Acta Cryst. (1965). **18**, 585

The Principle of Close Packing and the Condition of Thermodynamic Stability of Organic Crystals

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(*Received* 3 *May* 1964 *and in revised form* 28 *July* 1964)

The present paper gives an outline of a theory of structure and thermodynamic properties of organic crystals, based on the following assumptions.

1. Lattice binding energy may be calculated as total energy of interaction of all pairs of atoms of different molecules.
2. Free vibrational energy may be subdivided into intra- and intermolecular parts.

Methods have been devised for the calculation of thermodynamic properties of organic crystals, based on their structure. Several examples illustrate good agreement with experiment. It has been shown that the theory of close packing of molecules is a consequence of a more general theory with some additional simplifying assumptions.

Introduction

We believe it has been convincingly shown (Kitajgorodskij, 1945, 1959) that organic crystals are built according to the principle of close packing. This assertion means the following. It is possible to select sufficiently universal intermolecular radii with the help of which a certain shape may be given to a molecule. This done, a crystal will turn out to be a close packing of solids: adjacent molecules dovetail. When comparing an actual structure with imaginary ones having different cells and symmetry, we shall see that it is impossible to select structures that would be appreciably more closely packed than the actual one.

The theory of close packing has been supported, first of all, by our conclusion concerning the space groups possible for organic crystals. Rules of chemical organic crystallography thus obtained are rigorously observed. Quite recently Zorky & Poraj-Košic (1961) worked out a geometric method of selection of closest packings of arbitrarily chosen convex figures. The tightest structures have been theoretically derived for molecules of two different substances. In both cases the experimentally observed structure was found among the tightest packings.

In some simple cases (paraffins) the principle of close packing was successfully used for deducing possible structures. In most cases this work is impossible without limiting conditions because it is possible for a given molecule to have different crystal structures of closely similar densities. However, if the cell and symmetry are given, the packing of molecules can be often found from the condition of equality of all intermolecular distances of atoms of one kind. This indirect application of the close-packing idea is very often used in chemical organic crystallography.

Despite the obvious validity of the theory of close packing, the geometric aspect of this theory leaves one with a certain feeling of dissatisfaction. The actual structure corresponds to the condition of minimum free energy. But why is the geometric principle of close packing a consequence of minimum free energy? In the present paper we shall try to answer this question.

But the substantiation of the principle of close packing is not the goal *per se*. The present paper gives an analysis of the possibilities of building up a theory relating the structure of an organic crystal with its mechanical and thermodynamic properties. The geometric theory of close packing of molecules in a crystal is a consequence of the quantitative model proposed in the paper, with certain simplifying assumptions.

Free energy of an organic crystal

It is well-known (*e.g.* Leibfried, 1955) that when the energy difference between the ground and the first excited electron states is more than 1 eV (which is always the case in organic crystals, since they are quite perfect dielectrics) one can make use of the so-called adiabatic approximation which permits the reduction of the Coulomb interaction of nuclei and electrons to the interaction of atoms. In this case the potential energy of atomic interaction, which depends on the coordinates of nuclei ('centres' of atoms) only, appears to be equal to the energy of the ground electron level.

The free energy of an organic crystal is expressed by the equation

$$F = \Pi(r_i) + E - TS\,,$$

where Π is the equilibrium value of the potential energy, and E is the vibration energy of the atoms. The energy E and the entropy S are unambiguously defined by the values of the vibration terms.

Thus, quantum mechanics rigorously enables us to 'forget' about electrons and to reduce our problem to the study of the arrangement and motion of atoms. But in the case of organic crystals we can go somewhat further, if we subdivide free energy into two parts, inter- and intramolecular:

$$F = F_{\mathrm{cr}} + F_{\mathrm{m}}$$

where

$$F_{\mathrm{m}} = \psi(\mathbf{r}_i) + E_{\mathrm{m}} - TS_{\mathrm{m}}$$
$$F_{\mathrm{cr}} = \varphi(\mathbf{R}_i, \boldsymbol{\varphi}_i) + E_{\mathrm{cr}} - TS_{\mathrm{cr}}\,.$$

This subdivision of F is adequate because vibrational intermolecular states remain practically unchanged upon entering a crystal. The potential energy ψ also must correspond to the energy of a free molecule; it changes in specific cases only, which will be dealt with below.

