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Theoretical Calculation of the Spatial Distribution of Molecules in Crystals

T.V.Timofeeva, N.Yu.Chernikova, and P.M.Zorkii

The fundamental energetic and geometric framework of the interpretation and prediction of molecular packing is discussed on the basis of results published between 1960 and 1977. The atom-atom potential method is described, and the methods of selecting the parameters of these potentials are examined. An extended tabulation of theoretically determined molecular packing arrangements is presented, listing the form of the chosen potential function, the structure parameters which are treated as adjustable in the minimisation of the energy, and other aspects of the method of calculation. 271 references.

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I. INTRODUCTION

The *a-priori* determination of the distribution of molecules in a crystal structure without resorting to experimental data (or with a minimal use of such data) offers many attractive possibilities. Firstly, the very fact that prediction is possible confirms the validity of our views on the fundamental aspects of crystal structure. Secondly, there is now considerable practical interest in the theoretical calculation of structures in cases (e.g. polymers, layered polytypes) where X-ray diffraction cannot give full structural information but it can confirm *a-priori* calculations. Thirdly, these calculations can be useful in computations of approximate, model structures which can then be made more precise by using X-ray diffraction data. Therefore it is not surprising that the early theoretical calculations of the spatial arrangements of molecules in crystals were followed by a large number of publications on the same theme during the past 25–30 years.

The aim of this review is to analyse the results of that work and to assess the prospects of this field of science. We shall examine very recent results, which were not available to previous reviewers[1–4]. Furthermore previous writers[3–5] have tended to ignore work other than their own.

II. GEOMETRIC AND ENERGY INTERPRETATION OF MOLECULAR PACKING

The problem of determining the optimum structure reduces to finding the spatial distribution with a minimum energy. There are at present two ways of formulating the problem. One consists in finding the closest packing of particles, using van der Waals radii. In the absence of directionally specific interactions the tendency to give a close-packed structure is a good guide to finding the arrangement with minimum energy. The second (and stricter) approach is to calculate the arrangement corresponding to a minimum in the intermolecular interaction energy.

In general the calculation of the closest packing of bodies of arbitrary shape presents enormous mathematical difficulties. However in many crystal-chemical problems we can introduce substantial simplifications which allow us to reach a definite solution.

One of these simplifications is to assume that the elementary cell parameters are known. This variant of the problem was solved by Kitaigorodskii[6] for 2,6-dimethylnaphthalene by using a special apparatus (the "structure seeker"), and also for several other crystals[7–9] by computation. The combination of the principle of closest packing with experimentally measured lattice parameters forms the basis of the X-ray method of determining crystal structures developed by Gel'fand, Neigauz, and others[10,11] (the "gully" method).

Another simplification is possible in the case of polymeric molecules. Since the axes of these molecules must be parallel, one degree of freedom is lost. By virtue of this approximation the principle of closest packing allows us not only to predict the arrangement of chains in the cell but also to identify a very limited number of possible elementary cells. Studies of polyethylene by this method were reported by Kitaigorodskii[12,13] and by Segerman[14].

Zorkii and Porai-Koshits[15–17] combine the principle of closest packing with a quantitative calculation of the distribution of objects of arbitrary shape in a plane with the highest reticular density (the streamline trajectory method). This allows them to calculate the most compact type of packing of long-chain molecule (or planar molecules) in a layer whose plane coincides with the plane of the molecule. The crystal structures of $PdCl_2$,[18] $BeCl_2$,[19] Ni dimethylglyoxime[20], and Cu salicylalmethyliminate[21] have been successfully determined by the trajectory method.

The geometric approach continues to be an effective method of interpreting molecular crystal structures. Its value has been enhanced by the publication of an accurate set of van der Waals radii[22,23], obtained by a statistical analysis of a large amount of structural information. However, though it remains a simple and useful tool for qualitative and semi-quantitative estimates, the geometric model is not a serious contender for the quantitative *a-priori* prediction of molecular packing, i.e. the problem to which this review is devoted. The geometric approach is inferior to the energy approach (in that its postulates are less strict and well founded) without in any way making the calculation of the optimum structure (using a computer) more straightforward. Hence it is better to seek a solution of the molecular packing problem directly from calculations of the intermolecular interaction energy. The atom–atom approximation, which is discussed in detail in the next Section, offers a concrete method of calculating this energy.

The energy of a crystal structure consisting of rigid molecules can be expressed as a function of a series of structure parameters:

$$U(a, b, c, \alpha, \beta, \gamma, X_i, Y_i, Z_i, \varphi_i, \theta_i, \psi_i),$$

where a, b, c, α, β, γ are the lattice parameters, X_i, Y_i, Z_i are the coordinates of the centres of gravity of the symmetrical, independent molecules, and ϕ_i, θ_i, ψ_i are the Euler angles which characterise the orientation of these molecules. In special cases the number of independent parameters can be less: thus the energy of rhombic benzene is a function of six parameters only ($U(a,b,c,\phi,\theta,\psi)$). On the other hand the angles which characterise the conformation must be included among the parameters if the molecule cannot be treated as rigid.

By minimising the energy U we can find the structure parameters which offer the optimum molecular packing: in principle this should correspond to the crystal structure experimentally observed. Minimisation is usually applied to the potential energy of the structure. Thus we are in fact examining the structure of the crystal at a temperature close to the absolute zero. However we know experimentally that the vast majority of molecular crystals do not suffer phase transformations over a wide range of temperature (up to room temperature), and their geometric characteristics change very little. Hence the optimum structure for the absolute zero is often also the optimum for room temperature. However a strict formulation of the problem requires calculation of the free energy F of the crystal structure.

Consideration of the simplest model structure, consisting of an assembly of independent oscillators located at lattice sites, shows[24] that the free energy can be expressed as the sum of the following terms:

$$F = U_0 + E_0 + E_T - TS,$$

where U_0 is the potential energy of the structure at 0 K, and E_0 and E_T are the zero-point vibration and the thermal vibration energy respectively. The free energy of all molecular crystals is usually assumed to consist of these terms.

Molecular crystals are distinguished by a very large difference between the energies of their intramolecular and intermolecular interactions. For this reason Kitaigorodskii suggested[25] expressing the thermodynamic functions of molecular crystals as the sum of two terms: a "molecular" term and a "crystalline" term. The former is related to the structure of the molecules and to their internal vibrations, the latter to the relative position of the molecules and to their external vibrations:

$$U = U^{\text{intra}} + U^{\text{inter}},$$
$$S = S^{\text{mol}} + S^{\text{cryst}},$$
$$E_T = E^{\text{intra}} + E^{\text{ext}}.$$

Using these expressions the free energy of a molecular crystal can be written

$$F = E_0 + (U^{\text{intra}} + E_T^{\text{intra}} - TS^{\text{mol}}) + (U^{\text{inter}} + E_T^{\text{ext}} - TS^{\text{cryst}}) = E_0 + F^{\text{mol}} + F^{\text{cryst}}.$$

Our main interest lies in the evaluation of the term F^{cryst}. In the case of rigid molecules the minimum of the function F^{cryst} coincides with the minimum of the full free energy function.

Two specific ways of calculating F are known at present. The first, described in detail in Ref.26, includes a calculation of the full set of frequencies from the differentials of the potential energy with respect to the structure parameters (expressing the energy U in the atom–atom approximation). The standard free expressions in terms of the frequency distribution function (or density of states function) are then applied. Typical of this approach is a calculation[27] of the equilibrium parameters of the elementary cells of three hydrocarbons at different temperatures.

The second method of calculating the energy F is based on statistical mechanics, and involves a calculation[28] of the configurational integral

$$Q = \frac{1}{N!}\int_{\Omega}\cdots\int_{\Omega}\exp\left\{-\frac{U(q_1,\ldots,q_N)}{kT}\right\}\mathrm{d}q_1\ldots\mathrm{d}q_N,$$

where N is the number of molecules in the system, $U(q_1,\ldots,q_N)$ is the potential energy, and Ω is the volume in configurational phase space occupied by the system. In the calculation the configurations $q_1^{(i)},\ldots,q_N^{(i)}$ are randomly generated in phase space (Monte Carlo method) and the corresponding values of the integrand are averaged. Concrete calculations of this type have been reported for crystals of the intert gases[29,30], N_2,[31] and CO_2.[32] However this approach is too cumbersome for large (or even moderately large) molecules.

Excessive use of computer time can be avoided by using the cell model[33], whose application to the calculation of the thermodynamic functions of molecular crystals is discussed by Holt and coworkers[34]. According to this model the volume occupied by the system is divided into N cells whose centres form the lattice. Each cell contains one molecule whose position and orientation are described by the six-dimensional vector q (which includes three translational and three rotational components). The motion of each molecule is assumed to be independent of the motion of molecules in neighbouring cells. The quantity $U(q)$ is the interaction energy of a given molecule with its neighbours at the centres of their respective cells. If the equilibrium positions of the molecules in the crystal are taken as the centres of the cells, and denoted by $\bar{q}$, then the quantity $U(\bar{q})/2$ is the energy of the crystal structure.

The use of the cell model simplifies the calculation of the configurational integral, which in this case is written

$$Q = \left[\exp\left\{-\frac{U(\bar{q})}{2kT}\right\}\cdot V_t\right]^N.$$

In this expression V_t is the "free volume":

$$V_t = \int_{\Delta}\exp\left\{-\frac{U(q)-U(\bar{q})}{kT}\right\}\mathrm{d}q,$$

where Δ is the cell volume.

This approach, together with the atom–atom potential method[35,36], was used by Pertsin and Kitaigorodskii to calculated the optimum structure and to interpret the polymorphic transitions in benzene[37] and adamantane[38]. We shall discuss this work more fully in a later Section of this review.

