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Self-Crystallizing Molecular Models. II

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Structures of typical molecular crystals are discussed with reference to molecular models which simulate magnetically the electric multipoles of actual molecules. In many examples, structures given by the molecular models are found to agree with the actual crystal structures. From the packing of quadrupolar spheroids, it is inferred that the unknown space group for acetylene at lower temperatures is probably *Pnnm* (D_{2h}^{12}).

The structure of a molecular crystal is governed by the shape of the molecule as well as by the intermolecular force. However, it is a difficult problem to establish the relation between the molecular characteristics and the crystal structure. For the purpose of pursuing this problem the author has developed a novel type of molecular model constructed of pieces of magnets. (Kihara, 1960, 1963)*.

As there is a great variety in molecular crystals, it will be fruitful to choose several typical cases. Here we choose more or less symmetric molecules which have no dipole moment. Such a molecule has in general an electric quadrupole, octupole, or hexadecapole. If the moment of the multipole is sufficiently large, the multipole concerned will govern, together with the shape of the molecule, the structure of the corresponding molecular crystal.

Our molecular models consist of combinations of barium ferrite magnets simulating magnetically the electric forces between actual molecules. When their shapes and the magnetization are adequately patterned after a given molecule, a structure into which these magnetic models are assembled will simulate the actual structure of the molecular crystal under consideration.

The van der Waals force acts even between spherically symmetric molecules. The cohesive energy in the crystals of inert-gas molecules is entirely due to the van der Waals attraction. In fact, the structures of inert-gas crystals have been found to be closest-packings of spheres except helium, for which the quantum effects are dominant.

In general, the greater part (more than about 80%) of the cohesive energy of a molecular crystal originates in van der Waals attraction. However, the crystal structure is often not closest-packing, indicating that other types of intermolecular force are acting in addition to the van der Waals attraction.

Molecules which are not spherically symmetric have in general electric multipoles. The multipolar forces may be either attractive or repulsive according to the mutual orientation of molecules. Such being the case, the crystal structure is largely governed by the orientation-sensitive multipolar interactions when the multipole moment is sufficiently large.

The characteristic features of multipolar interactions will most clearly appear when the shapes of the molecules are simple. We shall first investigate spherical models, then spheroidal models, and then more complicated ones.

Structure data of actual crystals discussed below are mostly taken from Wyckoff (1948–1953) and Donnay, Donnay, Cox, Kennard & King (1963).

Octupolar sphere

The nearly spherical molecule of hexamethylenetetramine $(CH_2)_6N_4$ has the symmetry $\bar{4}3m$ (T_d), four nitrogen atoms forming a regular tetrahedron. Since electrons have affinity towards the nitrogen atoms, the surface of this molecule is composed of four poles of negative charge at the positions of the nitrogen atoms and four poles of positive charge in between. Thus the molecule may be approximated by an octupolar sphere.

We can make an octupolar sphere by combining together eight pieces of magnet, four pieces being magnetized outwards and the others inwards [Fig. 1(*a*)].

The structure obtained by assembling such models, shown in Fig. 2, represents the real crystal structure of hexamethylenetetramine; the space group is $I\bar{4}3m$ (T_d^3), with one body-centered cubic Bravais lattice of molecules.

The external shape of this molecular crystal, which is a rhombic dodecahedron as shown in Fig. 3, can also be reproduced by an assembly of our molecular models shown in Fig. 4.

Simple types of crystal dislocation can also be demonstrated by our molecular models. Fig. 5 represents a possible edge dislocation in the crystal of hexamethylenetetramine.

Axially symmetric quadrupolar sphere

The shape of the molecule of β-hexachlorocyclohexane $C_6H_6Cl_6$ as well as that of β-hexabromocyclohexane $C_6H_6Br_6$ is like an oblate spheroid, the six halogen

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* The paper of 1963 is referred to as part I.

atoms forming a ring outside the ring of carbon atoms. Since electrons have affinity towards the halogen atoms, the molecular surface is composed of one circular zone of negative charge and two caps of positive charge. Thus it may be approximated by an oblate spheroid with an axially symmetric quadrupole.

The prolate spheroid-like molecule of carbon dioxide has a linear quadrupole, in which two poles with an electric charge of the same sign are at the two ends and a charge of opposite sign is along a ring in between.