Intermolecular (crystal) free energy is defined by intermolecular vibration states connected with translational and vibrational movement of molecules. Each molecule vibrates as a solid with 6 degrees of freedom; thus $3N$ translational and $3N$ vibrational waves are propagated in the crystal. Accordingly, the potential energy of molecular interaction at equilibrium — the lattice binding energy — depends on the arrangement of the centers of gravity of molecules $\mathbf{R}_i$, as well as on their orientation determined by Euler angles.

The frequencies of intramolecular vibrations being measured in tens of cm^{-1}, room temperatures (and even temperatures of 150–200 °K) are high enough to make use of the approximation $1-\exp(-h\nu/kT) \simeq h\nu/kT$. The vibrational part of the energy

$$F_{\mathrm{cr}}^{\mathrm{vibr}} = kT\,\Sigma \ln\{1-\exp(-h\nu/kT)\}$$

is easily transformed to:

$$F_{\mathrm{cr}}^{\mathrm{vibr}} = E_{\mathrm{cr}} - TS_{\mathrm{cr}} = 6RT\ln(h\bar{\nu}/kT)$$

where $\bar{\nu}$ is the mean geometric frequency,

$$\ln\bar{\nu} = 1/(6N)\,\Sigma\ln\nu\,.$$

To bring this equation into agreement with the Debye interpolation formulae, one should introduce the 'Debye' temperature, $\theta = e^{1/3}(h\bar{\nu}/k)$.

The equation for the free energy is

$$F_{\mathrm{cr}}^{\mathrm{vibr}} = 6RT\ln\theta/T - 2RT\,.$$

At temperatures below 200 °K the Debye interpolation formulae may be used.

The characteristic temperature θ, as well as φ, is a function of the arrangement of molecules in a crystal. Thus, the condition of crystal stability in the general case (with the molecule unchanged) becomes

$$\delta F = \delta\varphi + 6RT\,.\,\delta\theta/\theta = 0\,.$$

In the case the variations $\delta\varphi$ and $\delta\theta$ are determined by changes in the mutual arrangement and orientation of the molecules. At absolute zero the condition of stability changes to $\delta\varphi = 0$. Vibrational zero-point energy may be disregarded: at a maximum value (6 frequencies of 80 cm^{-1} each), zero-point energy of intermolecular vibrations equals 0·5 kcal.mol^{-1}, its possible changes caused by variations in mutual arrangement of molecules not exceeding 0·1 kcal.mol^{-1}, whereas even for molecules of 10–12 atoms the heat of sublimation is more than 10 kcal.mol^{-1}.

Thus, if an organic crystal structure is stable at absolute zero, it means that the lattice binding energy for this structure is very near to a minimum value.

Energy of molecular interaction

The only possibility of any progress in studying potential energy of interaction is by assuming additivity. The study of this problem developed in a direction (*e.g.* Hirshfelder, 1954) where Φ was represented by the sum total of potentials Ψ molecule–molecule,

$$\Phi = \Sigma\Psi_{ik}\,.$$

For a condensed state of a substance such an approach creates insuperable difficulties owing to the strong orientational depence of Ψ_{ik}. Besides that, the principal fault of such an approach should be stressed, this fault being that the functions Ψ_{ik} are different depending on the kind of molecules. Having ascertained, on the strength of quite comprehensive experiments, the type of Ψ for molecules of one kind we are no further in understanding interaction potentials of other molecules. The finding of molecule–molecule potentials Ψ, as is done in the case of real gases with the help of virial coefficients, appears to be quite a futile occupation. It is even more hopeless to expect to achieve any progress in this way in studying lattice binding energy of molecular crystals.

