three-center bond

## 6. ANALOGIES

The electron-pair domains, obviously unobservable by the naked eye, can, however, be modeled by constructions in which space-requiring units have to arrange themselves in a given space. Walnut clusters and balloon clusters are especially handy for such a purpose. Clusters of both balloons and walnuts yield the same arrangements as described above for electron pairs in the valence shell. The balloon clusters are man-made as the openings of the balloons are joined whereas the walnut clusters grow on walnut trees. A closer look at the more flexible balloon clusters is especially instructive for they can be disturbed easily, forcing, for example, the tetrahedral cluster to take up a planar arrangement. As soon as, however, we let the cluster alone it rearranges itself at once into the previous tetrahedral configuration. Having both kinds of clusters is also instructive because they represent two different degrees of penetration into each other by the rather flexible balloons on the one hand, and by the rigid walnuts, on the other hand. Regardless of these differences, the arrangements are the same.

## 7. DOMAIN-SIZE AND POSITION

The arrangement of the electron pairs in  $AX_6$ ,  $SF_6$ , eg, and in  $AX_5E_1$ ,  $IF_5$ , eg, is octahedral (Fig. 2). The bond configuration of  $AX_6$  is also octahedral, whereas in  $AX_5E_1$  it is tetragonal pyramidal. The position of the lone pair can be chosen arbitrarily in  $AX_5E_1$  as all sites in the octahedral arrangement are equivalent. However, replacing a second bond by a lone pair, ie, in  $AX_4E_2$ , eg,  $XeF_4$ , the position of the second lone pair is predetermined and will be opposite the first one. The two lone pairs, having the largest domains around the central atom, will be at the largest possible distance from each other. The bond configuration of  $AX_4E_2$  will be tetragonal planar (Fig. 2).

In a five-electron-pair arrangement, ie, trigonal bipyramid, there are two different sites to start with. The axial positions are tighter whereas the equatorial positions are looser. This difference will determine that a larger domain will be found at an equatorial site and further larger domains will populate the remaining equatorial sites before taking up axial sites. Thus, for example,  $PF_5$  is obviously trigonal bipyramidal (tbp, Fig. 2).  $SF_4$  is  $AX_4E_1$ , thus its electron-pair arrangement is also tbp but its bond configuration will be determined by the fact that the lone pair is in an equatorial site (Fig. 2). Similarly, chlorine will be found at the end of an equatorial bond in  $ClPF_4$ , the two chlorines and the three chlorines all in equatorial positions in  $Cl_2PF_3$  and in  $Cl_3PF_2$ , respectively. Accordingly, the single fluorine ligand is found in axial position in  $FP_4Cl$  (Fig. 4).

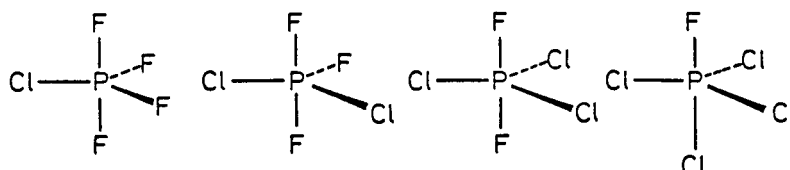


Fig. 4 - Configurations of trigonal bipyramidal fluoride-chlorides of phosphorus(V)

## 8. PHYSICAL BASIS

The search for a sound physical basis of the VSEPR model has gone on almost as long as the model has been around. Many workers have considered if not suspicious, then at least not very becoming for such an extremely simple model to work so well in so broad classes of compounds. There have also been some apparent exceptions which needed further scrutiny. At some point the model was considered to be merely a direct consequence of the Pauli exclusion principle, and it has even been suggested to call it Pauli mechanics.

Molecular orbital calculations [8] have produced geometries consistent with the predictions of the model. They also provided localized orbitals whose shape and size were in complete agreement with the predictions of the VSEPR rules. Unfortunately, there is always some arbitrariness in selecting the localized orbitals. Ideally, the total electron density distribution of a molecule should display all the features that the VSEPR model is based upon. Alas, it is not sensitive enough to such details as the core electron density distribution dominates the pattern. R.F.W. Bader [9] calculated the local concentrations and depletions of the total charge distribution by taking its second derivative. The emerging charge concentrations and their distribution reflect the valence shell electron pairs and their arrangement according to the VSEPR model. This approach, what is really the calculation of the negative Laplacian of the total electron density distribution, provides a sound physical basis of the VSEPR model. It does not, however, replace the model itself as it does not provide a simple means for accounting for, let alone predicting, variations in molecular geometry.

