Molecular coordination numbers in crystal structures of organic compounds

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The calculation of molecular coordination numbers (MCNs), and topological and geometrical analysis of the environment of molecules in the crystal structures of 23 067 organic compounds, shows that Kitaigorodskii's close-packing model, assuming the predominance of MCN = 12, works correctly in only a few cases, whereas MCN = 14 is the most frequent. To explain this fact the close-packing model is extended with the model of the thinnest covering of space by deformable molecules. It is shown that the packing of molecules of arbitrary shape and composition can be better described with geometrical, but not topological, parameters of their short-range environment, which is conveniently characterized by molecular Voronoi–Dirichlet polyhedra.

1. Introduction

At present, the principle of close packing suggested by Kitaigorodskii (1973) is commonly used to describe a molecular crystal. According to this model a molecule is represented as a solid bounded by exterior surfaces of overlapped van der Waals spheres, corresponding to the atoms of the molecule. The surfaces, bounding different molecules, should adjoin, but should not overlap each other and should not be in empty voids. It is the arrangements of molecules, providing a large number of contacts, which are termed close packings. In order to form a close packing, molecules tend to be occupied so that the 'bumps' of one molecule interact with the 'hollows' of another. To characterize the density of molecular packing, Kitaigorodskii used the packing coefficient (k), which is equal to the ratio of the volume of all the molecules in the unit cell to its volume, and also the number of molecules, surrounding a molecule in the crystal structure, which is termed the molecular coordination (or contact) number (MCN). In terms of the close-packing model, MCN is determined as the number of molecules, which have at least one contact with a given molecule. Kitaigorodskii assumed that the basis for close packing of organic molecules is a layer with MCN = 6. The superposition of such layers results in a close packing with MCN = 12. This model conforms topologically to the close-packing of hard spheres, commonly used in inorganic crystal chemistry (Wells, 1986), however, there is no strict proof of its correctness. Kitaigorodskii's analysis of the features of molecular packings in crystals of about 150 organic compounds has shown that MCN = 12 is the most common. At the same time, according to Kitaigorodskii (1973), MCN = 14 and 10 is less frequent and the model of close-packed layers could not give a reasonable explanation. Thus, Kitaigorodskii has given the packings of adamantane (k = 0.69) and hexamethylene-

tetramine (k = 0.72) molecules as examples of close-packed crystal structures. The adamantane molecules are arranged on a face-centred cubic (f.c.c.) lattice with MCN = 12, whereas in the crystal structure of hexamethylenetetramine the centroids of molecules are arranged on a body-centred cubic (b.c.c.) lattice and each molecule has 14 neighbours (Figs. 1a and b). Kitaigorodskii explained this fact by the 'convenient' shape of the hexamethylenetetramine molecule. However, both molecules have an identical symmetry, similar structure and a shape close to spherical. Therefore, the problem of why MCN = 12 is observed for one molecule, but another molecule has MCN = 14, remains unsolved. In later investigations (Fischer & Koch, 1979; Zefirov & Zorky, 1995) the predominance of MCN = 14 instead of 12 was found in crystal structures of organic compounds, but this fact was not fully explained. Evidently, the close-packing model as applied to organic crystals requires
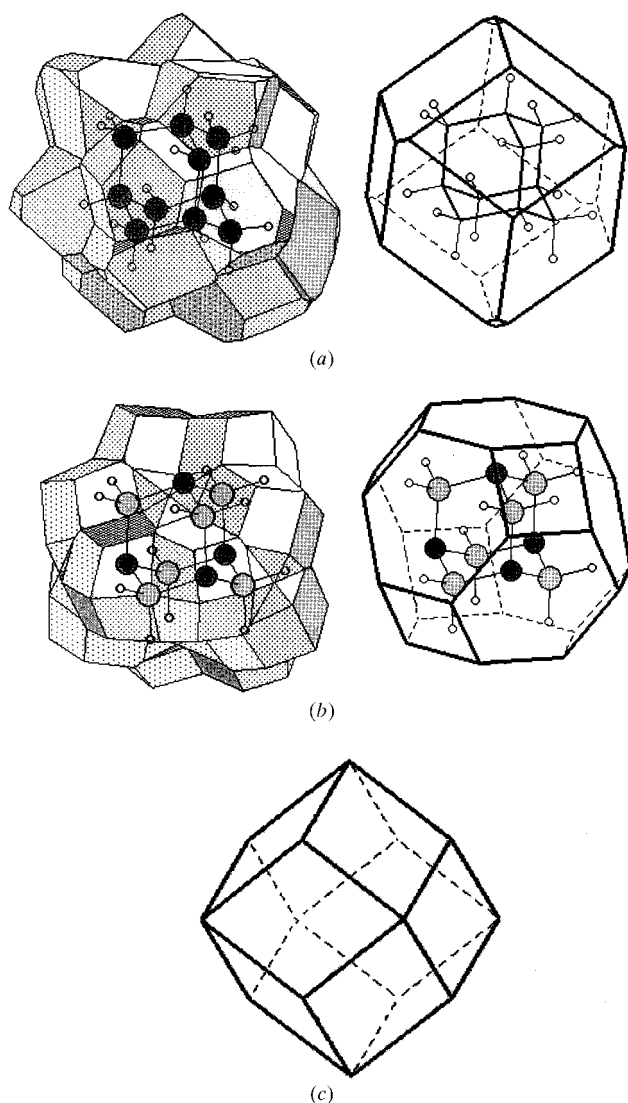

(a)

(b)

(c)

Figure 1
(a) Adamantane (T = 188 K) and (b) hexamethylenetetramine molecules, represented as molecular (left) and lattice molecular (right) VDPs. Topologically both lattice VDPs are Fedorov cuboctahedra, however, the lattice molecular VDP of the adamantane molecule is geometrically similar to a rhombododecahedron (c).

further development. Certainly, the molecules in a crystal tend to fit together closely, obeying the principle of the maximum filling of space (Vainshtein *et al.*, 1983). However, is this arrangement always similar to the close packing of hard spheres?

There is another way to describe molecular crystals. It is based on a model of the thinnest space covering (Blatov & Serezhkin, 1997). According to this model, structural groups (molecules in this case) are represented by spheres with different deformability (unlike the close-packing model, in which the molecules are represented by solids of fixed shape). Filling the whole empty space and mutually deforming the soft spheres, ultimately generates convex polyhedra (Voronoi–Dirichlet polyhedra, VDPs), thus forming a normal (face-to-face) partition of space. Once a sphere is circumscribed around each VDP, one can obtain a space covering, *i.e.* the arrangement of solids (intersected spheres in this case), where any point in space belongs at least to one of them. As in packing, a covering can be characterized by the covering coefficient (K_c), which may be calculated as the ratio of the volume of a sphere circumscribed around a VDP to the volume of the whole space. If all structural groups are equivalent to each other, the covering coefficient may be calculated as follows

$$K_c = V_s/V_{VDP}, \qquad (1)$$

where V_{VDP} and V_s are the volumes of a VDP and a sphere circumscribed around it, respectively. A covering with the minimum value of K_c is termed the thinnest. In three-dimensional space, the thinnest covering corresponds to an arrangement of the centers of intersected spheres on a b.c.c. lattice (K_c = 1.46), whereas the close packing of spheres is characterized by a larger value of K_c (2.09). The deformation degree of spheres forming a partition is proportional to the value of their overlapping (V_{os}) after the formation of the appropriate covering of space, since (Blatov & Serezhkin, 1997)

$$V_{os} = V_{VDP}(K_c - 1). \qquad (2)$$

Thus, the minimum value of K_c corresponds to the smallest deformation of soft spheres. Therefore, if the soft structural groups (atoms or molecules) tend to arrange so that the volume of empty space between them is a minimum, according to the principle of maximum filling of space, one can expect that their centroids should arrange on a b.c.c. lattice with coordination number 14 and a VDP in the form of the Fedorov cuboctahedron (truncated octahedron). The '14-neighbour rule' follows from this model (Blatov & Serezhkin, 1997), so that in compounds comprising easily deformable groups, each group tends to surround itself by 14 similar groups. The validity of this rule was proved by the analysis of crystal structures of ∼5000 mononuclear coordination compounds of various compositions (Blatov & Serezhkin, 1997) and of molecular crystal structures of simple substances (Peresypkina & Blatov, 1999).

