Y surfaces. It had not been realized that in both cases the inherent symmetry of the surfaces is higher, namely $Im\bar{3}m$–$Pm\bar{3}m$ and $Pn\bar{3}m$–$Fd\bar{3}m$, respectively. As a consequence, $C(S)$ surfaces are in fact P surfaces and Y surfaces are in fact D surfaces (*cf.* Koch & Fischer, 1992).

Fig. 1 shows a skew octagon with site symmetry $\bar{4}$..–2.. as was used for the generation of $C(S)$ surfaces. The octagon is subdivided by straight lines into eight congruent skew quadrangles and each of these quadrangles represents a generating polygon of a P surface as described, for example, in Table 2 of Fischer & Koch (1987). In fact, inspection of a model of the $C(S)$ surface shows the additional straight lines that form the boundaries of the small quadrangles.

Fig. 2 displays a skew hexagon with site symmetry ..2–..2 as was applied to derive the Y surfaces. The indicated subdivision yields eight congruent skew quadrangles, each of which can be used to generate a D surface (*cf.* Table 2 of Fischer & Koch, 1987).

The genus of the $C(S)$ and Y surfaces was stated to be 9 in previous papers (see, for example, Koch & Fischer, 1988; Fischer & Koch, 1989), whereas P surfaces as well as D surfaces have genus 3. The difference of these values is caused by the different sizes of the primitive unit cells of H_i and H_g. As the following diagrams show, the primitive unit cell of H_g is four times the size of H_i in both cases.

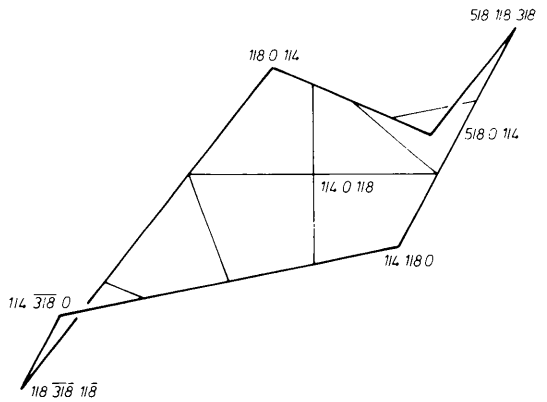

Fig. 2. Skew hexagon with site symmetry ..2–..2 subdivided into eight congruent skew quadrangles forming generating polygons of a D surface. The coordinates of the centre and the vertices of the hexagon refer to a conventional description of $I4_132$.

P surface:

$$\begin{array}{ccc} Im\bar{3}m(a) & - & Pm\bar{3}m(a) \\ \vert\,2 & & \vert\,2 \\ Pm\bar{3}n(a) & - & Pm\bar{3}(a) \\ \vert\,4 & & \vert\,4 \\ Ia\bar{3}d(2a) & - & Ia\bar{3}(2a) \end{array}$$

D surface:

$$\begin{array}{ccc} Pn\bar{3}m(a) & - & Fd\bar{3}m(2a) \\ \vert\,2 & & \vert\,2 \\ P4_232(a) & - & F4_132(2a) \\ \vert\,4 & & \vert\,4 \\ I4_132(2a) & - & P4_332(2a) \end{array}$$

An enlargement of the unit cell by a factor of n results in a change of the genus g to

$$g_n = 1 + n(g-1)$$

as shown earlier (Fischer & Koch, 1989). The values $n = 4$ and $g = 3$ (the genus of P and D surfaces) yield $g_n = 9$, the incorrectly stated genus of $C(S)$ and Y surfaces.

For all minimal balance surfaces known so far it has been checked that a similar error does not occur.

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Acta Cryst. (1993). A**49**, 210–212

Kitajgorodskij's categories.

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(*Received* 17 *June* 1992; *accepted* 22 *July* 1992)

Abstract

To a close approximation, the relative frequency of the space groups of molecular organic compounds is determined by ease of packing. Kitajgorodskij, with molecular organic structures in mind, divided the space groups of the triclinic, monoclinic and orthorhombic systems into four categories: 'closest-packed', 'limitingly close-packed', 'permissible' and 'impossible' [Китайгородский (1955). Органическая Кристаллохимия. Москва: Изд. Акад. Наук; Engl. transl: Kitaigorodskii (1961). *Organic Chemical Crystallography*. New York: Consultants Bureau]. Empirically, about a dozen of the 'impossible' space groups are not rare and several of them (Pc, $P2/c$, $C222_1$, $Fdd2$ and possibly other orthorhombic groups) can be recategorized as 'permissible' on Kitajgorodskij's own criteria. In addition, certain space groups (notably $C2/c$ and $Pbca$) requiring inherent molecular symmetry for close packing in

0108-7673/93/010210-03$06.00

Table 1. *The space groups of the triclinic and monoclinic crystal systems arranged in accordance with Kitajgorodskij's categories*

Revisions are indicated by placing the space-group symbol in round brackets in its original position and in square brackets in its new position. The superscript numerals give the number of examples found with the number of formula units (Z) appropriate for the molecular symmetry indicated.

