A topological and geometric outline for description and design of polymeric macromolecules with structure regularity*

F. Danusso, G. Tieghi, and T. Ricco†
Industrial Chemistry Dept., Macromolecular Chemistry and Materials Section, Polytechnic Institute of Milan (Italy)
(Received 15 August 1978; revised 19 December 1978)

The study of a chemical aggregate (molecule or molecular fragment) must proceed through the choice of a qualifying model. The structure of the aggregate (the way in which its model is constructed) can be defined and assigned through a system of levels, first topological and then geometric in nature. Different kinds of structural regularity may be defined, and their related properties studied, first considering one-row aggregates, and then multi-row aggregates which are considered as appropriate combinations of one-row aggregates. The complete topological and geometric systematics of regular one-row aggregates is derived. At geometric levels, complete regularity mathematically implies (in one-row aggregates) a generalized helical structure, which may be more expressively analysed in five (proper, limiting and degenerate) forms of their 'monoatomic equivalent' reticular skeleton. It is also shown how the choice of a more detailed equivalent model may lead to a wider shape classification. Examples of reticular skeletons of regular two and three-row unit aggregates are also given. Criteria are discussed in order to attribute a 'dimensionality' to the aggregates under study, and also in relation to their shape characterization.

GENERAL CONSIDERATIONS

Methodology and aim of the research

Both the main subjects mentioned in the title (description and design) require:

(a) a sharp definition of the object of interest, i.e. of the chemical aggregate (molecule or molecular fragment);

(b) since this is a complex, invisible object, a proper definition of the model by which we intend usefully to represent it, which itself becomes the object under study;

(c) the method by which the structure of the object (the model) can be assigned in all its features;

(d) definitions relating to structure regularity;

(e) the individualization, in a rational way, of all the possible forms the object (model) with the structure regularity under consideration can assume.

A method of studying this last point may be a convenient morphogenesis which can also be considered as the model for a synthesis operation. Such a model evidences the essential elements which have to be considered in a shape-based design.

The subject will here be dealt with from the point of view of the topology and geometry of the object, that is of those fundamental structural aspects which may be called 'compositive' and 'connective' and possibly 'figurative'. These are distinct from those of the 'attributive' structure, which, depending on the problems, will also include chemical, physical or biological features, associated with or supported by the topological and geometrical structure.

It seemed advisable to go back to primitive concepts, and then to re-establish them in a mathematical framework in a language which is hoped to be more straightforward, and of a higher degree of intuition and generality. This particularly refers to the balance between geometric and topologic means: the latter are largely used by chemists on intuitive grounds; however, their relationship with the former means, with which they should constitute a concerted approach to structure is not always clearly recognized.

It appears reasonable that such a methodology should lead to some valuable assistance along many lines of present macromolecular research, such as:

(i) to reach a better systematization of the large number of results so far obtained by macromolecular chemists;

(ii) to supply macromolecular chemists with more effective means for planning and forecasting in their work;

(iii) in particular, to offer more appropriate methodological means of designing the synthesis of two and three-dimensional macromolecules with a regular structure;

(iv) to help in the introduction of simulation of the more specifically chemical aspects of macromolecular research;

(v) to assist in dealing with the problems which arise in the study of relationships between the shape of macromolecules and their chemical, physical or biological functions.

In this paper a brief and not exhaustive idea will be given of the essential problems which arise in the deepening of the subject, as well as of the main results so far obtained[1].

---

* General lecture read by F. Danusso at the 3rd Italian Meeting of Macromolecular Science, Milan, October 17–19, 1977

† Present address: Istituto di Chimica Industriale del Politecnico, Sez. Chimica Macromolecolare e Materiali, Piazza Leonardo da Vinci 32, 20133 Milan, Italy

0032–386/79/070805–08$02.00

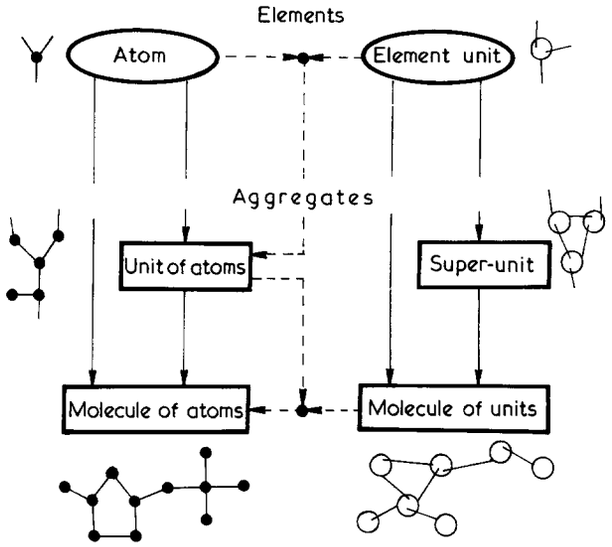

Figure 1 Genealogic relationship between elements usually considered and chemical aggregates

Chemical aggregates

The object under study is the chemical aggregate. This is the result of a chemical aggregation of elements. Every element is connected to another by at least a chain of elements and chemical bonds, and, in particular, is chemically juxta-connected to a number of adjacent elements equal to what is defined as its connection valency.

A chemical aggregate is stoichiometrically closed (molecule) when all the chemical bonds are established between its own elements and stoichiometrically open (molecular fragment) when some of the chemical bonds are established with foreign elements (or aggregates).

The elements usually considered by chemists are atoms but in some instances usefully chosen molecular fragments are considered (each as a whole) as primitive components, which may be given the name 'element units'.

Aggregates may thus be conceived as being made up either of atoms or of element units (or possibly by both of these kinds of elements, though atoms can be considered as a particular case of element units).