Thus, there are two basic approaches to the description of the structure of a molecular crystal:

(i) The traditional approach based on the close-packing model of molecules and on the related close-packing model of hard spheres. Within this approach, van der Waals radii of atoms are used to separate a domain of space belonging to a molecule and to find intermolecular contacts together with MCN (Bondi, 1964; Zefirov & Zorky, 1978).

(ii) The approach where VDPs of atoms and inter-dependent models of space partition and space covering are applied for the same purpose. Note that VDPs were first used for the determination of atomic coordination numbers by Frank & Kasper (1958).

In practice the distances between the atoms of adjacent molecules usually deviate from the sum of appropriate van der Waals radii. Therefore, the selection of intermolecular contacts by means of van der Waals radii is rather subjective (Zefirov & Zorky, 1978). If VDPs are used, the presence of an intermolecular contact is determined by the presence of common faces of VDPs of atoms belonging to different molecules. The strength of the contact can be estimated by values of solid angles Ω_i of these faces expressed as a percentage of the whole solid angle (4π sr). The value of Ω_i indicates the presence of an intermolecular contact, if it exceeds the triple error of determination of solid angles ($\sim 1.5\%$) and corresponds to a 'basic' face of VDP (i.e. if it intersects a segment connecting centers of considered atoms; Peresypkina & Blatov, 1999). If there are contacts between a pair of molecules, the relative force of the intermolecular interaction can be estimated by the sum of the solid angles Ω_i, corresponding to these contacts, normalized by the sum of solid angles for all non-valence bonds formed by a central molecule (Ω_Σ), thus

$$\Omega_{\mathrm{mol}} = \sum_i \Omega_i / \Omega_\Sigma \times 100\%. \qquad (3)$$

In this case, a molecule is represented by its '*molecular*' VDP constructed from the VDPs of separate atoms, which can be non-convex (Fig. 2a). If the interior structure of contacting molecules is ignored and only their centroids considered during VDP construction, the VDP obtained will be convex (Fig. 2b) and its shape characterizes the arrangement of molecules around the central one. Therefore, we shall term the VDP constructed in this way as a 'smoothed' molecular VDP. In particular, the number of faces of a smoothed molecular VDP is equal to MCN, and its dimensionless normalized second moment of inertia is

$$G_3 = \left(\frac{1}{3}\right)\left(\int_{\mathrm{VDP}} R^2 \mathrm{d}V_{\mathrm{VDP}}\right) / V_{\mathrm{VDP}}^{5/3}, \qquad (4)$$

where R is the distance between the centroid of a molecule and some point inside the VDP. G_3 characterizes the uniformity of the short-range environment of a molecule, and its degree of sphericity (the sphere has the minimum value of $G_3 = 0.07696$ among all three-dimensional solids; Peresypkina & Blatov, 1999). Note that the Fedorov cuboctahedron and the rhombododecahedron (Figs. 1b and c), corresponding to the arrangements of particles in the models of the thinnest covering and close packing, have a high degree of sphericity

($G_3 = 0.07875$ and 0.07854, respectively). As was shown by Peresypkina & Blatov (1999), the two described methods of MCN determination give similar results in most cases, but only the method using VDPs allows one to make unambiguous conclusions about the MCN value in the case of strongly distorted molecular packing.

To characterize the topology of molecular packing, Peresypkina & Blatov (1999) used VDP constructed from a sublattice of molecular centroids. Hereinafter we shall term this VDP the 'lattice' molecular VDP (Fig. 2c). Although lattice and smoothed molecular VDPs constructed for the same molecule in a given crystal structure can coincide with each other, in general, they are not identical to each other (Figs. 2b and c). A smoothed molecular VDP characterizes the local topology of molecular packing, taking into account only those molecules directly connected. In particular, smoothed molecular VDPs do not always form a partition of space. Lattice molecular VDPs characterize the global topology of a packing as a whole and form a partition of space, but the number of faces of such a VDP is not always equal to MCN
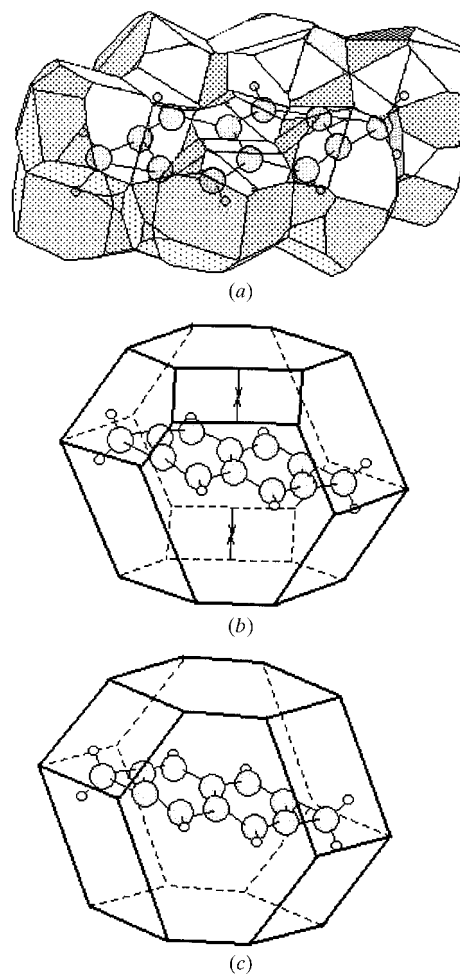

(a)

(b)

(c)

Figure 2
(a) Molecular, (b) smoothed and (c) lattice VDPs of a molecule of dicyclopropanaphthalene (SIWFUZ10). The smoothed VDP (type 14/22-1) can be transformed onto the lattice VDP (type 12/18-1) by 'tightening' two quadrangular faces, as shown by arrows.

