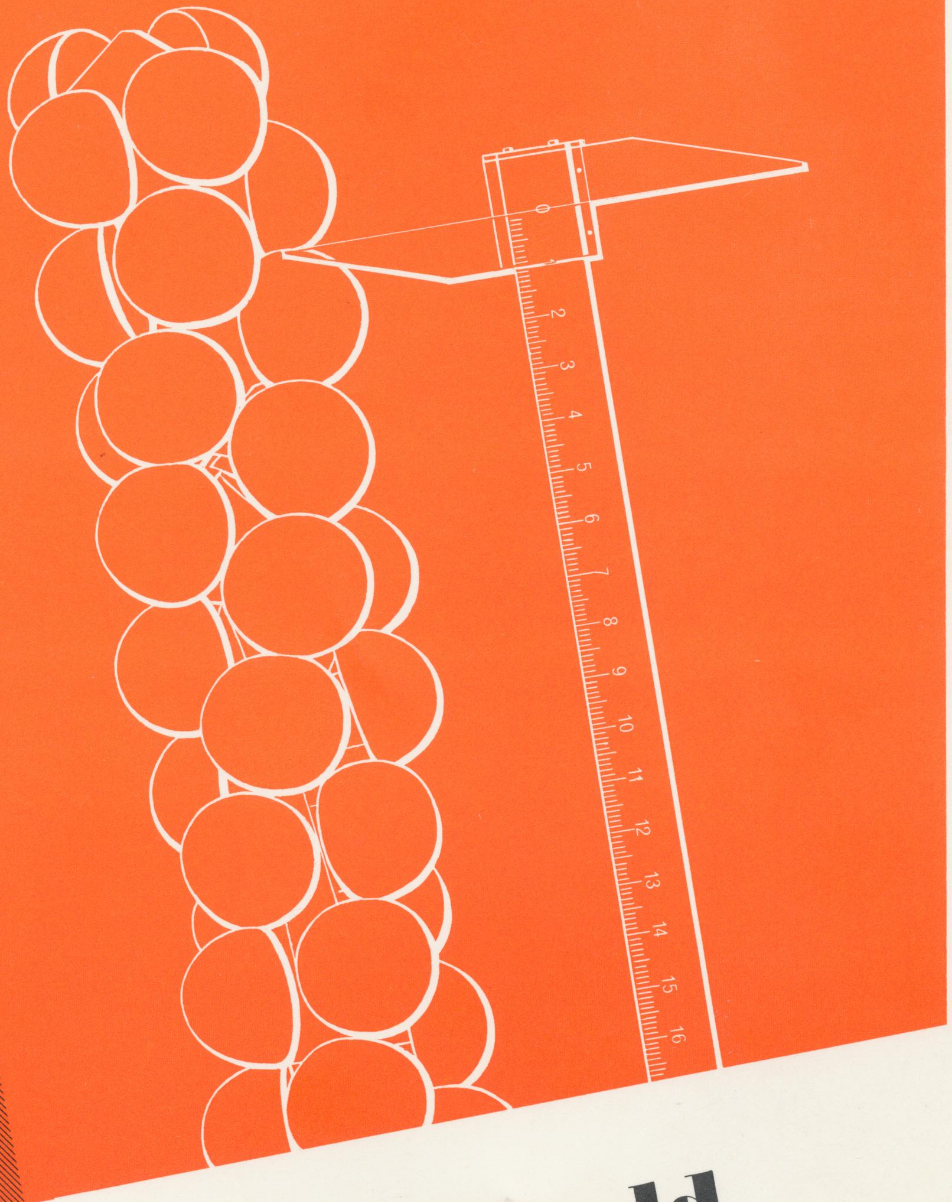
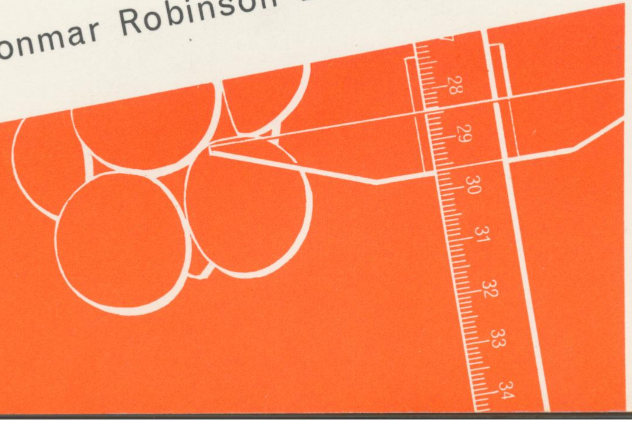


Courtauld Atomic Models

A DESCRIPTIVE TEXTBOOK

Conmar Robinson D.Sc., F.R.I.C.



GRIFFIN

The construction and use of

COURTAULD ATOMIC MODELS

by

Conmar Robinson, D.Sc., F.R.I.C.

(formerly of Courtaulds Limited)

A series of space-filling models manufactured
and supplied by Griffin & George Limited

GRIFFIN & GEORGE Limited
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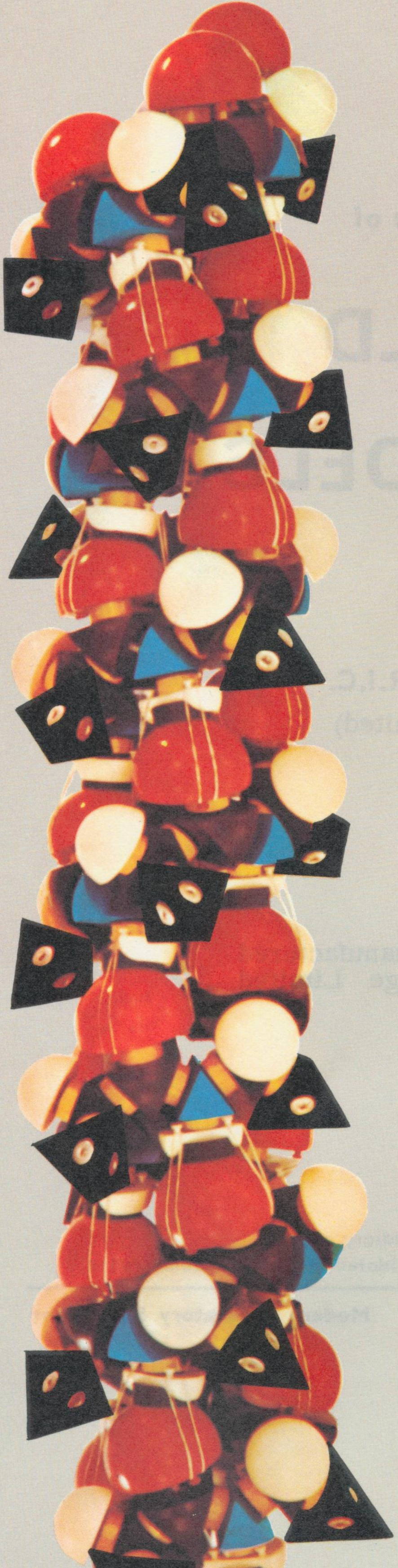

Fig. 1. Polypeptide chain in the α-helix conformation.
The side chains are represented by the β carbon atoms

Introduction to second edition

Since the first edition of this booklet in 1962, some important additions have been made to the models and their accessories. Specially designed bent links, corresponding to the bent bonds which have been shown to exist in cyclopropane, make possible the building of three-membered rings. Similar links have been introduced to improve the representation of four-membered rings. The tetrahedral carbon models have been improved by slightly truncating the corners and by providing cavities in three of the faces, which allow these models to be locked in the staggered conformation by bridging them with a nylon rod.

A new nitrogen atom has been introduced for use in five-membered rings, where previously it had been necessary to use the amide nitrogen model. A new oxygen model is provided for use in co-ordination compounds

Much of the text has been rewritten in the light of further experience and some new sections have been added. The new section on cycloalkanes, while describing models of molecules which can only be accurately represented by space-filling models having elastically-distortable valency bonds, also provides striking evidence in justification of the design of these atomic models.

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CONTENTS

1. The nature of atomic models

Atomic models may be divided into two classes, skeletal and space-filling. In the skeletal type, a system of rods is used to represent only the bond lengths and bond angles in the molecules, but no information is given about space-filling properties. In the space-filling type, the atoms are represented by solid models of such shape and size that when they are joined together to form the model of a molecule, not only are the bond lengths and bond angles represented, but the surface of the model indicates what would be the nearest approach of another molecule or unbonded atom. We may refer to this surface as the van der Waals envelope. The space-filling models are more generally useful, since it is only with them that direct observations of steric hindrance and molecular packing can be made. Such observations are particularly valuable when a large number of conformations, arising out of rotation about a number of bonds, has to be considered. In some cases, however, when accurate measurements of interatomic distances are required skeletal models may be found more convenient. The two types should, therefore, be considered to be complementary.

2. The principle of the Courtauld models

The Courtauld models are space-filling models made to a scale of 0.8 in.≡1 Ångström unit. In the earliest space-filling models, designed by Stuart(1), the opposing plane faces of atoms joined together by covalent bonds were in direct contact and there was consequently no possibility of allowing any distortion either of the valency angles or of the van der Waals envelope. In the Courtauld models, on the other hand, a link 0.4 in. long (≡0·5Å) is used for joining the atoms together, and the plane faces of the models are cut back correspondingly further so as to preserve the correct covalent distances between the centres of the atoms. This allows the linking mechanism to be designed so that the valency angle can be distorted from its normal value by several degrees, while a rubber collar which is fitted over the link supplies a restoring force that ensures that opposing faces will remain parallel when not under strain. At the same time rotation about single bonds is allowed. This principle, which greatly extends the usefulness of the models, was first introduced by Dr. G.S. Hartley(2) when on the staff of Courtaulds' Maidenhead Laboratory. The length of the link allows the direction of valency bonds to be seen clearly and also gives some much needed transparency to complicated molecules without sacrificing any appreciable area of the van der Waals envelope, while the elastic distortion of the link allows the deviation of the valency angles from their normal values caused by steric hindrance to be observed and also allows many molecules, e.g. those having strained rings, to be built which could not be built without this device. Stuart(3), after reviewing the relevant data estimates that the energy required to change the valency angle by 6° is from 0.150 to 0.550 kcal/mole. and so is less than the thermal energy at room temperature (0.6 kcal/mole.). Much more energy (2.5 to 4 kcal/mole.) is required to increase the length of a valency bond by 0.1Å. It can be seen from this that introducing elastically-distortable valency angles into the design of atomic models makes them much more realistic. (In actual molecules, steric hindrance will, of course, cause distortion of the van der Waals envelope as well as of the bond angle).

Wooden models constructed on this principle and as developed in Courtaulds' Maidenhead Laboratory (2,4,5) were previously supplied by Griffin & George Limited. The present models which are accurately moulded in polystyrene are on the same principle but the linking mechanism has been considerably improved as the result of further work in that laboratory up to 1962 and technical development by Griffin & George Limited. Since these models are hollow they are very light, which together with the stronger linking mechanism makes them particularly suitable for building large molecules.

3. The linking mechanism

The atoms are connected by a brass link, shaped at each end to fit the press-stud sockets mounted in the plane faces of the models. In recent production, the end of the link has been slightly flattened to increase the clearance between the link and the base of the socket.

The ends of the link are so designed that the link may be inclined 12° from the normal. A rubber collar is fitted over the link, and being slightly compressed by the linked atoms, it ensures that the opposite faces of these atoms will return to the parallel position after any stress is removed. Two types of plastic ring are provided, one coloured yellow and the other red. **For most purposes the yellow rings (length 0.314 in.) should be fitted over the rubber collars.** This has the effect of restricting the angle of inclination to a maximum of 6° from the normal. Users will find it convenient to keep most of the rubber collars permanently fitted with yellow rings. If it is required to build a model in which practically no distortion of the valency angles is possible, the red rings (length 0.370 in.) should be used. If an unfavourable combination of tolerances involved in the components of the linking system requires it, shims may be introduced to further reduce the degree of distortability. Fig. 2. shows an exploded drawing of the linking mechanism.