The identification of the deepest minima in a multidimensional energy surface constructed from the structure parameters involves calculations as cumbersome as those required by the search for the closest packing. Hence various simplifying assumptions are usually made, and in particular the structure class (the symmetry space group and the type of equivalent positions available to the molecule) is assumed to be known. Thus the reported calculations of molecular structure cannot be claimed to be fully *a-priori*.

The latter difficulty can be largely overcome by the potential function symmetry method developed in Refs.17, 39, and 40. This method allows us to find the structure class most likely to apply to molecules or polymer chains of a given symmetry, and to evaluate the relative probabilities of alternative classes[41,42]. In the calculation of the chain structures of $PdCl_2$ and $BeCl_2$ crystals[18,19] the potential function symmetry method allowed the optimum configuration of the chains to be identified without using an experimental information on the packing of the chains.

III. THE ATOM–ATOM APPROXIMATION AS A METHOD OF CALCULATING THE ENERGY OF ZERO-VALENT INTERACTIONS

Van der Waals (zero-valent) interaction is a quantum effect: in principle it can be described by the standard methods of quantum mechanics. However the difficulties encountered in attempting to solve the Schroedinger equation for systems containing a large number of atoms and molecules are still unsurmountable. Therefore empirical and semi-empirical approaches are almost universally used in concrete calculations of zero-valent interaction energies.

It is usually assumed that the van der Waals interaction consists of several, qualitatively different contributions. Though a strict quantum-mechanical interpretation does not support this assumption, in most cases good agreement between calculation and experiment is obtained by treating the van der Waals forces as consisting of the following terms: 1) an attraction due to dispersion interaction, 2) a repulsion resulting from the close approach of the electron clouds of atoms not bound by valency forces, 3) the electrostatic interaction of the fixed charge distributions, and 4) specific intermolecular interactions such as hydrogen bonds.

Numerous and varied investigations during the last 30 years have shown that all these contributions can be described with adequate precision by assuming additivity of the interaction energy of multi-atomic molecules with respect to the interaction energies of their constituent atoms. This approximation allows us to express the interaction energy of two molecules (in the absence of specific bonding forces) as the sum

$$U = \frac{1}{2}\sum_{ij}(\varphi_{ij} + \psi_{ij}),$$

where ϕ_{ij} are the atom–atom potentials describing the first two of the above contributions, and ψ_{ij} are terms allowing for the interaction of the effective charges on the atoms (the atoms i and j being part of different molecules).

The van der Waals interaction energy within a single molecule can be described in a similar way. If the method of evaluating ϕ_{ij} and ψ_{ij} is known, the conformation of the molecules can be calculated (including the orientation of groups able to rotate round an ordinary bond, and perturbations caused by steric hindrance). Indeed, the first successful application of the atom–atom approximation was in the solution of conformational problems. This approach was pioneered by Hill[43,44] and Barton[45], who worked with compounds in which the effective charges on the atoms were so small that only the repulsion energy and the attraction from dispersion interaction needed to be considered. A detailed description of the many conformational calculations made by the atom–atom approximation is given in Dashevskii's monograph[46].

Summation over the molecules in pairs (i.e. calculation of the energy of interaction of one molecule, taken as the central molecule, with the whole of its surroundings) allows us to express the potential energy of the molecular crystal (U_Σ) in the atom–atom approximation. This quantity is approximately equal to the heat of sublimation extrapolated to the absolute zero (assuming that sublimation does not produce significant changes in the conformation of the molecules or in the energy of intramolecular vibrations). By minimising the quantity U_Σ, treated as a function of the parameters which characterise the relative position of the molecules, the structure of a molecular crystal can (in principle) be calculated theoretically, as stated above.

The ϕ_{ij} potentials are usually approximated by the Lennard-Jones "6–12" potential[47] or by the modified Buckingham "6–exp" potential[48]:

$$\varphi_{ij} = -A_{mn}r_{ij}^{-6} + B_{mn}r_{ij}^{-12},$$
$$\varphi_{ij} = -A_{mn}r_{ij}^{-6} + B_{mn}\exp(-\alpha_{mn}r_{ij}),$$

where the first term describes the attraction and the second the repulsion, the subscripts m and n refer to the types of atom, A, B, and α are empirical parameters, and r_{ij} is the interatomic distance.

In Ref. 49 the atom–atom potentials are expressed in a more general form (as "6–exp, D" potentials):

$$\varphi_{ij} = A\exp(-Br_{ij})/r_{ij}^{D} - C/r_{ij}^{6}.$$

If $D = 0$ this reduces to the "6–exp" potential, and if $B = 0$ and $D = 12$ it reduces to the "6–12" potential.

Recent papers often refer to a "repulsion potential", which we shall denote by "d–d_0". This potential, first proposed by Williams[50], is defined as

$$V_{ij} = \omega(d_0 - d_{ij})^2 \text{ for } d_{ij} < d_0;\ V = 0 \text{ for } d_{ij} > d_0.$$

Here d_{ij} is the interatomic distance, and d and ω are parameters depending on the nature of the interacting atoms. The use of this potential greatly simplifies the minimisation procedure by allowing the method of least squares to be used. The main shortcoming of the "d–d_0" potential is that the quantity $\sum_{ij} V_{ij}$ is not the energy of the structure: it cannot be compared with real physical quantities such as the heat of sublimation. Calculations by the "d–d_0" potential occupy a position intermediate between the geometric and the energy approach.

The method of selecting the appropriate parameters is very important in the application of atom–atom potentials. The usual selection criterion is good agreement between calculation and experiment for several model compounds and several quantities (various thermodynamic functions such as heats of sublimation, compressibility coefficients, components of the elasticity tensor, etc.). The chosen values of the parameters are then applied to other substances, not too different from the model substances. One of the most reliable and widely used methods of choosing the parameters relies on fitting the calculated crystal structure to the experimentally observed structure. This method is discussed in the next Section. The frequencies of intramolecular and intermolecular vibrations in crystals[26] have been used in recent work for optimising the parameters of atom–atom potentials.

Approximate quantum-mechanical formulae are occasionally used in parallel with the purely empirical approach. This is specially true of the parameters A, which can be calculated by the London formula[51] or by the Slater–Kirkwood formula[52], as in Refs. 53–55. In that work the repulsion parameters were found by minimising the potential at the equilibrium distance, which was selected empirically.

The first systematic selection of the parameters of the "6–exp" atom–atom potential in crystal chemistry is due to Kitaigorodskii and Mirskaya[56,57]. Since the parameters A, B, and α have no clear physical significance, these workers used formulae including characteristics of the potential curve such as r_0 (the equilibrium distance), ε (the depth of the potential well), and D (the second differential at the minimum). The advantage of this aproach is that the quantities r_0, ε, and D vary only within narrow limits, and they are sensitive to several specific properties (r_0 to the geometric parameters of the structure, ε to the heat of sublimation, and D to the vibration frequencies and to the elasticity tensor).

A unique feature of Kitaigorodskii's and Mirskaya's approach is their use of the "universal" curve

$$\varphi_{ij} = -0.119\,(r/r_0)^6 + 4.2\cdot 10^4 \exp(-13.6\,r/r_0),$$

obtained by assuming identical potential wells of −0.067 kcal mole^{-1} for the three main types of atom–atom interaction in organic crystals (C...C, C...H, and H...H). The expression also assumes that $r_0\alpha = 13.6$. If the equilibrium distances are known (and they are taken to be 3.8, 3.3, and 2.8 Å for C...C, C...H, and H...H respectively) the parameters A and α can easily be calculated. The parameter B is found to be constant for the three types of interaction.

Table 1. Parameters of the "6–exp" potential used by Kitaigorodskii et al.

Type of interaction	A, $\frac{\text{kcal}}{\text{mole}}\cdot$ Å^6	10^3B, kcal mole^{-1}	α, Å^{-1}	References
C...C	358	42.0	3.58	59
C...O	313.2	57.1	3.85	59
O...O	259.4	77.7	4.18	59
S...S	2346	235.0	3.49	60
S...C	847	99.4	3.54	60
N...N	259	42.0	3.78	61
N...O	256	57.0	3.98	61
C...C	421	71.6	3.68	90
C...H	118	18.6	3.94	90
H...H	29	4.9	4.29	90

Even these "universal" parameters gave an acceptable level of agreement between the calculated energy of the structure and the measured heat of sublimation. However subsequent work led the authors[58] to conclude that the best agreement with experiment is obtained by using atom–atom potential curves with minima of different depth (−0.067, −0.057, and −0.048 kcal mole^{-1} for C...C, C...H, and H...H respectively). The final values of the parameters obtained by Kitaigorodskii and coworkers for these three types of interaction are listed in Table 1 together with their later results[59–61] for interactions involving N, O, and S atoms.

Various combination rules are used to obtain the parameters of interactions between unlike atoms. Thus Scott and Scheraga[54], Hendrickson[62], and Kitaigorodskii and coworkers[59] obtained the parameter α_{mn} by the formula $\alpha_{mn} = (\alpha_m\alpha_n)^{1/2}$. Dashevskii and coworkers[63] relied on another empirical expression: $\alpha_{mn} = 2\alpha_m\alpha_n/(\alpha_m + \alpha_n)$. Similar combination rules were used by these workers for the parameters A_{mn} and B_{mn} in the equation for the "6–exp" potential. Theoretical justifications of the combination rules are given in Refs. 64–66.

Whereas early workers tended to ignore electrostatic interactions in crystals, arguing that their contribution to the energy of the structure was negligibly small[67–69], in more recent work this term is almost invariably included (albeit in different forms).

