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A database survey of molecular and crystallographic symmetry

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The point of contact between molecular and crystallographic symmetries is that of the Wyckoff position, the position at which a molecule resides in a crystal structure. These Wyckoff positions may have the same symmetry as the molecules, some symmetry in common with the molecules or no symmetry at all. Using CSDSymmetry [Yao *et al.* (2002). *Acta Cryst*. B**58**, 640–646], a relational database containing information pertaining to the symmetry of molecules and the crystal structures that play host to them, the distribution of molecules over Wyckoff positions and the occupancy of Wyckoff positions in crystal structures is presented. Analysis of these data has led to the characterization of some relationships between molecular and crystallographic symmetry.

1. Introduction

The elucidation of relationships between space-group symmetry and molecular symmetry has occupied pioneering members of the crystallographic community for many years. The number of crystal structures available to study continues to increase rapidly and the temptation to find the guiding principles of molecular aggregation remains. There is no doubt that the ability to predict crystal structures given the molecular building blocks is a goal that has assumed ‘holy grail’ significance.

The first papers concerning space-group frequencies were published in the 1940s (Nowacki, 1942, 1943), when only a few hundred crystal structures were known. The field of symmetry relationships took a great leap forward with the publication of Kitaigorodskii’s book *Organic Chemical Crystallography* (Kitaigorodskii, 1961), in which he presented his principles concerning the close packing of molecules. Kitaigorodskii proposed that popular space groups would be those that provided good conditions for the close packing of molecules, taking into consideration the role that molecular symmetry could play. As noted by Brock & Dunitz (1994) in their review of molecular and crystallographic symmetry relationships, Kitaigorodskii’s predictions concerning space-group frequencies for symmetric and asymmetric molecules have proved ‘remarkably accurate’. The growth of crystallographic databases made studies of space-group frequencies and symmetry relationships more tractable. Wilson (1988, 1990, 1993*a*,*b*) used the Cambridge Structural Database (henceforth CSD; Allen, 2002; Bruno *et al.*, 2002) as the basis for his study of space-group frequencies and symmetry relationships. Wilson used extensively, and for the first time, the number of molecules in the asymmetric unit (Z') as a quantity that could be collated and which could reveal information about the nature of molecules that crystallize in the space groups. There have since been many further attempts to rationalize molecular and crystallographic symmetry relationships (see *e.g.* Scaringe, 1991; Zorky *et al.*, 1993; Belsky *et al.*, 1995; Steiner, 2000), and the review by Brock & Dunitz (1994, and references therein) provides an excellent summary of the field.

The CSD is the definitive database of published organic and metal-organic structures determined by X-ray and neutron diffraction techniques. Although the information contained in the database is primarily concerned with recording molecular structures in the context of their three-dimensional crystal structures, the CSD is a unique source of information about relationships between molecular and crystallographic symmetry. Recently, Cole *et al.* (2001) described a molecular-symmetry perception algorithm and its implementation in *RPluto* (Motherwell *et al.*, 1999).[1] The symmetry elements for each molecule are identified within certain geometrical tolerances, and the combination of the symmetry elements present for the molecule allows its assignment to a point group. The perception of molecular symmetry is performed using only the atomic coordinates, and no information regarding any coincident crystallographic symmetry is included in the analysis.

The application of this algorithm to many molecules, coupled with the ability to determine the symmetries of the occupied Wyckoff positions in crystal structures (Cole, 1995), has led to the development of a new database, CSDSymmetry (Yao *et al.*, 2002). CSDSymmetry is relational and stores data such as point group, space group, symmetry of occupied Wyckoff position, and Z and Z' for each of the 198 229 molecules in the CSD (Version 5.19 of April 2000). The inclusion of a number of auxiliary information tables allows molecules to be selected on the basis of the symmetry elements that characterize them or their membership in a space group that employs a particular symmetry operation. Yao *et al.* (2002) give more details about the creation and uses of CSDSymmetry. The present paper uses CSDSymmetry to probe the point of contact between molecular and space-group symmetry, namely the Wyckoff positions in crystal structures. In previous studies, relationships between molecular and crystallographic symmetry have relied heavily on the use of Z', which is only loosely correlated with molecular symmetry. We present for the first time a large-scale survey of structural data for which the symmetry of the occupied Wyckoff position and the symmetry of the molecule are known unambiguously.