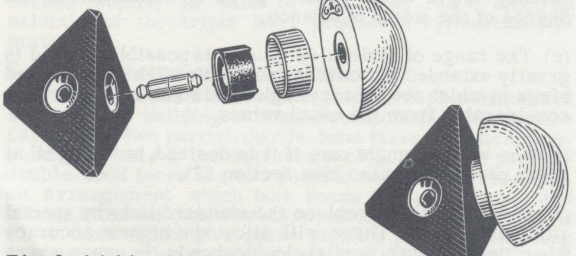
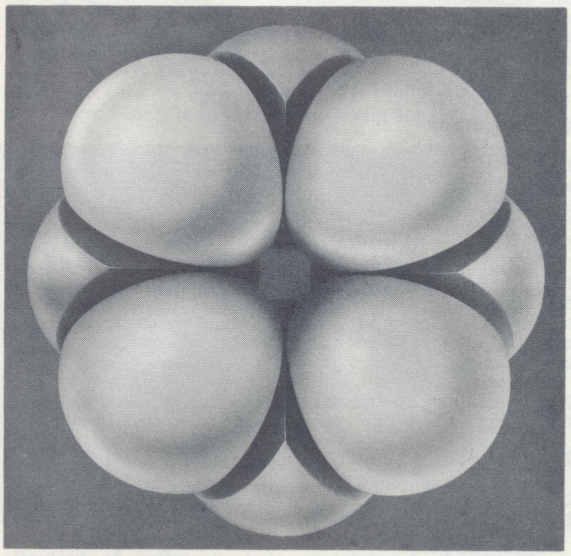


Fig. 2. Linking Mechanism

When it is desired to build four- and five-membered rings in which the bond angles differ considerably from the undistorted values given by the atomic models, then the rubber collars may be used without the plastic rings and the full 12° distortability becomes available (See Section 10). However, chains of atoms are greatly weakened if the plastic rings are not used, since their absence makes it much easier for chance movements to lever the links out of their sockets. Plastic rings, therefore, should always be used except when building rings of less then six atoms, or where the required degree of distortion can only be obtained by omitting them.

The strong springs with which the sockets are fitted are made to withstand a tension of 15 lb in a direction normal to the face of the atom, but the models are very easily taken apart if the links are inclined towards the plane faces before extracting them from the sockets. The collars have been designed so that the friction between them and the models allows a short chain of atoms to be posed in a chosen conformation. If for any purpose it is wished to increase the ease of rotation, their surfaces can be dusted with French chalk.

The method of attachment allows large molecules to be built rapidly and to be handled without falling to pieces.



Octasulphur, S_8.

4. The advantages of the distortable link

(a) The length of the links leaves the molecular structure more open than with the Stuart type of model so that it is easy to observe and measure bond directions and follow the internal structure of large molecules.

(b) When folding chains of molecules into complicated conformations (e.g. in protein structures) the additional pliability of the chain makes the manipulation much easier, while the restoring force of the rubber collar ensures that the normal valency angle will be assumed in the completed structure if the conformation does not involve strain.

(c) The models are constructed so that the radii of their spherical surfaces correspond to the van der Waals radii obtained from crystallographic data. (See Section 8).

(d) Where steric hindrance occurs, the distortion of the valency angle which results gives an indication of the degree of the steric hindrance.

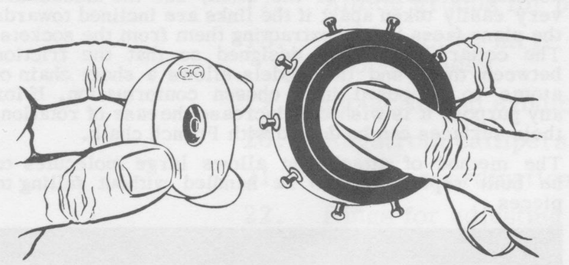
(e) The range of molecules which it is possible to build is greatly extended and covers many molecules with strained rings in which the valency angles and bond lengths deviate considerably from the usual values.

(f) The valency angle can, if it is desired, be 'wedged' at some particular value (See Section 22).

(g) It is possible to replace the standard links by special adjustable links. These will allow the highest accuracy when dealing with partial-double bonds, in cases where the exact value is not otherwise given by the combination of models used. (See Section 15).

5. Link magazine for inserting and extracting links

The strong spring used in the sockets of the plastic models makes inserting the links by hand a little hard on the fingers, especially when the models are new. (After the first couple of insertions the resistance decreases and settles down to a steady value.) A magazine has therefore been designed for facilitating the insertion and extraction of the links. This is a plastic disc in which ten links are arranged radially with their ends protruding. When the protruding end of one of the links is inserted in a model, a direct pull will leave the link in the socket of the model. On the other hand, if the magazine is levered against the surface of the model, the link will be retained in the magazine.



Link Magazine.

6. Bond order

Faces normal to the direction of single bonds are fitted with a single socket. Double- and triple-bond faces are each fitted with two sockets so that rotation about the bond is prevented; (in some cases, partial-double-bond faces are fitted with single sockets). On double-bond faces the sockets are placed 3/4 in. apart and on triple-bond faces they are 1 in. apart; this prevents the two kinds of faces being confused. In all cases the perpendicular through the centre of a single socket, or through a point midway between a pair of sockets, passes through the centre of the atom.

It is sufficient to use one plastic ring with a double- or triple-bond, although two rubber collars should be used.

7. Nylon rods for restricting rotation

In some cases it is necessary to restrict rotation about a bond represented by a single link. For example, the benzene carbon models are so designed that in the molecule of benzene built with them the six equivalent C-C bonds are represented by alternate double and single links, a design principle which allows any canonical form of an aromatic molecule to be represented. Rotation about double links is of course, impossible, but for accurate representation of these resonating systems it is necessary that rotation about the single links should also be restricted. For this reason the appropriate faces of the benzene carbons are supplied with cavities into which a nylon rod can be inserted parallel to the single link, so forming an additional connection between the two atom faces. Similar cavities have also been provided in the faces of other models where the partial-double bond is represented by a single socket and link. These are nos. 13, 18 (section 17) and 19a (section 10).

Since the previous edition of this publication cavities have been placed in three of the faces of tetrahedral carbon models (a cavity suitably placed in the fourth face would intrude on one of the other cavities.) These cavities are so located that if a nylon rod is inserted in the cavities in the opposing faces of two tetrahedra connected by the standard linking mechanism so as to form a bridge between them, it will hold them in the staggered conformation.

The limited flexibility of the nylon rods allows a few degrees distortion from planar or staggered conformation when stressed, which accords with the nature of chemical bonds.

8. Principles followed in the designs

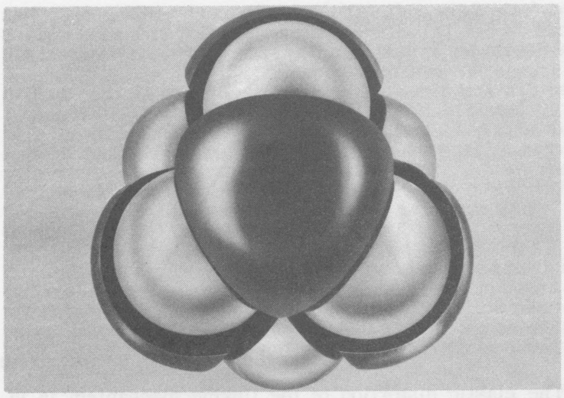
Accurate data exist for covalent radii and bond angles in many compounds. As is well known, single-bond and double-bond covalent radii can be attributed to each element which, when added together, will give values in good agreement with the known lengths of pure single and double bonds in many compounds. In some cases, however, the values will depend much more on the nature of the second atom with which a bond is formed (as in phosphorus and sulphur) and here in designing the models it was necessary to decide what values for covalent radii would make them most generally useful. This principle also applies to the choice of bond angles which are still more dependent than bond lengths on the nature of the adjacent atoms. **It should always be remembered that atomic models are in the nature of calculating machines and the result obtained in their use can only be true in so far as the data used in their design are relevant to the problem considered.** For the most accurate work the literature should be consulted for data for the molecule to be studied or for similar compounds. "Tables of Interatomic Distances and Configuration in Molecules and Ions", (London, The Chemical Society, 1958) greatly facilitates this.

In the Stuart models (and also in the later models developed by Briegleb(6)) it was impossible to base the design on the full values of the van der Waals radii as obtained from crystallographic data, i.e. from the interatomic distances for the minimum internal energy (the r^*_{min} of Stuart and of Briegleb), since with rigid models this would have prevented the building of many simple molecules and would have been unsuitable for dynamic, as distinct from static, problems, where the distance of nearest approach is in part determined by the thermal energy. Hence in these a smaller value, from 0.15 to 0.25Å less than r^*_{min}, was taken for the radius - the choice of this value, r^*_r, being somewhat arbitrary.

However, with the Courtauld models it has been possible, owing to the distortable link, in general to base the design on the unreduced and less arbitrary values obtained for the crystallographic data.

Since the opposing plane faces of bonded atoms are separated by the length of the link, there is no need to adjust the area of the faces to make them fit, as was done in the Stuart models in order to give a smooth surface to the molecules. Hence serious errors of the type pointed out by Wepster(7) when criticising the Stuart models, do not arise.

The van der Waals radii used for determining the non-bonding radii are in general those given by Pauling(8) who based them on ionic radii. An exception, however, is hydrogen, where if the value of 1.20Å given by Pauling had been used for this atom it would have been impossible to build many familiar compounds. Here the use of a



Phosphorous oxide, P_4O_6

smaller radius is justified since the van der Waals sphere of the hydrogen atom, which contains only one electron, is particularly easy to invade. A radius of 1.0Å was therefore chosen as a compromise which gave satisfactory results in a number of problems (See also Section 13). Thus for dibenzyl, which is known to be non-planar through the steric hindrance of the 2,2′hydrogen atoms, the model not only shows restricted rotation about the bond joining the benzene rings, but, thanks to the distortable valency angle, can easily be forced through the planar confirmation, in accordance with the fact that isomers cannot be resolved. Since the hydrogen model was originally designed much empirical evidence has accumulated from the use of the models to show that this value of 1.0Å for the van der Waals radius is, in fact, the most satisfactory choice for a rigid hydrogen model. The most recent evidence in support of this comes from models of medium sized cycloalkanes (See Section 14).

In the simplest cases the model is a segment of a sphere of radius equal to the van der Waals radius, and the distance of each plane face from the centre of the atom is equal to the covalent radius less half the length of the link. In the chlorine, bromine and iodine models, the spherical segment forming the model has been chamfered so as to allow the building of carbon tetrahalides and hexahalogen derivatives of benzene. This is justified since, as Pauling has pointed out (8), the effective van der Waals radius in a direction which makes only a small angle (less than 35°) with the direction of the convalent bond is smaller by about 0.5Å than in directions away from the bond. With ortho-substituted aromatic halogen compounds, however, this results in some loss of fidelity since the models do not show the observed bond angle distortion. For smaller atoms such as oxygen and fluorine the gap between the atoms provided by the length of the link makes the chamfering unnecessary.

In tetrahedral models the problem is somewhat different since there is no corresponding spherical surface and the tetrahedral shape of the model may be determined, as in the case of the tetrahedral nitrogen atom, by the intersection of four plane faces at right angles to the valency bonds. Originally the tetrahedral carbon model was designed in this way, but experience showed that the corners, which have no significance in reality, sometimes caused spurious steric hindrance, therefore in the latest production of this model, the corners are slightly truncated. (The modified model is shown in Fig. 2.).