Direct experimental evidence for lone pairs as well as bonds is provided by electron density difference maps. Such a map can be obtained by subtracting the charge densities of isolated atoms from the total charge density of the molecule. For  $(\text{CH}_3)_2\text{TeCl}_2$ , an  $\text{AX}_4\text{E}_1$  molecule, the tellurium lone pair in equatorial position is well seen as projected onto the plane of the two axial Te-Cl bonds, bisecting the equatorial angle C-Te-C (Fig. 5) [10].

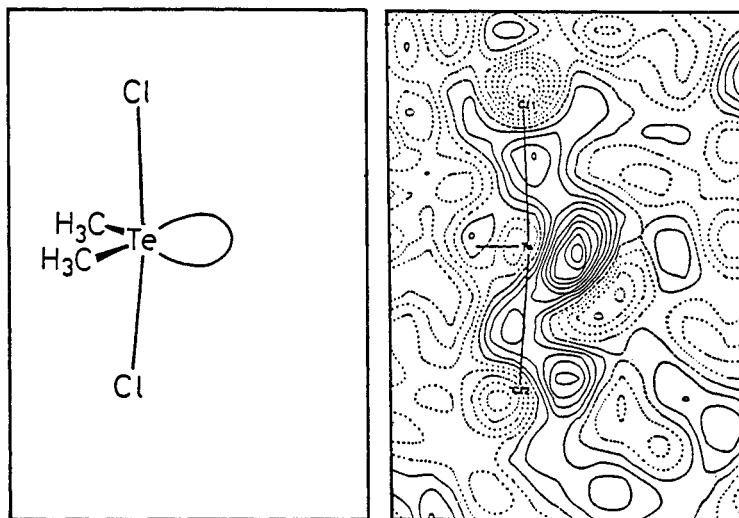


Fig. 5 - Dimethyltellurium dichloride; its trigonal bipyramidal configuration and an electron density difference map displaying the tellurium lone pair in equatorial position (after Ziolo and Troup [10])

## 9. LIMITATIONS

Consider now the hydrogen sulfide,  $\text{SH}_2$ , molecule (Fig. 6). There is only one bond angle, H-S-H, in it. There are two more angles involving its lone pairs, which cannot be measured experimentally but can be calculated by quantum chemical techniques [8]. This picture is again consistent with the relative domain sizes, and thus with the VSEPR model. For the sulfur difluoride,  $\text{SF}_2$ , molecule, the relationship between its angles will be analogous (Fig. 6). However, comparison of the two bond angles H-S-H and F-S-F merely on the basis of ligand electronegativity differences is not adequate for there are other interactions among the electron pairs which also bear the consequences of the electronegativity change. In this particular example the interactions involving the lone pairs far outnumber the bond/bond interaction. A generalized applicability test has been suggested to involve all possible interactions [11]. Seeming controversies can be removed by including all electron pairs in testing the applicability of the model [12].

The VSEPR model assumes a spherical core beneath the valence shell that does not affect the arrangement of the electron pairs in the valence shell. The original simple predictions are no longer valid when the spherical symmetry of the core is deformed as is often the case in transition metal chemistry. Further limitations of applicability occur with increasing relative ligand sizes (see next section).

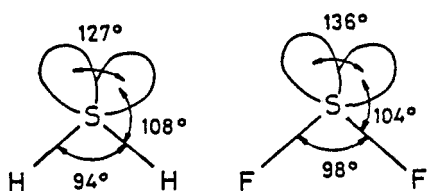


Fig. 6 - Computed angles in hydrogen sulfide and sulfur difluoride (Schmiedekamp et al. [8])

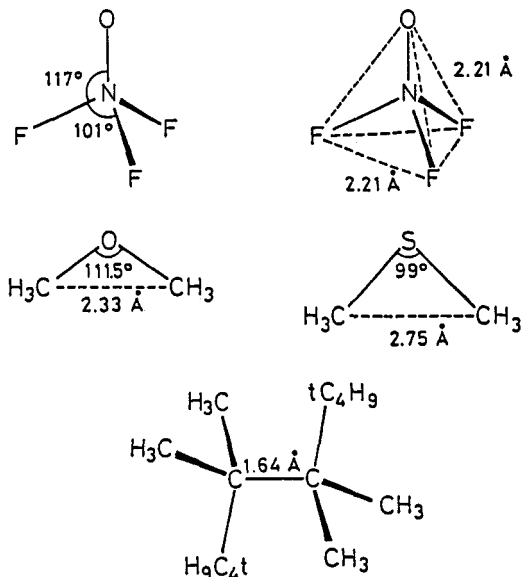


Fig. 7 - (a) Bond angles and nonbonded distances in  $\text{ONF}_3$  [13]  
 (b) Bond angle and nonbonded C...C distance in dimethyl ether and dimethyl sulfide [14]  
 (c) Bond-lengthening influence of the tert.butyl groups [16]