Category	Molecular symmetry	$1P$	$\bar{1}P$	$2P, 2C$	mP, mC	$s/mP, 2/mC$
Closest-packed	1		$P\bar{1}^{5946}$	$P2_1^{2552}$		$P2_1/c^{13131}$
						$[C2/c^{1456}]$
	$\bar{1}$		$P\bar{1}^{1477}$			$P2_1/c^{2658}$
	$\bar{1}$ or 2					$C2/c^{1626}$
Limitingly close-packed	$2/m$					$C2/m^{107}$
Permissible	1	$P1^{189}$		$C2^{260}$	$[Pc^{138}]$	$[P2/c^{74}]$
					Cc^{371}	
	2			$C2^{87}$		$[P2/c^{66}]$
	m				Cm^{18}	$P2_1/m^{215}$
Impossible				$P2^3$	Pm^1	$P2/m^0$
					(Pc)	$(P2/c)$

Kitajgorodskij's categorization may also be placed in the category allowing close packing for molecules in general positions; in such cases both enantiomers may be required.

Kitajgorodskij (Китайгородский, 1955; Kitaigorodskii, 1961) has divided the space groups of the triclinic, monoclinic and orthorhombic systems into four categories, which he called (i) 'closest-packed', (ii) 'limitingly close-packed', (iii) 'permissible' and (iv) 'impossible'. The categorization was based on a group-by-group analysis of the possibilities of (a) forming close-packed layers of molecules and (b) close-stacking the layers. Certain types of close or nearly close packing required that the molecules should possess and use inherent symmetry. From his analysis he expected that the frequencies of occurrence of the space groups would decrease in the order (i) > (ii) > (iii) > (iv), the last being 'impossible'.

This categorization has proved very successful in broad outline, but there are about a dozen anomalies. These are of two types. The first is 'impossible' space groups with a hundred or more examples; the second is space groups with many examples of molecules in general positions but for which the categorization would admit only molecules possessing and using some inherent symmetry. For the 'impossible' space groups, Kitajgorodskij's treatment of $P1$ may be applicable. This is categorized [Китайгородский (1955, p. 119); Kitaigorodskii (1961, p. 95)] as 'permissible (unlikely)' [Группа $P1 = C_1^1$ принадложит к допустиным (маловероятным)] without discussion, but the implicit argument on preceding pages seems to be that close-packed layers of molecules are possible in this space group but that the layers cannot be densely stacked unless the molecules are of suitable shape - for example, flat on both top and bottom. The space group is thus 'permissible' for molecules of such shape. There seems to be no reason why this argument should not be equally applicable to the space groups Pc and $P2/c$, thus transferring them from 'impossible' to 'permissible'.

Table 2. *The space groups of the orthorhombic crystal system arranged in accordance with Kitajgorodskij's categories*

Revisions are indicated by placing the space-group symbol in round brackets in its original position and in square brackets in its new position. The superscript numerals give the number of examples found with the number of formula units (Z) appropriate for the molecular symmetry indicated.

(a) Geometric class 222

Category	Molecular symmetry	$222P$	$222C$	$222F$	$222I$
Closest-packed	1	$P2_12_12_1^{5410}$			
Limitingly close-packed	1	$[P2_12_12^{114}]$			
	2	$P2_12_12^{69}$			
	222		$C222^0$	$F222^0$	$I222^3$
Permissible	1	$(P2_12_12)$	$[C222_1^{27}]$		
	2		$[C222_1^{33}]$		
Impossible		$P222^1$			$I2_12_12_1^1$
		$P222_1^1$	$(C222_1)$		

(b) Geometric class mm

Category	Molecular symmetry	$mm2P$	$mm2C$ ($2mmC$)	$mm2F$	$mm2I$
Closest-packed	1	$Pca2_1^{289}$			
		$Pna2_1^{148}$			
Limitingly close-packed	m	$Pmc2_1^7$	$Cmc2_1^{71}$		
	mm			$Fmm2^6$	
Permissible	2		$C2cb^{32}$	$[Fdd2^{99}]$	
	m	$Pmn2_1^{36}$	$C2cm^6$		$Ima2^3$
Impossible		$Pmm2^0$	$Cmm2^0$	$(Fdd2)$	$Imm2^0$
		$Pcc2^1$	$Ccc2^4$		$Iba2^{39}$
		$Pma2^2$	$C2mm^3$		
		$Pnc2^2$	$C2mb^1$		
		$Pba2^3$			
		$Pnm2^3$			