2. Symmetry relationships from the molecular point of view

We restricted our sample to structures in which there is only a single chemical species in the unit cell. Although it is not possible to search CSDSymmetry for structures that contain a single entity (residue in CSD terminology), it is possible to search for structures that have only a single entry in the database and for which the residue number is one. In the creation of a CSDSymmetry entry, a residue number is assigned to each molecule found in the asymmetric unit. Thus, by insisting that the residue number is unity and that there is only one entry (molecule) per structure in CSDSymmetry, we almost guarantee that the maximum Z' for these structures is one. This method is not infallible, but the resulting data set, which contains a very high percentage of structures with only one type of molecule, is very quickly and easily obtained. The data set, known henceforth as 'One-R' contains 95 836 structures and forms the basis of all searches outlined below.

One-R was searched for each of the 32 crystallographic point groups, and only molecular point groups that contained 75 or more structures were analysed further.[2] Molecules of point-group symmetry C_1 (1), *i.e.* molecules with no symmetry, dominate the data set, accounting for 71% (67 950) of One-R members. The largest subset of molecules with symmetry is that containing molecules belonging to point group C_i ($\bar{1}$), with 7786 members, followed closely by C_2 (2) with 7189 members and C_s (m) with 6181 members. These three point groups collectively represent 22% of One-R, and therefore molecules belonging to point groups of higher symmetry account for approximately 7%.

2.1. Retention of molecular symmetry in crystal structures

The principal aim of this study is to determine how molecular point-group symmetries are accommodated in three-dimensional structures. The frequencies of occurrence of the 32 crystallographic point groups in One-R are given in Table 1. For every point group, the symmetry of the site occupied by the molecule in each structure has been extracted. These occupancies have been collated and are presented in Table 2.

Inspection of the Wyckoff positions occupied by members of the simple molecular point groups C_i, C_2, C_s and C_3 has revealed a hierarchy in the retention of molecular-symmetry elements. The point groups are characterized by only one symmetry element other than the identity operation, and therefore in the crystal structure the molecule either retains its symmetry or resides on a general position. It can be seen that:

(i) Inversion centres are retained to a very high degree (99%).

(ii) Rotation axes are retained in 59 and 66% of structures built from C_2 and C_3 molecules, respectively.

(iii) Mirror planes are retained in only 26% of cases.

A consequence of a molecule's belonging to a higher-symmetry point group is that there is a choice of which, if any, symmetry elements are retained in the crystal structure. For example, the point group C_{2v} ($mm2$) contains a twofold axis and two mirror planes; hence the molecule could be found on Wyckoff positions of symmetry C_1 (1), C_2 (2), C_s (m) or C_{2v} ($mm2$). Inspection of Table 2 reveals the following:

(i) Clearly, molecules that belong to a point group that encompasses an inversion centre almost exclusively utilize

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[1] *RPluto* can be downloaded free of charge, for non-commercial research purposes, from http://www.ccdc.cam.ac.uk/prods.

[2] Data for the remaining crystallographic point groups with less than 75 members are included in the supplementary material for this paper, which is available from the IUCr electronic archives (Reference: BK0132). Services for accessing these data are described at the back of the journal.

Table 1
The frequency of crystallographic point groups in One-R in descending order of occurrence.