## 10. NONBONDED DISTANCES

Comparison of the bond angles in the  $\text{ONF}_3$  molecule (Fig. 7a) [13] shows that the angle between the NF bonds are considerably smaller than the angles involving the NO bond, considered to be represented by a large electron-pair domain. Thus the VSEPR predictions are fulfilled. It may also be noted that the four ligands of nitrogen represent a near-regular tetrahedron with practically equal edge lengths which may and may not indicate some importance of nonbonded interactions. A remarkable constancy of intramolecular nonbonded distances, such as O...O, O...F, F...F, etc., has been observed in various molecule series [14] which again may imply some importance of such interactions or, for example, some limits at which such nonbonded distances can be found. From such distance limits even a set of intramolecular or 1,3 nonbonded radii have been postulated [15] to the analogy of, for example, covalent radii and intermolecular van der Waals radii. These intramolecular or 1,3 nonbonded radii indicate the importance of space requirements in close nonbonded interactions. It has been noted, for example, that whereas the oxygen bond angle is larger than the ideal tetrahedral in  $\text{CH}_3\text{OCH}_3$ , it is much smaller than the ideal tetrahedral in the analogous sulfur derivative (Fig. 7b). If we compare the nonbonded C...C distances in these molecules with twice the intramolecular 1,3 nonbonded radius of carbon, 1.25 Å, ie, 2.50 Å, the following is observed. In spite of the relatively large angle of dimethyl ether, the two carbon atoms are 0.17 Å closer to each other than 2.50 Å. On the other hand, in dimethyl sulfide the two carbons are at 2.75 Å although the angle is much smaller. The rather short carbon-oxygen bonds bring the two methyl groups close to each other in dimethyl ether and the dominating effect is the nonbonded repulsions. The two methyl groups are well separated in dimethyl sulfide due to the rather long carbon-sulfur bonds, and the angle is determined by the arrangement of the bonding electron-pair domains as part of the tetrahedral electron-pair arrangement in the valence shell of sulfur.

Steric effects have been considered to be important in governing molecular shapes and in the variations of molecular parameters from the time when only very little was known about the details of molecular structure. Bulky groups may considerably change the structural features of a molecule if they have to elbow for space. An example is an ethane derivative where there is a bulky tert.butyl group at each end [16], and the central C-C bond is 0.1 Å longer than in ethane itself (Fig. 7c). There are numerous other examples, and the importance of these effects is well demonstrated in the magnitude of bond lengthening since changing a bond length is the most energy-consuming change of all structural changes.

## 11. ENERGETICS

At this point it is appropriate to introduce some information about the correlation of intramolecular forces and energies, just to see what kind of energetics may be involved in the geometrical changes under discussion [17]. As we describe molecular geometry, most conveniently, by bond lengths, bond angles, and angles of torsion, it seems most informative to indicate the energy requirements of their changes. Of course the amounts of energies are system-dependent so in order to generalize, the values quoted are approximate at best. For a C-C single bond, stretching or compression of 0.1 Å costs about 15 kJ/mol and this amount rises approximately proportionally for double and triple bonds. Bond angle deformation is less expensive than bond stretching. An angular distortion of 10° involves about one third of the energy of the distortion of a single bond by 0.1 Å. Torsion about the C-C bond by 10° from the minimum position in ethane, for example, costs about fifteen times less than a 10° deformation of a C-C-C bond angle. These approximate amounts indicate well that bond stretching is much more expensive energetically than torsion, with angular deformations falling somewhere in between. It is noted here that today's best determinations claim accuracies of a few thousandths of an Å for bond lengths and a few tenths of a degree for bond angles. A caveat should also be stressed, viz. that perturbation of any of the parameters in a molecular structure is accompanied by relaxation of the other parameters. Thus it is too rough an approximation to assume that the parameters change independent of each other in any real structural situation. Such situations arise, for example, when molecules undergo internal rotation [18], molecules dimerize or dissociate, and when molecules condense into crystal structures [19].

