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Theoretical Determination of the Geometrical Form of the Crystal of Anthracene

BY A. I. KITAIGORODSKY AND N. A. AHMED

Institute of Elemento-Organic Compounds, Academy of Sciences of the USSR, Moscow

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The form of a crystal of anthracene was determined by calculating from the atom-atom potentials the surface energies of all planes having simple indices and by drawing out a Wulff plot. Good agreement is obtained between the theoretical form and that of real crystals grown from solution.

Introduction

The relationship between the internal structure of a crystal and its external habit was first expressed by A. Bravais, who emphasized the importance of crystal planes of high density. The significance of the atomic array in determining crystal habit was then shown by Kossel (1928), Stranski (1928), Hartman (1958) and others. There were also several attempts at correlating crystal habit with surface free energy when plotted in spherical coordinates [Wulff's plot or 'γ plot' (Wulff, 1901; Yamada, 1924; Herring, 1950)]. Hartman & Perdok (1955) introduced the periodic bond chain method which serves as a preliminary investigation before an exact calculation of surface energy is carried out. Wulff & Gualtieri (1962) showed that differences between experimental and derived habits yield specific information with regard to the nature of adsorption, surface lattice deformation, and the character of bonding. In all this work there was no possibility of the calculation of exact values of surface energy since a method of calculating the internal forces was lacking. The introduction in chemical organic crystallography of the method of atom-atom potentials made possible the calculation of several properties (Kitaigorodsky, 1970). In this work the exact values of surface energy have been calculated and the geometrical form of the crystal of anthracene has been derived. Anthracene was chosen as it has a simple molecule containing only

carbon and hydrogen atoms, the interactions of which are known. Moreover the structure is known to a high degree of accuracy.

Calculation of the potential energy of nucleation

Any crystallization operation can be considered to consist of three steps:

- (1) achievement of supersaturation.
- (2) formation of crystal nuclei,
- (3) growth of crystals,

The formation of crystal nuclei is a difficult process: not only do the constituent molecules have to coagulate, resisting the tendency to redissolve, but they have to become orientated into a fixed lattice. Most probably, the mechanism of nucleation is as follows: minute structures are formed, first from the collision of two molecules, then from that of a third with the pair, and so on. Short chains or flat monolayers may be formed initially and eventually the lattice structure is built up. The most probable factor that influences the choice of molecules for coagulation is the binding energy.

For simplicity of calculating the potential energy of nucleation, the following model was assumed.

- (a) The initial state is an ideal gas.
- (b) Molecules are arranged from the very beginning according to the crystal lattice but not necessarily

with the lattice dimensions of the grown crystal as separating distances between them.

- (c) The molecules which are preferred for addition one by one to the original molecule are those which keep the energy of the system to a minimum.

Crystals of anthracene are monoclinic with the following unit cell dimensions: $a = 8.562$, $b = 6.038$, $c = 11.184$ Å, $\beta = 124^\circ 42'$ (Mason, 1964).

There are two centrosymmetric molecules in the unit cell, arranged according to the space group $P2_1/a$ with their centres at $0,0,0$ and $\frac{1}{2}, \frac{1}{2}, 0$. The molecule at the origin was taken as the basic molecule to which others will coagulate. The energies between this molecule and all others surrounding it were calculated individually, searching for the molecule which will join the first. The molecule at $\frac{1}{2}, \frac{1}{2}, 0$ was found to be the one which has an interaction energy less than others nearby. These two molecules were then taken as a basic system to which a third one was added and so on. In all calculations variation of the unit cell dimensions was considered, but the orientation of the molecule in the unit cell as given by Mason (1964) was not changed.

The energy

$$U = -Ar^{-6} + Be^{-\alpha r}, \quad (1)$$

was calculated using the constants A , B , α given by Kitaigorodsky (1966). U is the mutual energy of all interacting atoms of a system of N molecules, divided by N . Table 1 gives the values of U and the corresponding unit cell dimensions. Fig. 1 shows the order of adding molecules and the resulting shape after 25 molecules have been assembled. It must be mentioned that the positions of some molecules were not unique; sometimes more than one position gave the same energy, but the resulting final shape (Fig. 1) is the same. Fig. 2

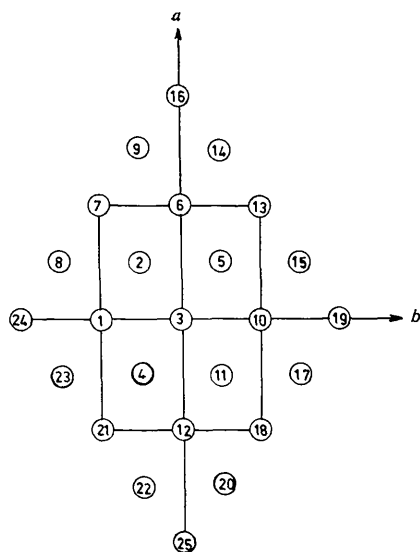


Fig. 1. Order of addition of molecules and the resulting shape after 25 molecules have been assembled.