Point group	Number of occurrences	% of data set
C_1 (1)	67 950	70.90
C_i ($\bar{1}$)	7786	8.12
C_2 (2)	7189	7.50
C_s (m)	6181	6.45
C_{2h} ($2/m$)	2036	2.12
C_{2v} ($mm2$)	1632	1.70
C_3 (3)	583	0.61
D_{2h} (mmm)	505	0.53
D_2 (222)	296	0.31
S_4 ($\bar{4}$)	294	0.31
C_{3v} ($3m$)	289	0.30
D_3 (32)	189	0.20
D_{2d} ($\bar{4}2m$)	151	0.16
S_6 ($\bar{3}$)	118	0.12
D_{3h} ($\bar{6}m2$)	114	0.12
D_{3d} ($\bar{3}m$)	89	0.09
T_d ($\bar{4}3m$)	79	0.08
D_{4h} ($4/mmm$)	75	0.08
C_{3h} ($\bar{6}$)	55	0.06
C_4 (4)	38	0.04
D_4 (422)	37	0.04
C_{4v} ($4mm$)	36	0.04
O_h ($m3m$)	22	0.02
D_{6h} ($6/mmm$)	20	0.02
C_{4h} ($4/m$)	17	0.02
T (23)	9	0.01
C_6 (6)	3	0.00
C_{6h} ($6/m$)	1	0.00
D_6 (622)	1	0.00
T_h ($m3$)	1	0.00
O (432)	1	0.00
C_{6v} ($6mm$)	1	0.00

Wyckoff positions of symmetry C_i or Wyckoff positions that encompass an inversion centre. Thus, molecules of symmetry D_{2h} (mmm) use C_i and C_{2h} ($2/m$) special positions to a high degree, combining to account for about 85% of the D_{2h} data set, and molecules of C_{2h} symmetry are found on special positions of C_i or C_{2h} symmetry in 95% of the subset.

(ii) Symmetry elements that are retained to a similarly high degree as inversion centres are S_4 ($\bar{4}$) and S_6 ($\bar{3}$).

(iii) Molecules belonging to point groups that contain rotation axes but no mirror symmetry [D_2 (222) and D_3 (32)] are found to retain one of their rotation axes in structures in approximately 50% of cases.

(iv) Molecules that belong to point groups that include mirror planes but no inversion symmetry, for example D_{3h} ($\bar{6}m2$) and C_{2v} ($mm2$), retain the mirror symmetry only in a minority of cases (usually 10–20%) and often to a lesser extent than available rotation axes.

(v) General positions host 30–60% of molecules belonging to point groups that do not encompass inversion symmetry.

(vi) Full point-group symmetry (for point groups other than the simplest, as defined previously) is retained in crystal structures quite infrequently, only accounting for 0–20% of cases. For example, a Wyckoff position of C_{3v} symmetry ($3m$) is occupied by molecules of C_{3v} symmetry in only 7% of cases, and molecules of D_{3d} ($\bar{3}m$) symmetry residing on Wyckoff positions of D_{3d} symmetry account for only 1% of the subset.

2.2. Molecules of C_1 (1) point-group symmetry

It is an inescapable fact that the majority of molecules contained in the CSD have no symmetry. This fact, however, does not make the C_1 data set unworthy of study; C_1 molecules are not evenly distributed through the space groups, thus highlighting the existence of molecular/crystal symmetry relations.

The histogram in Fig. 1 shows the percentage of C_1 molecules in a selection of space groups that belong to One-R. Examination of the 230 space groups shows that there are 13 space groups with only general positions and no special positions: all of these space groups have more than 70% of their structures built from C_1 molecules.[3] The other space groups that host a similarly large proportion of C_1 molecules are $P2_1/c$, $Pbca$, $C2$ and $P\bar{1}$, space groups that Kitaigorodskii identified as offering good close-packing conditions to molecules of C_1 symmetry. The remainder of the space groups shown in Fig. 1 have less than 60% of their structures built from molecules of C_1 symmetry, and space groups such as $Pnma$ and $P2_1/m$ exhibit few structures (< 1%) that contain C_1 molecules. The space groups whose structures are built from C_1 molecules in less than 60% of cases are those with special positions. The colour scheme adopted in Fig. 1 reflects this observation: blue indicates a space group with no special positions; red indicates a space group with special positions of a single symmetry; yellow, a space group with special positions of two symmetries; and black, more than two special positions of different symmetry. A general trend through the histogram can be seen; as the symmetry of the space group increases the percentage of C_1 molecules present decreases. Conversely and importantly, as space-group symmetry increases so does the percentage of high-symmetry molecules found in such structures.