## 12. CRYSTAL PACKING

Classical crystallography knows of 230 three-dimensional space groups. This is not a large number if considering that all crystals, naturally grown and man-made, must fall into one of the 230 groups. However, about three fourths of the organic crystals so far determined fall into only five of those 230 space groups, and 12 space groups account for almost 90 % of the compounds [20].

As first was sensed by Kepler, densest packing is probably the single most important concept for describing crystal structures. In atomic/ionic crystals the problem is reduced to the close packing of spheres. In molecular crystals, molecules, often with strange shapes, have to pack in such a way as to minimize the empty space among them. Thus the concave part of one molecule accommodates the convex part of the other molecule. This is also called dove-tail packing versus the less advantageous head-to-head packing. This also explains why a few low-symmetry space groups are the most probable for molecular crystals. Alexander I. Kitaigorodskii [21] analyzed all 230 three-dimensional space groups from the point of view of their ability for densest packing of molecules with arbitrary shape. He essentially predicted the above cited statistics of space-group distribution, long before those data became available, on the basis of a simple geometrical model. It is also remarkable that the 230 space groups were derived at the end of the last century, about a hundred years ago, well before X-ray diffraction began to be applied to crystal structures.

Space-group theory applies to infinite crystals, and, obviously, no crystal is infinite. Scale is important when short-range and long-range orders have to be defined. One of the advantages of the determination of molecular structure in crystals is that the crystal is an amplifier. It multiplies the scattering of X-rays and neutrons from a molecule by the number of molecules in the arrays of the crystal. However, the crystal need not be infinitely large for this purpose. It needs only be large enough to allow the determination of all those properties that are related to the crystal structure being infinite. The actual finiteness of the crystal can be ignored as long as the assumption of its infiniteness is a satisfactory one for the detection and determination of the properties sought [22].

## 13. QUASICRYSTALS AND FULLERENE MOLECULES

Only axes of rotational symmetry of orders 2, 3, 4, and 6 occur in the space groups to which all proper crystalline substances belong. Nevertheless, icosahedral arrangement has been considered for three-dimensional packing as it is the most symmetrical way to arrange twelve spheres. However, it is not the densest packing and it is not a crystallographic packing. When the icosahedra are packed together, they do not form a plane but curve up gradually and eventually form a closed system. There is marked similarity here to the C<sub>60</sub> cluster molecule called buckminsterfullerene, synthesized recently in measurable amounts [23].

Dan Shechtman et al. [24] published in 1984 the first experiment producing a fivefold symmetric point electron diffraction pattern from a sample of splat-cooled Al/Mn alloy. The experiment clearly indicated that the micron-sized grains of the alloy were indeed simple crystals. On the other hand, the pattern unambiguously displayed icosahedral symmetry. The term quasicrystal was coined by D. Levine and P.J. Steinhardt [25], also in 1984, and it refers to the mathematical term quasiperiodic which means a pattern that can be built up as the sum of a finite number of periodic waves. Fivefold symmetry is thus intimately involved with two new areas, quasicrystals in physics and buckminsterfullerene and similar molecules in chemistry [26]. Curiously, fivefold symmetry has played a conspicuous role in Nature and other fields of human endeavor as well [27].



#### 14. ENZYME ACTION

Emil Fischer discovered in 1894 that glycolytic enzymes can distinguish between stereoisomeric sugars, and this discovery led to the formulation of his famous lock-and-key hypothesis. The specificity of an enzyme (the lock) for its substrate (the key) arises from their geometrically complementary shapes. Again chemical intuition, experience, and modeling preceded a lot of hard-core knowledge as the chemical composition of enzymes was not firmly established until the 20s and 30s of the twentieth century. The first X-ray structure of an enzyme was then elucidated in 1965.

Geometrical complementarity thus means that a substrate-binding site is an indentation on the enzyme surface that is complementary in shape to the substrate. Enzymes, by virtue of their inherent chirality, form asymmetric active sites. This is their stereospecificity. Finally, there is also geometrical specificity in that the enzymes are selective about the identity of the chemical groups of the substrate. This latter is, however, not so strict a requirement as stereospecificity.

#### 15. MOTION

Whether individual molecules in the gaseous state or molecules locked into a crystal structure, intramolecular motion influences size and shape [4]. Bending deformation motion will make a linear molecule appear bent or a planar molecule appear puckered. Thermal ellipsoids well demonstrate the atomic displacement distribution in the crystal. Motion and thus shape and size are strongly temperature-dependent. Even if appropriate corrections can reduce such motion-averaged geometries to the equilibrium geometries corresponding to the minimum potential energy, the average structures have great practical importance as they represent best the systems participating in real events, for example, chemical reactions.