We have made an attempt to avoid the above difficulty by using atom–atom potentials (Kitajgorodskij, 1961). The main assumption is that, to a sufficiently good approximation, the potential energy of molecular interaction may be represented as the sum total of pair interactions atom–atom. Thus, the energy Φ of a molecular system is equal to $\Sigma\Phi_{ik}$, where the summation is taken over all pairs of atoms of different molecules.

In order that the statement of the problem in question should be of heuristic interest, we shall take the following approximation as a basis: we shall assume that each atom of a given chemical kind may be regarded as superposition of a 'universal neutral atom' and a residual electric charge Xe at the atom centre. The specific character of an atom in a given molecule will be reflected only by the value of this residual charge. Energy of interaction is considered in the form

$$\Phi_{ik} = U_{ik} - \frac{X_i X_k e^2}{r_{ik}}\,,$$

where U_{ik} are universal potentials for neutral atoms. For instance, all hydrocarbons are described in this approximation by three universal curves U_{CC}, U_{CH}, and U_{HH}.

The introduction of atom–atom potentials changes radically the approach towards the problem of intermolecular interaction: on the basis of detailed experimental research parameters of universal potentials may be found for a small group of 'standard' substances, while further these same curves will help to predict the properties of all other organic substances.

Later on we shall see that the heuristic possibilities of the method of atom–atom potentials are not all affected by the electrostatic component of intermolecular energy, which in our scheme allows for chemical specificity of atoms of a given molecule. The rôle of this component is either quite insignificant, or may be taken into account without any special difficulty.

An attempt at a calculation in which atomic interaction potential is regarded as a function of only the distance between the centres of atoms appears to be justified. There also exists, of course, a dependence of interaction energy on the direction of the radius vector in relation to the corresponding valence bonds. Thus, for instance, there are many indications of the fact that the equilibrium distance of hydrogen-atom interaction with the radius vector perpendicular to the valence bond exceeds by one or two tenths of 1 Å the equilibrium distance in the direction of the bond. This quite insignificant dependence is of little consequence for the calculation of intermolecular energy, as during the summation an automatic averaging of various directions of interatomic vectors in relation to the valence bonds takes place.

No doubt, the most suitable analytic dependence for $U(r)$ is a combination of an inverse sixth power and an exponential:

$$U(r) = -Ar^{-6} + B \exp(-r/\varrho) .$$

It is expedient to introduce the following parameters instead of A, B, ϱ: $Z = r/r_0$, where r_0 is the abscissa of the curve minimum; $\alpha = r_0/\varrho$; and $U_{2/3}$, energy at Z equal to $\frac{2}{3}$. Such a transformation is expedient inasmuch as it makes obvious *a priori* the approximate values of the independent parameters: r_0 values are known to us from the analysis of intermolecular distances in crystals*, $U_{2/3}$ values ($Z = \frac{2}{3}$ is, for instance, the distance between the closest non-bonded atoms in an aliphatic chain) are doubtless of the order of a few kcal. mol^{-1}, and α values may only be found in the relatively small interval from 11 to 15. Therefore we recommend that the foregoing equation should be rewritten thus:

$$U = U_{2/3}\left[\frac{1}{Z^6} - \frac{6}{\alpha}\exp\alpha \, . \exp(-\alpha Z)\right] \left[11{\cdot}4 - \frac{6}{\alpha}\exp\alpha/3\right] .$$

In our papers on interaction curves for hydrocarbons (Kitajgorodskij, 1961) α values were assumed to be equal to 13, and $U_{2/3} = 3{\cdot}5$ kcal.mol^{-1} for all interactions C · · · C, C · · · H, and H · · · H. These figures, as well as r_0 values for three curves 3·8, 3·15 and 2·6 Å are subject to refinement.

Lattice binding energy of a molecular crystal

The lattice binding energy of a molecular crystal related to one molecule is expressed by the equation

$$\Phi = \tfrac{1}{2}\Sigma\varphi_{ik} ,$$

where the summation takes place over all interatomic vectors connecting atoms of one molecule with all atoms of the remaining molecules.