In principle there are two possible ways of calculating U_{el}, which characterises the electrostatic interaction of two molecules. The first consist in expanding the energy U_{el} in a series with respect to multipoles:

$$U_{el} = U^{(q,q)} + U^{(q,\mu)} + U^{(q,Q)} + \ldots U^{(\mu,\mu)} + U^{(\mu,Q)} + \ldots,$$

where q is the net charge of the molecules, μ is the dipole moment, and Q is the quadrupole moment. The quantity q is finite in charge-transfer molecular complexes, whereas for homomolecular crystals (i.e. crystals composed of identical molecules) $q = 0$ and the corresponding terms in the formula also vanish. For practical purposes the multipole expansion is used relatively rarely: on the one hand, the values of the higher-order multipoles are usually unknown, and on the other hand it is not easy to ascribe to point multipoles (and in particular dipoles) a definite position and orientation with respect to a molecule.

The second method of calculating U_{el} relies on the atom–atom approximation. The continuous distribution of electron density is replaced by a discrete distribution, and an effective point charge (localised near the nucleus) is assigned to each atom in the molecule. Then we can write

$$U_{el} = \sum_{ij} q_i q_j / r_{ij}.$$

The effective charges can be calculated by various quantum-mechanical methods. Some workers[70–72] use the simplest computational scheme, in which the effective atomic charge is treated as the sum of the π- and σ-charges (the former calculated by the simple Hückel method, the latter by the Del Re method[74]). Other workers have used more complex quantum-mechanical approximations[55,75]. As an alternative, the charges (as well as other parameters of the intermolecular interaction potentials) can be evaluated by fitting the optimum structure to the experimentally determined structure[76,77].

The components of the intermolecular interaction listed above contribute (though to varying extents) to the structure of all molecular crystals. In addition, we sometime meet specific intermolecular forces, which are always associated with the presence in the molecule of some particular atoms or atomic groups. These forces include hydrogen bonds, bonds of the metal–metal and metal–oxygen type, and other bonds found in crystals of some inner complex compounds. The energy of these interactions is quite difficult to calculate: a successful method of calculation has been developed (so far) only for the hydrogen bond.

Various procedures have been described for evaluating the hydrogen bond energy. Some workers[55,78,79] have used the "6–exp", "10–12", and "6–12" atom–atom potentials, assigning specially chosen parameters to the atoms taking part in the hydrogen bond, and allowing for the part of the hydrogen bond energy which appears as interaction between effective atomic charges. Other workers have used special empirical and semi-empirical functions: Stockmayer potentials[80–81], and Lippincott–Shroeder[82,83] or Morse[84] potentials.

Afonina and coworkers[85] have used all the above methods of allowing for the energy of the hydrogen bond in their calculation of the heats of sublimation of various organic compounds. The best agreement with experimental data was obtained by using the last two potentials.

One of the most interesting approaches in the current development of the atom–atom potential method is the work of Scheraga and coworkers[86–88], who treat the interaction between electrons and nuclei by assigning positive charges (located in the nucleus) of 1, 4, 5, and 6e to the H, C, N, and O atom respectively, while the electrons are placed in the bonds or in the directions occupied by unshared pairs. The distances between electrons and nuclei are used as the parameters of the model. The potential energy consists of coulombic terms of the q_iq_j/r_{ij} type, describing the interactions between electrons and nuclei, and terms which allow for the attraction and repulsion between electrons in terms of the "6–exp" potential. The parameters of these potential functions are chosen by least squares from a large fund of experimental data on various properties of the molecules and of the molecular crystals (dipole moments,

barriers to internal rotation, difference in energy of conformational isomers, lattice energies and lattice constants, etc.). The main advantage of this model is that special potentials are not needed to allow for H-bonds, and the barriers to internal rotation can be described without introducing torsional potentials[46].

IV. SELECTION OF THE ATOM–ATOM POTENTIAL PARAMETERS FROM CRYSTALLOGRAPHIC DATA

The parameters of the atom–atom interaction potentials can be determined from data on the molecular packing in the crystal by two methods. The first consists in finding the optimum packing for different values of the parameters (i.e. the packing corresponding to minimum energy). The best choice of parameters is taken to be the set which gives a calculated structure as nearly as possible identical to the experimentally observed structure. The second method relies on the following considerations. The experimental structure is assumed to be identical to the equilibrium structure. Hence the differentials of the energy at the experimental point should vanish, and therefore the parameters of the potential are chosen so as to keep the differentials of the potential equal to zero. This method of selection avoids the repetitive calculation of lattice sums† and thus offers a substantial saving in computer time.

The first of these approaches is used by Kitaigorodskii and coworkers, and also by Giglio, Liquori, and others.

As was mentioned in the previous Section, Kitaigorodskii uses a universal potential curve for C...C, C...H, and H...H interactions[56]. The parameters of this curve have been progressively modified in successive papers[58,89,90]. One-dimensional and multi-dimensional sections of the energy surface (U) were drawn for different values of the parameters of the potential curve for methane[56], adamantane[57], benzene[58], etc., and the best values of the parameters (for which the position of the energy minimum corresponds to the real structure) were identified in this way. The depth of the minimum was corrected in accordance with the known heat of sublimation. The set of parameters ultimately chosen gave excellent results in the calculation of the optimum packing in crystals of coronene[91], biphenyl[92], dibenzyl[92], and others.

The parameters of the potential functions describing interactions with oxygen[59], sulphur[60], and nitrogen[61] atoms were established in a similar way from data on the structure and heat of sublimation of CO_2, S_8, and N_2O. Numerical values of all the parameters recommended by Kitaigorodskii's team are listed in Table 1.

Giglio, Liquori, and others[93–97] used a different approach: they did not vary the parameters of the potential to search for the optimum packing, but they adopted sets of parameters previously suggested by various workers (in particular, for conformational analysis). The best values of the parameters for the "6–exp,D" potential are given in Table 2.

In the course of this work it was shown that the position of the minimum of the atom–atom potential curve plays an essential role in the search for the optimum packing: the other characteristics of the potential are relatively unimportant. However this conclusion cannot be extended uncritically to other physicochemical properties.

†The lattice sums are expressions of the type $\sum_{ij} 1/r_{ij}^{6}$, $\sum_{ij} 1/r_{ij}^{12}$, $\sum_{ij} 1/r_{ij}$, etc., in which the summation is taken over all the atoms in the structure.

The second of the above methods of selecting the parameters of C...C, C...H, and H...H interactions was first applied by Williams in the case of the "6–exp" potential. The experimental data used as a basis for the optimisation were the structures, heats of sublimation, and other constants of nine aromatic[69] and nine aliphatic and condensed hydrocarbons[68]. Using these data he wrote approximately 100 expressions equating the U_Σ values to heats of sublimation, the first differentials of energy to zero, and the second differentials to the elastic constants.

Table 2. Parameters of the potential used by Giglio et al.[93, 94,96,97,108]

Type of interaction	10^3A, $\frac{\text{kcal}}{\text{mole}} \cdot \text{Å}^6$	B, Å^{-1}	C, $\frac{\text{kcal}}{\text{mole}} \cdot \text{Å}^6$	D
C...C	301.0	0.0	327.0	12
C...H	48.8	2.040	125.0	6
H...H	6.6	4.080	49.2	0
S...S	220.8	3.62	1430.0	0
C...N	340.0	0.0	340.0	12
N...N	387.0	0.0	354.0	12
C...Cl	239.0	3.970	653	0
Cl...Cl	220.8	3.620	1430	0
H...Br	25.6	3.557	366.7	0
C...Br	149.0	1.517	945.8	6
N...Br	165.2	1.517	983.8	6
O...Br	140.9	1.517	989.3	6
Me...Br	133.5	3.181	2836.0	0
S...Br	123.0	3.327	1977.2	0
Br...Br	65.8	3.033	2733.8	0
H...I	43.4	3.540	527.8	0
C...I	246.0	1.500	1361.0	6
N...I	272.7	1.500	1415.6	6
O...I	232.6	1.500	1423.6	6
Me...I	219.9	3.164	4081.0	0
S...I	206.8	3.310	2845.2	0
Br...I	107.6	3.046	3934.0	0
I...I	174.2	2.999	5661.0	0
O...O	105.7	4.608	125.1	0
O...H	19.8	3.840	497.6	0
O...C	178.5	2.304	202.2	6
O...Me	170.2	3.969	796.2	6
Me...Me	273.9	3.329	2942.0	0
Me...C	287.9	1.665	1235.0	6
Me...H	31.9	3.200	2089.0	0
Me...O	170.2	3.969	796.2	6

By using least squares Willams selected several sets of the A and B parameters most consistent with these equations. For convenience in the minimisation procedure the α parameters were not varied in the calculation of the lattice sums. The parameter α_{CC} was taken to be 3.60 Å^{-1} from calculations of the compressibility of graphite[98], and the parameter α_{HH} was taken to be 3.74 Å^{-1} from a quantum-chemical calculation of the repulsion between two hydrogen molecules[99]. The sets of parameters were obtained independently for the aromatic and the non-aromatic hydrocarbons: four for each of these two series of compounds. The difference between the sets was that the parameters A_{CH} and B_{CH} (either singly or jointly) were either treated as independent or calculated by the combination rules. The best of these sets was chosen by calculating lattice constants and molecular packing arrangements for different sets of parameters in several aromatic or aliphatic hydrocarbons. It was found that all the hydrocarbon crystals examined could be described satisfactorily by a single set of parameters (listed in Table 3).