In practice, depending on the problems, chemists deal with any of the following kinds of chemical aggregate:

(A) a unit of atoms (i.e. a fragment no longer considered as an element unit, but as a stoichiometrically-open aggregate of atoms);

(B) a super-unit (i.e. a larger fragment, stoichiometrically open, deriving from aggregation of two or more element units);

(C) a molecule of units (i.e. a stoichiometrically-closed aggregate of element units);

(D) a molecule of atoms (i.e. a stoichiometrically-closed aggregate of atoms).

The genealogical relationship between these elements and aggregates is represented in *Figure 1*, with a symbolic indication of their constitution. Clearly, the most detailed structural description is given by aggregates of atoms.

Models of aggregates

Any reasoning concerning chemical aggregate structure must proceed through the conception and consideration of a model, and is widely qualified by the choice of the kind of this model.

The most commonly used model of a chemical aggregate is the graphic model, which identifies elements with points and chemical or connective bonds between elements with segments. Another extreme model sometimes used is the solid model, which envisages the aggregate in a material way, with elements having their own volume (for example, the scale models constructed from laboratory kits). Depending on the problems, a wide variety of intermediate models may also be used, as illustrated below. These can be of mathematical or geometrical conception, or may be thought of as retaining some of the material character of the aggregate.

In graphic or solid models, at levels of topologic description, atoms and element units can be represented in the same way, for example, as points or small spheres, with the bonds converging to their centres. At levels of geometric description, however, atoms can again be represented in this way, whereas element units require a more complex representation, since the bonds of every unit do not converge in general towards a single centre. For this level of complexity, the element units have scarcely been applied so far in geometric considerations, but prevailingly introduced as units of atoms.

Equivalent models are more easily handled when dealing with aggregates of units: they substitute a simpler figure for each unit which retains some of the relevant features of the unit and is more fit for less detailed, but simpler, figurative considerations (for example, in the 'monoatomic equivalent' model each unit is replaced by a hypothetical single atom; in the 'biatomic equivalent' model by a suitable pair of hypothetical atoms, etc.).

Structure of a chemical aggregate

The structure of an aggregate is the way in which it, or rather its model, is made. Structure assignment (analysis, description, synthesis, etc.) in chemical practice is usually referred to connective structure. It is actually done by proceeding in insight steps, or levels, topological at first, then geometric in nature; this is done by assigning values or specifications to structural variables, selected to describe the variety of figures the model can assume.

In this way, the structure of a chemical aggregate identifies with a set of parametric specifications associated in an orderly manner, by levels, to part or all of the variables which among those describing the model chosen to represent the aggregate itself, directly or indirectly lead to information about compositive, topological or geometric features.

A homogeneous system of levels with relating structural variables is illustrated in *Table 1* for the graphic model of a molecule of atoms. The classification of the 2nd column is the customary one in modern chemistry.

At any level, a level structure is assigned, which implies knowledge of the structure of the lower levels, and which leaves out the structure of the higher levels (which may be unknown). Clearly a complete knowledge of the connective structure is reached at the highest level (the conformational one).

It is interesting to note that two aggregates have equal structure when they have equal corresponding structural parameters for the same model and the same set of structural variables. Such an equality may take place up to a certain level, and not at higher levels (isomerism). Generally, the structure equality of two aggregates has therefore to be stated, or assigned, with the specification of the level at which it occurs or is considered.

It may also be interesting to point out that equality defined in this way means the most intuitive topological or

Table 1 Level assignment of a molecular structure (molecule of atoms; graphic model)

Level qualification			Level name	Structural variables
Topology	Composition		Stoichiometric (Topologic–1)	Kinds of atoms and their number
Topology	Constitution		Constitutional (Topologic–2)	Pairs of juxta-connected atoms and kinds of bonds
Topology	Configuration	Orientational	(Topologic–3)	Labels ordering the juxta-connection set of each orientable atomic centre
Geometry	Configuration	Steric	(Geometric–1)	Descriptors of the steric arrangement of the juxta-connections around oriented atoms
Geometry			Metric (Geometric–2)	Bond lengths and angles
Geometry	Conformation		Conformational (Geometric–3)	Internal rotation angles

geometric superposability, which has different names and definitions in the mathematics*.

STRUCTURE SYSTEMATICS OF REGULAR ONE–ROW AGGREGATES

One-row aggregates

The description and morphogenesis of chemical aggregates with structure regularity will be carried out by studying first regular one-row aggregates, and then regular multirow aggregates. The latter can be generated through regular combinations of the former, that is by proper wielding or partial merging of more than one regular one-row aggregate in every unit.

A one-row aggregate† is an aggregate whose structural features can be completely and orderly described with logical or topological reference to points arranged along a line, in such a way that any pair of juxta-connected elements of the aggregate has a one-to-one correspondence with a pair of adjacent points on the line.

Structure regularity

Regularity is most generally taken to mean equality of parts and/or of relations between parts. Structure regularity means structure equality of parts and/or equality of structural relations between parts.

For the aggregates of interest in the present study the most important definitions will be reported in the following, bearing in mind that, holding the above equality to be referred to structural levels, any type of regularity will be understood as level regularity.

An aggregate has composition regularity when it can be divided into an integer number of units of equal structure‡.

The following are symbolic examples of one-row aggregates with composition regularity (at the configurational level)

(a) –AHAAHAAHAAHAAHAAHA–
unit: –AHA– (indifferent to orientation)

(b) –AHTTHATHAAHTAHTAHT–
unit: –AHT– (orientable)

(c) –ADADADCIACIAAD–
unit: –AD– (orientable and with orientable elements)

(d) –AYAYYAYAYAAY–
unit: –AY– (orientable)

An aggregate has juxta-connection regularity when it consists entirely of units of corresponding (or equal) structure, and is such that, for whatever pair of juxta-connected units, there is identical mode of connection and mutual orientation ('juxta-connection rule') of the two units.