As indicated above — and we shall revert to this later on — the crystalline-field influence upon a molecule is insignificant in the majority of cases. If a molecule is to be considered rigid, then all interatomic vectors, and hence lattice binding energy Φ, may be presented as a function of the coordinates of the molecular centre of gravity, XYZ, the Euler angles in relation to the lattice axes, and the parameters of the elementary cell.

The optimum structure may be found, in principle, if we construct multidimensional surfaces of the Φ function for all symmetry-consistent arrangements of the molecules. The coordinates of the absolute minimum of Φ solve the problem. This is, of course an unwieldy problem. Solution of the potential-energy problem as well as the application of the geometric principle of close packing can give us some minima of nearly equal depth. We should be wrong to choose the deepest among them because small differences can be of the order of quantities neglected in the proposed scheme of energy calculation.

But we are not now trying to solve the problem of investigating the energy surface without knowing the crystal symmetry. We are just trying to solve the following problem: let us consider the actual structure of a crystal and construct the Φ surface in the vicinity of a point representing this structure. For instance, in the case of a naphthalene crystal function $\Phi(\varphi_1, \varphi_2, \varphi_3, a, b, c, \beta)$ is constructed for the actual symmetry $P2_1/a$, the parameter values being varied about the experimental point. If the proposed approach is valid, then the surface has a minimum in the neighborhood of the said point. Surface shape in the vicinity of the equilibrium point may be compared with various experimental data. Suffice it to mention here that good fulfilment for organic crystals of the elasticity-coefficient equation

$$C_{ij} = \frac{\partial^2\Phi}{\partial\varepsilon_i\partial\varepsilon_j}$$

may serve as a basis for verification (Kitajgorodskij & Mirskaja, 1964). (Vibration-dependent components are small and can be accounted for.

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* It should be noted that there occurs a slight 'compression' upon the entry of a molecule into a crystal, and distances in the crystal will be 5-10% less than free equilibrium distances.

The study of elasticity coefficients and of the expansion tensor as a function of temperature makes it possible to verify the equation of lattice binding-energy surface. The potential-well depth is determined by the heat of sublimation. With the help of a special program for an electronic computer we made a calculation of some cross-sections of energy surfaces. Shown in Fig. 1 are Φ curves as a function of cell parameters in the case of naphthalene. The electrostatic component was not taken into account. This, still tentative, calculation is in quite satisfactory agreement with the small number of experimental data we have at our disposal.

Energy-surface cross-sections in which Φ changes as a function of Euler angles constitute a convincing proof of the validity of the proposed calculation chart. Fig. 2 shows such cross-sections for anthracene. Curve minima show good agreement with experimental values: the actual structure corresponds to the minimum of potential intermolecular energy.

The role of electrostatic energy

To find the role of the electrostatic energy as a lattice-energy component, it is necessary to obtain general energy equations, with explicit functional dependence of the energy on the lattice parameters and on the orientation of dipole and quadrupole moments relative to the symmetry elements. To bring about the solution of the problem in such a general form and, at the same time, to make the calculation results readily comparable with specific structures, we have considered cubic and hexagonal lattices of close-packed spheres.

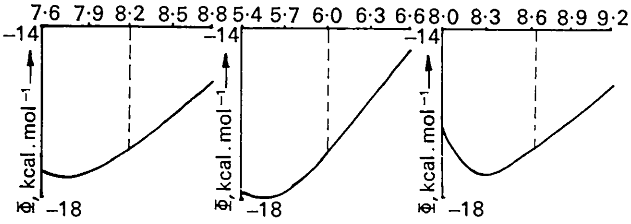

Fig. 1. Energy curves as a function of cell parameters for naphthalene.

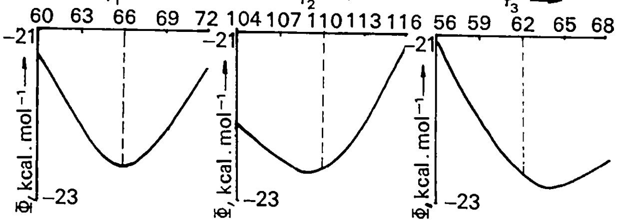

Fig. 2. Energy curves as a function of Euler angles for anthracene.