In his more recent work Williams has selected and tested a new set of parameters for the "6–exp" potential which allows for the electrostatic component[76,100] (following Warshel and Lifson[77], who first demonstrated the need to allow for

electrostatic interaction in hydrocarbons). The charges on the atoms were treated as parameters of the potential function, and were evaluated by the above method together with other parameters of the same series of compounds. The numerical values obtained are shown in Table 3. The contribution of the electrostatic component in the different hydrocarbons varies from 0 (for n-pentane) to 29% (for benzene). Only by allowing for the U_{el} term was Williams able to account for the polymorphic transition in benzene[100]. This suggests that even in hydrocarbons electrostatic forces are far from negligible. On the other hand the contribution of the electrostatic component to the energy of the benzene structure seems too high to be acceptable.

Table 3. Parameters of the "6–exp" potential used by Williams.

Type of interaction	A, $\frac{\text{kcal}}{\text{mole}} \cdot \text{Å}^6$	10^3B, $\frac{\text{kcal}}{\text{mole}}$	α, Å^{-1}	References
C...C	568	83.630	3.60	68
C...H	125	8.766	3.67	68
H...H	27.3	2.654	3.74	68
C...C	449	71.430	3.60	76
C...H	134.2	14.310	3.67	76
H...H	40.1	2.867	3.74	76

Notes: in Ref. 76 the parameters are given in kJ mole^{-1}; $q_H = q_C = 0.179$ e.s.u. [76]

Scheraga and coworkers used both the first and the second approach in their search for the parameters of the potential functions. They found a set of parameters describing the interaction of hydrocarbon molecules by the method of Williams, using as their experimental basis the heats of sublimation and structures of benzene measured at three temperatures[101].

More recently Scheraga and coworkers[55] used a wide range of compounds (including hydrocarbons, carboxylic acids, amines, and amides) to select and test a system of parameters to be used in calculations of the conformation of polypeptides and proteins. The energy of zero-valent interactions was calculated by using the "6–12" potential, the hydrogen bond energy by the "10–12" potential, and the U_{el} energy by Coulomb's law. The A coefficient, which characterises the attraction forces, was calculated by the Kirkwood–Müller formula in the "6–12" potential and by a quantum-mechanical formula in the "10–12" potential. The charges were calculated by the CNDO/2 method. Thus only the B parameter was varied, i.e. the parameter describing the repulsion between atoms not joined by valence bonds, and in particular between atoms taking part in hydrogen bonds.

The criterion for the validity of the parameters was the quantity σ, defined as

$$\sigma = \left[(1/N) \sum_{i=1}^{N} (l_i^{\text{calc}} - l_i^{\text{exper}})^2 \right]^{1/2},$$

where $l_i = a, b, c, \alpha, \beta, \gamma$ are the lattice parameters and N is the number of these parameters. The search procedure included two independent (but interrelated) minimisations: 1) minimising the energy by varying the lattice parameters, and 2) minimising the σ value obtained in the previous calculation by varying the B coefficients, using the formula

$$\frac{\partial}{\partial B} \{[a^{\text{exper}} - a^{\text{calc}}]^2 + \ldots + [\gamma^{\text{exper}} - \gamma^{\text{calc}}]^2\} = 0.$$

Different parameters were selected for different types of nearest-neighbour environment: thus, H atoms bound to an aromatic ring, to an aliphatic chain, to the nitrogen of an amino group, to the oxygen of a hydroxyl group, etc. were considered to be different.

Table 4. Parameters of the "6–12" potential used by Momany, Scheraga, et al.[55]

Type of interaction	A, $\frac{\text{kcal}}{\text{mole}} \text{Å}^6$	10^3B, $\frac{\text{kcal}}{\text{mole}} \cdot \text{A}^{12}$
H...H (aliph.)	45.5	14.10
H...H (amino, amido)	45.5	8.43
H...H (arom.)	45.5	14.39
H...H (carboxy, carbonyl)	45.5	11.69
C...C (aliph.)	370.5	906.03
C...C (carboxy, carbonyl)	766.6	1048.98
C...C (atom.)	370.5	475.30
N...N (amido)	363.1	732.54
N...N (in H bond)	401.0	374.94
O...O (carbonyl, carboxy)	369.0	170.19
O...O (hydroxyl)	217.2	125.63
S...S (heterocyclic, sulpho group)	249.0	363.18

The parameters thus obtained (Table 4) were tested by calculating the packing and the energy of the structure for crystals of monomeric[102] and of polymeric amino-acids[103,104]. The authors stress that the results given by these parameters are satisfactory only if the charges on the atoms are calculated in the CNDO/2 approximation.

The two possible approaches to the selection of the atom–atom potential parameters are compared in a paper by Hagler and Lifson[105]. A serious drawback of the second approach is shown to be the non-equivalence of the optimisation of the potential parameters from the differentials of the energy and from the experimentally observed structure. Thus in the case of points on gently sloping regions of the potential energy surface the differentials can be small, and yet the distance from the minimum may still be large. For this reason these workers proposed a method[105] in which the exact values of the parameters are obtained directly from the structure whilst avoiding the need for repetitive calculations of lattice sums.

The authors[105] explain their method by defining the vector $\boldsymbol{a}$ whose components are the structure parameters. The special feature of the method is that the quantity $\Delta\boldsymbol{a} = \boldsymbol{a}_{\text{calc}} - \boldsymbol{a}_{\text{exper}}$ is obtained directly, by the Newton–Raphson method, of calculating $\boldsymbol{a}_{\text{calc}}$: $\Delta\boldsymbol{a} = -F(\boldsymbol{a}_{\text{exper}})^{-1} \nabla_{\boldsymbol{a}} U(\boldsymbol{a}_{\text{exper}})$, where F is the matrix of the second differentials $F_{\alpha\beta} = \partial^2 U / \partial a_\alpha \partial a_\beta$, $\nabla_{\boldsymbol{a}} U$ is a vector whose components are the differentials $\partial U / \partial_\alpha$, and the numerical values of the differentials correspond to the experimentally determined structure.

The parameters of the potential, represented by the vector $\boldsymbol{p}$, are obtained by solving the equation

$$\delta \boldsymbol{p}^i = \boldsymbol{p}^i - \boldsymbol{p}^{i-1} = [(Z'Z)^{-1} Z' \Delta \boldsymbol{y}]^{i-1}$$

iteratively by least squares. In this equation $Z = \partial(F^{-1}\nabla U)/\partial \boldsymbol{p}$ is a matrix of the differentials of the deviations of the structure parameters (with respect to the parameters of the potential), and Δy is a vector of the deviation of the calculated from the experimental structure parameters.

In the first variant of the calculation the energy of the structure was described[106] by the formula

$$2U_{\Sigma}=-\Sigma A/r^6+\Sigma B/r^m+\Sigma qq'/r+2U_{H},$$

where m was taken to be 9 or 12. This formula includes a contribution from the hydrogen bonds (U_H), which was expressed by the Morse potential. However it was later shown that the hydrogen bond is adequately accounted for by the first three terms if the parameters of the potential and the charges are chosen for atoms taking part in hydrogen bond formation. The experimental material used in this calculation was a selection of structure data for eight amides, but heats of sublimation and dipole moments were also used in the minimisation procedure.

Table 5. Parameters of the potential used by Hagler, Lifson, et al.[106]

Type of interaction	A, $\frac{\text{kcal}}{\text{mole}}$ Å^6	10^3B, $\frac{\text{kcal}}{\text{mole}}\cdot$Å^{12}	q, e.s.u.***	A, $\frac{\text{kcal}}{\text{mole}}$ Å^6	10^3B, $\frac{\text{kcal}}{\text{mole}}\cdot$Å^{12}	q, e.s.u.***
	«6-12»			«6-9»		
H...H (att. to C)	32.9	1.15	0.10	15.0	0.445	0.11
O...O	502	275	−0.38	1410	45.8	−0.46
N...N	1230	2271	−0.28* −0.83**	2020	86.9	−0.26* −0.82**
C...C	532	1811	—	1230	38.9	—
C...C (in amides)	1340	3022	0.38	355	12.5	0.46
H...H(att. to N)	0	0	0.28* 0.41**	0	0	0.26* 0.41**

*In NH group; ** in NH_2 group, ***the CO, NH, NH_2, and CH_2 groups are assumed to be neutral.

The parameters of the potential functions selected in Ref.106 are listed in Table 5: we note that the "6–9" and the "6–12" potentials give equally good results in the calculation of equilibrium structures. The charges on the atoms obtained as parameters of the intermolecular interaction function were compared[106] with the charges found by quantum-mechanical calculations (*ab initio*, CNDO/2, and the Del Re method). The best agreement was obtained with the charges given by *ab initio* calculation.

The validity of the parameters thus obtained was tested by calculating the packing of molecules in ten crystalline amides[107]. For three of these the energy minimum was sought by varying every possible geometric parameter: only the number of molecules in the elementary cell was treated as known. The authors stress that this is the first reported calculation of this type.

Mirskaya and coworkers[90] compared the parameters of the potentials recommended by different authors for calculating the properties of crystalline hydrocarbons. Only those parameters having a clear physical significance were compared: the equilibrium distance r_0, the depth of the potential well ε, and the quantity $\lambda = r_0\alpha$ which characterises the steepness of the slopes towards the minimum for the "6-exp" potential. The authors point out[90] that the failure to ensure physical significance of the atom–atom potentials often leads to unrealistic potential curves. Thus the parameter $r_0^{HH} = 3.37$ obtained by Williams[68,69] is too high (when compared with the sum of the van der Waals radii). The values of ε^{CC} and r_0^{CH} obtained in Ref.77 are clearly too high. Momany and coworkers[101] obtained a curve for the C...C interaction without a minimum, and curves for the C...H and H...H interaction with excessively deep minima.