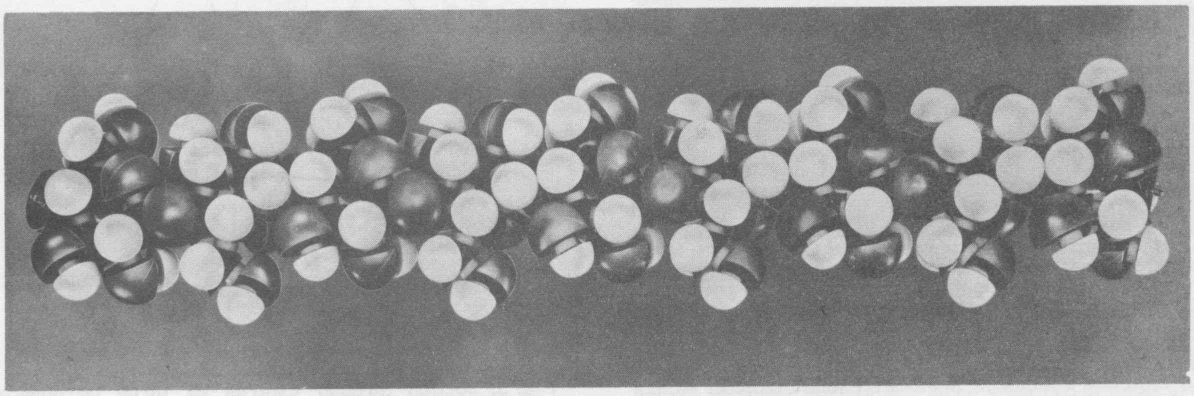
There remain, however, a few cases where this degree of truncation is insufficient, as discussed in the footnote to Section 13. With the larger tetrahedra (sulphur, phosphorus and silicon) the distance of the truncated corners from the centre of the atom equals the mean value of the covalent and the van der Waals radii; this was an arbitrary choice made in the absence of quantative data, but the exact value of this distance is generally of little importance.

In aromatic molecules, the π-electron orbitals result in the hydrocarbon rings having a thickness of 3.4Å at right angles to the planar bond systems, these rings being approximately flat. The benzene carbon model is therefore a triangular prism 3.4Å long, corresponding to a van der Waals radius of 1.7Å in a direction at right angles to the bond system. This same value has been used for the van der Waals radii of the acetylene carbon and allene carbon atoms, in each of which the two π-electron orbitals of the triple bond produce a cylindrical symmetry(6).

9. Six-membered aromatic rings

A benzene carbon model and a graphite carbon model are supplied for building aromatic compounds. The benzene carbon has two partial-double-bond faces and one single-bond face (this is the engraved face). One of the partial-double-bond faces has two sockets and the other has one, an arrangement which both keeps the ring planar and allows different canonical structures to be represented. If it is desired to give more rigidity to the planar ring system, the nylon rods supplied (See also Section 7) may be used as an additional connection between the partial-double-bond faces, which contain only a single socket, by inserting them in the holes provided in these faces. In fused-ring systems the graphite carbon, with three partial-double-bond faces of covalent radius 0.715Å, should be used to represent any carbon atom shared by two or more rings. Three partial-double-bond lengths, 1.39, 1.41 and 1.43Å, will then be given by the three possible combinations of the benzene and graphite bond radii and close approximations to the correct bond lengths in many fused-ring compounds will be obtained. For example, a model of the hydrocarbon coronene (in which six six-membered rings are symmetrically arranged about a central ring) will have all the bond lengths within 0.005Å of the values reported by Robertson and White (9). With the less symmetrical hydrocarbons anthracene and pyrene the bond lengths are still within 0.02Å, while with ovalene the discrepancy is somewhat greater. Naphthalene cannot be built accurately in this way, but a naphthalene block, C_{10}, is supplied. A benzene block, C_6, is also supplied to simplify the building of some aromatic compounds, but since it has six single-bond faces it cannot be used for building molecules containing fused rings.

It should be realised that much of the empty space which appears in models of substances containing aromatic rings (other than those where the benzene and naphthalene blocks are used) does not correspond to empty space in the actual molecule. This is because the links joining the atom prevent the representation of the unbroken surface of the van der Waals envelopes. However, since the spaces which result, including those through the centre of the rings, are not large enough for even a hydrogen atom to enter, they do not appreciably effect the degree of steric hindrance which is indicated by the model.



Portion of cellulose chain containing 6 glucose rings

10. Five-membered rings : purine bases

With atomic models having the usual rigid connections, it is necessary to design special planar atom models for five-membered rings in resonating systems. But with the Courtauld models the benzene carbon atoms may be used if the outer plastic ring is omitted in forming the bonds, so that the full distortability of the link allows the 120° valency angle to be reduced sufficiently for this pentagonal ring to be formed. However, since not more than two double links can be introduced into a five-membered ring, one of the models used in building the five-membered ring must have a single socket in each of the faces which are to be attached to its neighbours in the ring. Model No. 19A was therefore designed as a nitrogen atom for use in five-membered rings, each of its three planar faces being fitted with a single socket, but two of these faces giving a partial-double-bond radius of 0.62Å and the third giving a single-bond radius of 0.70Å.

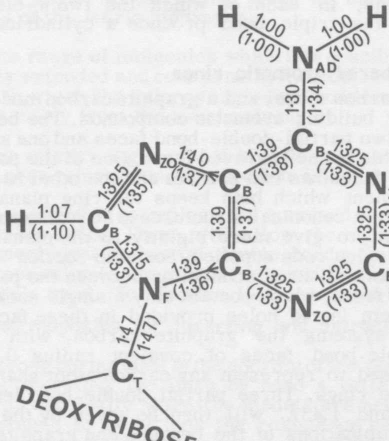


Fig. 3a. Adenine

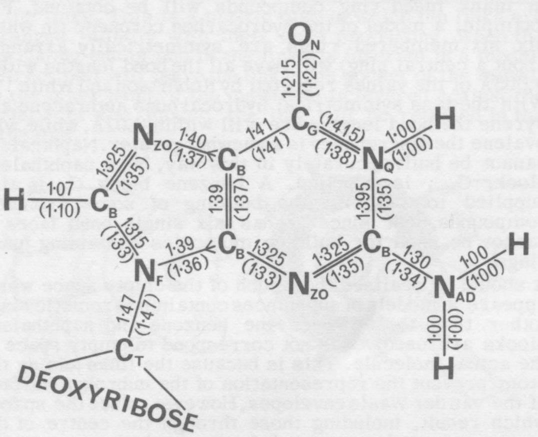


Fig. 3b. Guanine

Fig. 3. shows the construction of five-membered rings in the purine bases adenine and guanine which are constituents of the DNA molecule. The subscripts appended to the atomic symbols indicate the model used, and are as shown in the table of data on pages 14 and 15

The values in parenthesis are the bond distances in Ångström units proposed by Spencer(10) as the most likely values for the bond distances; the other values are those given by the models used. Instead of using graphite carbon models for the shared carbon atoms, which should be the general practice in building fused rings (See Section 9), benzene carbons are used, the single-bond faces being turned in the directions indicated by arrows in the diagrams. This results in the C-C distance being shorter, and the C-N distance longer, than they would have been if the graphite carbon models had been used, thus making the models more in accordance with Spencer's values. Graphite carbon models are also used for the carbon atoms to which the amino groups are attached. These are good examples of how the models may be used to simulate a molecule in which the bond character varies considerably.

11. Three-membered rings

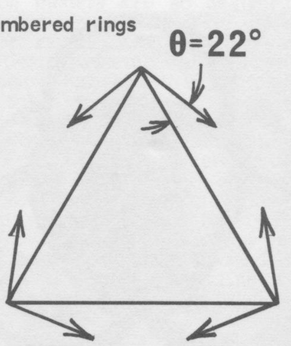


Fig. 4. Bond direction in cyclopropane

The elastic distortion of the linking mechanism is insufficient to allow three-membered rings to be built; nor is it possible to design a special carbon model for this purpose, since, as a drawing can show, some of the sockets would overlap.

For this reason bent links have been designed which allow the ordinary tetrahedral carbons to be used in building a model of cyclopropane. The use of such bent links to represent the valency bonds is not only mechanically convenient for our purpose but has some theoretical justification. In most molecules the bond direction, i.e. the maximum electron density, is assumed to coincide with the straight line joining the two attached atoms and it is believed that the hybridisation of the electron orbitals is modified in accordance with the geometry of the molecule so that the overlapping hybrids, which constitute the bond, each point in the bond direction. However, in cyclopropane, where the three carbon atoms are at the corners of an equilateral triangle, this is impossible, since as Coulson and Moffit point out(11), no two hybrids may make an angle of less than 90° with one another. Coulson and Moffit conclude from their theoretical treatment that the arrangement adopted in this molecule is as shown in Fig. 4., where θ, the angle between the direction in which hybrids point and the line joining the carbon atoms, is 22°, so that the angle between the hybrids is reduced from the tetrahedral angle to 104°.

It also follows from this theory that the H-C-H angle is **increased** to 116° and that the C-C length will be abnormally short. Experimental confirmation of these conclusions have been obtained(12) thus in cyclopropyl chloride the C-C distance is 1.513Å and the H-C-H angle is 114.5°; in tetramethyl cyclopropane C-C = 1.52Å and H-C-H is 114°; and in spiropentane C-C = 1.48Å. The shortest C-C distance which can be obtained if the three tetrahedral models are to have their centres at the corners of an equilateral triangle is when three of their edges are normal to this triangle and in contact with one another. Fig. 5. shows a section through C, C , C , the centres of the three tetrahedral carbons when arranged in this way. For the links to be satisfactory they must lie in this plane and each of their inclined halves must be normal to the model face in which the corresponding end of the link is inserted. If the lines CA, C B etc., which are normal to the atom faces and pass through the centres of the sockets are extended until they intersect at E, F and G, they will form a hexagon having three angles of 109.5°

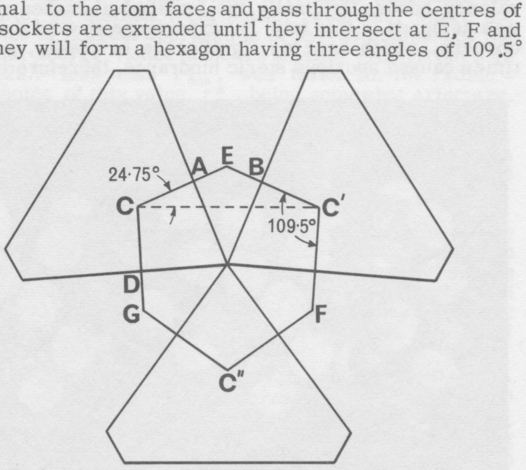


Fig. 5. Section through centres of three tetrahedral carbons joined by bent links

and consequently three of 130.5°. The link was therefore designed so that its two arms are inclined at 130.5°, and the distance from its centre to the surface of the model is 0.346Å (Fig.6a). The C-C distance when three tetrahedral carbon models are joined together with this link will be 1.56Å. With this arrangement (Fig.5.) the direction AE, DG, of the arms of the link may be looked upon as approximately indicating the directions of the carbon atom hybrids; and since the angle between them is near the tetrahedral angle, the angle θ which they make with the straight line between the atom centres is here 24.75°, compared to the theoretical 22°.

In building the three-membered rings the standard rubber collars should be used, which of course become compressed to the necessary wedge shape. The yellow rings, being incompressible, cannot be used, but the models built without them are sufficiently stable to be easily handled without coming apart.