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(Figs. 2a–c). The coincidence of these two types of molecular VDPs is usually observed in the case of packing with sufficiently isometric molecules. For instance, in the crystal structures of hexamethylenetetramine (HXMTAM) and the high-temperature modification of adamantane (ADAMAN02) the molecules are arranged according to models of the thinnest covering and close packing of spheres, respectively. Smoothed and lattice molecular VDPs in each of these crystal structures
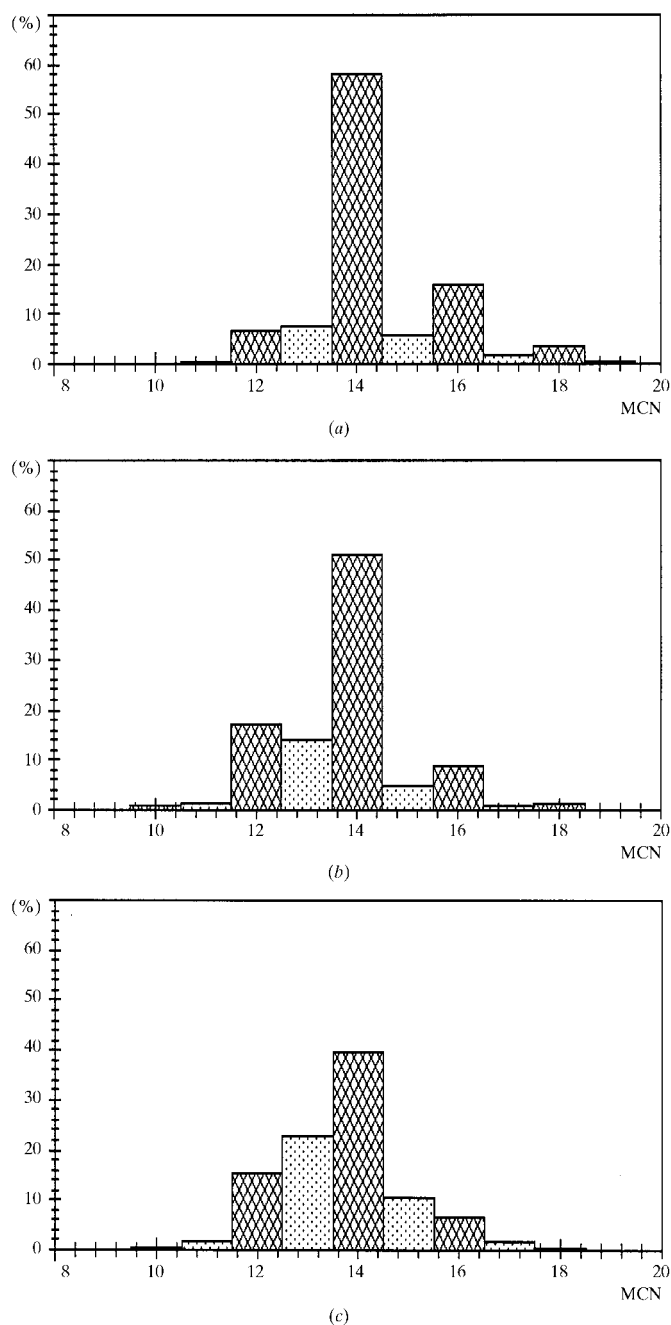

Figure 3
The distribution of MCNs for monosystem crystal structures, calculated considering (a) all intermolecular contacts and (b) only strong intermolecular contacts ($\Omega_{mol} > 1\%$). (c) The distribution of MCNs for the crystal structures containing crystallographically non-equivalent molecules of identical chemical composition, considering only strong intermolecular contacts.

are identical to each other: the Fedorov cuboctahedron and rhombododecahedron, respectively (Figs. 1b and c). Hereinafter the reference codes of compounds in the Cambridge Structural Database are given in brackets. In the low-temperature modification of adamantane (ADAMAN08) the molecular packing still has MCN = 12, but the lattice molecular VDP is the strongly distorted Fedorov cuboctahedron. This fact indicates that near each molecule two additional molecules occur, which are not immediately connected with this molecule (Fig. 1a). In addition to the topological features of lattice molecular VDP, its geometrical characteristics can also be used to analyze the features of molecular packing. In particular, packing (K_p) and covering (K_c) coefficients, calculated as the ratio of the volume of the insphere and circumsphere of the lattice molecular VDP, respectively, to its volume. It should be noted that K_p has a different meaning to the coefficient k used by Kitaigorodskii which characterizes the arrangement of molecular centroids, disregarding the interior structure of molecules. In particular, unlike k, K_p cannot exceed the value 0.7405, corresponding to the arrangement of molecular centroids on the lattice of one of the close packings. If the value of K_c is close to 1.46, the topology of the molecular packing considered is close to the topology of the thinnest covering of space by intersecting spheres. The uniformity of molecular packing is the dimensionless, normalized, second inertia moment of VDP obtained by averaging over lattice molecular VDPs of all Z non-equivalent molecules in a crystal structure and calculated according to the formula

$$\langle G_3 \rangle = \left(\frac{1}{3}\right)\frac{(1/Z)\sum_{i=1}^{Z}\int_{VDP(i)} R^2 dV_{VDP(i)}}{\left\{(1/Z)\sum_{i=1}^{Z} V_{VDP(i)}\right\}^{5/3}}. \qquad (5)$$

In particular, the $\langle G_3 \rangle$ value of a monosystem molecular packing ($Z = 1$) is equal to G_3 of lattice molecular VDP calculated using (4).

Thus, organic crystal chemistry needs to develop a uniform model which can explain the topological features of molecular packings, in particular, different values of MCN. Moreover, it is not known how effective is Kitaigorodskii's model, because it has not been tested with modern crystal structure data. This study was performed to define more exactly the field of applicability and the correctness of the models of close packing, and the thinnest covering to describe the features of molecular arrangements in crystal structures of organic compounds.

2. Experimental

For this investigation 27 886 structures without metals or disordered atoms were taken from the Cambridge Structural Database (1996). Crystal structures incompletely determined and compounds with errors in the experimental data found by the program package *TOPOS* (Blatov et al., 1999) were also omitted. The calculation of MCN for a compound was performed in two steps. First, the presence of interatomic contacts and their type (valent, van der Waals or specific) was

Table 1
MCN distribution for the sample with 23 067 organic compounds.

MCNs occupy no less than 1% of the sample.

Variant of MCN calculation considering all faces of molecular VDP			Variant of MCN calculation considering molecular VDP faces with $\Omega_{mol} > 1\%$		
MCN	Number of compounds	Relative part (%)	MCN	Number of compounds	Relative part (%)
14	13 362	57.9	14	11 809	51.1
16	3618	15.7	12	3921	17.0
13	1733	7.5	13	3209	13.9
12	1536	6.7	16	2000	8.7
15	1360	5.9	15	1107	4.8
18	787	3.4	18	296	1.3
17	398	1.7	11	273	1.1
The range of MCNs = 8–22			The range of MCNs = 6–22		

Table 2
The distribution of smoothed molecular VDPs on the combinatorial–topological types for the sample with 23 067 monosystem organic compounds.

The combinatorial–topological VDP types occupy no less than 1% of the sample. The combinatorial–topological VDP type is written as $f/v - k$, where f and v are the numbers of VDP faces and vertices, respectively, and k is the ordinal number of the VDP type with f and v given.

Variant of MCN calculation considering all faces of molecular VDP			Variant of MCN calculation considering molecular VDP faces with $\Omega_{mol} > 1\%$		
VDP type	Number of VDPs	Relative part (%)	VDP type	Number of VDPs	Relative part (%)
14/24-1	3142	13.6	14/24-1	2778	12.0
14/24-2	1629	7.1	12/20-1	1426	6.2
14/24-3	1072	4.6	14/24-2	1424	6.2
14/24-4	736	3.2	14/24-3	931	4.0
12/20-1	592	2.6	14/24-4	582	2.5
14/24-5	492	2.1	13/22-1	433	1.9
14/24-6	404	1.8	13/22-2	415	1.8
14/24-7	349	1.5	14/24-5	394	1.7
14/24-8	260	1.1	12/20-2	389	1.7
14/22-1	234	1.0	13/22-3	336	1.5
16/28-1	226	1.0	14/24-6	291	1.3
			14/24-7	272	1.2

determined in the crystal structure using the program *AutoCN* (Blatov *et al.*, 1999). The second step involving construction of the molecular VDP, the corresponding smoothed and lattice molecular VDPs, and the calculation of MCN was carried out using the program *ADS* (Blatov *et al.*, 1999). Out of 27 886 compounds, 2477 contained crystallographically different molecules of identical chemical composition and 2342 compounds contained chemically different molecules. This last group was not considered, because the features of packing in their crystal structures depended on differences in the shape and size of non-equivalent molecules. In particular, MCNs of these molecules are frequently too large (up to MCN = 36) or too small (MCN = 4). For instance, in the crystal structure of *N*-benzoylglycyl-L-histidyl-L-leucine pentahydrate (FACCIV10), the tripeptide molecule, being much larger than a molecule of water, has MCN = 35, whereas the water molecules have MCN = 6, 7 or 8. The smallest MCN = 4 is realised for water molecules in the crystal structure of methyl-2-acetamido-2-deoxy-β-D-glucofuranosidono-3,6-lactone

monohydrate (HANNUF). Thus, all conclusions were based on the analysis of two samples, comprising 23 067 monosystem and 2477 polysystem molecular crystal structures, respectively.