Table 6. Comparison of the characteristics of the potential curves proposed by various authors for hydrocarbon crystals[90] (ε in kcal mole^{-1}, r_0 in Å).

C...C			C...H			H...H			Refs.
ε	r_0	λ	ε	r_0	λ	ε	r_0	λ	
0.080	3.80	14.0	0.049	3.30	13.0	0.030	2.80	12.0	90
0.067	3.80	13.6	0.067	3.30	13.6	0.067	2.80	13.6	89
0.095	3.88	13.97	0.048	3.31	12.1	0.010	3.37	12.6	68,69
*	*	«6-12»	0.259	2.73	«6-12»	0.423	2.61	«6-12»	101
0.185	3.62	«6-9»	—	—	—	0.003	3.55	«6-9»	77

*No minimum.

Subsequently[55,106] these same workers[77,101] reconsidered their recommended potential parameters and compared r_0 and ε values (Tables 7 and 8) as had been done in Ref.90. We see from these Tables that the discrepancy between the r_0 values for the curves proposed by different authors is much smaller than the discrepancy between the ε values. One reason for the large differences between the ε values is that the overall energy of the intermolecular interaction (which alone can be compared directly with experiment) depends not only on ε but also on the effective charges on the atoms, which vary quite markedly according to the method of calculation and are even ignored altogether in some cases. It follows that the methods of calculating the component of the energy which is determined by the "6–exp", "6–12", etc. potentials, and the method of calculating the electrostatic component, should be mutually consistent.

Table 7. Comparison of the characteristics of the potential curves proposed in Refs.106, 109, and 110 (ε in kcal mole^{-1}, r_0 in Å).

ε	r_0	Refs.	ε	r_0	Refs.	ε	r_0	Refs.
H...H (attached to C)			C...C (in amides)			N...N		
0.0025	3.54	106	0.042	3.75	106	0.161	4.01	106
0.038	2.75	106	0.148	4.06	106	0.167	3.93	106
0.122	2.4	109	0.11	3.4	109	0.20	3.1	109
0.076	2.6	110	0.138	3.6	110	0.212	3.3	110
C...C			O...O			H...H (attached to N)		
0.184	3.62	106	0.198	3.65	106	0.0	0.0	106
0.039	4.35	106	0.228	3.21	106	0.0	0.0	106
0.11	3.4	109	0.23	3.04	109	0.122	2.4	109
0.138	3.6	110	0.172	3.2	110	0.076	0.26	110

V. TABULATION OF THEORETICAL CALCULATIONS OF MOLECULAR PACKING

In this Section we shall try to present as fully as possible, in tabular form (Tables 9–16), all the results obtained in theoretical calculations of crystal structures using atom–atom potentials. These investigations began in 1961, when

Kitaigorodskii proposed this method of identifying the energy minimum in a crystal. Since then, and up to 1977, the number of papers published on this topic has risen to 180.

Table 8. Comparison of the characteristics of the potential curves proposed by various authors (ε in kcal mole^{-1}, r_0 in Å).

ε	r_0	Refs.	ε	r_0	Refs.	ε	r_0	Refs.
H...H (aliph.)			C...C (aliph.)			O...O (carbonyl, carboxyl)		
0.037	2.92	55	0.038	4.12	55	0.200	3.12	55
0.0045	2.936	111	0.196	4.228	111	0.230[365]	3.00	111
0.0025	3.548	77	0.185	3.616	77	0.325	3.10	261
0.033	3.36	261	0.049	4.16	261	0.124[59]	3.25	262
0.060	2.80	262	0.060	3.80	262	0.106	3.32	263
0.010	3.37	68	0.095	3.88	68	N...N (amino)		
0.027	3.08	263	S...S			0.107	3.51	55
C...C (arom.)			0.043	3.78	55	0.194	3.60	111
0.073	3.70	55	0.361	3.91	261	0.165	3.52	261
0.095	3.90	261	0.333[60]	3.90	262	0.076	3.80	263
0.095	3.88	68				0.081	3.60	264

Table 9. Publications by Kitaigorodskii and coworkers on molecular packing calculations.

Year	Compound	Adjustable parameters	Refs.	Remarks
1961	Methane[a]	a	56	—
1961	Methane, adamantane	a	57	—
1964	Hydrocarbons (6 compounds)[a]	a, ψ	89	ΔH
1968	Benzene[a]	a, ψ	112	—
1969	Naphthalene, anthracene	a, ψ	113	a ($t°$)
1969	Naphthalene	ψ, X	114	ν ($t°$)
1969	CO_2^b	a	59	Q
1970	Coronene	a, ψ	91	ΔH
1971	Naphthalene, anthracene, biphenyl	ψ, X	115	ν, ν ($t°$)
1971	S8(rhombic), CS_2^b	a, ψ	60	ΔH
1970, 1971	C(Ph)4, Si(Ph)4, Sn(Ph)4, Pb(Ph)4[d]	a, ψ, φ	116, 117	—
1972	N_2O, α-N_2, hexamethylenetetramine[e]	a, ψ	61	Q, ΔH
1972	3,6-Diphenyl-s-tetrazine	ψ, φ	118	ΔH
1972	Biphenyl, dibenzyl	a, ψ, φ	92	ΔH
1972	p-Diethynylbenzene	ψ	119	Xsa
1974	Naphthalene[a]	—	90	ΔH, el. const.
1975	Acenaphthene, tolane, biphenyl*	SC a, ψ, X	120	—
1975	Benzene	ψ, X	41	A
1976	Adamantane	ψ, X	38	A, polymorph.
1976	Coumarin	a, ψ, X	121	ΔH
1976	Naphthalene, anthracene	ψ, X	42	A
1976	Binary acenaphthene–α-nitronaphthalene system	ψ, X, φ	122	—

*The "6–12" potential was used in this calculation, the "6–exp" in all the others. New parameters used for: (a) C, H, (b) O, (c) S, (d) Si, Sn, Pb, (e) N.

The most important contributions to this area of research came from the teams of Kitaigorodskii, Williams, Giglio, Simonetti, Scheraga, Lifson, Sarko, and Zugenmaier. The work of these groups accounts for more than 50% of the published material, and is presented in Tables 9–15. Publications from other laboratories are listed in chronological order in Table 16.

It is clear from the Tables that the number of papers dealing with this topic has risen steeply in recent years: approximately 60 papers between 1961 and 1970, as compared with over 100 papers between 1971 and 1977. The greatest number of publications appeared in 1974–1975. Whereas the early papers dealt with crystals consisting of molecules containing a small number of atoms (halogens, methane, benzene), and a limited number (one or two) of types of atom, the scope of the more recent papers has become much wider.

Table 10. Publications by Williams and coworkers on molecular packing calculations.

Year	Compound	Adjustable parameters	Refs.	Remarks
1966	Aromatic hydrocarbons (9 compounds)[a]		69	—
1966	Dibenzoylmethane*	ψ, X	8	Xsa
1967	n-Hexane, n-pentane, and other hydrocarbons (9 compounds)[a]	ψ, X	68	—
1968	Benzene, naphthalene, phenanthrene[a]*	ψ	123	—
1969	3,4-Dihydro-2,4,6-triphenyl-s-tetrazin-1,2(2H)-yl*	ψ, X	124	Xsa
1969	Aromatic hydrocarbons (4 compounds)*	ψ, X, φ	50	—
1972	p,p'-Bitolyl	ψ, X, φ	125	q
1973	2,4,6-Triphenylverdazil*	ψ, X, φ	126	Xsa
1974	18 hydrocarbons[a]	a	76	q
1975	Benzene (2 modifications)	a, ψ, X	100	q, polymorphic
1977	18 hydrocarbons[a]	ψ, X	127	q

*"d–d_0" potential: in all the other calculations the "6–exp" potential was used.

[a]New parameters used for C and H.

Table 11. Publications by Giglio and coworkers on molecular packing calculations.

Year	Compound	Adjustable parameters	Refs.	Remarks
1967	Hexamethylbenzene	ψ	128	—
1967	5-α-Androstan-3,17-dione	ψX	129	—
1968	Adamantane[a]	a, ψ	93	—
1968	S8(rhombic)*[b]	a	94	—
1969	$(SO_3)_n$*	a, φ	95	—
1969	Dimethylglyoxime**	ψ	80	H-b
1970	Ethylene, deutero-ethylene*	ψ, X, φ	130	ν
1970	N_2, dicyanogen, octachlorocyclobutane[c]	a	96	—
1970	Diketopiperazine**	ψ	131	H-b
1970	Hexabromomethylbenzene, iodoform[d]	a, ψ	97	—
1971	N,N'-Dicyclohexylurea*	ψ, X, φ	132	H-b, Xsa
1972	N-Methylacetamide	ψ, X	133	H-b
1972	Bromoform	SC a, ψ, X	134	μ
1972	Complexes of desoxycholinic acid with p-diiodobenzene and phenanthrene	ψ, X, φ	135	Xsa
1973	5-α-Androstan-3,17-dione*	ψ, X	108	Xsa
1974	Poly(fluoroethylene), polyethylene*	SC ψ, φ	136	—
1974	Coumarin*	ψ, X	137	Xsa
1977	Benzene, naphthalene, anthracene, phenanthrene[a]	a, ψ, X	138	ΔH

*The "6–exp,D" potential was used, **"6–12" potential (in all other calculations the "6–exp" potential was used). New parameters used for: (a) C, H, (b) S, (c) C, N, Cl, (d) Br, I.

At present most of the workers in this field are concerned with amides, mono- and poly(amino-acids), and other compounds of relevance to developing methods of calculation for complex, biologically important substances such as polypeptides and proteins. At the same time metal–organic and inorganic substances are beginning to be studied by the atom–atom potential method.