The summation technique for dipole arrangements corresponding to different spatial groups will be published elsewhere. We shall give here the result for a dipole arrangement corresponding to the space group $P2_1/a$ with $Z=4$:

$$\Phi_{\mathrm{el}}=(\mu^2/a^3)\ \{0{\cdot}857[-3+(\sqrt{8}\sin\psi\cos\varphi+\cos\psi)^2]\}$$

where μ is the dipole moment, a is the shortest inter-dipole distance, and ψ is the dipole angle with the normal to the close-packed layer.

This equation is typical enough to attract our attention to the slow rate (probably in most cases) of change of Φ_{el} with angles φ, ψ as compared with the similar dependence of Φ_{neutr}. The maximum value of $\dfrac{1}{\mu^2/a^3}\,\dfrac{\partial\Phi}{\partial\Psi}$ $=0{\cdot}13\ \mathrm{deg}^{-1}$. Let us assume that we have under consideration a molecule with a dipole moment of 4 Debye and a mean diameter of 7 Å. In this example $\partial\Phi/\partial\Psi$ is of the order of 0·09 kcal. mol.$^{-1}$deg^{-1}. If we consider the above-mentioned typical curve $\Phi_{\mathrm{neutr}}(\varphi)$, it becomes obvious that dipole–dipole interaction forces cannot move a molecule out of the state $\delta\Phi_{\mathrm{neutr}}=0$ even in the case of molecules with a high dipole moment.

In the case of non-dipole molecules, the quadrupole–quadrupole interaction energy may be estimated in the same way.

It does not follow from the above that the electrostatic interaction has no effect at all upon the structure of a molecular crystal. Differences between maximum and minimum values of electrostatic energy, though not great, are not negligible either. In the foregoing dipole example Φ_{el} ranges from $+3{\cdot}5$ kcal. mol^{-1} to $-2{\cdot}0$ kcal. mol^{-1}. There are grounds for believing that dipoles will fall in the neighbourhood of the $-2{\cdot}0$ kcal. mol^{-1} minimum, *i.e.* dipole angles in this example will be close to $\psi=90\%$.

As the surface of Φ_{neutr} as a function of the parameters has a plurality of minima, an arrangement of molecules is formed in which the structure is to be found at one of the lowest minima of Φ_{neutr}, Φ_{el} being also minimal in such an arrangement.

In the case of hydrocarbons the effect of electrostatic interaction may be neglected.

The condition of structure stability and the principle of close packing

The condition of stability of structure at absolute zero is expressed by the equation:

$$\delta\Phi_{\mathrm{neutr}}+\delta\Phi_{\mathrm{el}}=0\ .$$

As we saw in the preceding section, electrostatic energy is a rather slowly-varying function of the structure parameters. Thus, if the Φ_{el} surface is superposed on the surface of Φ_{neutr} as a function of the parameters the shift in the position of the minima of Φ_{neutr} is insignificant, but the minima may change places, as shown in Fig. 3. The presence of the electrostatic component leads to the assumption that a stable structure does not necessarily correspond to the absolute minimum of Φ_{neutr}. All we can say for certain is that *one of the lowest minima of* Φ_{neutr} *corresponds to the actual structure.*

At arbitrary temperature the entropy factor comes into play. Of two minima with the same depth, that one is realized for which the conditions of molecular vibration favour a greater entropy (making use of a mechanical model we can say that the minimum with a wider potential well is more suitable), or to put it differently, that minimum is realized for which the characteristic temperature is lower.

A phase transition with an increase of T occurs when an increase in lattice binding energy $U_1 - U_0$ may be compensated by an increment of $T\Delta S$ (Fig. 4). If a phase transition occurs, it means that the potential well U_1 is wider than the potential well U_0. When the temperature goes up so that $T\Delta S$ becomes equal to $U_1 - U_0$, the phase transition occurs. If there are no sufficiently "wide" wells among "higher" ones, then the substance will melt.