3. Results

Our results (Table 1, Fig. 3*a*) show that MCN values in monosystem crystal structures vary in the range 8–22; MCN = 14 is the most frequent and MCN = 16 is next. Other MCN values, including MCN = 12, do not exceed 10% of the sample. 23 067 smoothed molecular VDPs, corresponding to the MCNs determined, are divided into 4555 combinatorial–topological types, and only 11 VDP types are realised frequently enough (for each of them the frequency exceeds 1% of the sample size, Table 2). Among these 11 types seven tetradecahedra and one hexadecahedron are combinatorially similar to the Fedorov cuboctahedron, *i.e.* can be transformed to it by a small number of elementary steps of 'tightening' faces or edges, or 'splitting' edges or vertices (Blatov & Serezhkin, 1997, Figs. 4*a*–*c*), rather than to the rhombododecahedron (1–4 steps rather than 4–8 steps, respectively). The Fedorov cuboctahedron is the most frequent among all VDPs (13.6% of the total amount of VDPs and 23% of all tetradecahedra). Note that almost all frequent smoothed VDPs belong to the so-called general combinatorial–topological types. All their vertices are trihedral (*i.e.* three edges meet at each vertex) and the number of vertices of a VDP (v) depends on the number of faces (f) (Blatov & Serezhkin, 1997)

$$v = 2f - 4. \tag{6}$$

As mentioned by Blatov & Serezhkin (1997), general VDPs are combinatorially stable: their topology does not alter over sufficiently small (for instance, thermal) motions of atoms. VDPs, for which (6) is not fulfilled, are termed special and are usually rare. Thus, the above-mentioned rhombododecahedron is an example of a special combinatorial–topological VDP type. Only one type of tetradecahedron (14/22-1) of all the VDP types given in Table 2 is special (it has two vertices, at each of which four edges meet, Fig. 2*b*), and can be easily transformed either to the Fedorov cuboctahedron or to the rhombododecahedron. The only type of dodecahedron, which gives more than 1% of the total number of VDPs, is a slightly distorted rhombododecahedron (can be transformed by 'tightening' four, usually small, faces to vertices).

To determine the influence of the presence of weak intermolecular contacts on the results of MCN estimation, another calculation which considers only the contacts with $\Omega_{mol} > 1\%$ was performed. As a result, the predominance of MCN = 14 is observed, but with slight changes in the MCN distribution (Table 1, Fig. 3*b*), namely:

(i) the range of MCN values is extended;

(ii) the number of compounds with MCN = 12 and 13 increases sharply;

(iii) the number of compounds with MCN = 14 and 16 decreases.

A similar distribution is also observed in the crystal structures of compounds containing crystallographically non-equivalent molecules of identical composition (Fig. 3c), however, the number of odd values of MCNs is larger compared with the distributions for monosystem crystal structures.

The distribution of smoothed molecular VDPs on combinatorial–topological types obtained without considering weak

Figure 4
Three-stage step-by-step transformation of smoothed VDP (type 14/24-4) for a molecule of 2,2,4,4,6,6-hexaphenylcyclotriphosphazatrien (HPCYPN) onto its lattice VDP (the Fedorov cuboctahedron, type 14/24-1) by (a) 'splitting' an edge into a face, (b) 'tightening' an edge to a vertex and 'splitting' it to another edge, *i.e.* by 'reversing' an edge, and (c) 'tightening' a face into an edge. The arrows show the path of transformation, thin lines indicate the position of edges and faces after the transformation.

molecular interactions also changes compared with results of the exact calculation (Table 2), namely:

(i) the total number of combinatorial–topological VDP types in the sample decreases from 4555 to 3836;

(ii) three types of tridecahedra appear among the most frequent polyhedra;

(iii) the relative part of dodecahedra increases. The VDP type 12/20-1 (a distorted rhombododecahedron) takes second place after the Fedorov cuboctahedron; the VDP type 12/20-2 appears among 12 types of VDPs, giving more than 1% of the sample, increasing by 1.1%;

(iv) the relative part of all tetradecahedra and hexadecahedra decreases.

These changes in the topology of the environment of molecules can be explained by the disappearance of faces of molecular VDPs caused by neglecting weak intermolecular contacts. If a molecule with some atoms connected by such contacts with atoms of a central molecule has other stronger contacts, ignoring the weak contacts yields a decreasing number of faces of the appropriate molecular VDP. In that case, the shape and number of faces of the smoothed molecular VDP should be kept and MCN remains unchanged. If a molecule is connected with the central molecule only by these forgotten weak contacts, this molecule should no longer be considered to be in contact with the central molecule. Therefore, the number of faces of the smoothed VDP of a central molecule and, consequently, the MCN decrease by unity. Thus, considering only strong intermolecular contacts during the MCN calculation results in a decrease in the relative part of the large MCN = 14–22 and an increase in the relative part of the small MCN = 6–13. The decrease of the total number of combinatorial–topological VDP types can be explained by the transformation of some VDP types to other types already presented in the sample, caused by the loss of one or several faces. Since the break or appearance of weak intermolecular contacts can be formally considered a result of the small motion of molecules, neglecting contacts with $\Omega_{mol} > 1\%$ causes the decrease of the number of combinatorially unstable smoothed VDPs with small faces. Thus, the above-mentioned special type 14/22-1 is not included in the list of frequent VDPs, since it is transformed mostly in the dodecahedron 12/18-1 by 'tightening' two small quadrangular faces (Fig. 2b). In some cases, it also loses one or both tetrahedral vertices, for instance, being transformed to a VDP of the type 12/19-1 or 12/20-1. At the same time, the analysis shows that almost all the frequent general types of polyhedra keep the leading position if one considers all or only strong intermolecular contacts. Henceforth, we shall analyze only the results of the analysis of the monosystem molecular crystal structures without considering the weak intermolecular contacts ($\Omega_{mol} > 1\%$).

The rather small number of combinatorially different lattice VDPs (487 types, Table 3) indicates that each type of lattice VDP corresponds to several types of smoothed VDP, the number of which depending on the composition and structure of the molecules packed identically. At the same time, analysis of the distributions of values of geometrical characteristics
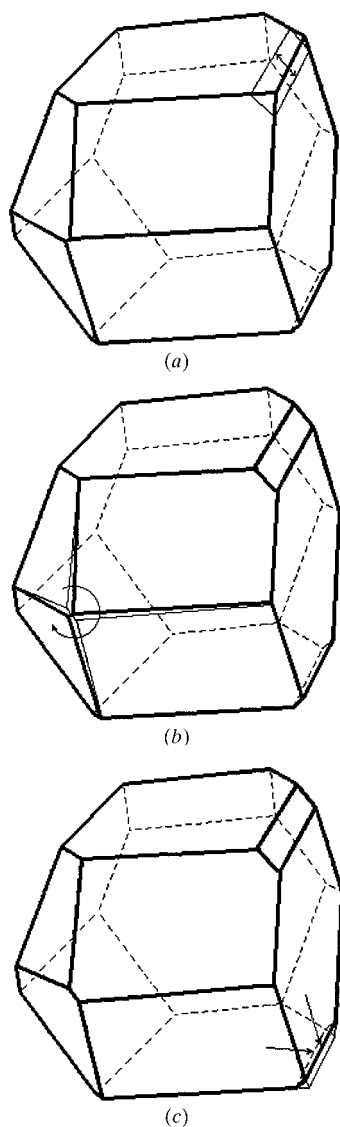
Table 3
The distribution of lattice molecular VDPs on their combinatorial–topological types for the sample with 23 067 monosystem organic compounds.