Examples of one-row aggregates with juxta-connection regularity (at the configurational level) are the following ones (superunits):

(a) –AHAAHAAHAAHAAHAAHA– unit: –AHA–

(b) –ADADADADADAD– unit: –AD–

(c) –AYAYAYAYAYAY– unit: –AY–

(d) –ACADADADACAC– units: –AC– and –AD–, for which a correspondence is established between –C– and –D–.

An aggregate has insertion regularity when it entirely consists of units of corresponding (or equal) structure, and is such that every unit has a same mode of insertion in the aggregate ('insertion rule'), i.e. a same set of connection and mutual orientation modes with its juxta-connected units, orderly considered.

The following are examples of one-row aggregates with insertion regularity (at the configurational level)

(a) . . . –AHAAHAAHAAHAAHAAHA– . . . unit: –AHA

(b) . . . –AHTAHTAHTAHTAHT– . . . unit: –AHT
. . . –AHTTHAAHTTHAAHTTHA– . . .

(c) . . . –AYAYAYAYAYAY– . . . unit: –AY–

(d) . . . –ACIAADCIAACCIA– . . . units: –AC– and –AD–, for which a correspondence is established between elements –C– and –D–.

An aggregate has complete regularity when both composition and insertion regularity are present in it.

From these definitions, properties of regular aggregates can be derived, as well as relations between regularities of different kinds.

For example, in an unlimited (finite or infinite) one-row aggregate, when complete regularity is present, juxta-

* At the topological levels such an equality essentially conforms to the concept of isomorphism. At the conformational level it corresponds to what is variably referred to as direct equality (elementary geometry), proper congruence (e.g. Weyl), compatible equality or congruence (e.g. Shubnikov), and direct isometry (e.g. Coxeter). This is different from what is named opposite equality (elementary geometry), improper congruence (e.g. Weyl), mirror equality (e.g. Shubnikov) and opposite isometry (e.g. Coxeter): such an equality frequently implies, in our view, a difference of structural parameters already at the configurational level

† Frequently also called 'linear', or, if appropriate, 'branched' or 'cyclic'. When open, it corresponds to a 'tree' of graph theory; when closed it results in a single cycle. In the case of a branched structure, every branch (side group or chain) has to be considered part of a single element along the row

‡ The dividing operation is here postulated as the splitting of bonds and not, as a rule, of elements. In the former case units result in a stoichiometrically proper aggregate (stoichiometrically proper unit); in the latter the unit is only a speculative improper aggregate (stoichiometrically improper unit). The bonds are in turn postulated as connective bonds: between two juxta-connected units only one 'connective' bond is considered along the row, whatever the number of 'chemical' bonds

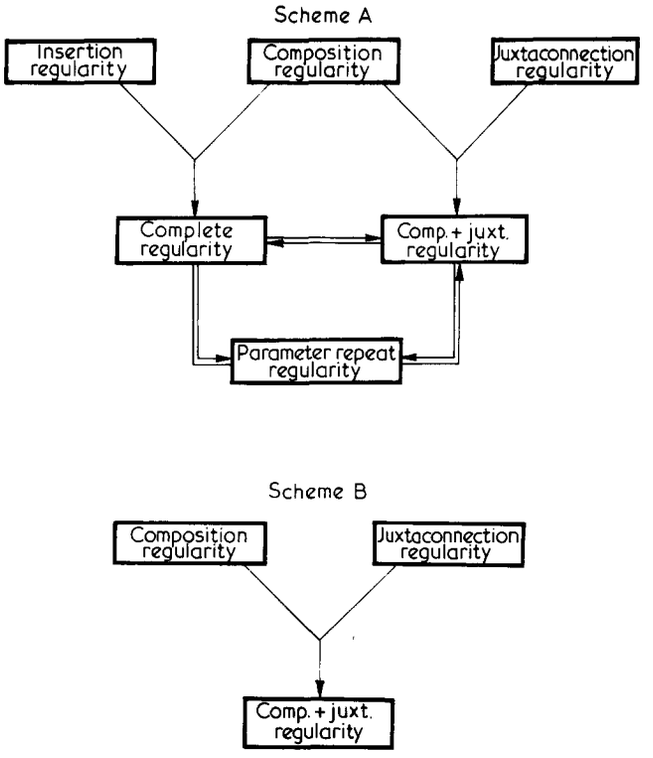

Figure 2 Relationship between regularities of different types in one-row aggregates. Scheme A, unlimited aggregates; Scheme B, limited aggregates, when juxta-connection unit is orientable (juxta-connection regularity can also take place in limiting form). Scheme A, limited aggregates, when juxta-connection unit is indifferent to orientation (juxta-connection regularity can also take place in limiting or degenerate form)

connection regularity is also present, with a unit equal to once or twice that of the insertion regularity if this latter is orientable, and equal to the latter if it is indifferent to orientation. At the topological levels, when the units are indifferent to orientation, composition regularity implies also, with the same unit, both insertion and juxta-connection regularity.

A limited (and then finite) regular one-row aggregate may have either insertion or juxta-connection regularity, or both, depending on the kind of units, their number and connection pattern. With insertion regularity the aggregate consists of only two insertion units; for this reason complete regularity of a limited aggregate is more typically designated as binodal regularity. With insertion regularity, juxta-connection regularity may be present in a proper way, but also as a limiting (only two units) or degenerate case (only one limiting unit).