Thus, heat fluctuations may transfer a structure from a lower minimum to a higher one, but do not bring the structure out of Φ_{neutr} surface minima. Therefore, the condition $\delta\Phi_{\text{neutr}} = 0$ is the universal condition of structure stability, to which it should be added that *the actual minimum is not necessarily an absolute, but is one of the lowest minima.*

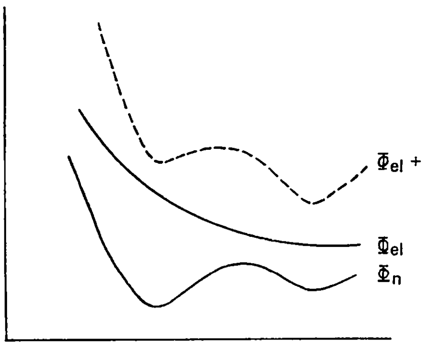

Fig. 3. Electrostatic interactions do not violate close packing. They lead only to the choice from several of the most close-packed structures of the one which has the advantage in electrostatic energy.

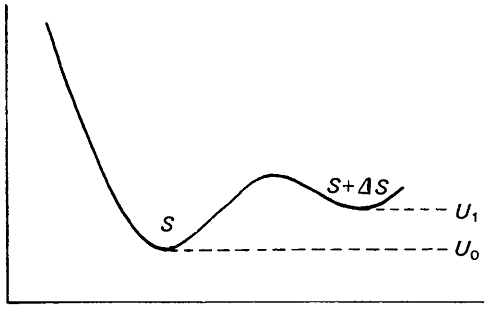

Fig. 4. Phase transition transfers a structure from the deepest minimum to the next one.

The condition of structure stability, as well as the condition of minimum potential energy of molecular interaction, doubtless leads us to the principle of close packing of solid molecules. The following simplification is necessary for this transition: interaction curves of all pairs of atoms are characterized by uniform depth of potential wells (which we have already assumed), and the curve is replaced by a vertical straight line in the repulsion region. Under these conditions minima on the energy surface should coincide with those on the analogous volume surface.

A rigorous proof of such an assumption would be a rigorous proof of the principle of close packing. Having no such proof we can only refer to the already-quoted paper by Zorky & Poraj-Košic (1961), where it is shown for particular cases that one of the deepest minima on the volume surface built for solid molecules leads to the parameters of the real structure.

Together with a trend towards close packing, a molecule in a crystal tends to retain part of its symmetry elements, provided this retention does not cause a serious loss of density. This tendency is believed to be of an entropic nature. It seems natural to assume that in a more symmetric position a molecule has a greater freedom of vibrations (the structure occupies a wider potential well on the multidimensional energy surface). Unfortunately this assumption, too, is purely hypothetical, though an attempt at a rigorous proof is not utterly hopeless. It is to be supposed that some structures, in which a molecule occupies a special position on the symmetry axis or plane, are unstable at low temperatures; however, high barriers of phase transformation prevent a more stable structure from manifesting itself.

The effect of the crystalline field upon the shape of the molecule

Using the proposed idea for calculating intermolecular interactions we can calculate the crystalline-field potential at any point of the lattice. This potential is formed by the field of neutral atoms (this field being different for different types of atom) and the electrostatic potential. It is difficult to evaluate the electrostatic potential in a general form, as this potential represents a small difference between large quantities. As mentioned above, the electrostatic potential changes in value from one point to another considerably slower than the potential of neutral atoms. Approximate evaluations show that the electrical potential gradient appears negligible as compared with that of the neutral-atom potential, at any rate when the residual electrical charges of atoms are not too great. The intensity of the field of neutral atoms may be estimated from the equations given above (a chart of the crystalline field may be plotted for particular cases). Calculations show that these forces do not exceed 10^{-7} dyne in order of magnitude. It is quite obvious that the forces are directed into the molecule, since the crystalline field as a whole exerts pressure upon the molecule.