All faces with $\Omega_{mol} > 1\%$ were taken into consideration during VDP calculation; the VDPs occupy no less than 1% of the sample. See also the headnote to Table 2.

VDP type	Number of VDPs	Relative part (%)
14/24-1	8802	38.2
12/18-1	2756	12.0
14/24-4	2697	11.7
14/24-2	2425	10.5
16/28-2	808	3.5
14/24-7	739	3.2
14/24-8	737	3.2
16/28-3	481	2.1
16/28-4	444	1.9
18/32-1	235	1.0

(K_p, K_c and G_3) of lattice molecular VDPs, relating to the same combinatorial–topological type, shows that there is no unambiguous correspondence between the topology of a polyhedron and its geometrical shape. Moreover, statistically the VDP type can be considered random, because the distributions of K_p or K_c values for any given VDP type and also for a random sample of compounds, corresponding to arbitrary VDP types, are similar to each other and close to the Gaussian (polynomial) distribution with small positive skewness.

As in the models of molecular packing described above where an arrangement of spherical objects is considered explicitly or implicitly, one can expect that these models should correctly describe isometric molecules whose shape is close to spherical. Therefore, 130 structures with quasi-spherical molecules were studied in detail, with a sphericity degree for their lattice molecular VDPs of $0.07854 \leq G_3 \leq 0.07875$. In this case, these VDPs fall between the ideal Fedorov cuboctahedron and the ideal rhombododecahedron, depending on the degree of deviation from a sphere. The values of K_p for quasi-spherical molecules also form a pseudo-Gaussian distribution with small positive skewness and vary in the range 0.56–0.74. The average $\langle K_p \rangle = 0.66$ is closer to the value characteristic of the thinnest covering (0.6802) than to the value typical of close packing (0.7405). Only five compounds of the whole sample with completely solved crystal structures may be described by an undistorted close packing of spheres, namely acetylene (ACETYL02), hexaaminobenzene (ZZZWOU01), hexachlorocyclohexane (HCCYHB), congressane (CONGRS) and dodeca-(dimethylamino)-cyclohexaphosphazahexaene (PNDMAM10, see Figs. 5a–e). The values of K_c in the sample considered form a similar distribution within the range 1.46–2.09, with a mean of 1.72. One can see that the values of K_c for quasi-spherical molecules lie within the range limited by the typical values of the thinnest covering and close packings. The value $K_c = 2.09$, characteristic of close packing, corresponds to the five aforementioned compounds with $K_p = 0.74$. The ideal covering with $K_c = 1.46$ corresponds to molecules of only three compounds, namely, hexamethylenetetramine, dodecamethyl-hexasila-tetrapho-

spha-adamantane (HMSIPA) and dodecamethyl-hexasila-tetraarsa-adamantane (MESIAD), see Figs. 1(b) and 6(a)–(c).

(a)

(b)

(c)

(d)

(e)
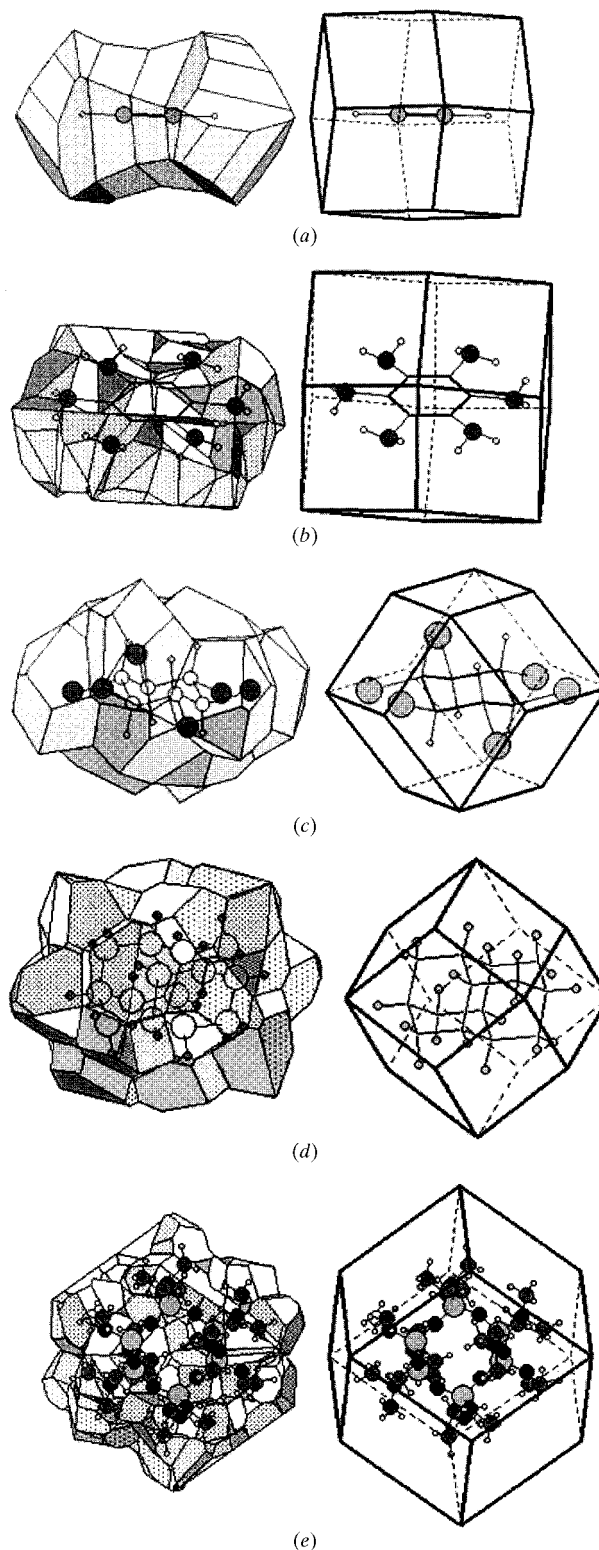
Figure 5
Molecules with packing topologically equivalent to a close packing of hard spheres: (a) acetylene, (b) hexaaminobenzene, (c) hexachlorocyclohexane, (d) congressane and (e) dodeca(dimethylamino)cyclohexaphosphazahexaene, represented as molecular (left) and lattice molecular (right) VDPs.

It should be noted that there is no strict correspondence between the coefficients of packing and covering, although there is correlation between their values. For instance, the range K_p = 0.575–0.680 corresponds to the packings of hexamethylenetetramine (HXMTAM), tetracyanomethane (TCYMET), trimethylamineboran (ZZZVPE01), 3,7,10-triaza-2,4,6,8,9,11-hexasilabicyclo(3.3.3)undecane (LEBWIY) and 2,6,15-trithia(3–4,10–7)-metacyclophane (VAMMEB), see Figs. 7(a)–(d), with $K_c \simeq$ 1.46–1.47.