#### 16. IN LIEU OF CONCLUSIONS

Using up available space by electron pairs, elbowing for space by bulky atomic groups, dove-tail packing of molecule with molecule or enzyme with substrate, all this shows the importance of space in chemical structures, and accordingly, chemical properties. Chemical reactions occur by way of transition states as reactants become products, and spatial properties of the transition states are being increasingly investigated.

Johannes Kepler understood something important in the governing principles of the microworld when he was looking at snowflakes. It is true, however, that his space considerations also counted for the spectacular failure of his planetary model based on regular polyhedra enveloping each other. He would be amused though by recently discovered cluster molecules, metal carbonyls, for example, in which one regular polyhedron frame of atoms envelopes another regular polyhedron frame of atoms.

This paper is not presenting a closed area of knowledge, rather, it is merely calling attention to the importance of simple space considerations in chemistry. It is hoped that by doing so, it will stimulate truly synergic interactions of chemistry with other fields.

#### REFERENCES

- Fuller, R.B.: *Synergetics: Explorations in the Geometry of Thinking*. New York: Macmillan 1975, pp. 108-109
- Kepler, J.: *Strena seu de nive sexangula. Fracoforti ad Moenum: Godefridum Tampach 1611*. English translation, *The Six-Cornered Snowflake*. Oxford: Clarendon Press 1966
- Lewis, G.N.: *J. Am. Chem. Soc.* 38, 762 (1916)
- Domenicano, A., Hargittai, I., eds.: *Accurate Molecular Structures*. Oxford: Oxford University Press 1992
- Sidgwick, N.V., Powell, H.M.: *Proc. Roy. Soc.* A176, 153 (1957)
- Gillespie, R.J., Nyholm, R.S.: *Quart. Rev. Chem. Soc.* 11, 339 (1957)
- Gillespie, R.J., Hargittai, I.: *The VSEPR Model of Molecular Geometry*. Boston: Allyn and Bacon 1991
- Schmiedekamp, A., Cruickshank, D.W.J., Skaarup, S., Pulay, P., Hargittai, I., Boggs, J.E.: *J. Am. Chem. Soc.* 101, 2002 (1979)
- Bader, R.F.W., MacDougall, P.J., Lau, C.D.H.: *J. Am. Chem. Soc.* 106, 1594 (1984)
- Ziolo, R.F., Troup, J.M.: *J. Am. Chem. Soc.* 105, 229 (1983)
- Hargittai, I., Chamberland, B.L., in: *Symmetry: Unifying Human Understanding*, pp 1021-1038 (I. Hargittai, ed.). New York: Pergamon Press 1986
- Hargittai, I.: *Inorg. Chem.* 21, 4334 (1982)
- Plato, V., Hartford, W.D., Hedberg, K.: *J. Chem. Phys.* 53, 3488 (1970)
- Hargittai, I.: *The Structure of Volatile Sulphur Compounds*. Dordrecht: Reidel 1985
- Bartell, L.S.: *J. Chem. Phys.* 32, 827 (1960); Glidewell, C.: *Inorg. Chim. Acta* 20, 113 (1976)

16. Winicker, R., Beckhous, H.-D., Ruckhardt, C.: Chem. Ber. 113, 3456 (1980)
17. Bernstein, J., in: Ref. 4, Chapter 19, p. 469
18. Scharfenberg, P., Hargittai, I.: J. Mol. Struct. 112, 65 (1984)
19. Hargittai, M., Hargittai, I.: Phys. Chem. Minerals 14, 413 (1987)
20. Mighell, A.D., Himes, V.L., Rodgers, J.R.: Acta Cryst. A39, 737 (1983); Donohue, J.: Acta Cryst. A41, 203 (1985)
21. Kitaigorodskii, A.I.: Molekulyarnie kristalli. Moscow: Nauka 1971
22. Mackay, A.L.: Acta Cryst. 22, 329 (1967)
23. Huffman, D.R., Lamb, L.D., Kratschmer, W.: Nature 347, 354 (1990)
24. Shechtman, D., Blech, I., Gratias, D., Cahn, J.W.: Phys. Rev. Lett. 53, 1951 (1984)
25. Levin, D., Steinhardt, P.J.: Phys. Rev. Lett. 53, 2477 (1984)
26. Hargittai, I., ed.: Quasicrystals, Networks, and Molecules of Fivefold Symmetry. New York: VCH 1990
27. Hargittai, I., ed.: Fivefold Symmetry. Singapore: World Scientific 1992