As the range of compounds being studied becomes wider, suitable parameters of the potentials have to be chosen. Papers dealing with this problem are mentioned in the Notes of the Tables.

Table 12. Publications by Simonetti and coworkers on molecular packing calculations.

Year	Compound	Adjustable parameters	Refs.	Remarks
1967	2-Bromo-1,1-diphenylprop-1-ene***	φ	139	φfree
1967	2-Bromo-1,1-ditolylethylene	φ	140	—
1968	Biphenyl	ψ, φ	141	—
1969	*p,p'*-Bitolyl	ψ, φ	142	—
1971	1,1-Di(*p*-nitrophenyl)ethylene*	φ	143	*q*, φfree
1971	Polyethylene*	*a*, ψ	75	*q*, φfree
1971	11,11-Difluoro-1,6-methano[10]annulene**	*X*	144	Xsa
1972	1,6:8,13-Butan-1,4-diylidene[14]annulene*	ψ	145, 146	*q*, φfree, Xsa
1972	1,6:8,13-Propan-1,3-diylidene[14]annulene*	ψ	147	*q*, φfree, Xsa
1973	*p*-Nitrobiphenyl*	ψ, φ	148	*q*, φfree
1973	Naphthalene, anthracene, pyrene, etc. (9 compounds)	ψ, *X*	149	ν
1975	Anthracene, adamantane, dibenzo-1,4-cyclooctа-3,7-diene**	*a*	27	*A*, ν
1975	Hydrocarbons, molecules containing N and O (25 compounds)	ψ, *X*	150	reorient.
1976	F-substituted aromatic compounds (5 compounds)[a]	ψ, *X*	151	Δ*H*, ν

*"6–12" and "6–exp" potentials used; **a special potential was used in this calculation, the "6–exp" potential in all other calculations; ***form of the potential not stated.

[a]New parameter for the potential of F.

Table 13. Publications by Scheraga and coworkers on molecular packing calculations.

Year	Compound	Adjustable parameters	Refs.	Remarks
1968	Benzene[a]	*a*	101	*a* (*t*°)
1971	Poly(*L*-alanine), poly(β-benzyl-*L*-aspartate)	*a*, ψ, φ	103	*q*
1974	Amino-acids (14 compounds)[b]	*a*, φ	102	*q*
1974	Hydrocarbons, carboxylic acids, amines, amides (14 compounds)	*a*	55	*q*
1974	Poly[β-(*p*-chlorobenzyl)-*L*-aspartate]	*a*, ψ, *X*, φ	104	*q*, *A*
1975	Hydrocarbons, alcohols, amines, ice (8 compounds)*[c]	*a*, φ	86	*q*, μ, ν
1975	n-Hexane, n-octane, methylamine, methanol, α-*D*-glucose*	*a*, φ	88	*q*
1975	Acetic and formic acid	*a*, φ	152	*q*, μ, ε

*The "6–exp" potential was used in the approximation of the electron–nucleus interaction model; in all other calculations the "6–12" potential was used.
New parameters for the potentials of: (a) C, H, (b) C, H, N, O, S, (c) C, H, N, O.

It is clear from Tables 9–16 that the "6–exp" and "6–12" potentials have been used most frequently. The "6–exp, *D*" potential often appears in the papers from Giglio's laboratory. More recently some workers have successfully used the "d–d_0" potential proposed by Williams. All these types of potential are described in Section III. Special potentials of a non-standard type are only rarely used.

The complexity of the calculations reported can be judged by the column headed "Adjustable Parameters" in the Tables. Most of the authors have treated the space group, the number of molecules in the cell, and the type of position taken up by the molecules in the cell as known (from experimental data) when seeking to optimise the packing of the structure: in other words, they have assumed a given structure class. However some workers have considered different structure classes: this is indicated by the abbreviation SC in the Adjustable Parameters column. The following abbreviations are also used in that column to indicate the structure parameters which were varied during the optimisation procedure: *a*—the parameters of the elementary cell, ψ—the Euler angles which characterise the orientation of the molecules, *X*—the coordinates of the centres of gravity of the molecules, and φ—parameters describing the conformation of the molecules (usually the angular rotations about single bonds).

Table 14. Publications by Lifson and coworkers on molecular packing calculations.

Year	Substance	Potential	Adjustable parameters	Ref.	Remarks
1969	α-N_2	6-12	ψ, *X*	153	ν
1970	α-N_2^a	6-12,6-exp	ψ, *X*, φ	154	*Q*, ν
1970	Alkanes (13 compounds)[b]	6-12,6-9,6-exp	*a*, ψ, *X*, φ	77	*q*, Δ*H*, ν
1971	n-Hexane	6-9,6-12,6-exp	• ψ, *X*	155	*q*, ν
1974	Benzene, biphenyl, 9,10-trans-β-ionylidene-γ-crotonic acid	6-12,6-9,6-exp	SC *a*, ψ, *X*, φ	156	ν
1974	Chalcones (4 compounds)	6-exp	*a*, φ	157	—
1974	Amides (6 compounds)[c]	6-9	*a*, ψ, *X*	105	*q*
1974	Amides (9 compounds)[c]	6-9,6-12	*a*	106	*q*, μ, H-b, Δ*H*
1974	Amides (10 compounds)	6-9,6-12	SC *a*, ψ, *X*	107	*q*
1975	Naphthalene, benzene	6-exp	*a*, ψ, *X*	158	ν
1975	α-N_2, γ-N_2^a	6-12	ψ, *X*, φ	159	Δ*H*, ν, ν (*t*°)
1975	Urea, formamide, adipamide	6-9,6-12	*a*, ψ, *X*	160	*q*, H-b, ν
1976	Ice (hexagonal)	modified 6-exp	*a*, ψ, *X*	161	*q*
1976	*N*-Methylamide, amides, peptides	6-9,6-12	SC, *a*, ψ, *X*, φ	162	—

New parameters for the potentials of (a) N, (b) CH, (c) C, H, N, O.

Table 15. Publications by Sarko, Zugenmaier, and coworkers on molecular packing calculations.

Year	Compound	Adjustable parameters	Refs.	Remarks
1972	6-monosaccharides (α and β glucose, etc.)	ψ, *X*	163	H-b
1973	B-Amylose.H_2O	SC *a*, ψ, *X*, φ	164	H-b, Xsa
1974	Cellulose I	SC *a*, ψ, *X*, φ	165	H-b
1974	Mannan	ψ, *X*, φ	166	—
1974	Dimethylsulphoxide-amylose complex	ψ, *X*	167	Xsa
1976	Cellulose II	*a*, ψ, *X*, φ	168	H-b, Xsa
1976	Cellulose III_1	*a*, ψ, φ	169	H-b
1976	V-Amylose	ψ, *X*	170	H-b, Xsa, φfree
1977	β-*D*-Glucone acetate	ψ, *X*	171	Xsa, φfree

*New parameters for the potentials of C, H, O. The "d–d_0" potential was used in all calculations.

In the early work the number of adjustable parameters was usually small, but as computer techniques become more generally available the complexity of the calculations increased. The record for the number of parameters varied in the calculations is held by Scheraga's group, who treated

all the parameters listed above as adjustable and took only the number of molecules in the cell as given.

Table 16.

Substance	Adjustable parameters	Refs.	Remarks
1	2	3	4
	1962		
Chlorine, iodine[I]	SC *a*, ψ	172	—
	1964		
Methane	SC *a*, ψ, φ	173	*q*
Chlorine[I]	SC *a*, ψ	174	*Q*
	1965		
Naphthalene	ψ	175	μ, *Q*
	1966		
Polyethylene	*a*, ψ	176	—
β,β-Dimethyladipic acid	ψ	9	—
	1967		
Chlorine[I]	SC *a*, ψ	177	*q*
Benzene[IV,a]	ψ	178	ν
Naphthalene, anthracene	ψ, *X*	179,180,181	ν
	1968		
$(CH_2O)_n$	ψ	182	ν
Chlorine, fluorine[I]	SC *a*, ψ	183	*q*, *Q*
$(CH_2O)_n$[b]	*a*, ψ	184	—
Benzene[V]	*a*	185	*Q*
C_2N_2[I]	ψ, *X*	186	*Q*, ν
	1969		
1,3,5,7-Tetramethylocta-1,3,5,7-tetraene	ψ	187	—
Ethylene[IV]	ψ, *X*	188	ν
Benzene	ψ	189	ν
Benzene[IV]	ψ, *X*	190	ν
Chlorine[I,IV]	ψ	191	*q*, ν
Chlorine	ψ	192	—
	1970		
Benzene, deuterobenzene	ψ	193	ν
α-N_2[I]	ψ, *X*	194	*q*, ν
Acenaphthene	ψ	63,195	ν
Deutero-anthracene	ψ, *X*	196	ν
Naphthalene	ψ, *X*	197	ν
Formic acid[IV,b]	—	198	*q*
Anthracene	ψ, *X*	199	ν
Polyethylene	*a*, φ	200	—
	1971		
p-Dichlorobenzene, *p*-dibromobenzene[II]	ψ	201	—
Acetylene[IV]	ψ	202	*Q*
Methane	SC ψ, *X*	203	Δ*H*, polymorph.
α-O_2, β-O_2[I]	ψ, φ	204	*Q*, ν (*t*°)
α-, γ-N_2; α-, γ-CO[I,IV]	SC *a*, φ	205	*Q*, μ, ν, polymorph.
CO_2[I,c]	ψ, *X*	206	ν (*t*°)
Adamantane	*a*, ψ	207	Δ*H*, reorient., polymorph.
	1972		
Cyclobutane	SC *a*	208	—
Planar molecules	ψ, *X*	209	*q*
Iodoform, chloroform, bromoform	SC	210	μ, Xsa
Biphenyl	ψ, *X*	211	ν
Trans-dichloroethane	ψ	212	
	1972		
Polyethylene[VI,a]	*a*, ψ	213	—
α-Chitin[III]	ψ, *X*, φ	214	Xsa
Benzene, naphthalene	ψ, *X*	215	ν
	1973		
Chloro-substituted benzenes (3 compounds)[d]	ψ, *X*	216,217	Δ*H*, ν
Benzene, deuterobenzene	ψ, *X*	218,219	μ, ν
Triphenylphosphine	φ	220	φ_{free}
Ethylene[VI]	SC ψ	221	ν
Hexamethylenetetramine	ψ, φ	222	ν
Acenaphthylene	ψ	223	—
Benzene, SO_2	ψ	224	*q*
N-Methylacetamide	ψ, *X*	225	*q*, H-b
Mucondinitrile and 8 organic complexes[II]	ψ	226	reorient.
	1974		
Hexachlorobenzene[I]	*a*, ψ	227	*q*, ν
Aromatic compounds (8 compounds)	ψ	228	Δ*H*, reorient.
Tetraphenylsilane[I]	ψ, φ	229	*q*, Δ*H*, ν
Cl_2, Br_2[IV,VI]	ψ, *X*	230	ν, ν (*t*°)
H_2, N_2, O_2, F_2, Cl_2, Br_2, I_2	SC *a*, ψ, *X*	231	*Q*
α-O_2[I]	SC ψ, *X*	232	—
α-N_2, γ-N_2[e]	*a*, ψ	233	ν
Methane	SC *a*, ψ	234	ν