Examples (at the configurational level) of limited one-row aggregates (all, but one, superunits):

(i) –AHAAHAAHAAHAAHAAHA–
6 juxta-connected units –AHA–; 2 insertion units –AHAAHAAHA– (in general: even number of indifferent juxta-connected units; 2 insertion units)

(ii) –AHAAHAAHA–
3 juxta-connected units –AHA–; 2 improper insertion units $-AHAA(H)_{1/2}-$ (in general: odd number of intrinsically indifferent juxta-connected units; 2 improper insertion units)

(iii) –AHAHAH–
3 orientable juxta-connected units –AH–; no insertion regularity (in general: *n* orientable juxta-connected units; no insertion regularity)

(iv) –AHHAAHHAAHHA–
3 juxta-connected units –AHHA–; 2 insertion units –AHHAAH–

(v) –AHAAHA–: 2-juxta-connected units –AHA– (limiting case); 2 insertion units –AHA–;
–AHAH–: 2 juxta-connected units –AH– (limiting case); no insertion regularity;
–AHHA–; MA–AM (molecular aggregate) degenerate juxta-connection regularity; 2 insertion units.

Other general properties are as follows: an aggregate with complete regularity is such that a hypothetical observer, first placed on a particular insertion unit and then transferred to another, cannot distinguish between the two positions in the aggregate; in other words, the (topologic or geometric) dispositions of the insertion units in the aggregate are all equivalent (a primitive and generalized expression of symmetry).

In particular, complete one-row regularity can be defined or recognized as parameter repeat regularity: a hypothetical observer, who proceeds along the unlimited row of the aggregate and records values and specifications for all the structural parameters (in the order the corresponding structural features are met and analysed according to a level system), finds a periodic sequence of values and specifications. The period sequence is the parameter repeat unit.

In unlimited aggregates this parametric unit, mathematical in nature, physically corresponds to the juxta-connection unit, and retains all information about the structure of this latter unit and its juxta-connection rule. For binodal regularity, parameter repeat cannot be present in the normal way since the aggregate is limited. However, it can be considered present by using an appropriate convention – an unlimited pendular running along the limited row of the aggregate, within its two ends. In this way, when insertion regularity is present, the parameter repeat unit corresponds to a pair of insertion units (that is, to the limiting case of the whole aggregate); when insertion regularity is not present, the parameter repeat unit corresponds to the double of the entire aggregate, so that the parameter repeat becomes a degenerate case of regularity.

In unlimited aggregates, when the parameter repeat recording is the same in both of the opposite running directions along the row, the aggregate is indifferent to orientation, whereas if the two recordings are different, the aggregate is orientable. In limited aggregates, binodal regularity makes the aggregate indifferent to orientation in any case.

The genealogic relationship between regularities of different type is summarized in *Figure 2*.

Possible one-row aggregates with parameter repeat regularity: topologic systematics

Using the definitions and properties of regular structures, it is easy to state precisely what types of parameter repeat regular, one-row aggregates are possible at the highest topological level.

The possible parameter repeat units can be distinguished into orientatable and indifferent to orientation. The indifferent ones can in turn be distinguished into: (a) intrinsically indifferent, and (b) indifferent as the result of coupling between two insertion units with opposite orientation. Symbolic examples of possible units are:

(a) orientable: –AH–, –AHT–, –B–, –ABC–, –ABA–, –AY<,M–;

(b) intrinsically indifferent: –A–, –AHA–;

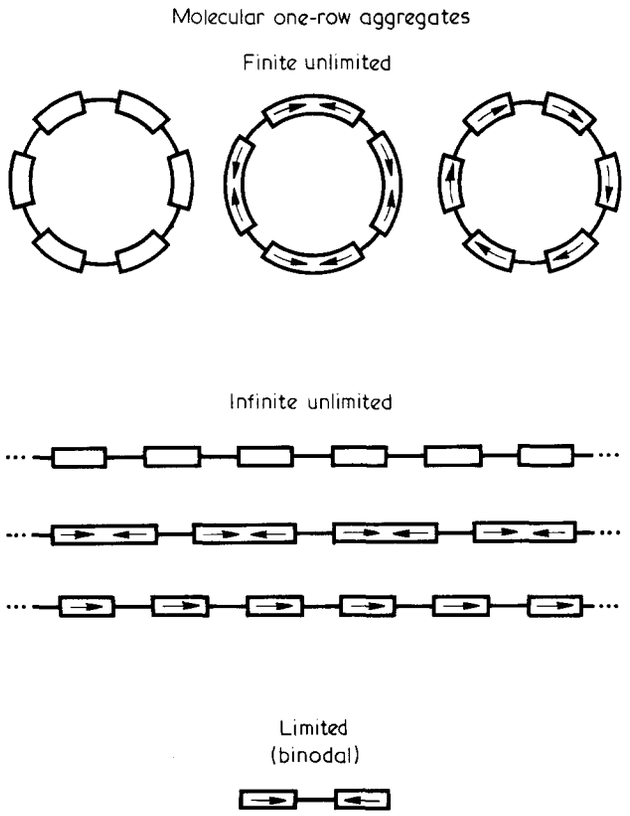

Figure 3 Topological classification of the possible molecular one-row aggregates with parameter repeat regularity (configurational level)

(c) indifferent because of opposite coupling; –AHHA–, –ADCIA–.

Depending on the type of unit and its connection pattern, corresponding whole aggregates are accordingly orientable or indifferent to orientation.

All the parameter repeat regular aggregates should be unlimited. For one-row aggregates this condition can be reached in either of two ways: with (finite) cyclic aggregates or with infinite open aggregates.

The binodal aggregates are physically finite and limited. However, in a mathematical sense, they can also be seen as unlimited through the already mentioned expedient of pendular running on the finite row. This is theoretically possible, for example in the limiting situation of the 'squashing' of an unlimited running on a cyclic aggregate. If this view is accepted, in a complete pendular period two parameter repeat units are generally encountered, and the aggregate can be put in correspondence with a finite (double) row bearing two parameter repeat units at its ends, in agreement with the most relevant feature of binodal regularity.

The whole topology for molecular aggregates is schematically illustrated in *Figure 3* (the degenerate case of binodal regularity has been omitted). This same topology can be extended to stoichiometrically open aggregates, i.e. superunits, when these have only half-bonds which are lateral with respect to their row. For superunits which also have end half-bonds, and are therefore limited, only binodal regularity is possible.