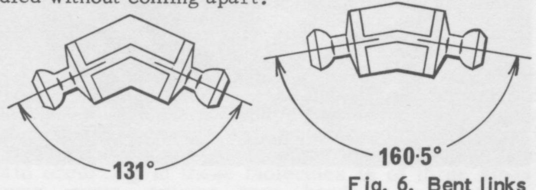


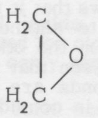
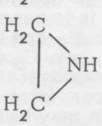
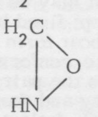
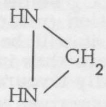
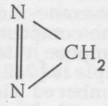
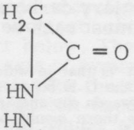
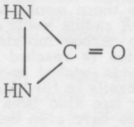
Fig. 6. Bent links

(a) 3-membered rings (b) 4-membered rings

Figs. 7. and 8. show models of cyclopropane and spiropentane built with these links.

The bent rings may also be used to construct three-membered rings in which one or two of the carbons are replaced by other elements. Fig.9. shows a model of ethylene oxide, in which model No. 21 was used for the oxygen atom; epoxides may be similarly constructed.

The following ring compounds and their derivatives may be constructed using the atom models indicated by the symbols in the last columns. (The model S_{DI} cannot be incorporated in three-membered rings as its edge protrudes beyond the centre).

Ring Compound.		Models Used.
Ethylene Oxide		C_TO_{DI}
Aziridine		C_TN_{AN}
Oxaziridine		$C_TO_{DI}N_{AN}$
Diaziridine		C_TN_{AN}
Diazirine		C_TN_{ZO}
Aziridinone		$C_TC_CN_{AN}$
Diaziridone		C_TN_{AN}

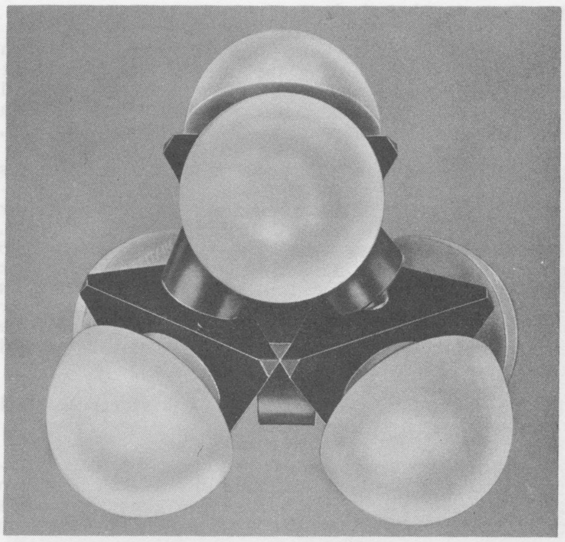


Fig. 7. Cyclopropane

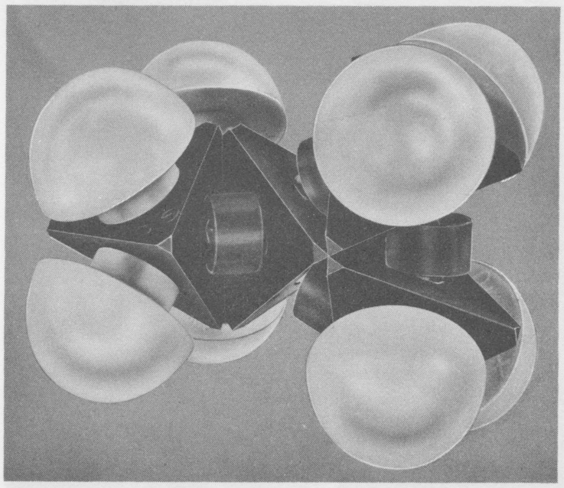


Fig. 8. Spiropentane

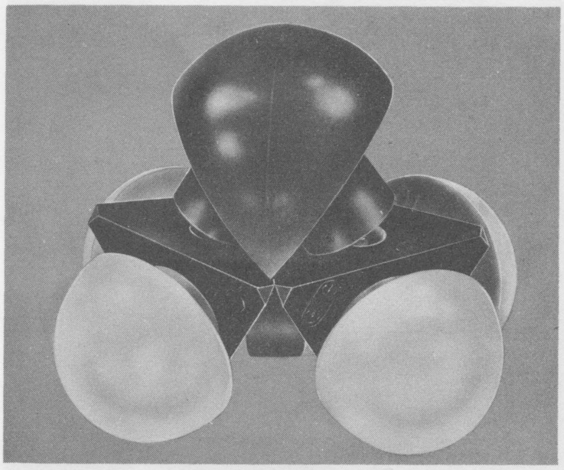


Fig. 9. Ethylene Oxide

In general in these heterocyclic rings the C–C distance is even shorter than in cyclopropane, e.g. ethylene imine 1.48Å, ethylene oxide 1.47Å. It may therefore sometimes be an advantage to represent the carbons by the tetrahedral nitrogen models N_T, since when two of these are joined by a bent link the C-C distance will be 1.4Å.

12. Four-membered rings

It is just possible to build four-membered rings with the standard links (using the rubber collars without yellow rings) but the rings are greatly strained and easily fall apart. A bent link has therefore also been designed for use in four-membered rings. (Fig. 6b).

In cyclobutane the four carbon atoms are at the corners of a square and here again Coulson and Moffit(11) concluded that the hybrids are inclined at an angle to the line joining the carbon atom, θ being 9° and H-C-H 111°. The link for the four-membered ring was designed so that two arms are inclined at 160.5° and the distance from the centre of the link to the model surface is 0.263Å, so that C-C = 1.54Å. When a ring of four tetrahedral models is built with these links, using the rubber collars only, the arms of the link will be normal to the model faces and so θ will be 9.75°.

13. The elastically-distortable link and stereochemical problems

All the usual stereochemical problems that can be illustrated with rigid space-filling models can be shown more clearly, as the length of the link gives the models transparency and allows the bond directions to be seen easily. But there are also many cases where, thanks to the elastically-distortable link, the model can do much to show why one of several conformations is assumed or likely to be assumed, and where such evidence could not be obtained from rigid models. Good examples are found in the cycloalkanes, and other alicyclic compounds.

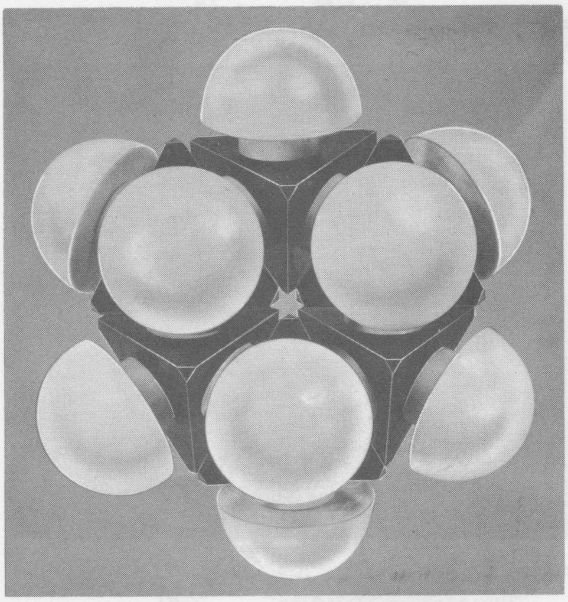


Fig. 10a. Cyclohexane, chair conformation

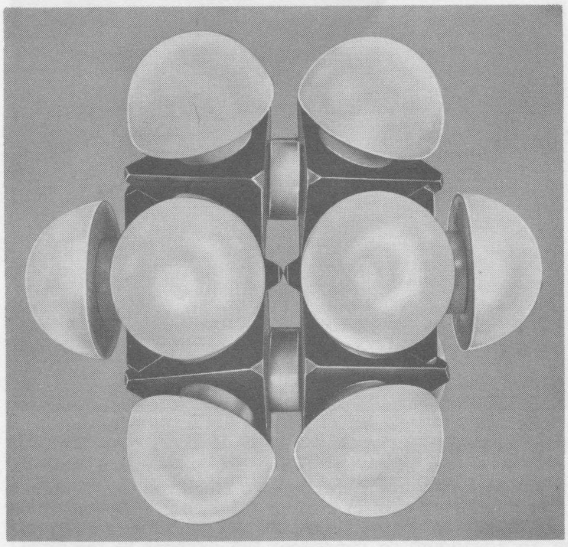


Fig. 10b. Cyclohexane, boat conformation

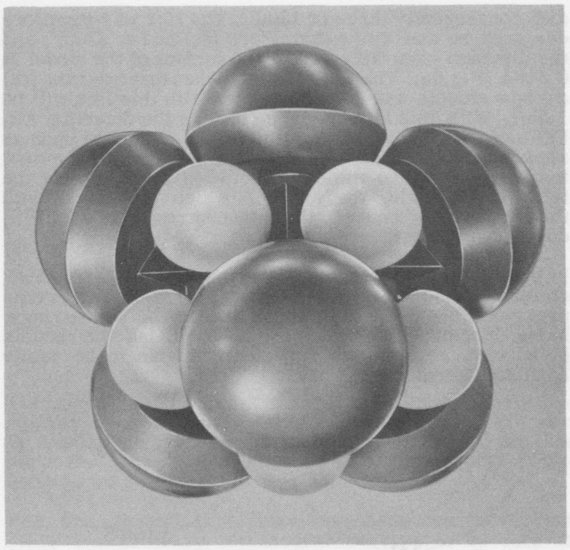


Fig. 11. γ-1 : 2 : 3 : 4 : 5 : 6 Hexachlorocyclohexane ("Gammexane") Carbon ring in chair form. Three C-Cl bonds axial (a), three equatorial (e) viz., a a a e e e.

In cyclohexane, since the 6° distortion of the valency bonds allows the tetrahedral angle of the carbon atoms to be increased to over 120°, the model may be posed in the highly-strained planar conformation and it is therefore possible to carry out the boat-chair transformation without breaking the ring (Fig. 10). The model not only shows that this chair conformation is unstrained (since all the tetrahedral angles are undistorted and all the carbon atoms are "staggered" with respect to their neighbours), but also shows that it is impossible to pass from this conformation to another without increasing the tetrahedral angles. On the other hand, in the boat conformation it can be seen that the pairs of carbons joined by two of the bonds are in the eclipsed conformation, so that there is considerable Pitzer strain (See Section 14); but here it is possible to pass from one boat conformation (where C_1 and C_4 are at the bow and stern) to another (where, say, C_2 and C_5 are at the bow and stern) without the tetrahedral angles being increased. (This mobility of the boat form and the contrasting rigidity of the chair form may be clearly demonstrated if the bond angles are kept fixed by using red rings). If the transition from one boat form to another is stopped half-way, an intermediate conformation is obtained in which the distance between the pair of hydrogens attached to C_1 and C_4 **above** the ring and the distance between the pair attached to C_3 and C_6 **below** the ring is the same (2.3Å). In this conformation (referred to as either the skew, or twisted, boat), it will be seen that the Pitzer strain is considerably less than in the "true"* boat and it is therefore energetically favourable.

Calculation has shown that at room temperature only about one in a thousand cyclohexane molecules will exist in the boat form; but in some compounds, as the models can show, the substituents impose this conformation on the ring. An interesting example is [2, 2, 2,] - bicyclo-octane, where the three six-membered rings, each of which is formed by the two tertiary carbons and two of the three bridges joining them, must each be in exactly the "true" boat conformation.

*The so-called "true" boat is that in which the six C-C bonds most resemble a boat, and here the C-H bonds in the positions of flagstaff and bowsprit are inclined towards one another so that the H-H distance is 1.83Å, and consequently there would be transannular strain and the hydrogen models of 1.0Å radius would overlap. Actually however, the "corners" of the two carbon models at the centre of the ring interfere before this position is reached (See Fig. 10b). In the exceptional cases, where it is wished to demonstrate this extreme position, the corners may easily be filed further back. This additional truncation of the corners has also been found necessary in other bridged ring systems which have been built e.g. the chlorinated insecticide "Dieldrin".