Table 16 (contd.).

Substance	Adjustable parameters	Refs.	Remarks
1	2	3	4
	1975		
CH_4, CO_2, C_6H_6, $C_6H_5NO_2$	*a*, ψ, *X*	235	*q*, Δ*H*
n-Butane	*a*, ψ, *X*	236	ν
Pyridazine derivatives (2 compounds)	ψ	237	*q*, μ
Durol	ψ, φ	238	ν, Δ*H*
	1976		
Imidazole, pyrazine, urea, cyanuric acid[I]	ψ, *X*	239	ν
Biphenylene	*a*, ψ	240	ν, Δ*H*
Adrenaline	*a*, ψ, *X*, φ	241	*q*, H-b, φ_{free}
Anthracene	SC *a*, ψ	242	reorient.
Hydroquinone clathrates[I]	ψ, *X*	243	*q*
Hexamethylenetetramine, (α, β)	ψ	244	reorient.
α-CO[I,c]	ψ, *X*, φ	245	*Q*, ν
Hexachlorobenzene	ψ, *X*	246	μ, ν
CO_2, N_2, C_6H_6[I,IV]	*a*, ψ	247	*Q*, Δ*H*
Methane, adamantane, 2,2-paracyclophane, 3,3-paracyclophane	*a*, ψ	248	*a* (*t*°) reorient., polymorph.
Benzene	ψ, *X*, φ	249	ν
Hexaphenylbenzene, triphenylbenzene, triphenyltriazine	*a*, φ	250	φ_{free}
Phenoselenazine[V]	ψ, *X*, φ	251	—
	1977		
n-Alkanes (5 compounds)	ψ, *X*	252	Δ*H*, reorient., polymorph
$Sb(Ph)_5$, $P(Ph)_5$, $As(Ph)_5$	SC ψ, φ	253,254	*q*
	1977		
$M(Ph)_5 \cdot \frac{1}{2}C_6H_{12}$ (M = P, As, Sb)	SC *a*, ψ, *X*	255	*q*
Acetic acid	SC ψ	256	*q*, H-b
TCNQM-phenanthroline[II]	ψ	257	reorient., Xsa
2-Methyl-5,8-dihydroxy-1,4-naphthaquinone[III]	ψ, *X*, φ	258	Xsa
α-N_2[I,IV,e]	ψ, *X*	259	*Q*, ν, ν (*t*°)
Formic acid	ψ	260	*q*, *Q*

Notes. The following potentials were used: (I) "6–12", (II) "6–exp, *D*", (III) "*d*–d_0", (IV) a specially defined potential, (V) "6–exp" and "*d*–d_0", (VI) "6–exp" and "6–12" (in all other cases the "6–exp" potential was used). New parameters for the potentials of: (a) C, H, (b) C, H, O, (c) C, O, (d) C, H, Cl, (e) N, (f) C, H, N.

The column headed "Remarks" gives some additional information on the method of calculation or on the purpose of the investigation. The following abbreviations are used: *q*, μ, and *Q* denote allowance for the electrostatic interactions in the monopole, dipole–dipole, and quadrupole–quadrupole approximation respectively, ε denotes allowance for the dielectric constant in the calculation of the electrostatic component, H-b shows that the energy of the hydrogen bond has been allowed for, Δ*H* that the calculated results have been compared with the experimental heat of sublimation, el.const. that the results have been compared with the experimental elastic constants of the crystal, reorient. that the reorientation of molecules in the crystals has been considered, Xsa that the optimum structure was calculated in the course of an X-ray structural analysis, polymorph. that the work was aimed at interpreting a polymorphic transformation, ϕ_{free} that the conformation of the molecule in the crystal has been compared with the calculated conformation of the free molecules, *a*(*t*°) that the temperature dependence of the lattice parameters has been calculated, *A* that the thermodynamic functions have been calculated, ν that the vibration frequencies in the crystals have been calculated, and ν(*t*°) that the temperature dependence of the frequency has been calculated.

We note that a discussion of calculated frequencies of internal and external molecular vibrations lies outside the scope of this review. Special review articles have appeared on this topic[26,266]. Work on the calculation of frequencies

is included in the Tables only in so far as it involves minimisation of the intermolecular interaction energy by varying the structure parameters.

In most of the work listed in Tables 9–16 the structure class of the crystals under study is taken from X-ray diffraction data, i.e. the problem of optimising the packing of the molecules is solved for a given structure class. However some workers have formulated the problem more widely, and have treated the structure class as a variable. A brief outline of publications in which packing arrangements for different structure classes are compared is given below.

Brock and Ibers[253,254] tried to account for the square-pyramidal coordination of antimony in $Sb(C_6H_5)_5$ (structure class $P\bar{1}$, $Z = 2(1)$) as compared with the trigonal-bipyramid coordination found in $P(C_6H_5)_5$ and $As(C_6H_5)_5$ (structure class Cc, $Z = 4(1)$). For each of the three compounds the potential energy of the crystal structure was minimised for a coordination polyhedron taken either as a tetragonal pyramid in the class $P\bar{1}$, $Z = 2(1)$, or as a trigonal bipyramid in the class Cc, $Z = 4(1)$. The calculation was satisfactorily consistent with experiment, but only after allowing for the electrostatic component.

Kitaigorodskii and coworkers[120] studied acenaphthene (structure class $Pcm2_1$, $Z = 4(m,m)$), biphenylene ($P2_2/a$, $Z = 6(1,\bar{1})$), and tolane ($P2_1/a$, $Z = 4(\bar{1},1)$) to explain the existence of quasi-heteromolecular crystal structures, in which identical molecules can occupy more than one system of equivalent positions. To this end they calculated the optimum packing of acenaphthene molecules in the $P2_1/a$, $Z = 4(1)$ structure class, and of biphenylene and tolane in the $P2_1/a$, $Z = 2(\bar{1})$ structure class, i.e. they examined the normal packing arrangements in which all the molecules are symmetrically equivalent. Only in the case of acenaphthene was the potential energy of the real structure lower than the energy of the hypothetical packing arrangement. For biphenylene and tolane the energies of the real and the hypothetical packing were found to be almost identical.

The aim of Derissen and Smit[256] was to explain the specific behaviour of acetic acid during crystallisation. Unlike most of the other carboxylic acids, acetic acid forms a structure (structure class $Pna2_1$, $Z = 4(1)$) in which the molecules are connected by hydrogen bonds in infinite chains (rather than in dimers). The most likely alternative to the real structure of acetic acid was taken to be that of fluoroacetic acid ($P2_1/c$, $Z = 4(1)$). Minimisation of the potential energy for this structure class gave two minima of similar depth. Their energy was practically identical to that of the real structure. Thus the authors[256] could not reach any firm conclusion on the reasons for the anomalous structure of crystalline acetic acid. However they correctly point out[256], like other workers[120], that this type of problem cannot be finally resolved without calculating the free energy. In all probability the lack of success of a number of investigations[172,174,177,183] of the crystal structure of chlorine is also due to the use of the potential energy (instead of the free energy) of the structure in the minimisation procedure.

We shall now turn to a more detailed discussion of some special aspects of the calculation of the energy of molecular packing, noted in the "Remarks" column of Tables 9–16.

1. Comparison of the Conformation of the Free Molecule and the Conformation of the Molecule in the Crystal

If the molecule contains atomic groups able to rotate about an ordinary bond the crystal field may be sufficient to affect the conformation when such a molecule is introduced into a crystal. This effect has along been recognised in comparisons of X-ray diffraction results with the results of analytical methods sensitive to the geometry of "free" molecules (electron diffraction of vapours, and microwave spectroscopy).

Minimisation of the energy of zero-valent interactions in the atom–atom approximation allows us to interpret and to predict the influence of a crystal field on molecular conformation. The classical work in this area was contributed by various authors[92,141,125], who calculated the conformation of biphenyl molecules in the vapour and in the crystalline phase. In complete agreement with experiment, the calculations indicated a planar structure for the molecule in the crystal and a non-planar conformation (with an angle between the phenyl rings between 30° and 42° according to different authors) in the free state.