4. Discussion

The results obtained do not confirm Kitaigorodskii's assumption that MCN = 12 is preferable for molecular crystals of organic compounds and allow the predominance of MCN = 14 to be discussed. According to the model of thinnest
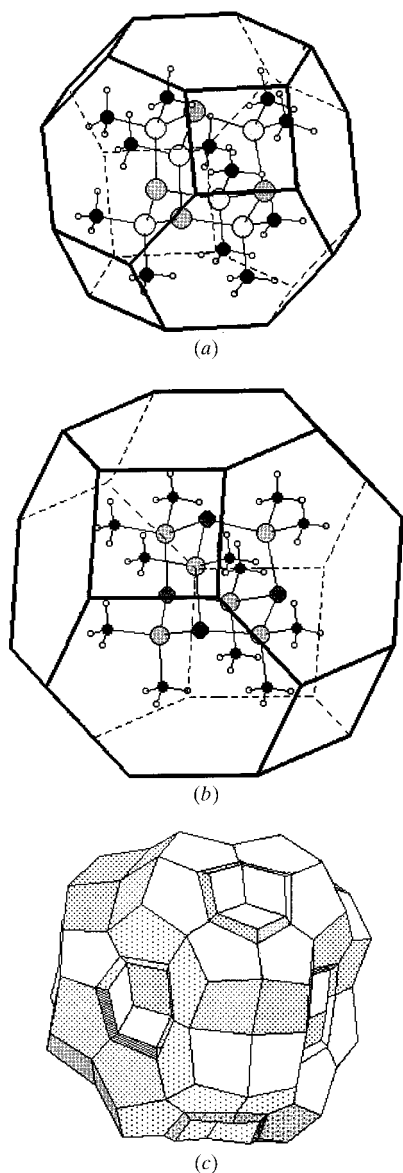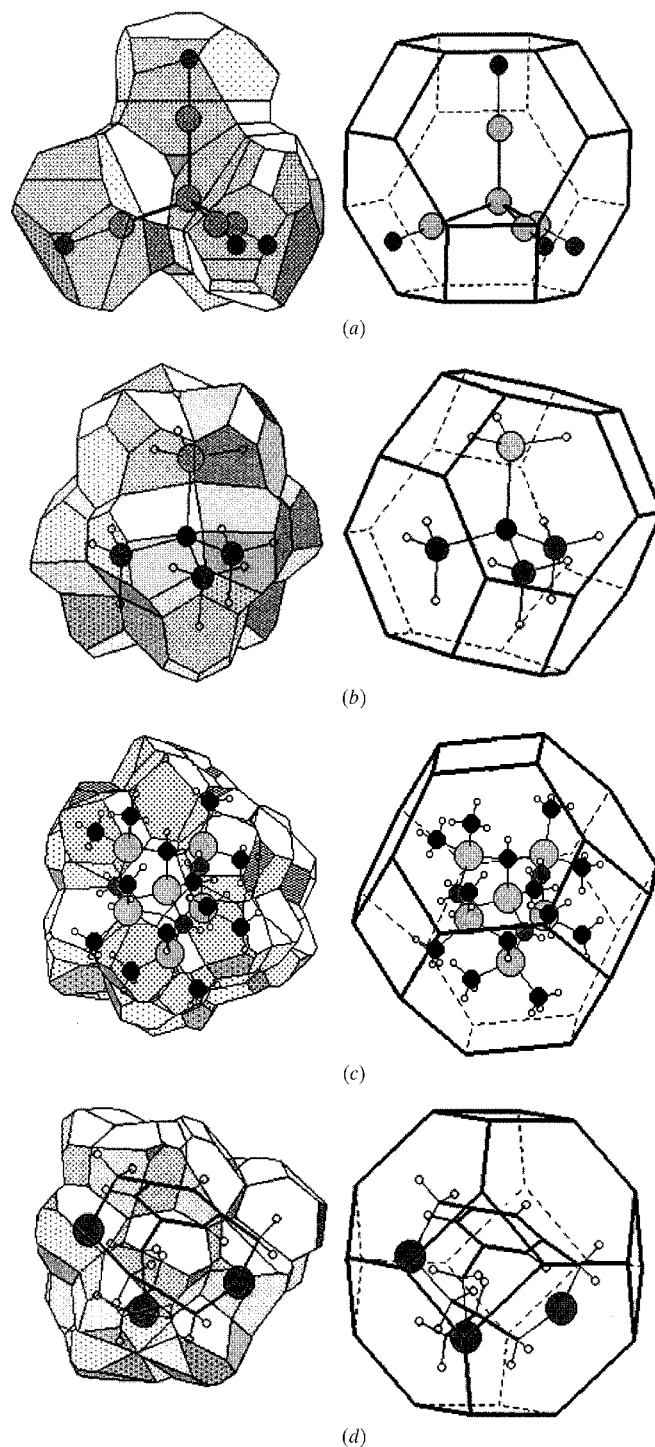

Figure 6
The molecules of compounds, whose packing corresponds to the ideal covering of space, represented as their lattice VDPs: (a) dodecamethyl-hexasila-tetraarsa-adamantane; (b) dodecamethyl-hexasila-tetrapho-spha-adamantane. Both molecules have topologically similar molecular VDPs (c).

Figure 7
Molecular (right) and lattice molecular (left) VDPs of molecules of (a) tetracyanomethane, (b) trimethylaminoborane, (c) 3,7,10-triaza-2,4,6,8,9,11-hexasilabicyclo(3.3.3)undecane and (d) 2,6,15-trithia(3–4,10–7)-metacyclophane.

covering, this fact indicates that most of the molecules in the crystal structures investigated are essentially deformed. Evidently, most of the real molecules are not absolutely hard or absolutely soft; they have a different degree of hardness. To consider the molecules from this point of view, let us accept the coefficient of covering its lattice VDP as a measure of hardness (softness). For quasi-spherical molecules ($G_3 \leq 0.07875$) the values of this criterion vary in the range $1.46 \leq K_c \leq 2.09$; the greater value of K_c the harder the molecule. It should be emphasized that one should consider the 'softness' of a molecule not only as a deformity, but also as a degree of deviation from the spherical shape, because the asphericity of a molecule stipulated by its structure features can be considered as a result of the 'deformation' of a hypothetical isomer of spherical shape. For instance, the molecule of hexamethylenetetramine can be considered as 'soft', although, evidently, it has a similar deformity to the adamantane molecule of similar shape (Figs. 1a and b). At the same time, in comparison to adamantane, it is already 'distorted' because four methine groups are substituted on the smaller N atoms. However, packing with $K_c \simeq 1.46$ is more often formed by molecules,

which can be represented as hard quasi-spherical nuclei wrapped in an outer layer of voluminous and easily deformable groups such as the aforementioned adamantane derivatives (HMSIPA, MESIAD). In other cases the outer layer is not dense enough and allows the penetration of adjacent molecules according to the 'bumps and hollow' principle as, for instance, in tetracyanomethane molecules (TCYMET, Fig. 7a), whose packing is characterized by the values $K_p = 0.66$, $K_c = 1.47$ and MCN = 14. The molecule of pentaerythritol (PERYTO, Fig. 8) should be considered as 'hard', because its exterior surface is formed by slightly deformable hydroxyl groups. The packing of pentaerythritol molecules is characterized by $K_p = 0.73$, $K_c = 2.06$ and MCN = 12. The trans-1,4-dichloro-1,4-dinitrosocyclohexane molecule (BOCNOW, Fig. 9) has an intermediate degree of hardness. The large substituents located on different sides of the conventional plane of the cyclohexane ring make its motion rather difficult, but not enough to forbid some deformation. In this case the covering and packing coefficients are equal to 1.74 and 0.70, respectively, MCN = 14, where the smoothed molecular VDP is the Fedorov cuboctahedron. For comparison, the voluminous substituents at C atoms in the hexachlorocyclohexane molecule (HCCYHB) make the motion of a molecule so difficult that it behaves as a hard sphere in terms of the packing topology (Fig. 5c). Taking into consideration that the shape of the overwhelming majority of molecules in the sample is far from spherical, one can assume that the model of the thinnest covering should be realised for crystals of organic compounds much more often than the close-packing model. This hypothesis explains the predominance of MCN = 14 in the whole range of G_3 values for the molecules of an arbitrary shape.