As a first approximation to these molecules let us choose a sphere with axially symmetric quadrupole. We can make such a quadrupolar sphere by combining together two hemispheres magnetized in opposite directions [Fig. 1(*b*)].

The structure obtained by assembling such models (Fig. 6) represents the real crystal structures composed of the molecules mentioned above. The space group is $Pa3$ (T_h^6), with four simple cubic Bravais lattices of molecules, on each of which the molecular axes are mutually parallel and along one of the four body-diagonals.

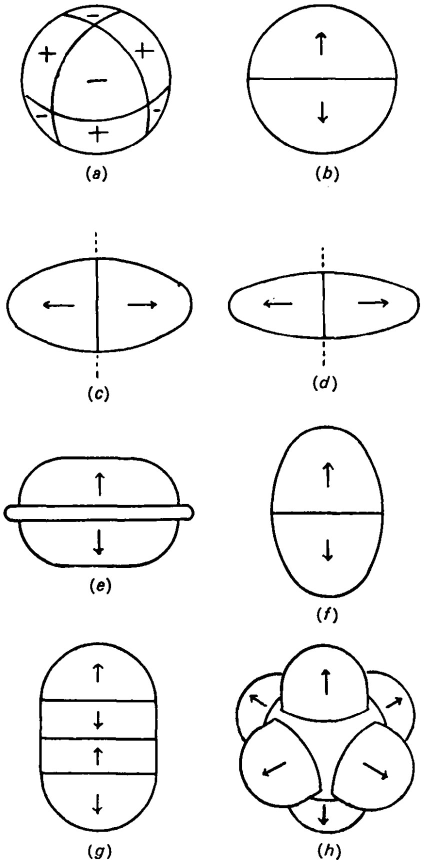


Fig. 1. Molecular models made of barium-ferrite magnets. (*a*) Octupolar sphere. (*b*) Axially symmetric quadrupolar sphere. (*c*), (*d*) Quadrupolar oblate spheroid. (*e*) Model of benzene molecule. (*f*) Quadrupolar prolate spheroid. (*g*) Model of biphenyl-type molecules. (*h*) Model for UCl_6 and WCl_6 discussed in part I.

Thus we draw the following conclusion. *The deviation from a sphere of the molecular shapes of carbon dioxide and β-hexachlorocyclohexane plays no essential role in the symmetry of their crystal structure.* This statement does not apply, however, to thinner or slenderer molecules, as we shall see in the next two sections.

Oblate spheroids and similar models

An oblate spheroid which is magnetized radially from the axis can be composed of six uniformly magnetized divisions (Figs. 7–9). The number six is chosen so as to simulate actual flat molecules to be considered.

An oblate spheroid with the axis ratio 2 to 1 [Fig. 1(*c*)] is very close in shape to the molecule of β-hexachlorocyclohexane or β-hexabromocyclohexane. In fact the structure obtained by assembling such models perfectly simulates the actual crystal structures, the space group $Pa3$ (T_h^6) being the same as in the case of spherical models (Fig. 7).

This structure cannot be obtained when the model is very flat. The model with the axis ratio 3 to 1 [Fig. 1(*d*)] gives an orthorhombic $Cmca$ (D_{2h}^{18}) structure shown in Fig. 8 and a monoclinic $P2_1/c$ (C_{2h}^5) structure shown in Fig. 9.

Typical examples corresponding to the monoclinic structure are:

Hexachlorobenzene C_6Cl_6
Hexabromobenzene C_6Br_6

Spheroidal models with the axis ratio 5 to 2 can be assembled into any one of these cubic, orthorhombic and monoclinic structures.

The crystal of benzene C_6H_6 belongs to the orthorhombic structure $Pbca$ (D_{2h}^{15}), which is, as one might say, between cubic $Pa3$ and orthorhombic $Cmca$ (see Cox, 1958). This structure can be given by the molecular model shown in Fig. 1(*e*), which simulates the benzene molecule more closely than oblate spheroids. Fig. 10 shows the result. In it, the molecular model is made to have an 'equator' consisting of a slender plastic ring corresponding to the six hydrogen atoms in C_6H_6.

Prolate speroids

A quadrupolar prolate spheroid can simply be made by combining two magnetized hemispheroids [Fig. 1(*f*)].