In substituted cyclohexane compounds the models demonstrate how the equatorial positions are more roomy than the axial ones. Fig.11. shows a model of γ-hexachlorocyclohexane ("Gammexane"). The three chlorines in the top of the photograph are in the axial positions. The model can only be built because the distortable valency angles allow the first and third C-Cl bonds (not visible in the photograph) to be inclined outwards. This distortion of the valency angles is in accordance with the X-ray findings. This model is a good example of the numerous cases where the three-dimensional structure shown by the model would be difficult to visualise from the structural formula as written on paper.

Fig.12. shows a model of cholesteryl iodide from which the hydrogen atoms have been removed to allow the structure to be seen more clearly. It illustrates how the open structure given by the linking mechanism makes the models suitable for the study of steroids.

14. Medium sized cycloalkanes

Although cyclohexane forms a strain-free ring, with more carbon atoms in the ring, strains are introduced which, as the heats of combustion show, increase steeply until a maximum occurs with cyclodecane, to be followed by a large decrease on reaching cyclododecane. The strain occurring in these molecules is of three kinds: Baeyer strain, arising from bond angle distortion; Pitzer strain, arising from distortion from staggered partial conformations; and transannular strain, arising from the interaction of hydrogen atoms coming into contact across the ring. The conformations assumed by the molecules are such that the energy due to these three causes is a minimum. It used to be assumed that the last two of these effects determined the conformations, but the recent X-ray work of Dunitz(13) and his co-workers which has established the actual conformation of several of these rings shows that Baeyer strain plays a large part. It follows that models of these molecules cannot be built from atomic models having rigid links.

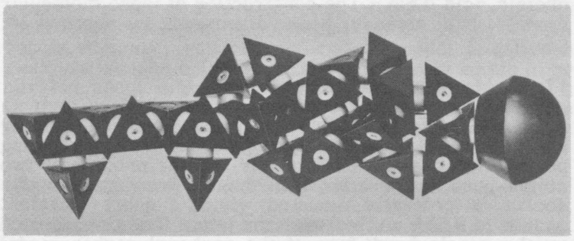


Fig. 12. Cholesteryl iodide. The hydrogen atoms have been removed for clarity. (built with early non-truncated carbon models)

Models of cyclononane, cyclodecane and cyclododecane have been built with the Courtauld models. The close agreement obtained with the X-ray results of Dunitz and co-workers, not only underlines the great advantages of the elastically-distortable link but fully justifies the design and accuracy of the models used. The results are therefore given in some detail in what follows. The ring of carbon atoms for each model was first arranged so as to have approximately the partial conformations found by these workers and the hydrogen atoms models were then added so that the final conformations were taken up as the result of any steric hindrance due to the latter.

Fig.13. shows the model of cyclododecane. There are four hydrogens just in contact above the ring and four similarly in contact below. The latter are rotated 60° clockwise about the axis of symmetry with respect to the former, this accounting for the shape of the space in the centre. (It follows that left-handed molecules will exist in equal quantities in which the rotation is 60° anticlockwise). The model showed the following points:-

(1) The twelve carbon atoms show little deviation from the staggered conformations (i.e. Pitzer strain is small) but the greatest deviation is about the bonds at the centres of the four sides of the "ring".

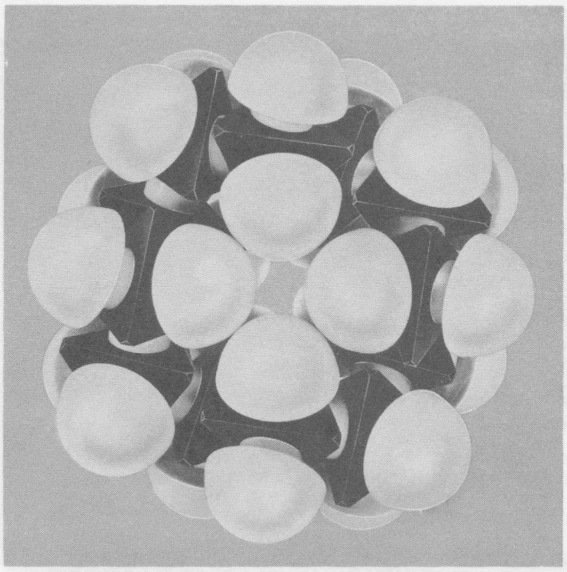


Fig. 13. Cyclododecane

(2) The C-C-C angles at the four corners are increased to approximately 117°, the other C-C-C angles are close to 110°.

(3) The model shows no transannular strain but since there are hydrogen models of 1.0Å radius just in contact this agrees with the X-ray results that their nearest approach is 2.0Å. All this is in agreement with Dunitz' and co-workers' results.

Similar good agreement with the established structure is found for cyclodecane, Fig. 14. Here the Baeyer strain is greater, all the C-C-C angles being increased by several degrees above the tetrahedral value and there is Pitzer strain about two of the bonds. There are two triangular groups of three hydrogens, one above and one below the ring. The hydrogens in each of these groups are found to be pressed together under considerable tension, indicating considerable transannular strain. All this is in

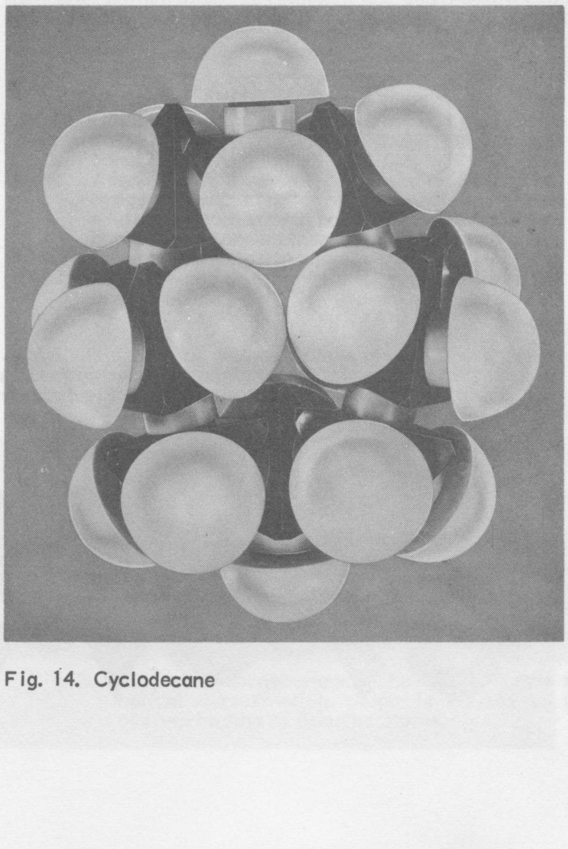


Fig. 14. Cyclodecane

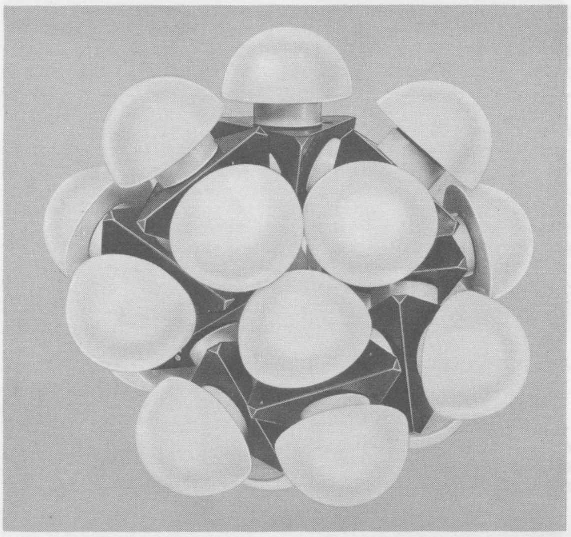


Fig. 15. Cyclononane

accordance with the X-ray results. When all six of the hydrogen atoms were removed it was found that the ring of tetrahedral carbon atoms could be rearranged so as to give staggered conformations throughout and to leave all the tetrahedral angles undistorted. This makes it clear that the Baeyer and Pitzer strains in this molecule are imposed on it as a result of the considerable stress which is required to reduce the nearest approach of two hydrogen atoms to 1.8Å. This, together with the fact that no change is produced in the model of cyclododecane on removing the hydrogen atoms, shows that the choice of 1.0Å for the radius of the hydrogen atom in the Courtauld model was the most practical choice for a rigid model. (See Section 8).

With cyclononane Fig. 15 the model is again in agreement with the experimental results. Here again there are three hydrogens in contact above and three below the ring and each group of three is under tension. The conformation is less regular than in the two previous molecules. The model shows considerable Baeyer strain in six of the angles, while Pitzer strain is much more marked than in the other molecules, there being a marked departure from the staggered conformation about all but one of the bonds.

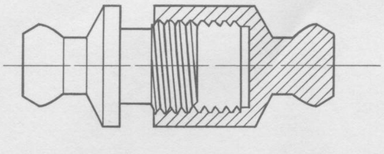


Fig. 16. Adjustable link

15. Adjustable links

Where a sufficiently accurate value for a partial-double-bond length is not given by combining two atomic models with the standard link, the adjustable link (Fig.16.) may be used. This is available in two lengths covering a range of adjustment about the length of the standard link (0.5Å) of – 0.1 to 0Å and of 0 to + 0.1Å respectively. Each link consists of two threaded members which may be locked in position by means of a touch of solder or adhesive after being adjusted to the required lengths.

16. Hydrogen bonds

A special hydrogen model (No.11) is supplied for forming hydrogen bonds, in which the unbonded spherical surface of radius 1.0Å has been partly cut away so as to form a plane surface and a cylindrical surface of radius 0.5Å. The plane face contains a circular groove into which is fitted a strip of vulcanised fibre sheet in the form of a ring. Both this model and the double-bonded oxygen model are fitted with three pegs. If these two models are held together by looping elastic bands over these pegs, the fibre ring will ensure a linear hydrogen bond in which the H...O distance is 1.90Å and the NH...O distance 2.90Å (Figs. 1. and 17.). If on the other hand the fibre strip is removed, the model may be used to form a non-linear hydrogen bond, as in a chelate ring, the cylindrical surface then maintaining the H...O distance at 1.90Å (Fig. 18.). To form a hydrogen bond with the di-univalent oxygen model the elastic bands must be looped over the two links joining this atom to its neighbours. In a similar way a hydrogen bond may be formed with the nitrogen model (No. 16), e.g. when it is used for the bonding of purine and pyrimidine bases in nucleic acids, and here the linear NH...N bond length will be 3.10Å.

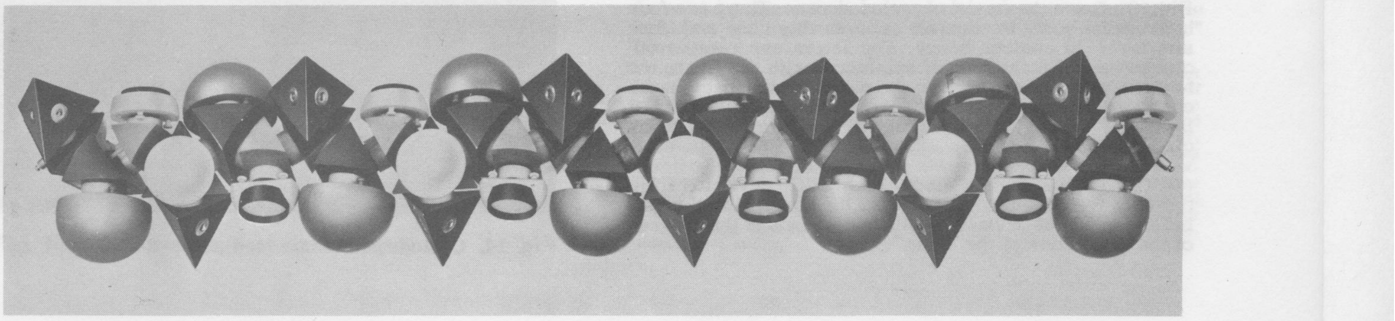
Fig.19.(right) shows a representation of hydrogen bonding to both oxygen and nitrogen atoms as it occurs, according to Watson and Crick(14), between the bases thymine and adenine and between cytosine and guanine in deoxyribonucleic acid (DNA). The construction of these molecular models has already been discussed in section 10. See Fig. 3

17. Amide group for polypeptides

A special nitrogen model (No. 13) has been designed for building the planar amide group needed for constructing polypeptide chains. This is a triangular prism with two single-bond faces and a third face (in which a single socket is centrally mounted) giving a short covalent radius of 0.55Å so that when the latter face is connected to the single-bond face of the carbonyl carbon model the correct partial-double-bond OC...NH distance of 1.30Å is obtained. As only one link is used for this bond, one of the nylon rods, already referred to in section 7 must be inserted in the holes supplied for the purpose in the opposing faces of the two models. The flexible plastic rod keeps the group planar when not under strain, but allows the two ends of the amide group to be rotated a few degrees out of the planar conformation. (Pauling estimates that 0.1 kcal/mole. is needed to produce 3° rotation about this bond).