3. Symmetry relationships from the crystallographic point of view: occupation of Wyckoff positions in crystal structures

One-R has been analysed in terms of the occupancy of Wyckoff positions in space groups with a minimum of 450

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[3] A number of space groups that strongly 'favour' C_1 molecules are chiral. Thus, an enantiomerically pure substance is obtained when a molecule that does not possess an inversion centre or mirror plane crystallizes in a chiral space group. The structures that are represented in the histogram and which belong to a chiral space group are enantiomerically pure. However, any molecule (possessing any symmetry) may crystallize in a chiral space group. The observation that space groups with no special positions appear to 'favour' molecules of C_1 symmetry is true whether or not the space group is chiral. For some structures belonging to the enantiomorphous space groups (such as $P3_1$ and $P3_2$), the 'absolute configuration' is known (the crystallographer has determined that the structure belongs to a particular space group of the pair), and for other structures, it is not. The presence of an unknown number of structures for which the absolute configuration has been determined in each space group invalidates the combination of statistics for the enantiomorphous pairs of space groups.

Table 2
The distribution of molecules of particular point-group symmetries over Wyckoff positions in crystal structures.

Point group	Symmetry of occupied Wyckoff position	Number of occurrences	% of data set (to nearest % point)
C_i ($\bar{1}$)	C_i ($\bar{1}$)	7675	99
	C_1 (1)	105	1
C_2 (2)	C_2 (2)	4252	59
	C_1 (1)	2932	41
C_s (m)	C_1 (1)	4559	74
	C_s (m)	1612	26
C_{2h} ($2/m$)	C_i ($\bar{1}$)	1778	87
	C_{2h} ($2/m$)	172	8
	C_1 (1)	55	3
	C_2 (2)	16	1
	C_s (m)	14	1
C_{2v} ($mm2$)	C_1 (1)	989	61
	C_s (m)	271	17
	C_2 (2)	267	16
	C_{2v} ($mm2$)	104	6
C_3 (3)	C_3 (3)	384	66
	C_1 (1)	198	34
D_{2h} (mmm)	C_i ($\bar{1}$)	367	73
	C_{2h} ($2/m$)	61	12
	C_1 (1)	47	9
	C_2 (2)	10	2
	D_{2h} (mmm)	9	2
	C_s (m)	6	1
	C_{2v} ($mm2$)	4	1
	D_2 (222)	1	0
D_2 (222)	C_2 (2)	146	49
	C_1 (1)	101	34
	D_2 (222)	49	17
S_4 ($\bar{4}$)	S_4 ($\bar{4}$)	216	73
	C_2 (2)	49	17
	C_1 (1)	28	10
C_{3v} ($3m$)	C_s (m)	120	42
	C_1 (1)	119	41
	C_3 (3)	28	10
	C_{3v} ($3m$)	21	7
D_3 (32)	C_1 (1)	66	34
	C_2 (2)	52	28
	C_3 (3)	36	19
	D_3 (32)	35	19
D_{2d} ($\bar{4}2m$)	C_2 (2)	44	28
	C_1 (1)	36	24
	S_4 ($\bar{4}$)	31	21
	D_{2d} ($\bar{4}2m$)	22	15
	C_s (m)	7	5
	C_{2v} ($mm2$)	6	4
	D_2 (222)	5	3
S_6 ($\bar{3}$)	S_6 ($\bar{3}$)	79	67
	C_i ($\bar{1}$)	39	33
D_{3h} ($\bar{6}m2$)	C_1 (1)	47	41
	C_2 (2)	23	20
	C_s (m)	18	16
	C_{3h} ($\bar{6}$)	15	13
	C_3 (3)	6	5
	C_{3v} ($3m$)	3	3
	D_3 (32)	2	2
D_{3d} ($\bar{3}m$)	C_i ($\bar{1}$)	43	48
	S_6 ($\bar{3}$)	29	33
	C_{2h} ($2/m$)	10	11
	C_s (m)	4	5
	D_{3d} ($\bar{3}m$)	1	1
	C_2 (2)	1	1
	C_1 (1)	1	1
T_d ($\bar{4}3m$)	C_1 (1)	28	35
	T_d ($\bar{4}3m$)	11	14
	C_2 (2)	9	11
	S_4 ($\bar{4}$)	7	9
	C_s (m)	7	9
	C_3 (3)	6	8
	D_{2d} ($\bar{4}2m$)	4	5
	T (23)	3	4
	C_{3v} ($3m$)	3	4
	D_2 (222)	1	1
D_{4h} ($4/mmm$)	C_i ($\bar{1}$)	47	63
	C_{4h} ($4/m$)	8	11
	C_{2h} ($2/m$)	7	9
	C_1 (1)	6	8
	S_4 ($\bar{4}$)	3	4
	C_4 (4)	2	3
	C_s (m)	1	1
	C_{2v} ($mm2$)	1	1