Study at geometric levels – reticular skeleton

The geometry of an aggregate depends on all its structural detail and offers an infinite variety of possibilities. If one wishes to describe all the possibilities in a simple way, it is necessary to define typical forms comprehensible in a finite classification.

The figurative structure of an aggregate can be generally thought of as deriving from the combination of two elements: (a) the 'skeleton', and (b) the 'substance' which covers the skeleton. The 'substance' can realize an infinite set of possibilities, but the 'skeleton', if regular, can be classified in a relatively small number of fundamental forms. This number depends on the way in which the skeleton is defined; that is, on the simplicity of the model chosen to represent the aggregate schematically.

A reticular skeleton is defined as the geometric figure obtained when in an aggregate with complete regularity, observed at the conformational level and with all its structural variables settled at parametric values or specifications, we can substitute a simpler figure for each unit and for each row crossing the unit a line of a defined geometric form (directrix line). Usually, it is this line (or a system of these lines) that allows one to define the shape of the aggregate.

Possible shapes of molecular one-row aggregates with parameter repeat regularity – monoatomic reticular skeleton

Particularly simple and expressive is the reticular skeleton obtained by a monoatomic equivalent model, that is by substituting in general an atom (point) for every unit and a pair of bonds (segments) for each row crossing the unit. Thus every row assumes the shape of a polygonal line, whose vertices represent the units on the row, and the sides the connection bonds between units*. The substitutive atoms (vertices) can be placed on a point arbitrarily chosen on every unit but in corresponding position in all the units.

It can be demonstrated in a completely general mathematical manner that when in a one-row aggregate complete regularity is present, corresponding points of the parameter repeat units lie equidistant along the same cylindric circular helix. Therefore, the monoatomic reticular skeleton of the same aggregate will be in general a helical polygonal line, inscribed in a cylindric circular helix passing through its vertices.

The corresponding shape has helical appearance only in the reticular skeleton of a part of the infinite unlimited aggregates. In other one-row aggregates such a skeleton assumes shapes mathematically derivable from the helical one, but representing particular, limiting or degenerate cases of the cylindrical circular helix. These shapes can be classified in four other expressive forms.

The five possible monoatomic forms are represented in *Figure 4*, with an indication of a morphogenesis of projective type as an example of a rational derivation of every form from the fundamental, with proper helical shape. Among these, the cyclic and binodal ones can also be recognized, as already foreseen in the topological systematics.

In the same *Figure 4* a sixth form is indicated (single point), which is doubly degenerate, and corresponds to the very particular case of degeneration of parameter repeat regularity (for example, degeneracy of the binodal case).

Relationship between juxta-connection parameters and shape–shape generator

For the design of a completely regular aggregate two elements have to be established: (a)the structure of the units and (b) their mode of juxta-connection. All the parameters relat-

* If appropriate, in this model the polygonal line representing the row can be substituted by another expressive directrix line (helix, circle, etc.)

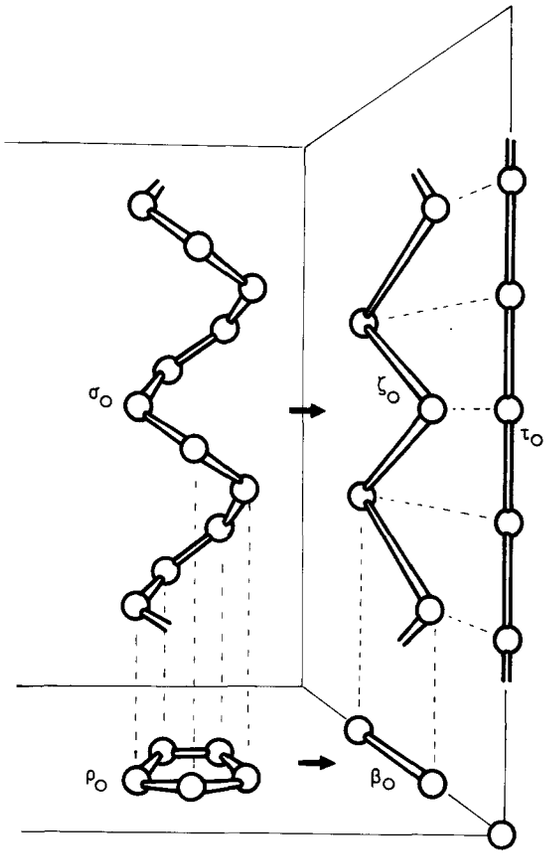

Figure 4 Five forms of 'monoatomic' reticular skeletons of parameter repeat regular one-row aggregates (conformational level; corresponding shape generators are indicated)

ing to both these elements are contained in the parameter repeat unit; when this unit is singled out, we have information concerning the whole molecular structure and a possible means for its geometric synthesis. The latter is based on a repetitive and cumulative juxta-connection operation which simulates polymerization. The corresponding 'operator' is also the one which, when applied to a given unit, determines the shape of the aggregate, i.e. its morphogenesis*.