When the group -NH-CO-CHR- is built with models Nos. 6, 7, 10, 11, 13 and 20, the bond lengths will all be within 0.02Å of those given by Pauling, Corey and Branson(15) for the polypeptide chain and the bond angles will also have the values given by them, except that the CCN angle will be 5° too small.

Fig. 17 A portion of the polypeptide chain shown in Fig. 1, in the fully extended conformation. The fibre strips for assuring linear hydrogen bonds with Model No. 11 are clearly shown. The nylon rods inserted between Models Nos. 6 and 13 to maintain the planar conformation of the amide group can just be seen.



18. Constructing large molecules : polypeptides

In designing the models, particular care has been taken to make them suitable for the study of the intricate stereochemical problems which arise with both synthetic and natural high polymers. Long chains of atoms can be rapidly assembled with the models, and folded into complex conformations without their falling apart, while the accuracy of the models justifies confidence in measurements of, for instance, repeat distances. The advantages of the models for such problems can be seen in the case of polypeptide chains. In synthetic polypeptides or in proteins these are held together in various conformations by intra- or inter-chain hydrogen bonding and the stereochemical problems arising in this expanding field are almost unlimited. Fig. 1. shows a polypeptide chain wound into the α-helix of Pauling, Corey and Branson, by hydrogen bonding each -NH- group to the -CO- next but three along the chain. These authors showed by a calculation based on the known bond distances and angles in simple peptides that this conformation would give linear hydrogen bonds and hence be favoured by its stability. Its occurrence in many polypeptides and proteins was subsequently proved by X-ray observations. The model of the polypeptide chain can be folded into the α-helix with ease, the hydrogen bonds being formed with elastic bands as described in section 16. The flexibility of the chain facilitates the folding, while the degree of friction between the rubber and the surface of the model is sufficient to allow a portion of the chain to be suitably poised before hydrogen-bonding it into position. When the folded model is examined it will be found that all the hydrogen bonds are linear, that no bond angle is strained out of position, and that the projection of one amino-acid residue on the axis of the helix is 1.5Å long (in accordance with the value obtained from X-ray diffraction and by calculation). If the model is twisted so as to alter the pitch of the helix, when the torsion is released the original pitch, giving a 1.5Å repeat distance, will be restored. A model of eighteen residues weighs only 5 lb and is sufficiently stable to be carried about in one hand without becoming distorted. It is thus possible to manipulate two or more such models to find, for instance, how different side-chains may affect inter-chain packing.

19. Isotactic and syndiotactic polymers

The models are very suitable for studying and demonstrating the structures arising in isotactic and syndiotactic polymers. Here, since steric factors play a large part in determining the helical or other conformation assumed by the molecule and since a large number of atoms may be included in the repeat distance, accurate space-filling models which do not easily fall apart are essential.

In isotactic vinyl polymers where overcrowding of the side chains prevents the main chain from being straight, a helical conformation results. The additional space for the side chains is obtained partly by rotation about single bonds in the main chain but also by opening up the tetrahedral angles of carbon atoms (e.g. to 114.5° in polypropylene and to 116.5° in polystyrene). It follows that a true representation of these conformations can only be made with models having distortable valency angles. Fig. 20 shows the helical conformation which is assumed by polytetrafluoroethylene as a result of similar overcrowding. The model shows a repeat distance of 16.8Å for thirteen CF_2 groups which is the value found in an X-ray investigation by Bunn and Howells(16). The molecules of this substance form left- and right-hand helices in equal numbers.

20. Ångström callipers

Since the link joining two atom faces together is comparatively long and since the faces of the models into which it is inserted are always flat, the Courtauld models are more suitable than other space-filling models for making accurate measurements of the repeat distances in polymer molecules. A pair of callipers has been designed for this purpose. (Fig 20).

The scale has a range of 28Å subdivided into tenths of a unit (0.8 inch is equivalent to 1.0Å). Two sliding transparent Perspex jaws are provided which are tapered so that they can be inserted between bonded atoms and are spring-loaded against the scale. One of these is symmetrical while the other is not. The position of the latter on the scale may be reversed, depending on whether 'inside' or 'outside' measurements are to be made. The distance from an inside to an outside face may be measured with the unsymmetrical jaw in either position.

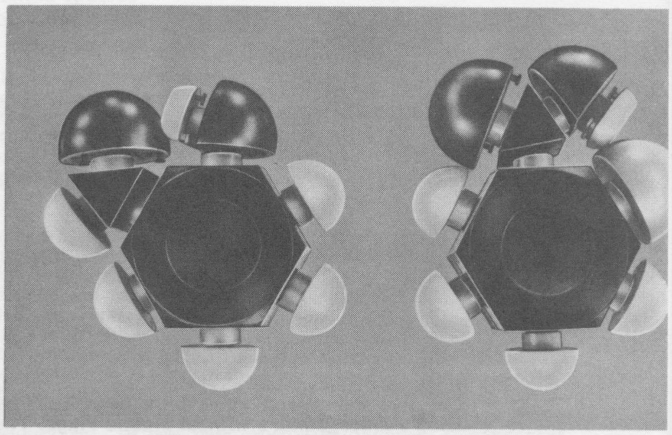


Fig. 18. These models show how Model No. 11 can be used for the formation of non-linear hydrogen bonds by using it without the fibre strip.
Left: Salicylaldehyde. Right: o-Fluorobenzoic acid.

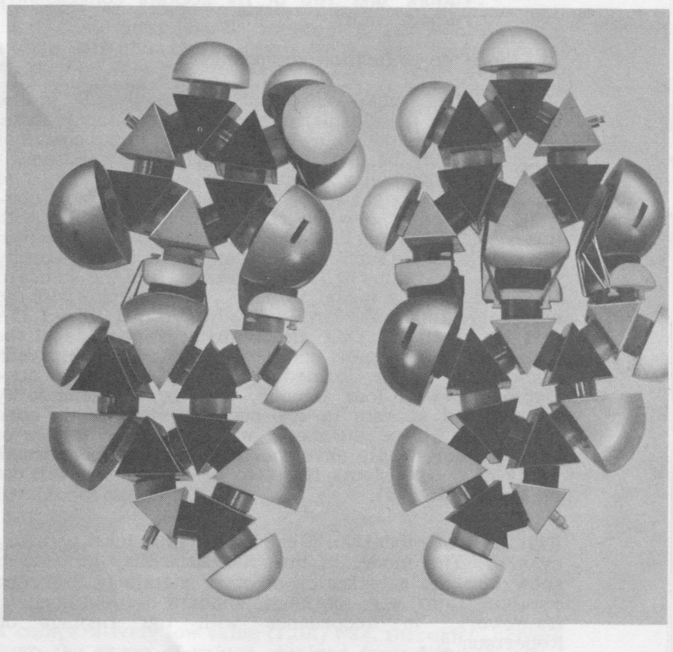


Fig. 19. Complementary pairs of purine and pyrimidine bases in the structure proposed for deoxyribonucleic acid.
Left: Adenine and thymine held together by two hydrogen bonds. (The bare links protruding from a nitrogen atom in each base indicate the valency bond, which connect these to one of the two intertwined polynucleotide chains).
Right: Cytosine and guanine held together by three hydrogen bonds.

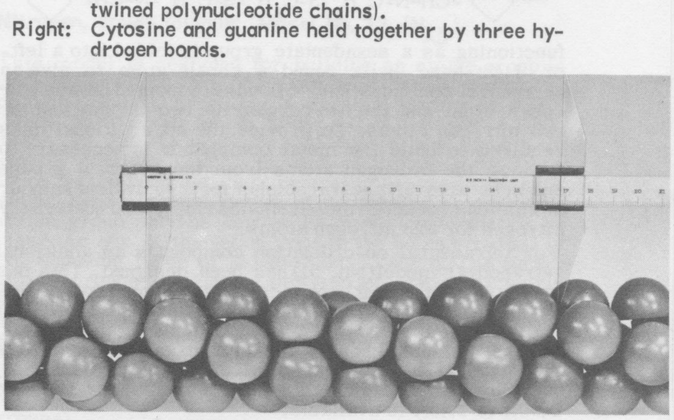


Fig. 20. Polytetrafluoroethylene. The model shows the helical conformation which is caused by the over-crowding of fluorine atoms.

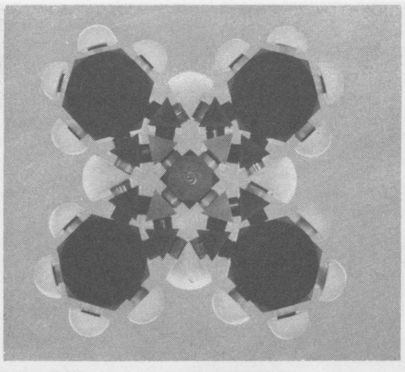


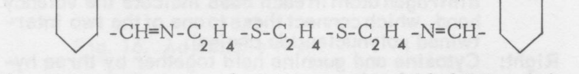
Fig. 21. Nickel phthalocyanine.
The five-membered rings have been built by using rubber collars without plastic rings. The alternate double links used in the resonance system were made visible in the photograph by not using rubber collars on the upper-most links. Model No. 50 has been used to represent the nickel atom in the square planar configuration, and two of its sockets consequently remain empty.

21. Metal co-ordination compounds

For building metal co-ordination compounds in the octahedral or square-planar configuration a model in the form of a cube and having a single socket in the centre of each face may be used to represent the metal atom. It is not commercially practical to supply a series of such plastic models which would cover the almost continuous range of covalent radii that is called for with different metals and different ligands. However, one such model (No. 50) is supplied, each face of which corresponds to a covalent radius of 1.25Å when used with the standard link and, if this model is used in conjunction with the adjustable links, any covalent radius from 1.15 to 1.35Å can be obtained. This allows many compounds of the transition metals most commonly found in co-ordination compounds to be formed. (The square-planar configuration, with four ligands, may be represented by leaving the sockets in two opposite sides of the cube unoccupied. Here the model will give no indication of the van der Waals envelope in these positions, but in many of the problems likely to be studied this will not be a disadvantage).

Fig. 21 shows model No. 50 used in building nickel phthalocyanine. The model of this substance may be used to show how the substitution of other metals of different covalent radii, e.g. platinum, distorts the surrounding framework, in accordance with the findings of Robertson(18).

An interesting example of the use of this model is to show how a molecule of the substance



functioning as a sexadentate group is folded into a left- or right-hand helix round a cobalt atom to give an octahedral configuration(17). Bonds are formed between the cobalt atom and the two oxygen, the two sulphur and the two nitrogen atoms. To provide the six additional links required to build the metal complex it is necessary to remove the hydrogen atoms from the hydroxyl groups and substitute tetrahedral sulphur for di-univalent sulphur atoms (one socket in these remains empty) and quaternary nitrogen for azo nitrogen atoms.