[1] In some cases, the sum of Wyckoff positions occupied for a molecular point group does not equal the total number of molecules given for the same point group in Table 1. The difference in totals ($< 2\%$) is due to errors in the symmetry perception algorithm: the perceived symmetry of the molecule and its Wyckoff position is incompatible. These data have not been included in Table 2.

members. The frequencies of occurrence for the space groups in One-R are given in Table 3. Each space group is broken down by the percentage occupancy of Wyckoff positions, and these data are presented in Table 4. As mentioned in §1, the work of Kitaigorodskii, particularly his proposals concerning the close packing of structures through the utilization of appropriate special positions, has proved accurate over the years. We have found little to contradict those findings. However, there are a few notable points:

(i) There is no space group for which more than 19% of its structures are built from molecules residing on an inversion centre. Space groups such as $P2_1/c$, $P\bar{1}$ and $Pbca$ [which only have Wyckoff positions of symmetry C_i ($\bar{1}$)] are popular with molecules of C_1 symmetry, which indicates that the close-packing conditions offered by these space groups through occupancy of their general positions is very satisfactory.

(ii) The space groups $C2/c$ and $Pbcn$ have 42 and 60%, respectively, of their structures built with C_2 axes occupied.

(iii) Mirror-containing space groups $Pnma$ and $P2_1/m$ are observed only very rarely without their mirror planes being occupied.

Table 3
The frequency of occurrence of space groups with 450 or more members in One-R.

Space group	Number of occurrences	% of data set
$P2_1/c$	38 291	39.95
$P\bar{1}$	16 662	17.38
$P2_12_12_1$	11 150	11.63
$C2/c$	6839	7.14
$P2_1$	5591	5.83
$Pbca$	4602	4.80
$Pna2_1$	1547	1.61
$Pnma$	1197	1.25
$Pbcn$	911	0.95
$C2$	653	0.68
$P2_1/m$	450	0.47
Total		91.69