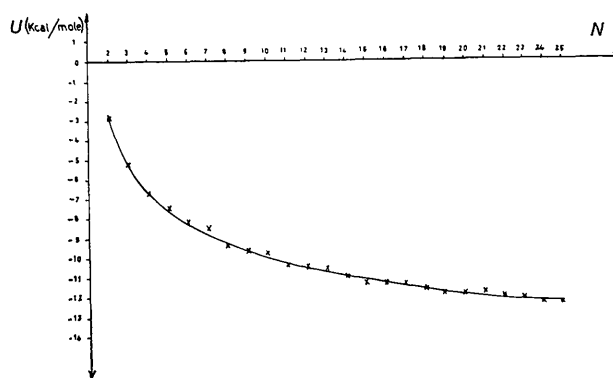


Fig. 2. Relation between the number of molecules N and the corresponding energy U .

shows the relation between the number of molecules N and the corresponding energy U . The calculation was stopped after adding 25 molecules because the energy per molecule reached a steady value as shown in Fig. 2. After such a number of molecules the potential energy of the system has a value between the extreme values of energy obtained after adding various numbers of molecules to the system, *i.e.* the energy is fluctuating around the constant value shown in the Figure. The calculation of the dimension of the nucleus is not possible by the method described; but the number 25 gives an idea of the smallest size of nucleus that exists during crystallization. As is shown in Fig. 1 all molecules are in the a - b plane. Arrangement in the third direction could not be achieved according to the proposed rule of minimum energy. This result is quite understandable as it is known that crystallization oc-

Table 1. Values of U and corresponding unit cell dimensions

N	U (Kcal. mole ⁻¹)	a (Å)	b (Å)
2	-2.77	8.295	6.390
3	-5.18	8.665	5.860
4	-6.71	8.670	5.860
5	-7.43	8.573	5.863
6	-8.11	8.560	5.868
7	-8.47	8.552	5.895
8	-9.43	8.610	5.855
9	-9.67	8.545	5.895
10	-9.77	8.605	5.847
11	-10.36	8.602	5.845
12	-10.48	8.540	5.890
13	-10.51	8.597	5.840
14	-10.91	8.597	5.853
15	-11.28	8.600	5.843
16	-11.30	8.597	5.840
17	-11.28	8.595	5.865
18	-11.55	8.600	5.840
19	-11.80	8.535	5.870
20	-11.80	8.590	5.840
21	-11.77	8.595	5.835
22	-11.97	8.590	5.845
23	-12.17	8.590	5.840
24	-12.35	8.595	5.840
25	-12.33	8.590	5.840

curs in three dimensions only in the presence of lattice defects.

However, the resulting two dimensional shape shown is in agreement with the experimental crystals described by Groth (1919) as plates containing the a and b axes with the faces $\{001\}$, $\{110\}$, $\{20\bar{1}\}$ and sometimes $\{11\bar{1}\}$ as the most common forms.

Another method for obtaining the form of the crystal was tried: namely calculation of the surface energy.

Surface energy calculation

Gibbs (1928) found that the crystal is in equilibrium with its own vapour phase when for a constant volume, its total surface energy is a minimum:

$$\sum_i^n \sigma_i A_i = \text{minimum}$$

where A_i is the area of the i th face of a crystal bounded by n faces and σ_i is the surface free energy per unit area of the i th face. Wulff (1901) showed that this statement is equivalent to the equation:

$$\frac{\sigma_1}{h_1} = \frac{\sigma_2}{h_2} = \dots = \frac{\sigma_i}{h_i} = \text{constant}$$

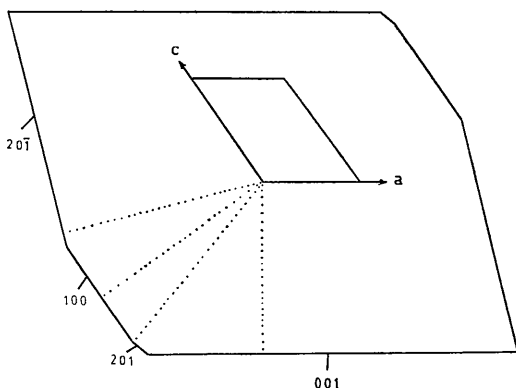


Fig. 3. (010) Projection of Wulff plot. The dotted lines show the directions of normals.

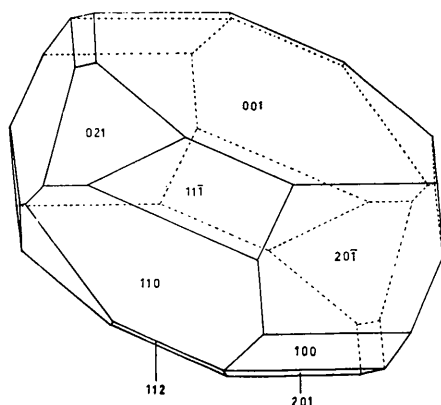


Fig. 4. Resulting form of the crystal.

where h_i = central distance of the i th crystal face. Gibbs pointed out that a crystal will assume the equilibrium form only when it is of microscopic dimensions. Macroscopic crystals, which are growth forms, possess the same planes as the equilibrium forms (Stranski & Kaishev, 1935). Only the relative sizes of the various planes usually differ in the two forms.