For tetrahedral co-ordination compounds an additional tetrahedral model (No. 51) has been designed. This is a regular tetrahedron each face of which corresponds to a covalent radius of 1.35Å (which is the tetrahedral covalent radius for copper) when used with the standard link. The regular tetrahedra of the sulphur and silicon models (1.0 and 1.17Å radius respectively) may also be used, so that with the adjustable links a continuous range of 0.90Å to 1.45Å is available.

In some cases tetrahedra or cubes which only approximate the right size may give a useful qualitative picture. Thus models Nos. 50 and 51 can be used to show how β,β,β-triaminoethylamine, $N(CH_2CH_2NH_2)_3$, which functions as a quadridentate group, forms a tetrahedral structure with either nickel or platinum, while steric hindrance makes the planar configuration normally adopted by these elements impossible.

22. Rings for adjusting bond angles

A device for inclining a link by a known number of degrees from the normal may be made by cutting one of the red rings in two halves as shown in Fig. 22 which shows a section at right angles to the plane of the ring. The ring is divided into two halves by the plane XY which passes through the centre O of the section and which is inclined at an angle, say 5°, to DC. In Fig 22a the two halves are arranged so that AB is parallel to DC. If the top half is rotated about the bottom half the angle which AB makes with DC increases continuously until the maximum inclination (10° in this case) is reached after 180° rotation (Fig. 22b). Since some material is lost in the cutting, it is only possible to obtain one half from each red ring). If the rings are graduated it will be necessary to indicate the direction as well as the size of the wedge angle. This is best done by marking the number of degrees, 2, 4, 6, etc., on each of the halves in such a way that when two similar figures, say two 4's, are brought opposite one another, their position represents the thick end of a (in this case) 4° wedge, given by the two halves when combined in that position. When this device is used between any two atoms P and Q, in general the angles made between the bond P-Q and all other bonds involving either P or Q will be altered. When either P or Q is a univalent atom, this is often of no consequence, but in most other cases, even if it is required to adjust only a single angle, it may become necessary to insert wedges throughout the molecule to restore the remaining angles to their original values. Although in most cases where the angles of the molecules are different from those of the model the wedges allow a more accurate representation, in some cases an exact representation may be impossible for geometric reasons. In adjusting the angles in a ring it will sometimes be found that it is necessary to insert a wedge of a larger angle than the alteration in the half bond angle which is required at that point. Consequently the adjustments which can be made are sometimes less than that which the 12° available distortion of the link direction might at first suggest.

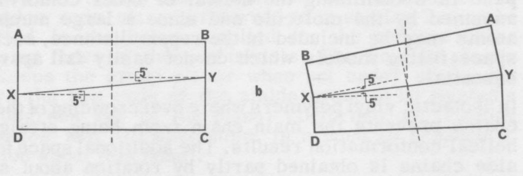


Fig. 22. Suggested device for adjusting bond angles

23. Hydrates

Model No. 22a (co-ordination oxygen) has been designed for building compounds in which H_2O is a ligand. This is a prism of triangular cross-section with a single socket mounted in each of three faces. Fig. 23 shows $CuCl_2, 2H_2O$ as an example of the square-planar co-ordination compound built by using this model for the oxygen atoms and model No. 50 for the copper atom. The values in brackets are those obtained by Peterson and Levy(19) for the bond lengths and bond angles by electron diffraction, whilst the unbracketed values are those given by the models. All the atoms are in one plane.

Zinc acetate dihydrate is an example of an octahedral conformation where by using Model No. 50, although the covalent radius is too short when the standard link is used, the qualitative nature of the distorted octahedron can be seen.

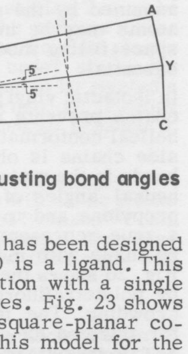


Fig. 23

Characteristics of Atomic Species

See pages 14 and 15 for Table of Data

Bromine. Model No. 1. (Br)

The bromine, chlorine and iodine atoms are chamfered so as to allow six halogens to be attached to a benzene ring and four to a tetrahedral carbon atom. No cutting back is necessary in the case of the smaller fluorine atom.

Carbon, acetylene. Model No. 2. (C_{AC})

This model is a disc of radius 3.6Å (Briegleb(6) has pointed out that for practical purposes the two π electron orbitals give cylindrical symmetry about the direction of the triple bond).

One face has two sockets placed at a distance apart (1 in.) which allows it to be attached only to other triple-bonded atoms (Nos. 2, 15 and 17). The second face has one socket for the single bond.

Carbon, allene. Model No. 3. (C_{AL})

A disc having one pair of sockets in each face so that the line through one pair is perpendicular to that through the other.

Carbon, benzene. Model No. 4. (C_B)

This is a prism of triangular cross-section. One face contains two sockets and one a single socket and two holes in either of which a nylon rod can be inserted to maintain the planar conformation (See Section 7). Each of these faces gives a partial-double-bond covalent radius of 0.70Å. In building a benzene ring these faces should be arranged so that double and single links alternate in the ring. The third face (the engraved face) contains a single socket, mounted centrally, but no holes; this gives a single-bond covalent radius of 0.77Å. (N.B. Since all the bond angles are 120° the section of the model is an equilateral triangle, but the bond lengths for the partial-double-bond faces are made different from that for the single-bond face by mounting the sockets on the former off-centre. The centre of the atom is therefore not quite at the centre of the model).

Benzene ring, C_6, Model No. 5. (-)

This is a block of hexagonal cross-section, having a socket mounted on each of the six sides. It is so designed that these faces correspond to the covalent radius of single-bonded carbon, 0.77Å, and it cannot, therefore, be used as part of an aromatic fused-ring system. The height of the block corresponds to a van der Waals radius of 1.70Å.

Carbon, carbonyl. Model No. 6. (C_C)

A van der Waals radius of 1.6Å has been used in the construction of this model. This value (rather than that of 1.7Å used in Models 4 and 7a) allows the model to be used for constructing the α-helix of Pauling, Corey and Branson(15).

Carbon, tetrahedral. Model No. 7. (C_T)

The model is a regular tetrahedron, with slightly truncated corners.

Carbon, graphite. Model No. 7a. (C_{GR})

This model is intended to be used wherever the carbon atom is shared by two or more aromatic rings (while Model No. 4 is used for the unshared carbon atoms in the ring system). The model is a prism, the section of which is an equilateral triangle. As with Model No. 4, two sockets are mounted on one face and one on each of the other two, but in this graphite carbon model each of the three faces corresponds to a covalent radius 0.715Å (the value found in graphite). The height of the model corresponds to a van der Waals radius of 1.70Å, also as found in graphite. The two sockets on one face are necessary so that the model may be used in conjunction with No. 4, but they also allow the models to be arranged so as to represent the single- and double-bond arrangements of any canonical structure.

If in building condensed ring aromatic systems, the graphite carbon is used whenever a carbon is shared by two or three rings, and the benzene carbon is used where the carbon is not shared, there will be three covalent distances of 1.39, 1.41 and 1.43Å corresponding to three possible combinations of these two models.

This principle allows a model of the hydrocarbon coronene (in which six-membered rings are symmetrically arranged about a central ring) to be built so that all the bond lengths are within 0.005Å of the values reported by Robertson and White(9). With the less symmetrical hydrocarbons anthracene and pyrene, the bond lengths are still within 0.02Å, while with ovalene the discrepancy is somewhat greater. The benzene carbon model should always be arranged in the ring system so that the single-bond face points outwards. The bond lengths in naphthalene cannot be accurately reproduced in this way and Model No. 7b has been specially designed to represent this molecule.

Naphthalene block, C_{10}. Model No. 7b. (-)

It is not possible to build an accurate naphthalene model by using Nos. 4 and 7a since the structure is 'abnormal' in that the bond length between the two shared carbon atoms has the same length as the two bonds parallel to it. For this reason, and for convenience in building dye molecules, a naphthalene (C_{10}) block has been designed based on the X-ray data of Abrahams, Robertson and White(20). The block has a hexagonal cross-section with two opposite sides longer than the other four. One socket is mounted on each of the four short sides while two are mounted on each of the longer sides. The model has six sides instead of ten, as a result of the cutting back of the van der Waals radius to the extent demanded by the length of the links. A more accurate design would have had a V-shaped cut in the centre of each long side, but as this would have been less than 0.2Å deep it was eliminated for practical purposes.

Chlorine. Model No. 8. (Cl)

See Model No. 1.

Fluorine. Model No. 9. (F)

See Model No. 1.

Hydrogen. Model No. 10. (H)

The energy required to reduce the van der Waals radius of hydrogen is less than in the case of other atoms. A comparatively low value (1.0Å) was, therefore, chosen from the range of values obtained from different compounds. (See also Section 13).

Hydrogen, bonded. Model No. 11. (H_B)

For the description and use of this model See Section 16.

Nitrogen, amide (planar). Model No. 13. (N_{AD})

This model is designed for building an amide group in conjunction with No. 6. One face has a centrally-mounted socket providing a covalent radius of 0.53Å which, with Model No. 6, gives a C-N distance of 1.3Å, which is the OC$\underset{\cdots}{-}$NH partial-double-bond length in simple peptides, etc. In each of the other two faces there is one socket, not centrally mounted, giving a single-bond covalent radius of 0.70Å. The atoms of the amide group may be kept in the planar conformation by inserting one of the nylon rods in the holes provided in the opposing faces of Models Nos. 13 and 6. The planar amide groups built with this model are particularly suitable for building polypeptide chains since the bond angles and bond distances in the models of the chains will correspond to those given by Pauling, Corey and Branson(15), except that the N-C-C angle will be 5° too small. Model No. 13 may also be used to build an NH_2 group. (Model No. 18 should be used for NO_2 groups).

Nitrogen, amine (pyramidal). Model No. 14. (N_{AN})

Each of three plane faces has a single socket giving the single-bond covalent radius.

Nitrogen, azide. Model No. 15. (N_{ZI})

The model is a disc with two double-bond sockets on one face and two triple-bond sockets on the other. The double-bond covalent radius was chosen so as to give a bond length of 1.25Å when it is combined with model No. 16, as in methyl azide.

Nitrogen, azo. Model No. 16 (N_{ZO})

A segment of a sphere with two sockets on one face and one on the other, each giving a partial-double-bond radius of 0.63Å. This gives 1.26 and 1.40 for the N=N and N-C distances in trans-azobenzene as compared with the observed values of 1.23Å and 1.41Å. (The C-N=N angle will be within 1° of the observed values for either trans-azobenzene or methyl nitrile). When used for pyridine it gives the N-C bond distance 1.33Å (observed = 1.34Å). It may also be used in purine bases, such as adenine and cytosine.
If it is incorporated in a non-resonating system the C-N distance will be too short (e.g. 1.40Å in methyl azide, compared with 1.47Å observed).

Nitrogen, nitrile. Model No. 17. (N_N)

The model has a planar triple-bond face. The ellipsoidal shape of the unbonded surface is determined in part by the "π-electron radius" and in part by the "σ-electron radius".

Nitrogen, quaternary, aromatic. Model No. 18. (N_Q)

This is designed to give a regular hexagon when combined with the benzene or graphite carbon models, and gives an N-C distance of 1.39Å. The single-bonded face has the socket mounted in the centre and must face away from the ring.

It may be used, for instance, as a quaternary nitrogen atom in the six-membered ring of purine bases. An NO_2 group may be represented by combining this model with one carbonyl oxygen and one negatively-charged oxygen.

Nitrogen, quaternary, tetrahedral. Model No. 19. (N_T)

A regular tetrahedron with four single-bond faces.