The Fedorov cuboctahedron is the most frequent among lattice molecular VDPs (Table 3). The difference in relative parts of the polyhedra in the form of the Fedorov cuboctahedron among smoothed (12.0%) and lattice (38.2%) molecular VDPs shows that there are rather effective coverings, whose local topology differs from the topology of the thinnest covering. Evidently, their occurrence is caused by the asphericity of molecules. For the combinatorial types listed in Table 2, the frequency dependence of lattice molecular VDPs of a given type on their degree of sphericity (and, therefore, the sphericity of appropriate molecules), expressed by G_3, indicates the predominance of Fedorov cuboctahedron VDPs in the G_3 values where there are lattice molecular VDPs in an overwhelming majority of molecules (Fig. 10a). The minimum G_3 value of the sample is 0.07854, with a maximum of
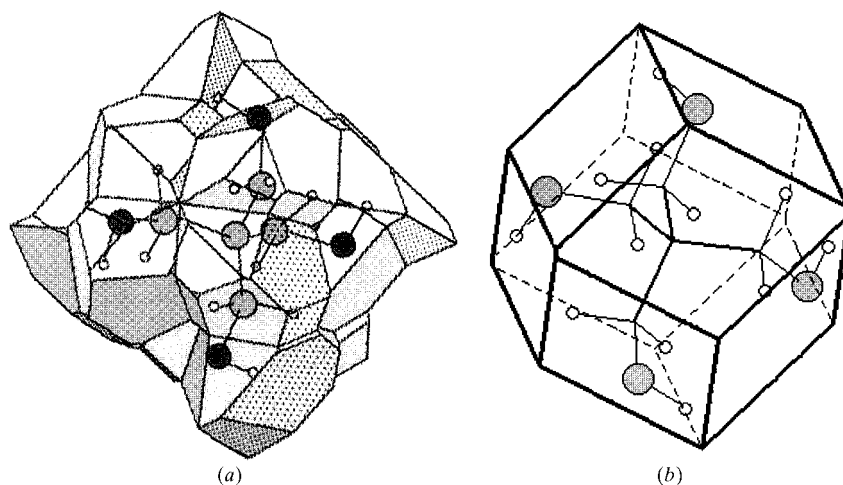

(a)   (b)

Figure 8
(a) Molecular and (b) lattice molecular VDPs of the pentaerythritol molecule.

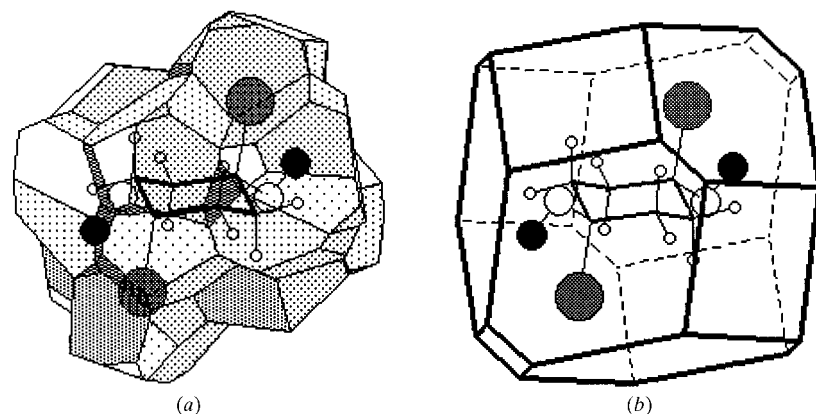(a)   (b)

Figure 9
(a) Molecular and (b) lattice molecular VDPs of the trans-1,4-dichloro-1,4-dinitrosocyclohexane molecule.

0.58898 [for the lattice VDP of dimers of octadecanoic acid (STARAC07, Fig. 11)]. In this case, 97% of all lattice VDPs are characterized by G_3 varying from 0.07854 to 0.11000. At the minimum G_3 value all lattice molecular VDPs are Fedorov cuboctahedra. At increasing G_3 (decreasing the uniformity of crystal structure, because in this case $\langle G_3 \rangle = G_3$) the number of VDPs of a given type decreases (Fig. 10a). Within the range $0.07854 \leq G_3 \leq 0.07875$, conventionally accepted for quasi-spherical molecules, the Fedorov cuboctahedron is much more frequent than lattice VDPs of any other type, which does not exceed 20% (Fig. 10b). In the range corresponding to non-spherical molecules the number of lattice VDPs of the Fedorov cuboctahedron decreases, but yields no other type.

It was mentioned above that the ideal close packings or the thinnest coverings are scarcely realised in molecular packings. How can we explain the fact that the Fedorov cuboctahedron is the most frequent lattice VDP, but the rhombododecahedron is so rare that in the sample studied only 18 lattice VDPs of this type were found? It is of interest that all 18 rhombo-dodecahedra have $G_3 \leq 0.08250$ and nine of them have $G_3 = 0.07875$, i.e. are ideal (they correspond to close packings in the crystal structures of various modifications of the five compounds mentioned above). At the same time the range of G_3 values, where the Fedorov cuboc-tahedron exists, is much wider. The minimum G_3 value of the sample corresponds to the ideal Fedorov cuboctahedron and the maximum value ($G_3 = 0.58898$) also corresponds to this VDP type, although it is strongly distorted (Fig. 11). At least two aspects cause such a rare frequency of rhombododecahedra. Firstly, the narrow G_3 range where the rhombododecahedron exists is stipulated by its combinatorial instability, because it is a special VDP. With an arbitrarily small motion of molecular centroids, the tetrahedral vertices can be split onto two vertices, so that the combinatorial properties of the VDP changes. Therefore, a rhom-bododecahedron can deform without changing the topology in only high-symmetry crystal struc-tures, where all molecules of one packing type move coherently. Secondly, a rhombododecahedron is infrequent even in the packing of quasi-spherical molecules ($G_3 \leq 0.07875$), because it has the maximum covering coefficient ($K_p < 2.09$ for all other combinatorial VDP types found with $G_3 \leq 0.07875$). Therefore, a close packing can be considered as the 'worst' covering among all sufficiently uniform arrangements of molecules, so it can only be realised for hard quasi-spherical molecules. At the same time the K_p value, corre-sponding to the thinnest covering, is insignificantly 'worse' than the maximum K_p value; therefore, the Fedorov cuboctahedron can describe the packing topology of
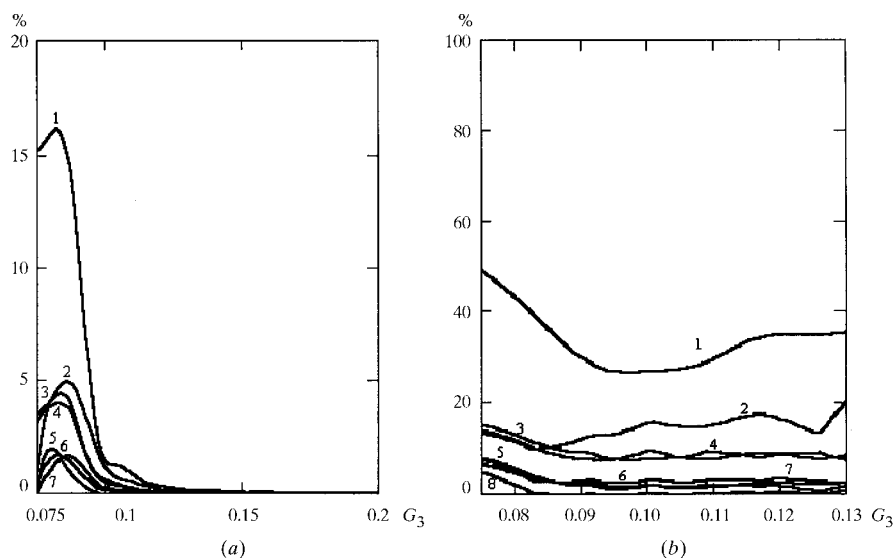

