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Abstract

Full Text

Crystallography

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CALCULATION OF THE STRUCTURE OF LAYERS IN CRYSTALS OF NICKEL DIMETHYLGLYOXIMATE ON THE BASIS OF THE THEORY OF CLOSE PACKING OF MOLECULES

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A. I. Kitaigorodskii, in his works ([1,2]), showed that a necessary characteristic of molecular crystals is a sufficiently high packing density. However, at the present time there are practically no methods for finding noncompact arrangements of bodies in space and of figures in a plane. As a result, when considering a particular packing in a crystal, we have no way of judging whether it is noncompact and, if not, to what extent and in what respect the real packing differs from the noncompact one. Yet without resolving this question it is impossible to form a clear idea of the causes determining the structure of molecular crystals.

We have developed a graphical method for determining the densest arrangements of figures in a plane. The method makes it possible to find the densest lattice packings of figures of arbitrary shape when the elementary cell contains no more than two figures ($Z \leqslant 2$).

Fig. 1. Areas of cells S of possible dense arrangements at $Z = 1$

In the present work this method was applied to calculating the packing in a layer of flat molecules of nickel dimethylglyoximate. From the data of X-ray structural analysis of single crystals ([3]), only the fact was used that the structure consists of layers coinciding with the planes m, in which the flat molecules are situated. This made it possible to rely on the procedure developed for the two-dimensional case.

To carry out the calculation we used a model of the molecule with symmetry mmm, constructed on the basis of the commonly occurring values of interatomic distances, valence angles, and intermolecular radii ([1]). The distance Ni—N and the angle N—Ni—N in the chelate ring were taken in accordance with the data of structural investigations ([4–6]); the remaining angles were uniformly corrected so

that the molecule retained a planar structure. The group CH_3 was conventionally represented in the form $-C<\begin{matrix}H\\H\end{matrix}$, with the H atoms arranged symmetrically to the line C—CH_3 at a distance of 1.7 Å from one another. The quantities used for constructing the model, and the corresponding X-ray structural analysis data ([3]), are given in Table 1.

As the vector $\mathbf{x}_n$, describing the position of the molecule in the plane, the direction Ni—midpoint of the C—C bond in the chelate ring was chosen.

Table 1

Characteristics of the molecule used in the calculation, and experimental structural data [3]

Bond / fragment	Interatomic distances, Å — used in calculation	Interatomic distances, Å — experimental (mean)	Angle / fragment	Valence angles, degrees —used in calculation	Valence angles, degrees —experimental (mean)	Atom / fragment	Intermolecular radius, Å
Ni—N	1.85	1.89	In the ring: N—Ni—N	80	80	N	1.57
N—C	1.35	1.23	In the ring: Ni—N—C	115	119	O	1.36
N—O	1.4	1.38	In the ring: N—C—C	115	111	C (in the ring)	1.75
C—C (in the ring)	1.45	1.53	Outside the ring: Ni—N—O	123	120	C (in the CH_3 group)	1.80
C—CH_3	1.5	1.49	Outside the ring: N—C—CH_3	123	126	H	1.17
C—H	1.1	—					

Fig. 2. Dependence of the cell area S on the angle φ between the vectors of translationally nonequivalent molecules for $Z = 2$.

Figure 2: Fig. 2. Dependence of the cell area S on the angle φ between the vectors of translationally nonequivalent molecules for $Z = 2$.

When the cell of a layer contains one molecule ($Z = 1$), the vectors $\mathbf{x}_n$ of all molecules are parallel (the molecules constitute one system of covector figures). In this case, if the arrangement is dense, it can be characterized by one parameter x. As such a parameter we used the projection of the distance O_0O_1 between the centers of two contacting molecules onto the vector $\mathbf{x}_0$. By a dense arrangement we here understand a packing in which each molecule has coordination number 6 in the layer.

If $Z = 2$, then, in order to attain a dense arrangement, the vectors $\mathbf{x}_n$ of four of the six molecules touching the given one must form with the vector of the given figure an angle φ not equal to zero (two systems of covector figures). In this case, the value of φ usually characterizes the dense packing to within two variants. When this is not so, one may choose the two densest packings. Since the symmetry of the molecule is mmm, the independent range of variation of the angle φ is taken from 0 to 90°.

Fig. 2. Dependence of the cell area S on the angle φ between the vectors of translationally nonequivalent molecules for $Z = 2$.

Consideration of all possible dense arrangements for $Z = 1$ and $Z = 2$ made it possible to construct the graphs shown in Figs. 1 and 2, in which the area of the layer cell S is represented as a function of x and φ.

For $Z = 1$, the existence of three densest arrangements was established (three minima in Fig. 1) with an approximately identical packing-density coefficient in the layer, equal to 0.85. These three arrangements give an oblique lattice with the parameters: 1) $a = 7.8$ Å, $b = 11.7$ Å, $\beta = 71°$; 2) $a = 9.7$ Å, $b = 11.7$ Å, $\beta = 50°$; 3) $a = 11.8$ Å, $b = 11.6$ Å, $\beta = 39°$.

It is important, however, to note that over a very broad range of values of x (from 0.75 to 11 Å)* the packing-density coefficient remains greater than 0.83 and becomes somewhat smaller than this value only at values of x close to zero.

On the curve describing the case $Z = 2$ (Fig. 2), the values of S for two packing variants at a given φ are plotted to the right and to the left of the ordinate axis. Here two lowest minima, A and B, are observed, corresponding

* The independent range of variation of x is from 0 to ~ 11 Å.

arrangements with packing-density coefficients of 0.83 and 0.82. In addition, low values of S are found at small angles φ, when the packings are essentially close to those obtained for $Z = 1$. The packing lattice corresponding to minimum B has parameters $a = 21.1$ Å, $b = 8.4$ Å.

The arrangement giving minimum A at $Z = 2$ proved to be very close to the real structure (3). It, like all the other arrangements represented on the curve $S(\varphi)$, has an orthogonal cell and the plane symmetry group Pgg. A comparison of the characteristics of this packing with the quantities found from X-ray structural data is given in Table 2. It is interesting to note that, despite the rather considerable discrepancy in the lattice parameters, which is most likely due to the inaccurate specification of the molecular shape, the atomic coordinates found by calculation for minimum A differ from the experimental ones on average by only 0.15 Å.

Table 2

Comparison of packing A, found by calculation, with the real structure (3)

Structural characteristics	Calculation data	Structural-analysis data
Angle φ between molecular vectors	83°	86°
Symmetry of the layer lattice	Pgg	Pgg
Lattice parameters in Å: a	18.2	16.7
Lattice parameters in Å: b	9.7	10.4
Area of the layer cell in Å^2	176.5	173.7
Packing-density coefficient: in the layer	0.83	0.84
Packing-density coefficient: in space	–	0.77

Thus, the calculation carried out showed that:

1. The packing realized in nature, with an orthogonal cell, corresponds to one of the minima on the curve $S(\varphi)$ at $Z = 2$.
2. Several somewhat denser packings with an oblique cell at $Z = 1$ are possible in principle.

At present it is difficult to give a definite answer to the question of why the realized packing proves to be preferable. The explanation may lie in more favorable conditions for the superposition of layers. The latter should be checked by means of a three-dimensional calculation. We are developing the corresponding methodology.

The accumulation of such computational data will probably help to study more precisely the factors determining the structure of molecular crystals.

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Note: Figure translations are in progress. See original paper for figures.