Nitrogen, five-membered ring. Model No. 19a. (N_F)

A planar atom having three faces each fitted with a single socket. Two of these faces give a partial-double-bond covalent radius of 0.62Å. When undistorted, the bond angle between these two bonds is 115°. The third face gives a single-bond radius of 0.70Å. See Section 10.

Oxygen, carbonyl. Model No. 20. (O_C)

The segment of a sphere with two sockets mounted in the plane face. The pegs on this face allow the model to be connected to No. 11 with elastic bands when it is wished to form a hydrogen bond.

Oxygen, di-univalent. Model No. 21. (O_{DI})

The bond angle of 105° used in this model is that found in water. In many substances, however, the bond angle formed by the oxygen atom is considerably larger.

Oxygen, negatively-charged. Model No. 22. (O_N)

The covalent radius of this model has been chosen so as to give, when linked to a single-socket face of model No. 6 or 28, the observed value for C-O or S-O distances in carbonate or sulphate groups. The P-O or Si-O distances obtained by linking it to model No. 23 or 25 will be about 0.05Å shorter than those found in phosphates or silicates.

Oxygen, co-ordination. Model No. 22a. (O_{CO})

The model is designed for co-ordination compounds in which water is a ligand. Each of the three faces of the trigonal prism corresponds to a covalent radius of 0.66Å and is fitted with a single socket. One of the bond angles (that between the hydrogen atoms) is 105° and the other two are 127.5°.

Phosphorus, tetrahedral. Model No. 23. (P_T)

The model has three single-bond faces and one double-bond face and is consequently not a regular tetrahedron.

Phosphorus, tervalent. Model No. 24a. (P_{TR})

Each of the three plane faces corresponds to a single-bond covalent radius. A van der Waals radius of 1.9Å has been used for the residual portion of spherical surface.

Silicon, tetrahedral. Model No. 25. (Si_T)

A regular tetrahedron with four single-socket faces, with the corners removed to avoid spurious steric hindrance.

Sulphur, di-univalent. Model No. 26. (S_{DI})

The bond angle of 105° is based on that found in dimethyldisulphide and dimethyltrisulphide and, as the model also gives the correct C-S and S-S bond lengths for these materials, it is suitable for building the important cystine links in proteins.

Sulphur, double-bonded. Model No. 27. (S_{DB})

The segment of a sphere with two sockets mounted in the plane face to give the double-bond radius.

Sulphur, tetrahedral. Model No. 28. (S_T)

The model is a compromise. It is a regular tetrahedron with one socket mounted in each of the four faces. Each of these faces gives a covalent radius of 1.00Å, which is the mean of the single- and double-bond radii. Combined with the negatively- charged oxygen atom (No. 22) it gives the S-O bond distance of 1.50Å as found in sulphate ions. The model may be used with No. 22 to build useful representations of sulphonic acids, sulphones and sulphuric esters but the $S\overset{\cdots}{-}O$ bond length will be too long (1.50Å compared with the observed 1.43 - 1.44Å) and the C-S bond length will be too short (1.77Å compared with 1.80Å observed). The single compromise model, however, has advantages in simplicity and cost over the several irregular tetrahedra which would have been necessary for more accurate representation of these classes of compounds. As with Model No. 25, the corners of the tetrahedron have been cut back.

Metal, cube. Covalent radius 1.25Å. Model No. 50 (M)

This is a cube with a single socket in each of the six faces. It is intended for building metal co-ordination compounds in the octahedral, or in the square planar configuration. In the latter case two sockets on opposite faces of the cube will remain unoccupied (See Section 21).

The octahedral covalent radii of the transition elements are in a number of cases close to this value.

Copper, tetrahedral. Model No. 51. (Cu)

A regular tetrahedron, having four single-socket faces, each giving a covalent radius of 1.35Å. The corners of the tetrahedron have been truncated so that each of these faces becomes a regular hexagon.

The model is intended for building co-ordination compounds, and, since Models Nos. 25 and 28 may also be used for this purpose, a continuous range of tetrahedral covalent radii, from 0.90 to 1.45Å, may be obtained by using the adjustable links.

Summary of Instructions

1. The flat faces corresponding to single bonds are fitted with single sockets; those corresponding to double bonds generally have two sockets. Triple-bond faces also have two sockets but spaced further apart so that they can only be attached to other triple-bond faces.

2. Some partial-double-bond faces only have one socket but these faces also have cavities into which nylon rods can be fitted to restrict rotation.

3. To connect two atoms by a single bond, insert a standard link in the socket of one, place a rubber collar surrounded by a yellow ring over it, and attach the second atom to the link. Two links with collars and rings are used for attaching faces having two sockets.

4. Always use the link magazine for inserting or extracting links. This much reduces the effort required when inserting, and after extraction these links are neatly packed and ready to hand.

5. Consult the table of bond angles and radii in order to select atom models.

6. Models such as that for the benzene carbon (C_B) have two equivalent partial-double-bond faces, one bearing one socket and the other two. Arrange the atoms so that the alternating double and single links will give the desired canonical structure. Take care not to confuse a single-bond face with a partial-double-bond face having only one socket.

7. When building fused aromatic rings, use the graphite carbon model (C_{GR}) for carbon atoms shared by one or more rings.

8. Models primarily constructed for six-membered aromatic rings may be used in five-membered rings if the yellow rings are dispensed with; but since there cannot be more than two double links in such a ring, a special nitrogen atom for five-membered rings is provided which has only **one** socket on each partial-double-bond face.

9. Always use a **yellow** ring on a rubber collar **except** when building five-membered planar rings or compounds where the link direction is greatly distorted. These rings not only restrict the angular distortion to an amount desirable for most purposes, but also greatly increase the effective tensile strength of the chain of atoms.

10. Only use **red** rings when it is required to avoid bond angle distortion.

11. Use the adjustable links if the desired bond lengths cannot otherwise be obtained.

12. When some particular model is not provided, consider substituting a model of another element having nearly the same bond angles and radii.

13. For hydrogen bonds, use the "bonded" hydrogen atom and attach this to the oxygen or nitrogen atom with which it forms a hydrogen bond by elastic bands.

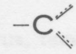
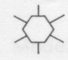
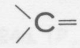
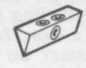
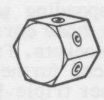
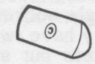
14. In quantitative work, remember that the models are in the nature of a calculating machine, and therefore consider whether the data used in designing the models used are appropriate to the problem.

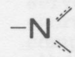
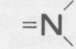
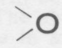
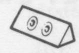
REFERENCES

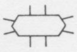
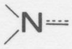
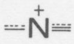
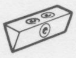
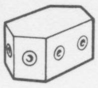
1. Stuart, Zeit physik. Chem. B, 1934, **27,** 370
2. Hartley and Robinson, Trans. Far. Soc., 1952, **48,** 847
3. Stuart, Die Struktur des freien Moleküls (Springer, Berlin, 1952)
4. Robinson and Ambrose, Trans. Far. Soc., 1952, **48,** 854
5. Robinson, Discussions of the Faraday Society, 1954, **16,** 125
6. Briegleb, Fortschritten der Chemischen Forschung, 1950, **1,** 642
7. Wepster, Rec. trav. chem., 1946, **65,** 318
8. Pauling, "The Nature of the Chemical Bond", Oxford Univ. Press, 3rd Edition, 1960
9. Robertson and White, J. Chem. Soc., 1945, 607
10. Spencer, Acta Cryst. 1959, **12,** 59
11. Coulson and Moffit, Phil. Mag., 1949, **40,** 1; Coulson, "Valence", (Oxford Univ. Press) 2nd Edn., 1961
12. Friend and Daly, J. Chem. Physics, 1958, **29,** 577
13. Dunitz et al., Helv. Chim. Acta, 1960, **43,** 3, 18; 1961, **44,** 2033; also Raphael, Proc. Chem. Soc., 1962, 97
14. Watson and Crick, Nature, 1953, **171,** 737, 964
15. Pauling, Corey and Branson, Proc. Nat. Acad. Sci., 1951, **37,** 205
16. Bunn and Howells, Nature, 1954, **174,** 549
17. Dwyer and Lions, J. Amer. Chem. Soc., 1950, **72,** 1545
18. Robertson, J. Chem. Soc., 1935, 615; 1936, 1195; 1937, 219; 1940, 36
19. Peterson and Levy, J. Chem. Phys., 1957, **26,** 220
20. Abrahams, Robertson and White, Acta Cryst., 1949, **2,** 233, 238

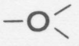
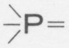
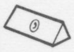
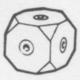
Characteristics of Atomic Species:

Table of Data overleaf ▷

Atom species		Bromine	C-acetylene	C-allene	C-benzene	C-benzene ring	C-carbonyl	C-tetrahedral
Catalogue No. S 33-405/		MODEL 1	MODEL 2	MODEL 3	MODEL 4	MODEL 5	MODEL 6	MODEL 7
Bond arrangement		−Br	−C≡	=C=				
Model outline								
Colour		blue-green	black	black	black	black	black	black
Bond angle		—	180°	180°	120°	60°	124° 124° 112°	109.5°
Covalent radii, Å	Single bond	1.14	0.75	—	0.77	0.77	0.77	0.77
	Double bond	—	—	0.67	0.695 (partial)	—	0.665	—
	Triple bond	—	0.605	—	—	—	—	—
van der Waals radii, Å		1.95	1.7	1.7	1.7	1.7	1.6	—

Atom species		N-azo	N-nitrile	N-quaternary	N-tetrahedral	N-Planar	O-carbonyl	O-di-univalent
Catalogue No. S 33-405/		MODEL 16	MODEL 17	MODEL 18	MODEL 19	MODEL 19a	MODEL 20	MODEL 21
Bond arrangement			≡N				=O	
Model outline								
Colour		blue	blue	blue	blue	blue	red	red
Bond angle		120°	—	120°	109.5°	122.5° — 115°	—	105°
Covalent radii, Å	Single bond	—	—	0.70	0.70	0.70	—	0.66
	Double bond	0.63 (partial)	—	0.70 (partial)	—	0.62 (partial)	0.55	—
	Triple bond	—	0.55	—	—	—	—	—
van der Waals radii, Å		1.6	1.5 1.6	1.7	1.5	1.70	1.4	1.4

C-graphite	C-naphthalene	Chlorine	Fluorine	Hydrogen	H-bonded	Iodine	N-amide	N-amine	N-azide
MODEL 7a	MODEL 7b	MODEL 8	MODEL 9	MODEL 10	MODEL 11	MODEL 12	MODEL 13	MODEL 14	MODEL 15
		−Cl	−F	−H	−H	−I			
									
black	black	grass-green	light green	cream	cream	dark green	blue	blue	blue
120°	—	—	—	—	—	—	120°	109.5°	180°
— 0.715 (partial) —	0.77 — —	0.99 — —	0.64 — —	0.30 — —	0.30 — —	1.33 — —	0.70 0.53 (partial) —	0.70 — —	— 0.62 0.55
1.7	1.7	1.8	1.35	1.0	0.5 1.0	2.15	1.5	1.5	1.6

O-negative	O-co-ordination	Phosphorus	P-tervalent	Si-tetrahedral	S-di-univalent	S-double bond	S-tetrahedral	Metal	Cu-tetrahedral
MODEL 22	MODEL 22a	MODEL 23	MODEL 24a	MODEL 25	MODEL 26	MODEL 27	MODEL 28	MODEL 50	MODEL 51
$-O^-$						=S			
									
red	white	purple	purple	grey	yellow	yellow	yellow	silver-grey	copper
—	105° — 127.5°	109.5°	100°	109.5°	105°	—	109.5°	—	109.5°
0.50 — —	0.66 — —	1.10 1.0 —	1.10 — —	1.17 — —	1.02 — —	— 0.94 —	1.0 1.0 —	1.25 — —	1.35 — —
1.4	1.40	1.9*	1.9	2.0*	1.85	1.85	1.85*	—	—

*See para 7, section 8

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