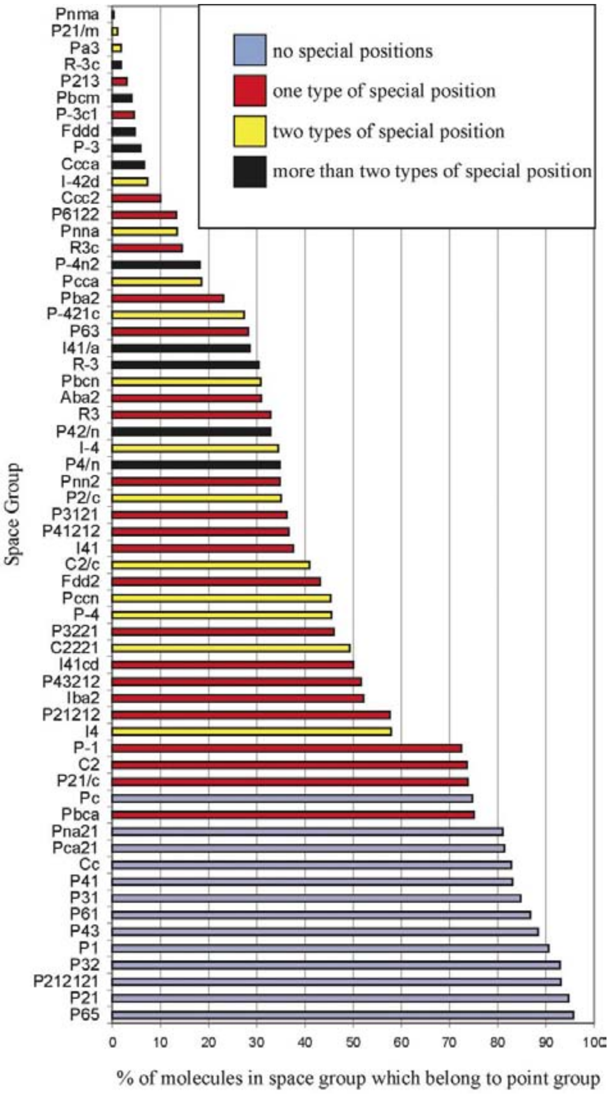

Figure 1
A histogram showing the percentage of molecules that are of C_1 (1) symmetry in each space group listed. The histogram has been sorted in descending order. The bars of the histogram are coloured for the number of types of special positions, according to the key shown. The 11 enantiomorphous pairs of space groups are treated individually.

Table 4
The occupancies of available Wyckoff positions in space groups with 450 or more members in One-R.

Space group	Symmetry of occupied Wyckoff position	Number of occurrences	% of data set (to nearest % point)
$P2_1/c$	C_1 (1)	32 930	86
	C_i ($\bar{1}$)	5361	14
$P\bar{1}$	C_1 (1)	13 496	81
	C_i ($\bar{1}$)	3166	19
$P2_12_12_1$	C_1 (1)	11 150	100
$C2/c$	C_1 (1)	3283	48
	C_2 (2)	2872	42
	C_i ($\bar{1}$)	684	10
$P2_1$	C_1 (1)	5591	100
$Pbca$	C_1 (1)	4082	88
	C_i ($\bar{1}$)	519	12
$Pna2_1$	C_1 (1)	1535	100
$Pnma$	C_s (m)	1165	97
	C_1 (1)	23	2
	C_i ($\bar{1}$)	7	1
$Pbcn$	C_2 (2)	539	60
	C_1 (1)	330	36
	C_i ($\bar{1}$)	40	4
$C2$	C_1 (1)	500	77
	C_2 (2)	153	23
$P2_1/m$	C_s (m)	420	93
	C_1 (1)	23	5
	C_i ($\bar{1}$)	7	2

4. Locations of molecules in crystal structures

A survey of molecular and crystallographic symmetry relationships would not be complete without looking at the consequences of the above preferences, *i.e.* the locations of molecules of a particular symmetry in terms of Wyckoff position *and* space group. The histograms in Fig. 2 show this information; the colours of the bars in the histograms indicate the symmetry of the occupied Wyckoff position (see key). Thus:

(i) Molecules that contain an inversion centre (for example molecules that belong to point groups C_i, C_{2h}, D_{2h} and D_{4h}) are commonly found residing on the inversion centre in one of four space groups (namely $P\bar{1}$, $P2_1/c$, $Pbca$ and $C2/c$) that Kitaigorodskii identified as offering good close-packing conditions to molecules containing an inversion centre.

(ii) Molecules with only twofold rotation-symmetry elements (for example C_2 and D_2) are most commonly found in $C2/c$ on the twofold axis. Thus, the close packing offered in $C2/c$ (with occupancy of the C_2 axis) is as satisfactory as the near-ideal close packing that is available through occupancy of the general positions in $P2_1/c$.