In a more recent paper of this type[250] the energy of the free molecule and the energy of the crystal structure are calculated as a function of the angle of rotation of the phenyl rings about the ordinary bond for hexaphenylbenzene, 1,3,5-triphenylbenzene, and 1,3,5-triphenyltriazine. The result of the calculation is that the isolated molecule has a higher symmetry, and that the rotation angles of the phenyl rings are slightly altered (by less than 10°) when the molecules are introduced into a crystal.

Calculations of molecular conformation in a crystal can be used to establish the location of atoms or atomic groups not detected with sufficient precision by X-ray diffraction. The calculation of the coordinates of hydrogen atoms in methyl groups is an example of this type of work[162,267].

2. Application of Optimum Packing Calculations in X-ray Diffraction Analysis

In this work an initial model of the molecule is usually assumed, based on standard bond lengths and bond angles, and supplemented if necessary by conformational analysis. Data on the structure class and on the elementary cell parameters are obtained from X-ray diffraction. The distribution of the molecules within the cell corresponding to a minimum energy is obtained from that information. If more than one distribution is found to be possible the R-factor is calculated in each case, and the structure corresponding to the lowest R-factor is identified by the standard methods of X-ray analysis. This method has been used, for example, in Williams' calculations of the structure of organic compounds containing nitrogen heterocyclic rings[124,126]. Simonetta and coworkers[145–147], having calculated the conformation of several derivatives of annulene, established their packing in the crystal to within $R \cong 5–8\%$. Similarly, Giglio and coworkers identified the structures of N,N'-dicyclohexylurea[132], 5α-androstan-3,17-dione[108], coumarin[137], and other compounds. The second structure in this list could not be determined by conventional methods of X-ray analysis.

The search for optimum packing as a means of determining structure is particularly valuable in the case of polymers. Perfect crystals, suitable for X-ray structural analysis, are seldom formed by polymers. By minimising the energy of the crystal structure we can build a model of the polymer which is then modified or confirmed by X-ray diffraction results.

A good example of this method of evaluating polymer crystal structures is given by the work of Sarko, Zugenmaier, and others (Table 15) on the crystal structure of carbohydrates and polysaccharides. These workers used the "$d–d_0$" potential (see above), with parameters chosen on the basis of six model monosaccharides[163]. This potential allowed them to calculate the effect of hydrogen bonds as well as ordinary intermolecular interactions. The packing of two model chains was considered in the work on the structure of

mannans[166]: these models gave very similar energy terms, and only by interpreting i.r. spectral data could one of them be chosen as the more likely.

The structure of different modifications of a material as important as cellulose could not be established until calculations of packing were applied to the problem. The first step in this type of work is a conformational analysis of the free molecule. Choosing the most probable conformations, and using experimental data on the space group and on the parameters of the elementary cell, 185 initial models were assembled. Minimisation of the energy reduced this number to 24 variants, from which the packing arrangements with the largest number of hydrogen bonds were chosen. The model was further refined by using experimental values of the structure amplitudes. It was shown that cellulose I consists of parallel chains and has a triclinic (and not monoclinic, as previously thought) unit cell. The *R*-factor of this structure was 29%. The modification known as cellulose II was characterised to an *R* value of 15.1%: it consists of antiparallel chains and contains a greater number of hydrogen bonds, which explains is greater stability. For the cellulose III modification the *R*-factor was 20.3%: in this modification the chains are parallel, as in modification I. Thus the polymorphic transformations in cellulose are now fully characterised.

3. Calculation of Thermodynamic Functions and Interpretation of Polymorphism

Methods of identifying the optimum packing by minimising the free energy were described in Section II. The problem of evaluating the thermodynamic functions is often encountered in various aspects of this type of work (not only in the calculation of the optimum structure). Several workers have calculated thermodynamic quantities through the frequency distribution functions. Thus in a study of crystalline benzene[190] the zero-point vibration energy and the specific heat for the range 60–220 K are calculated; the heat of sublimation at 0 K has also been obtained[77] from calculations of the optimum crystal structure, of the vibration frequencies, and of the molecular conformation in the gas and the crystalline phase.

Thermodynamic functions have also been calculated[35,36] through the configuration integral on the basis of the cell model. Thus the free energy, the specific heat, and the entropy at different temperatures have been obtained for naphthalene, benzene, and anthracene crystals.

One of the most important and interesting applications of the calculation of thermodynamic quantities is the explanation and prediction of polymorphism in molecular crystals. The simplest way of interpreting polymorphism is to demonstrate the presence of two minima, of similar depth, in the potential energy surface. Various attempts have been made[207,224] to account for polymorphism in this way, often successfully. Nevertheless the method is not universal because several minima of comparable depth can be found on the potential surface, and not all of these correspond to real modifications.

A strict interpretation of polymorphism requires calculation of the free energy. Pertsin and Kitaigorodskii[37,38] used the atom–atom potential method and the cell model to calculate the entropy and the free energy of benzene and adamantane as a function of temperature and pressure. At each point the free energy was minimised with respect to the structure parameters. The calculation was carried out for two modifications of each compound (treating the structure class as known): the intersection of the two free energy curves thus obtained gave the polymorphic transformation. In this way the phase transition temperature of adamantane was obtained, in excellent agreement with experiment. In the case of benzene the free energy isotherms intersected in the negative pressure region: the authors point out that the change in free energy with pressure is small, and comparable with the error of the calculation. However it is important to note that even in this case it was possible to obtain at least a qualitative prediction of the polymorphic transformation induced by changes in pressure.

4. Molecular Reorientation and Orientational Disorder

The symmetry or pseudo-symmetry present in some molecules can produce minima of identical (or similar) depth in the potential energy surface of the crystal for different values of the Euler angles. If the barriers separating these minima are low, reorientation is possible in the crystal (a sudden rotation of the molecule with a negligibly small effect on the position of the centre of gravity). On the other hand if the barrier is fairly high, and the molecule lies in substantially different positions before and after the change in orientation, orientational disorder can occur with molecules of suitable shape.

Reorientation can be observed experimentally through the NMR spectra, from which the height of the barrier can also be calculated. Orientational disorder is detected from X-ray diffraction data. However it should be noted that dynamic reorientation and static orientational disorder are almost impossible to distinguish by X-ray diffraction. Therefore published reports of orientational disorder should be accepted with caution.

This uncertainty can often be avoided by calculating the height of the reorientation barrier. In the case of planar molecules the simplest method of calculating the barrier height is the following. The molecule is rotated about an axis passing through its centre of gravity and normal to the plane of the molecule. The other molecules are considered to be rigidly fixed in the positions indicated by X-ray structural analysis. The plot of intermolecular interaction energy against angle of rotation gives the most favourable orientations and the height of the barrier opposing the orientational transitions.

Calculations of this type have been reported for benzene[67], for polycyclic aromatic molecules (naphthalene, coronene, pyrene, etc.)[228], and for a group of planar molecules including derivatives of benzene and naphthalene and some heterocycles[150]. The authors[150] point out the difference between: 1) crystals in which reorientation is easy (benzene, hexamethylbenzene, thiophen), 2) crystals in which reorientation is hindered (hexachlorobenzene), and 3) crystals in which reorientation is impossible (2-bromonaphthalene). This classification correctly reflects the qualitative conclusions obtained from NMR spectra. However not all the calculated reorientation barriers agree quantitatively with the experimental values.

Similar calculations have been carried out for organic molecular complexes[223,257], but unfortunately no allowance was made for the electrostatic component, which in this case can be expected to play an important role.

Calculations[226] on the TCE–naphthalene and TCE-paracyclophane complexes (where TCE is tetracyanoethylene) have shown the existence of the TCE molecule in two positions of similar energy differing by a 90° rotation of the molecule in its own plane. The barrier between these positions is unsurmountable in practice. This suggests the possibility of orientational disorder in these complexes, a conclusion which is consistent with X-ray diffraction data for the latter

complex[268], in whose crystals 25% of the molecules occupy one of the possible positions and 75% the other. However in the case of the TCE–naphthalene complex X-ray diffraction gives no evidence of orientational disorder[269].

The energy curve describing the rotation of the naphthalene molecule (in its own plane) in the naphthalene–TCE and naphthalene–TCB complexes (where TCB is tetracyanobenzene) has two minima separated by an angle of ~35° and by a barrier whose height (~3 kcal mole^{-1}) is much lower than the corresponding barrier for the TCE molecule. X-ray diffraction studies[269–271] have indicated the presence of disorder in these crystals, corresponding exactly to the calculated disorder, but with a lower barrier, which therefore does not exclude the possibility of dynamic reorientation.

The plots of energy against rotation angle for anthracene molecules in complexes with TCB and tetracyanoquinonedimethane show only one minimum. However this minimum is quite broad, and the molecules can perform large-amplitude librations in their own plane. This conclusion is consistent with X-ray results.

A calculation[244] of the reorientation barriers in crystals of adamantane (α and β modifications) and of hexamethylenetetramine was complicated by the absence of a direction which could be identified with the axis of rotation of the molecule. The authors considered two possible directions as the axis of rotation, corresponding to the diad and triad symmetry axes of the molecule, and two possible positions of the neighbouring molecules. The reorientation barrier of the molecules in the β modification was found to be higher than in the high-temperature (α) modification. Molecular rotation in hexamethylenetetramine crystals is strongly hindered by the intermolecular hydrogen bonds.

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Lomonosov Moscow State University
Chemistry Faculty
Institute of Element–Organic
Compounds of the USSR Academy
of Sciences