If the spheroid is not far from a sphere, an assembly of such molecular models gives the cubic structure $Pa3$ (T_h^6), which corresponds to the crystal structure of carbon dioxide. On the other hand, an assembly of thinner spheroids gives the orthorhombic $Pnnm$ (D_{2h}^{12}) structure, with two primitive Bravais lattices of molecules. An assembly of critical prolate spheroids with the axis ratio 3 to 4 gives both the cubic and orthorhombic structures mentioned above.

The crystal structure of acetylene C_2H_2 above −140°C is similar to that of carbon dioxide. Below −140°C the crystal system is orthorhombic, but the

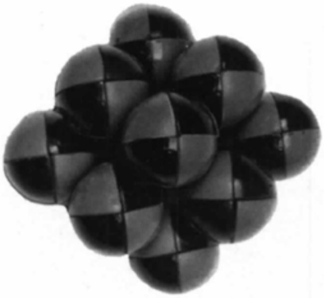


Fig. 2. Cubic $I\bar{4}3m$ structure of octupolar spheres.

Fig. 5. A model of edge dislocation in the crystal of hexamethylenetetramine.

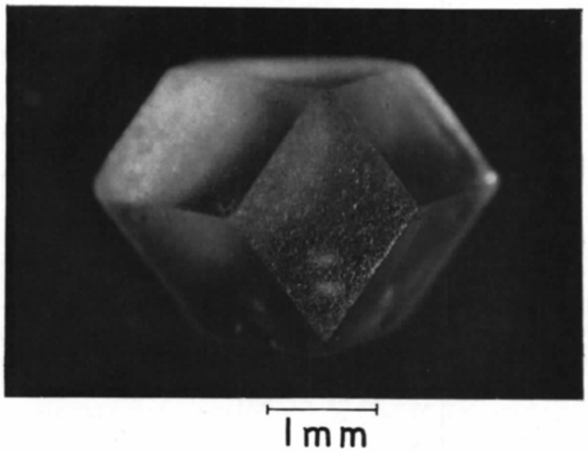


Fig. 3. A crystal of hexamethylenetetramine $(CH_2)_6N_4$.

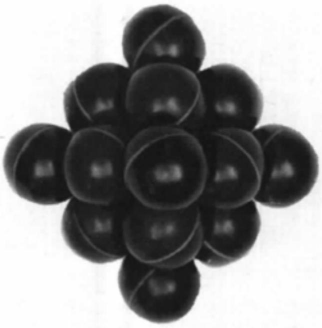


Fig. 6. Cubic *Pa*3 structure composed of quadrupolar spheres.

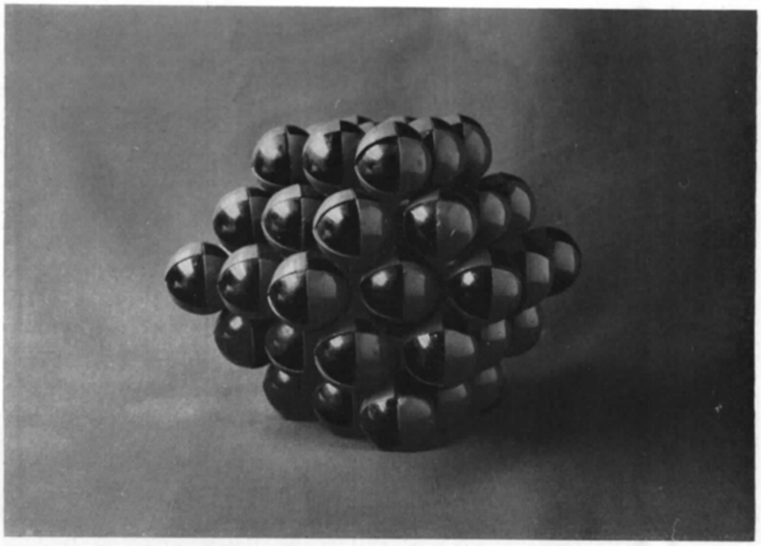


Fig. 4. An assembly of molecular models simulating the crystal of hexamethylenetetramine.

Fig. 7. Cubic *Pa*3 structure composed of quadrupolar oblate spheriods whose axis ratio is 2 to 1.