A practical way of reasoning may be the following: the parameter repeat unit can be represented on the graphic model of a unit of atoms at the conformational level, by a matrix which collects, in an orderly manner, the values of the parametric triads, l_i, θ_i and ϕ_i (bond lengths, supplementary bond angles and internal rotation angles) relating to all the atoms met with along the row. From these parameters, the passage to the monoatomic reticular skeleton can be made by calculating the corresponding matrix of the parameter repeat unit of the monoatomic equivalent model, consisting of a single triad L, Θ, Φ (the unit reduces to a single substitutive atom). In general:

$$\begin{vmatrix} l_1 & l_2 & l_3 & \dots & l_n \\ \theta_1 & \theta_2 & \theta_3 & \dots & \theta_n \\ \phi_1 & \phi_2 & \phi_3 & \dots & \phi_n \end{vmatrix} \longrightarrow \begin{vmatrix} L \\ \Theta \\ \Phi \end{vmatrix}$$

From this triad, the non-dimensional parameters Θ and Φ can be selected, generally characterizing a shape generator, $\gamma(\Theta;\Phi)$, such that, depending on the values or ranges of values of Θ and Φ, the monoatomic reticular skeleton assumes the shape of any of the five fundamental forms. To each of them a specific generator can be made to correspond according to the following Table:

Helical polygonal line	$\sigma_0 =$	$\gamma[\Theta \neq 0, \pi; \Phi \neq 0\pi]$ *
Planar zig-zag	$\zeta_0 =$	$\gamma[\Theta \neq 0, \pi; \Phi = \pi]$
Straight line	$\tau_0 =$	$\gamma[\Theta = 0; \Phi$ indef.]
Planar polygon	$\rho_0 =$	$\gamma[\Theta = 2\pi/k; \Phi = 0]$ (k = integer > 2)
Dumb-bell	$\beta_0 =$	$\gamma[\Theta = \pi; \Phi$ indef.]

* The helical polygonal line is rational when:

$$\text{arc cos}\frac{1}{2}(\cos\Theta + \cos\Phi + \cos\Theta\cos\Phi - 1) = \frac{m\pi}{n}$$

(m,n = integers) and otherwise is irrational

Orthogonal biatomic reticular skeleton

As an example of a more detailed skeleton model, we will mention here the orthogonal biatomic equivalent model, according to which every parameter repeat unit is substituted by one consisting of two hypothetical biconnected atoms, both having bond angles of $\pi/2$ and two end bonds colinear with the end bonds of the real unit. As shown in *Figure 5* (top for a unit, and bottom for two juxta-connected units), the substitutive unit can be constructed by prolonging the first and the last bond of the real unit and by intersecting the two segments (in general skew) with a third one, orthogonal to both the former, which represents the shortest distance between them as well as the bond between the two hypothetical atoms (placed on the two intersection points).

In the same *Figure 5* four parameters are indicated, sufficient to characterize the model unit completely, and which can be calculated from the real values*:

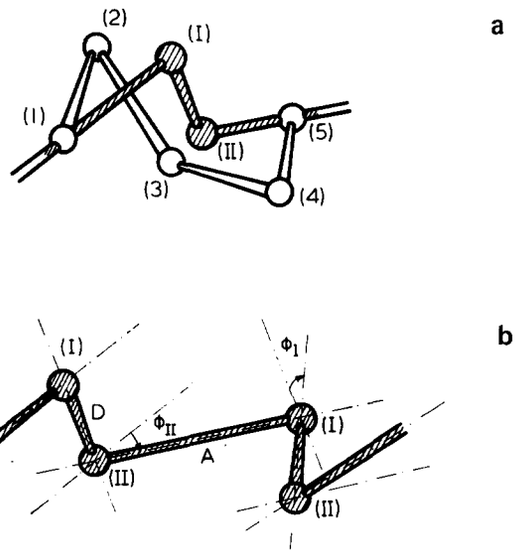

Figure 5 'Orthogonal biatomic' equivalent model of one-row aggregates. (a) construction of the orthogonal biatomic equivalent unit (I–II) from the real unit (1–2–3–4–5); (b) parameters A, D, Φ_I, Φ_{II} characterizing structure and juxta-connection of two orthogonal biatomic equivalent units along the row

* The relative simplicity of these considerations reflects the particularly low 'information content' of completely regular aggregates; the synthesis 'message' of these is simpler than that of any other aggregate of comparable size

* It is to note that there are particular conditions in which A and Φ_{II} are indeterminate. The enunciation of the model in these cases provides conventions which keep these parameters determinate, unless they happen to be indefinite[1]

$$\begin{vmatrix} l_1 & l_2 & l_3 & \dots & l_n \\ \theta_1 & \theta_2 & \theta_3 & \dots & \theta_n \\ \phi_1 & \phi_2 & \phi_3 & \dots & \phi_n \end{vmatrix} \longrightarrow \begin{vmatrix} A & D \\ \pi/2 & \pi/2 \\ \Phi_I & \Phi_{II} \end{vmatrix} \longleftrightarrow \begin{vmatrix} A \\ D \\ \Phi_I \\ \Phi_{II} \end{vmatrix}$$

From this tetrad, three non-dimensional parameters can be selected, characterizing the shape generator:

$$\gamma(D/A; \Phi_I; \Phi_{II})$$

Table 2 Shape generators of reticular skeletons of completely regular one-row aggregates according to the 'orthogonal biatomic' equivalent model

Shape generators	D/A	Φ_I	Φ_{II}
σ_0	0	$\neq 0, \pi$	$\neq 0, \pi$
σ_1	0	$\neq 0, \pi$	0
σ_2	$\neq 0$	$\neq 0, \pi$	$\neq 0, \pi$
σ_3	$\neq 0$	$\neq 0, \pi$ / 0	0 / $\neq 0, \pi$
ζ_0	0	π	$\neq 0, \pi$
ζ_1	0	π	0
ζ_2	$\neq 0$	$\neq 0, \pi$ / π	π / $\neq 0, \pi$
ζ_3	$\neq 0$	0 / π	π / 0
ρ_0	0	0	$\frac{2\pi}{k}$ $(k > 2)$
ρ_1	$f_1 = 0; f_2 = \frac{2\pi}{k}$ $(k > 2)$		$\frac{2\pi}{k}$
ρ_2	$\neq 0$	π	π
τ_0	0	Indefinite	0
τ_1	0	0	0
τ_2	$\neq 0$	0	0
β_0	0	Indefinite	π

$$f_1 = \frac{1 + \cos\Phi_{II}}{\sin\Phi_{II}} + \frac{D}{A}\frac{\sin\Phi_I}{1 - \cos\Phi_I}; f_2(\Phi_I, \Phi_{II})$$

$$f_2 = \arccos \frac{1}{2}(\cos\Phi_I + \cos\Phi_{II} + \cos\Phi_I \cos\Phi_{II})^{-1}$$

A classification of the possible orthogonal biatomic recticular skeletons is presented in *Table 2*, as a list of specific shape generators. In *Figure 6* the corresponding shapes are illustrated.