A crystal equilibrium form may be derived by varying the central distance of each crystal plane until each distance is proportional to the specific surface energy (Stranski, 1965) (Wulff's method). Wulff's method in two dimensions uses a polar diagram of the specific surface energy of the various planes which belong to a particular zone. The crystal form which corresponds to the lowest surface energy may be obtained by selecting the planes enclosing the smallest area. The respective planes are orthogonal to lines drawn from the origin, and intersect these lines at distances proportional to the specific surface energy of the specific plane. In three-dimensional representation the specific surface energies σ_i of all planes are plotted in spherical coordinates.

The specific surface energy σ_i is defined as being half the energy per unit area required to separate the crystal along the i th plane. According to this definition the energy must be positive if the energy is calculated according to equation (1). The summation was carried out on all interactions between the constituents of a unit of repetition in the specific plane and the constituent atoms of all other molecules at one side of that plane. As an example, for the plane (100), the interactions between the repeated unit containing the molecules (1), (4) and (21) (Fig. 1) and all molecules (including those in the third dimension) above the line showing the direction of the b axis, were considered. Half this energy was then divided by the area of that plane. The calculated values of σ_i for planes of simple indices using the lattice parameters and atomic coordinates given by Mason (1964), are shown in Table 2. The equilibrium form was derived using Wulff's method by drawing several projections of the three-dimensional representation of the energies σ_i of these given planes. As an example one projection is shown in Fig. 3. It is clear that although some planes have approximately equal energies, the directions of their normals influence the areas of their faces. Fig. 4 shows that the resulting form of the crystal is a plate containing the axes a and b with the biggest face as (001).

Table 2. Calculated values of σ_i for planes of simple indices using the lattice parameters and atomic coordinates given by Mason (1964)

Plane	σ erg.cm ⁻²	Plane	σ erg.cm ⁻²
100	87.98	201	90.14
010	117.50	20 $\bar{1}$	91.94
001	75.70	021	111.70
110	90.34	111	98.87
011	103.20	11 $\bar{1}$	105.50
101	90.80	112	94.20
10 $\bar{1}$	119.25	11 $\bar{2}$	122.00

The presence of more planes in this derived equilibrium form than the growth form described by Groth (1919), is quite normal. This difference is probably due to the velocity of growth of crystals in solutions.

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On Least-squares Refinement of the Phases of Crystallographic Structure Factors

BY D. SAYRE

Mathematical Sciences Department, IBM Thomas J. Watson Research Center, Yorktown Heights, New York 10598, U.S.A.

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A least-squares technique for direct refinement of the phases of structure-factors of crystals which obey the equations $a_n F_n = \sum_k F_k F_{n-k}$ is described. It is shown by tests carried out under somewhat idealized conditions that the initial phases need not be of a completeness or accuracy sufficient to resolve the atoms of the structure. The technique may be able to provide a bridge in protein crystallography and structure determination generally between preliminary phasing techniques and final refinement of atom parameters.

The refinement techniques in current use in crystallography (least-squares refinement of atomic parameters, Fourier refinement of atomic parameters and phases simultaneously) have the property that they cannot commence until the structure determination has progressed to the point where an approximate set of atom parameters, or equivalently a set of phases sufficiently complete and accurate to yield a Fourier map from which such parameters can be read off, is available. Frequently, however, a less complete and accurate set of phases will be available at an earlier point in the determination. In protein crystallography, for example, phases to 3.0–2.5 Å resolution can be obtained by the method of multiple isomorphous replacement (m.i.r.). It may also be noted that Hauptman (1969) and Karle (1970) have given procedures which from the observed magnitudes alone produce rough approximations to the phases for any structure. Thus a refinement technique which operated directly on phases rather than on atom parameters, and which was able to commence from an initial set of phases of less than atom-resolution quality, could be an important aid in completing protein structures and perhaps in determining structures generally.

In the present paper we consider, as a possible technique of this kind, minimization of the expression $\sum_h |a_h F_h - \sum_k F_k F_{h-k}|^2$ as a function of the phases. This minimization may be regarded as a reciprocal-space analog of the ordinary least-squares refinement of atom parameters. Starting with an initial set $\{\varphi_j^0\}$ of phases the process generates a sequence of approximations $\{\varphi_j^1\}, \{\varphi_j^2\}, \dots$ tending toward the set $\{\varphi_j\}$ at which the function is a minimum. Preliminary tests of the method conducted under partially realistic conditions are reported to show that the final set $\{\varphi_j\}$ can indeed be adequately close to the set $\{\Phi_j\}$ of true phases and that convergence to $\{\varphi_j\}$ can occur even when the initial set $\{\varphi_j^0\}$ is considerably below atom-resolution quality. $\{\varphi_j\}$ may alternatively be thought of as a least-squares solution of the equations

$$a_n F_n = \sum_k F_k F_{n-k} \quad (1)$$

(Sayre, 1952) without the usual approximation involved in replacing equation (1) by its corresponding set of triple-product relationships.

We may pause briefly to put the present technique