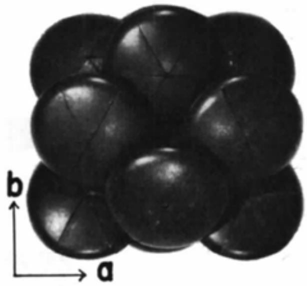


Fig. 8. Orthorhombic *Cmca* structure composed of quadrupolar oblate spheriods whose axis ratio is 3 to 1.

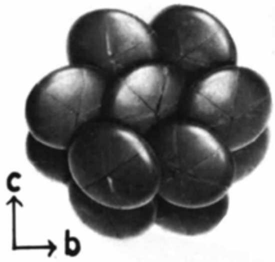


Fig. 9. Monoclinic $P2_1/c$ structure composed of quadrupolar oblate spheroids with the axis ratio 3 to 1.

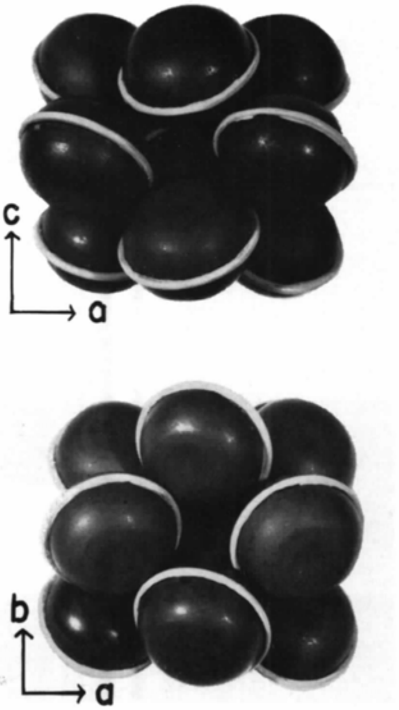


Fig. 10. Orthorhombic *Pbca* structure simulating the crystal structure of benzene.

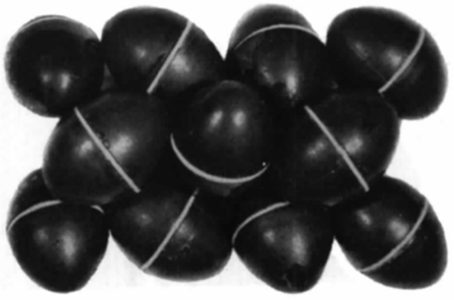


Fig. 11. Cubic *Pa*3 structure simulating the crystal structure of acetylene at higher temperatures seen from (110).

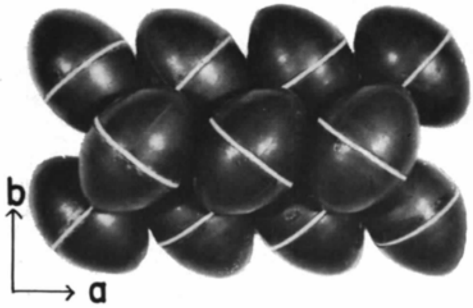


Fig. 12. Orthorhombic *Pnnm* structure, which probably corresponds to the crystal structure of acetylene at lower temperatures.

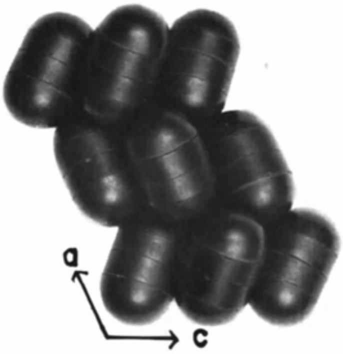


Fig. 15. $P2_1/c$ structure composed of two monoclinic Bravais lattices.

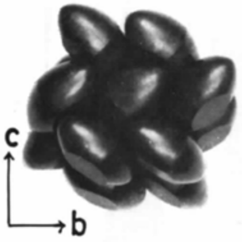


Fig. 13. Monoclinic $P2_1/c$ structure composed of models of quinone-type molecules.

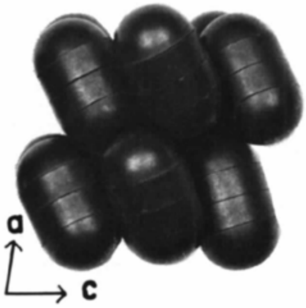


Fig. 16. $P2_1/c$ structure composed of four monoclinic Bravais lattices.