When $D = 0$, and Φ_I and Φ_{II} assume appropriate values, shape generators become those of the simpler monoatomic model (zero indexed); when $D \neq 0$ more numerous and complex shapes can be derived. In these latter cases, binodal regularity has been omitted from classification, the biatomic model not being especially suited to evidence varieties in such a simple case of regularity.

REGULAR MULTIROW AGGREGATES

The geometric synthesis of completely regular aggregates whose units belong to more than one row, can be systematically made by combining together two or more regular one-row aggregates on every unit in a given way. This operation has to be performed according to rules which preserve parameter repeat along each of the combined rows.

At the geometric levels, the possible varieties of multirow reticular skeletons depend on the model chosen to describe the one-row components being made up.

In *Figure 7* examples are shown of monoatomic multirow reticular skeletons obtained by combination of 2 and 3 one-row components. The morphogenetic operator of each of them is indicated as the 'product' of the generators of the composing one-row reticular skeletons.

The study of the complete systematics of multirow-unit aggregates is still in progress.

DIMENSIONALITY AND SHAPE

Chemists frequently speak of the dimensionality of macromolecules. Using the most usual models of the graphic type, any molecule or macromolecule (or its skeleton) is an intrinsically one-dimensional object. Nevertheless, if observed in three dimensions, it has a shape which depends on the way it develops in the space, and which cannot be intrinsically perceived.

On the other hand, when the major proportion of the atoms in a molecule may preferably be seen as lying essen-

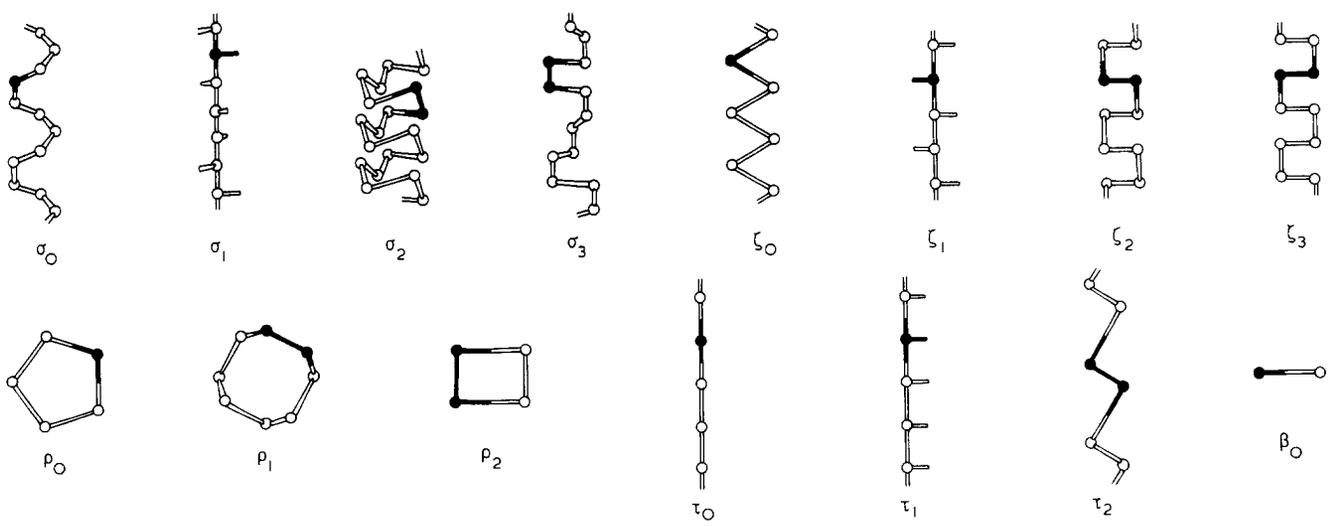

Figure 6 Possible 'orthogonal biatomic' reticular skeletons of parameter repeat regular one-row aggregates (characterizing shape generators are listed in *Table 2*)