(iii) Molecules that retain a mirror plane in crystal structures are most likely to be found in *Pnma* and, to a lesser extent, $P2_1/m$. However, the most popular destination for mirror-symmetric molecules is a general position in $P2_1/c$. The stacked close-packed layers achievable in *Pnma* through occupancy of the mirror plane appear less satisfactory than the close-packing conditions available in $P2_1/c$.

5. Conclusions

The development of the relational database CSDSymmetry has allowed, for the first time, a large-scale survey of the interplay between molecular and crystallographic symmetry, where the symmetry of the occupied Wyckoff position is known unambiguously. It is hoped that the data presented in

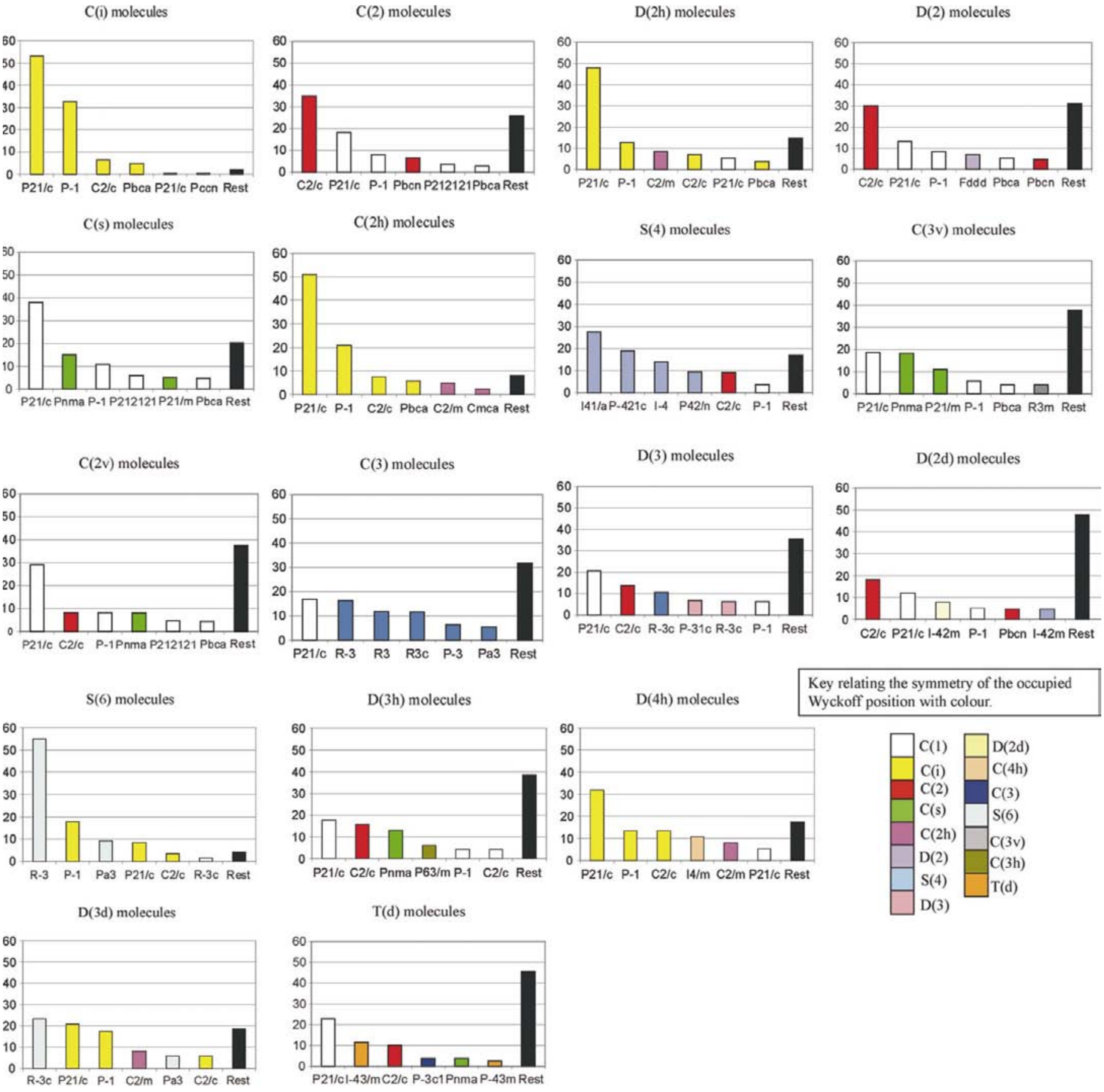

Figure 2
Histograms showing the top six locations in crystal structures for molecules of 17 crystallographic point groups with more than 75 members, in One-R. The colour coding indicates the symmetry of the Wyckoff positions occupied within the space group, for example, C_1 (1) white, C_i ($\bar{1}$) yellow, C_2 (2) red and C_s (*m*) green. A key is included. The vertical axis indicates the percentage of structures of each point group that belongs to the space-group/Wyckoff-position subset.

this paper provide valuable information to crystallographers who 'have come to expect the loss of molecular symmetry (except inversion) upon crystallization' (Lloyd & Brock, 1997). The following is a summary of our observations of crystal/molecule symmetry relationships determined from One-R, the data set of structures built from one type of molecule.

5.1. Crystal symmetry

The seminal work of Kitaigorodskii (1961) has shown that the desire for close-packed structures is a good rationale for explaining observed space-group frequencies. Thus, space groups that offer good close-packing conditions are popular. Those that do not offer good close-packing conditions are rare or are only utilized by molecules with specific symmetry. These observations have led to the idea of 'good' symmetry operators, *i.e.* those that are present in popular and close-packing space groups, and 'poor' symmetry operators, *i.e.