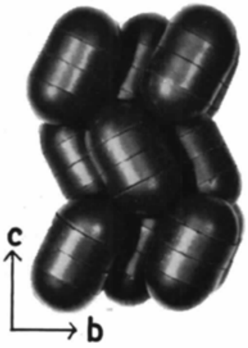


Fig. 14. Orthorhombic *Cmca* structure.

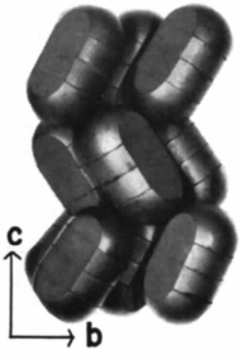


Fig. 17. Orthorhombic *Pbca* structure.

detailed structure is still unknown (Sugawara & Kanda, 1952).

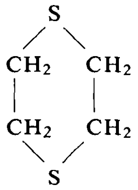
It is conceived, however, that the molecule of acetylene may be approximated by a model of spheroidal shape with the axis ratio close to $\frac{3}{4}$. Since the thermal motions result in the enlargement of the effective size of molecules, the molecular shape at high temperatures is effectively closer to a sphere than at low temperatures. Thus one may infer that the unknown orthorhombic structure of acetylene at low temperatures is probably *Pnnm*, as is shown by our molecular model.

Figs. 11 and 12 demonstrate how the molecules change their orientations at the phase transition. In fact one can demonstrate that the whole assembly (say, of fourteen spheroids) makes the transition from one structure to another when a few spheroids are set into appropriate orientations.

Model of quinone-type molecules

The shapes of the following quadrupolar molecules are like a prolate spheroid with two plane-parallel cuts:

trans-1,4-Dichlorocyclohexane $C_6H_{10}Cl_2$
trans-1,4-Dibromocyclohexane $C_6H_{10}Br_2$
trans-1,4-Diiodocyclohexane $C_6H_{10}I_2$
p-Dichlorobenzene $C_6H_4Cl_2$
p-Dibromobenzene $C_6H_4Br_2$
p-Benzoquinone $C_6H_4O_2$
1,4-Dithiane:



The crystal structures of these molecules are monoclinic $P2_1/c$ (C_{2h}^5), with two Bravais lattices of molecules.

Fig. 13 represents the symmetry and general characteristics of these molecular crystals. (A prolate spheroid with two plane-parallel cuts is closer to reality than the axially symmetric spindle-like model mentioned in part I. In fact, the present model gives only one configuration, whereas the spindle-like model results in several structures and does not give a unique structure.)

Model of biphenyl-type molecules

A model composed of four magnets as shown in Fig. 1(*g*) is a good approximation to some types of long molecule. This model gives the three kinds of structure shown in Figs. 14, 15 and 16.

The structure shown in Fig. 14 is orthorhombic *Cmca*, which is reduced to *Pbca* (D_{2h}^{15}), shown in Fig. 17, when the axial asymmetry reduces the elements of the symmetry group. The following are actual examples belonging to the *Pbca* structure:

Hexamethylenediamine $NH_2(CH_2)_6NH_2$
p-Dimethoxybenzene $CH_3–O–C_6H_4–O–CH_3$
Dimethyl terephthalate $C_6H_4(COOCH_3)_2$

The structures shown in Figs. 14 and 15 are monoclinic $P2_1/c$, composed of two and four Bravais lattices of molecules, respectively. Actual examples appropriate to the former are

Dicyanoacetylene $C_2(CN)_2$
Diethyl terephthalate $C_6H_4(COOC_2H_5)_2$
Biphenyl $(C_6H_5)_2$
Bibenzyl $(C_6H_5CH_2)_2$
Diphenyldiacetylene $C_6H_5–C{\equiv}C–C{\equiv}C–C_6H_5$
p-Azotoluene $CH_3–C_6H_4–N{=}N–C_6H_4–CH_3$

and those appropriate to the latter are

Azobenzene $C_6H_5–N{=}N–C_6H_5$
Stilbene $C_6H_5–CH{=}CH–C_6H_5$
Diphenylacetylene $C_6H_5–C{\equiv}C–C_6H_5$

The single crystal of hexamethylenetetramine shown in Fig. 3 was prepared by Dr T. Ninomiya, to whom the author is grateful.

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