(c) Geometric class mmm

Category	Molecular symmetry	$mmmP$	$mmmC$	$mmmF$	$mmmI$
Closest-packed	1	$[Pbca^{1798}]$			
	$\bar{1}$	$Pbca^{268}$			
Limitingly close-packed	1	$[Pbcn^{158}]$			
	2	$Pbcn^{278}$			
	m	$Pnma^{673}$			
	$2/m$		$Cmca^{35}$		
	mm	$Pmma^0$			
		$Pmmn^{11}$			
	mmm		$Cmmm^0$	$Fmmm^1$	$Immm^0$
	222		$Ccca^8$		
Permissible	1	$(Pbca)$			
		$[Pccn^{96}]$			
	$\bar{1}$	$Pccn^{90}$			
	m	$Pbcm^{44}$			
	$2/m$	$Pbam^1$			
Impossible		$Pmmm^0$	$Cmcm^{43}$	$Fddd^{17}$	$Ibam^{21}$
		$Pnnn^2$	$Cccm^2$		$Ibca^3$
		$Pccm^0$	$Cmma^1$		$Imma^4$
		$Pban^2$			
		$Pnna^{28}$			
		$Pmna^5$			
		$Pcca^{18}$			
		$Pnnm^{18}$			

For the second type of anomaly, space groups having many examples with molecules in general positions but categorized as requiring the molecules to possess and use inherent symmetry, Kitajgorodskij's argument may be taken a stage further. From a purely formal standpoint, if two molecules in general positions are related by a symmetry element, the resultant is a structural dimer with the symmetry postulated by Kitajgorodskij. If the two molecules form a dimer in a chemical as well as a structural sense, so much the better for the packing. Space groups placed by Kitajgorodskij in categories requiring molecules with inherent symmetry may thus also be placed in categories permitting molecules in general positions; in such cases both enantiomers may be required. Such recategorization immediately removes two serious anomalies; $C2/c$ and *Pbca* (merely 'permissible') become 'closest-packed' [(i)] for molecules in general positions. Kitajgorodskij, in fact, uses an argument similar to this in discussing multilayer structures [Китайгородский (1955, p. 129); Kitaigorodskii (1961, p. 105)] but apparently did not realize its implications for the categorization of space groups.

The categorization of the triclinic and monoclinic space groups is given in Table 1. Alterations in the light of the arguments are enclosed in square brackets; if a space group is transferred, its original position is indicated in round brackets. The table also gives (as superscripts) the number of examples of the space group with the number (Z) of formula units in the unit cell appropriate for the molecular symmetry indicated, as recorded in the Cambridge Crystallographic Data File (Allen, Kennard & Taylor, 1983) in January 1992; for the 'impossible' space groups the total number of examples is given without regard to Z. Disordered *etc.* structures were excluded, as in previous work (Wilson, 1988, 1990, 1991). It will be seen that after the recategorization the agreement is good; space groups categorized as 'closest-packed' have thousands of examples; those categorized as 'limitingly close-packed' or 'permissible' (except *Cm*) have hundreds; and 'impossible' have very few.

The space group $C2/c$ has been badly served by the translators. The Russian text (p. 121) reads: Группа $C2/c = C_{2h}^6$ для молекул в частом положении с симметрией $\bar{1}$ плотнейшая, а для молекул в частом положении с симметрией 2 – предельно плотная. This means: The group $C2/c = C_{2h}^6$ is closest-packed for molecules with symmetry $\bar{1}$ and limitingly close-packed for molecules with symmetry 2. The translation [Kitaigorodskii (1961, p. 97)] has exactly reversed the meaning. It is not readily possible to divide the 1626 examples of $C2/c$ using molecular symmetry into those with symmetry $\bar{1}$ (closest-packed) and those with symmetry 2 (limitingly close-packed) without consulting the original publications. A check of these in recent volumes of *Acta Crystallographica*, Section C, showed that symmetry 2 out-numbered symmetry $\bar{1}$ by about two to one. It is not possible to say whether this reflects better packing with symmetry 2 or a greater number of molecules with the required symmetry.

The categorization of the orthorhombic space groups is given in Table 2. The recategorization of *Pbca* as 'closest-packed for molecules in general positions' has removed the greatest anomaly. Other orthorhombic space groups that occur too frequently for their category are $C222_1$ and *Fdd*2. The first is categorized as 'impossible' because 'permissible' layers are stacked by twofold axes. However, $P2_12_12$ has closest-packed layers stacked by twofold axes but is nevertheless categorized as 'permissible'. It is therefore reasonable to transfer $C222_1$ to 'permissible'. The space group *Fdd*2 is categorized as 'impossible' because it involves quadruple layers and 'multilayer structures are exceptionally rare', although the layers themselves are 'permissible'. In other words, the categorization was based on the structures known in 1955, not on basic theory, and in 1992 it may be recategorized as 'permissible'. There remain a few space groups (*Iba*2, *Pnna*, *Pcca*, *Pnnm*, *Cmcm*, *Fdd*, *Ibam*) categorized as 'impossible' but having 17 to 43 examples. These have not been considered in detail.

In later publications (for example, Kitaigorodsky, 1973), Kitajgorodskij discussed the relative frequency of space groups from a somewhat different standpoint and without specific reference to the four categories. His conclusions relating to the commonest space groups were not affected but the 'impossible' space groups were not considered and he also concluded that the use of molecular symmetry *mmm* would be very improbable. Table 2 shows that, empirically, molecular symmetry 222 is rare.

I am indebted to Professors Carolyn Brock, Jack Dunitz and Theo Hahn and Dr Peter Wheatley for helpful discussion.

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