* those that are destructive to close packing (Filippini & Gavezzotti, 1992). Examples of 'good' symmetry operators are inversion centres, screw axes and glide planes that lead to favourable 'bump-to-hollow' molecular interactions. An example of a 'poor' symmetry operator is a mirror plane that generates unfavourable 'bump-to-bump' intermolecular interactions. Our survey of the occupancy of Wyckoff positions in space groups reaffirms this view. A small percentage of structures belonging to centrosymmetric space groups have an inversion centre occupied because unoccupied inversion centres are not destructive to close packing. Conversely, mirror planes in crystal structures are occupied to a high degree because close-packed structures are hard to achieve when the mirror plane is left unoccupied.

5.2. Molecular symmetry

A hierarchy in the retention of molecular-symmetry elements was observed from our survey of molecules in crystal structures. It was found that molecules that possess an inversion centre retain this symmetry element in their crystal structures in more than 80% of cases. Similarly high degrees of retention were observed for two other symmetry elements, namely S_4 and S_6. These symmetry elements can, like an inversion centre (which is equivalent to an S_2 axis), be described as 'point-acting'; rotation followed by reflection in a plane perpendicular to the rotation axis transposes all atoms (in the case of a molecule) through a point at the intersection of the plane with the rotation axis. The preference for 'point-acting' symmetry is useful in predicting the probable site of a molecule in a crystal structure. For example, in the crystal structure of benzene, the molecule of D_{6h} ($6/mmm$) symmetry does not utilize any special position of sixfold symmetry or mirror symmetry in the crystal structure; rather it is found residing on an inversion centre (Cox *et al.*, 1958).

Rotation axes were retained by molecules in approximately 50% of cases and mirror planes were usually retained in less than 30% of cases. Thus, symmetry elements described by an axis or a plane are retained to a lesser extent than point-acting symmetry elements. Using similar logic to that of Kitaigorodskii, we propose that molecular-symmetry elements that promote dense structures are retained in crystal structures, whereas molecular-symmetry elements that are not conducive to densely packed structures are lost. Preliminary results support this hypothesis and will be the subject of a further publication.

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