Crystalline-field forces are offset by intramolecular forces, *i.e.* by the elasticity of valence-bond compression, the elasticity of valence-angle deformation, and elasticity of rotation about ordinary bonds.

Using typical values of bond and angle elasticities we immediately find the corresponding deformations to be negligible and undetectable by methods of X-ray diffraction analysis. It is only for compressing non-bonded atoms within the first 5 to 15% fractions of equilibrium distance that an insignificant force of the order of 10^{-7} dyne is necessary. Therefore such compression, including the corresponding rotations about ordinary bonds, will be the only consequence of crystalline-field influence upon a molecule (at any rate, in the case of molecules of hydrocarbon type, whose atoms do not carry any charges)*. Thus, distortion of flat aromatic molecules, observed in X-ray diffraction analysis of crystals, is caused by the action of intramolecular forces only.

The smallness of intermolecular forces brings about a situation in which the conformation of a molecule in a crystal (with the exception of the already-mentioned case) is very close to the extreme conformation with respect to the value of intramolecular energy. For the most part, a molecule possesses the same conformation in a crystal as in a gas, *i.e.* the arrangement of atoms corresponds to the minimum of potential energy. But there may be cases when the conformation of a molecule in a crystal corresponds to the maximum of energy. We shall observe such cases when the conformation of a molecule with a maximum energy is, at the same time, minimal in relation to the molecule's own volume. Indeed, bearing in mind that the crystalline field exerts pressure upon a molecule, it seems natural that such cases are possible when an increase in the molecule's own energy is compensated by a decrease in the lattice energy, this decrease being due to the possibility of packing molecules in a smaller volume. Examples of this type are known in the literature: molecules of biphenyl and hexachlorobenzene, which are not flat in the gas, become flat in the crystal.

The above-mentioned assumption could be verified by comparing the heat of sublimation of these substances with the calculated lattice binding energy, but it would be somewhat premature to make such a calculation at present as atom–atom potentials are not yet sufficiently defined.

Intermolecular hydrogen bonds

The presence of strong hydrogen bonds between molecules considerably complicates the problem. The lattice binding energy increases quite sharply and the condition of structure stability is the minimization of the sum total of potential-energy components, already discussed in the present paper, and the hydrogen-bond energy. As the energy of each hydrogen bond amounts to several kcal.mol^{-1} it is obvious that, in the first place, the structure is built up so as to saturate the maximum number of hydrogen bonds. In a number of cases this circumstance probably involves sacrifices on the part of the potential energy of neutral-atom interaction. Practical experience in crystallochemistry has shown that this sacrifice is not very great. Usually a crystal is formed in which the tendency towards close packing is realized simultaneously with the saturation of all hydrogen bonds. Nevertheless, the theory is greatly complicated. Hydrogen bonds are directed, and deviations of the atoms forming it from a straight line are connected with a certain loss of energy which is not easy to estimate.

It is also obvious that the dynamics of the lattice, transformed by hydrogen bonds into a three-dimensional skeleton or into a system of band or chains, undergoes substantial changes.

The development of a theory of organic crystals with hydrogen intermolecular bonds is a problem for future research.

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* It seems to me that this circumstance should be made use of in the X-ray diffraction analysis of organic crystals. It is quite clear, for instance, that all sides of the benzene molecule are of equal length and their inequality may be only due to experimental error; similarly, planar symmetry of the naphthalene molecule is beyond doubt, and any differences in the length of bonds in the crystal should be due to experimental and calculation errors and do not reflect the real state of things. We can be equally sure of the identity of two crystallographically non-equivalent molecules in such crystals as acenaphthene.

When we try to find a structure with the help of the least-squares method, we should take into account these necessary equalities of bond lengths and angles. This reduction in the number of parameters will, quite naturally, increase the degree of accuracy in determining other parameters. It is possible to determine the optimum structure by finding a structure built up of molecules with regular symmetry, which is closest of all to the system of experimentally found maxima. It seems still better to introduce the requirements of molecular symmetry into eht least-squares program, *e.g.* according to the chart proposed by Waser (1963).