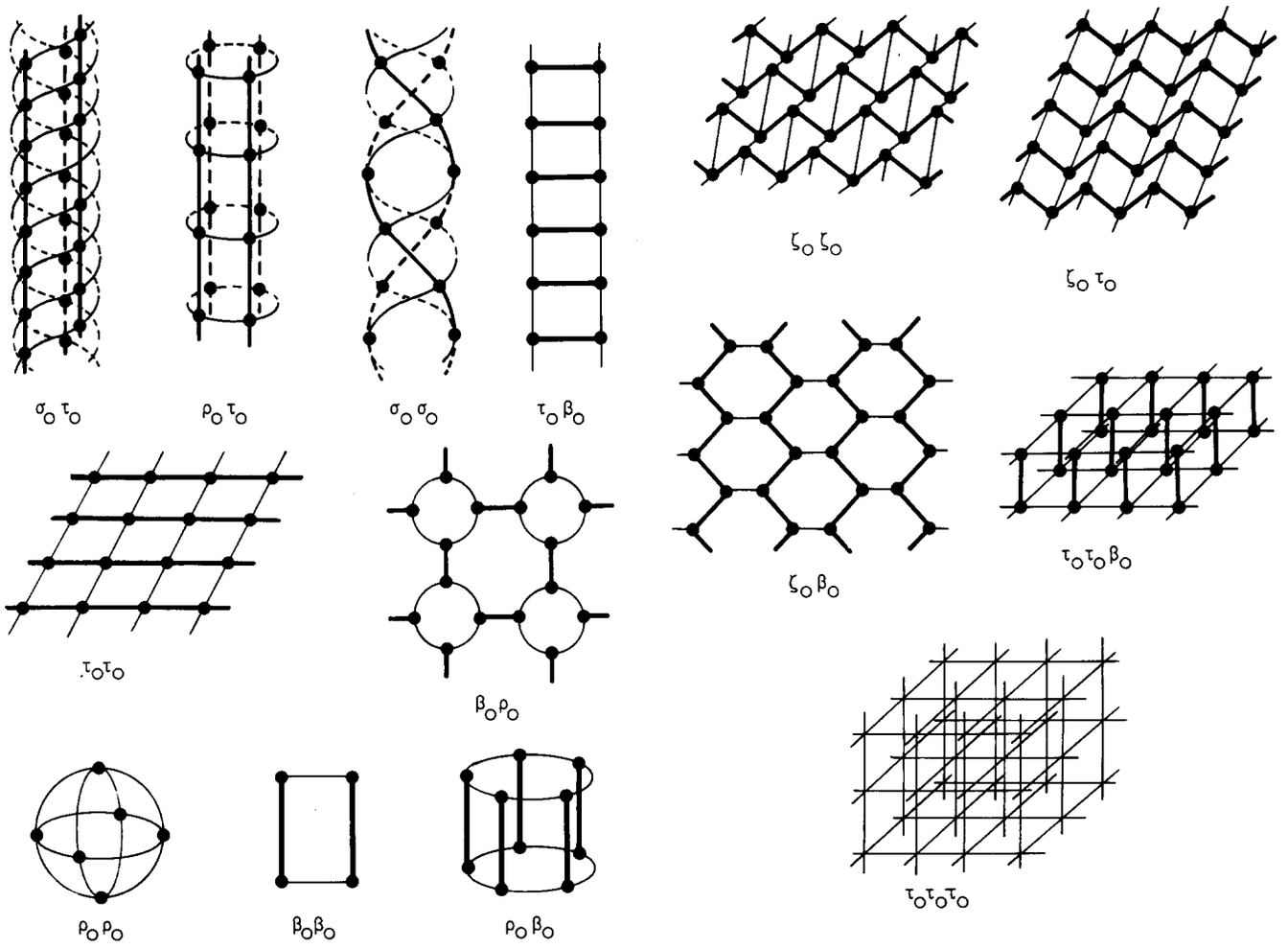

Figure 7 Examples of 'monoatomic' reticular skeletons of parameters repeat regular two and three-row aggregates (characterizing shape generators are simply indicated as the 'product' of the shape generators of the composing rows)

tially along a possible directrix surface (instead of directrix lines), the molecular skeleton can be conceived as an intrinsically two-dimensional object, having the shape of that surface observed in three dimensions. Thus, for example, regular molecules of generators $\tau_0\tau_0$ or $\zeta_0\beta_0$ (*Figure 7*) can be considered to be planar in shape; those of generators $\sigma_0\tau_0$ or $\rho_0\tau_0$ have cylindrical surface shape; those of $\rho_0\beta_0$ or $\rho_0\rho_0$ have spherical surface shape. It is interesting to note that the model has been changed and the molecular skeleton is no longer conceived of as a graphic type, but is assimilated by definition with a surface (possibly embedding the 'graphic' skeleton).

Similarly, if the density of matter may be seen as concentrated in a solid region of the three-dimensional space, the molecule may appear as an intrinsically three-dimensional object. If finite in at least one of its three dimensions, it still has a shape; if infinitely developed in all its dimensions, it has no longer a shape (mathematically it does have a shape in four or more dimensions). Also in this respect a different model has been chosen, according to which a solid (finite or infinite) directrix figure is taken to represent the skeleton of the molecule. For example, three-dimensional molecules can be considered those whose skeletons arise from $\tau_0\tau_0\beta_0$ (solid lamina), and $\tau_0\tau_0\tau_0$ (infinite, three-dimensional bodies).

Similar considerations can be made if one chooses a model of the 'solid' type for any particular molecule. In this case the molecule is constantly conceived an intrinsically three-dimensional object. In this respect, regular figures arising from generators like τ_0, $\tau_0\tau_0$ and $\rho_0\rho_0$, may be respectively considered as rods, laminae, spherical shells and even pierced laminae or shells.

In general, judgement on the shape may possibly include appreciation of the relative 'thickness' of the material constituting the object, such as thin rod (e.g. τ_0); thin ring (e.g. ρ_0); thin ribbon (e.g. $\tau_0\beta_0$); thick lamina (e.g. $\tau_0\tau_0\beta_0$); thin or thick cylinder (e.g. $\sigma_0\tau_0$) thin or thick spherical shell; full cylinder or sphere; thin or thick cylindrical (or prismatic) network; thin or thick planar network, etc.

The shapes discussed here, which are due to regular aggregates at the molecular level, are evident in nature: for example 'infinitely developed' three-dimensional bodies in diamond and other covalent crystals ('polymeric crystals'); thin laminae in mica and graphite; filaments, rods, hollow cylinders or spheres (polyhedra) in the housing or encapsulating structures of small living organisms (e.g. viruses, spores), or thick networks in their inorganic skeletons (e.g. in spores, in diatoms), etc.*

REFERENCES

1 Topics and problems introduced in this paper will be the object of more detailed publication in this Journal

* In the realm of living organisms, regular structures appear to be especially suited to the building up of morphologic elements not directly concerned with living and genetic processes. This is clearly because of their low 'information content', i.e. synthesis 'message' simplicity which results in an economic convenience as well as evolutionary soundness for living organisms