Figure 10
(a) Amount of the most frequent lattice molecular VDPs (in percentage of the sample), depending on their sphericity degree. The curves 1–7 characterize the parts of the VDP types 14/24-1 (the Fedorov cuboctahedron), 12/18-1 (with hexagonal faces), 14/24-2, 14/24-4, 14/24-7, 14/24-8 and 16/28-2 in the sample, respectively. (b) Relative parts of the most frequent lattice molecular VDPs (of the amount of VDPs with a given G_3 value), depending on their sphericity degree. The curves 1–8 characterize the parts of the VDP types 14/24-1 (the Fedorov cuboctahedron), 12/18-1 (rhombododecahedron with hexagonal faces), 14/24-2, 14/24-4, 14/24-8, 16/28-2, 14/24-7 and 12/14-1 (rhombododecahedron) in the sample, respectively.
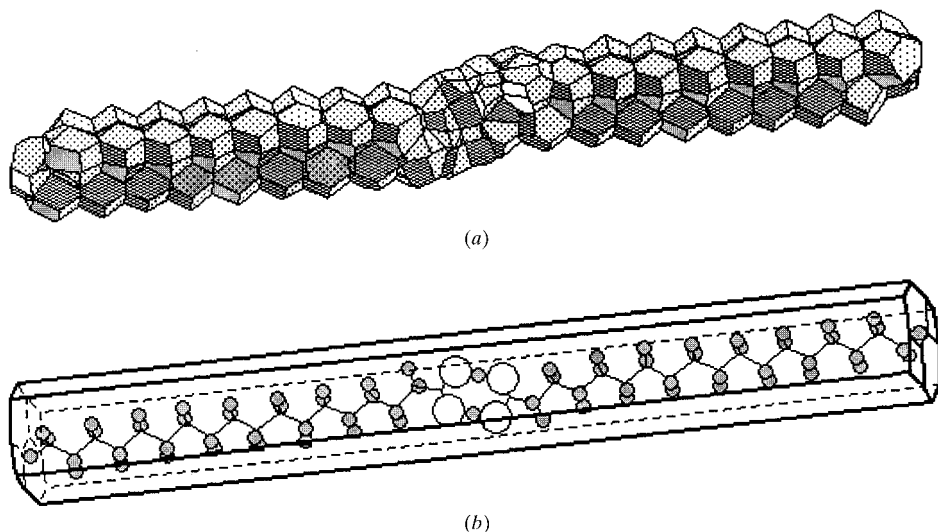

Figure 11
(a) Molecular and (b) lattice molecular VDPs of a dimer of octadecanoic acid.

many molecules with intermediate hardness or softness. With an arbitrary arrangement of molecules, the Fedorov cuboctahedron is likely to predominate over other lattice VDP types owing to its higher frequency. The regular Fedorov cuboctahedron has 14 rather large faces with little difference in area, therefore, it could be considered as being combinatorially stable, *i.e.* being able to keep its combinatorial properties under the motions of the crystal structure over wider limits compared with lattice VDPs of other types. This explains the difference in ratios of VDP types at small and large G_3 values (Figs. 10*a* and *b*). The sample of quasi-spherical molecules is characterized by the rather large number of lattice VDPs with the combinatorial properties of the Fedorov cuboctahedron. The more significant the deviations of sphericity, for a set of molecules whose centroids are arranged on a b.c.c. lattice, the more probable the presence of small VDP faces. The presence of small faces of the VDP disturbs its combinatorial stability, because these faces and the corresponding weak intermolecular contacts can easily disappear by distorting the crystal structure. With large G_3 values the Fedorov cuboctahedron becomes combinatorially less stable, its frequency in the sample of lattice molecular VDPs decreases, but remains the most frequent (Fig. 10*b*). Thus, in the range of G_3 values which corresponds to the majority of molecules, the VDPs with the combinatorial properties of the Fedorov cuboctahedron are the most favorable statistically and, consequently, a molecule of 'random' shape prefers this type of VDP. Therefore, it is the combinatorial stability of the Fedorov cuboctahedron that results in advantages for the model of the thinnest covering of space over the close-packing model of spheres for the description of organic compounds containing molecules of an arbitrary shape and hardness.

5. Conclusions

The results of this study show that the topological properties of molecular VDPs (namely, MCN or combinatorial propererites), used as the main characteristics of molecular packing in the papers cited previously, have a random nature and are not directly related to the physical characteristics of molecules. The use of the geometrical parameters of VDP (G_3, K_p and K_c), which do not strictly correlate with the topological properties of VDP, is physically more valid. In particular, the occurrence of MCN = 12 does not yet indicate the close packing of molecules, because the K_p value can be small enough. Similarly, *vice versa*: MCN = 14 does not allow one to state unambiguously that the packing of molecules cannot be described with the close-packing model; it is necessary to take account of the K_c value. Certainly, in some classes of organic compounds, whose molecular packings are characterized by a narrow range of variation of geometrical characteristics of molecular VDPs, the topological changes of the molecular environment allow one to catch fine effects of structure reorganization. A typical example is the aforementioned change in the number of faces of the lattice molecular VDP at the transition between the low- and high-temperature modifications of adamantane. A more detailed investigation of this problem is the subject of further research.

References

Blatov, V. A. & Serezhkin, V. N. (1997). *Acta Cryst.* A**53**, 144–160.
Blatov, V. A., Shevchenko, A. P. & Serezhkin, V. N. (1999). *J. Appl. Cryst.* **32**, 377.
Bondi, A. (1964). *J. Phys. Chem.* **68**, 441–451.
Cambridge Structural Database (1996). Version 5.11. Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, England.
Fischer, W. & Koch, E. Z. (1979). *Z. Kristallogr.* **150**, 245–260.
Frank, F. C. & Kasper, J. S. (1958). *Acta Cryst.* **11**, 184–190.
Kitaigorodskii, A. I. (1973). *Molecular Crystals and Molecules.* New York: Academic Press.
Peresypkina, E. V. & Blatov, V. A. (1999). *J. Mol. Struct. (Theochem.)* **489**, 225–236.
Vainshtein, B. K., Fridkin, V. M. & Idenbom, V. L. (1983). *Modern Crystallography.* Vol. 2, Berlin: Springer-Verlag.
Wells, A. F. (1986). *Structural Inorganic Chemistry.* Oxford: Clarendon Press.
Zefirov, Yu. V. & Zorky, P. M. (1978). *Vestn. MGU*, **19**, 554–558.
Zefirov, Yu. V. & Zorky, P. M. (1995). *Usp. Khim.* **64**, 446–461.