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Three-dimensional hydrogen-bonded frameworks in organic crystals: a topological study

Igor A. Baburin[a,b] and Vladislav A. Blatov[a]*

[a]Samara State University, Ac. Pavlov Street 1, Samara 443011, Russia, and [b]International Max Planck Research School 'Dynamical Processes in Atoms, Molecules and Solids', Noethnitzer Strasse 38, Dresden 01187, Germany

Correspondence e-mail: blatov@ssu.samara.ru

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1551 homomolecular single hydrogen-bonded frameworks in organic crystals have been classified into 148 topological types of three-periodic nets. Different representations of hydrogen-bonded frameworks as nets of molecular centroids, edge or ring nets are discussed. To study the influence of hydrogen bonds on the topology of molecular packings, 42 270 molecular crystals without hydrogen bonds have been considered. The topologies of molecular packings are found to be independent of hydrogen bonding. Analysis of 231 homomolecular frameworks composed of crystallographically different molecules shows that molecules not related by symmetry tend to form the same hydrogen-bond pattern. The relations between net topological types, space-group symmetry of crystals, site symmetry and point-group symmetry of molecules are discussed. As a result, a set of rules for the crystal design of molecular frameworks is proposed.

1. Introduction

The hydrogen bond is one of the most important intra- and intermolecular interactions that influences the physicochemical properties and structure of crystals (Jeffrey, 1997). Recently, hydrogen bonds have also attracted much attention in the field of crystal engineering as a 'tool' to synthesize supramolecular ensembles held by non-covalent interactions (*cf. e.g.* Krische & Lehn, 2000; Burrows, 2004). In doing this, hydrogen bonds are quite convenient in the sense that they are relatively strong compared with other intermolecular interactions, but at the same time flexible and depend on the mutual geometries of active functional groups as well as on the arrangement of molecules as a whole, thus providing a variety of possible architectures to be built up.

A theoretical description of hydrogen-bonded motifs in crystal chemistry was started by Wells (1954) who characterized the topologies of hydrogen-bonded networks in organic and inorganic solids by representing molecules as points and hydrogen bonds as lines originating from these points. He gave a survey of inorganic crystals with hydrogen bonding, namely, inorganic acids, salts, clathrates (Wells, 1986). In the study of three-dimensional nets (1954, 1977) he also drew attention to some organic structures with hydrogen bonds (*e.g.* β-hydroquinone).

Kuleshova & Zorky (1980) developed Wells' approach further and systematically studied hydrogen-bond patterns in organic crystals with symmetrically equivalent molecules. To take advantage of the graph-theoretical methods, the authors assigned a graph to each crystal structure by identifying a

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molecule with a graph node, the degree of which is equal to the number of hydrogen bonds formed by the molecule. To characterize the topologies of hydrogen-bonded networks, they used the symbols $G_m^n(k)$, where n and m refer to the number of hydrogen bonds formed by a molecule and the number of molecules linked to a given one by hydrogen bonds, respectively; G is the dimensionality of the hydrogen-bonded network (dimers, trimers *etc*., chains, layers or frameworks) and the sequence k specifies the sizes of the smallest rings in the graph. The authors found that the most common hydrogen-bond pattern is a simple one-dimensional chain, whereas frameworks are quite rare and represent unusual hydrogen-bond patterns. Note that this classification deals mostly with the local topology of hydrogen bonds; the overall topology is ignored, as a rule. Only in a few cases did the authors briefly mention that some hydrogen-bonded three-periodic nets are similar to the diamond structure.

Special graph-theoretical tools were further developed to analyze hydrogen-bond patterns in more detail (Etter, 1990; Grell *et al.*, 2002). All methods of this kind are mainly concerned with the characterization of rings, chains and other topological elements of hydrogen-bond patterns. Again, the global topology of hydrogen bonds is not considered. An attempt was also made to predict hydrogen-bond patterns directly from the structures of molecules or from the presence of some functional groups (Allen *et al.*, 1999; Infantes & Motherwell, 2005).

In the last few decades the global topology of three-periodic nets has been widely investigated, especially relating to applications in the crystal engineering of porous frameworks and to the methods of their classification (*cf. e.g.* Delgado Friedrichs *et al.*, 2005; Koch *et al.*, 2006; Hyde *et al.*, 2006; Carlucci *et al.*, 2007). Recently, Ockwig *et al.* (2005) analyzed the topologies of metal-organic frameworks (MOFs) and proposed a ‘grammar’ for crystal design. However, an analogous treatment of hydrogen-bonded frameworks has been performed on interpenetrating crystal structures of inorganic compounds (Baburin *et al.*, 2005). Moreover, less attention is paid to how the topological properties of crystal structures are reflected in their crystallographic symmetry, although for molecular crystals correlations between molecular and crystal symmetry (*e.g.* Brock & Dunitz, 1994), and between space-group types and packing patterns (Pidcock & Motherwell, 2004) were investigated in detail. Thus, the aim of this paper is to give a detailed account of three-dimensional hydrogen-bonded single frameworks in organic crystals from the topological viewpoint and to discuss relations between the space-group symmetry of the corresponding three-periodic nets, site symmetry and point-group symmetry of molecules. Only *homomolecular* organic crystals have been studied, *i.e.* containing molecular units of the same chemical composition and structure, but are likely to be distinguished by crystallographic symmetry and conformation. We do not consider the arrays of interpenetrating three-periodic nets; this is the subject of a separate publication (Baburin *et al.*, 2007).

2. Experimental

Crystallographic data on homomolecular organic crystals were selected from the Cambridge Structural Database (2006) by means of the program package *TOPOS* (http://www.topos.ssu.samara.ru; Blatov, 2006*a*). All the crystal structures are completely refined (including hydrogen positions) with $R_f \leq 0.1$, and contain no metal atoms. To determine intra- and intermolecular bonds we used an improved geometrical scheme as proposed by Peresypkina & Blatov (2000) and implemented into the *AutoCN* program of the *TOPOS* package. The improvement concerns the opportunity to recognize hydrogen bonds among other non-valence interactions. To consider the $\mathrm{H}\cdots A$ contact in a fragment $X-\mathrm{H}\cdots A$ (X = N, O, S; A = N, O, S, Se, F, Cl, Br, I) as a hydrogen bond, the following formal criteria should hold simultaneously (*cf.* Steiner, 2002; Baburin *et al.*, 2005):

(i) $d(\mathrm{H}\cdots A) \leq 2.5$ Å;

(ii) $d(X\cdots A) \leq 3.5$ Å;

(iii) $\angle\ X-\mathrm{H}\cdots A \geq 120°$ (three- and four-centered, symmetrical and resonance hydrogen bonds can be recognized as well). For the third-row atoms (S, Cl), the fourth-row atoms (Se, Br) or the fifth-row atoms (I) the maximum $d(\mathrm{H}\cdots A)$ and $d(X\cdots A)$ values are increased by 0.2, 0.3 or 0.4 Å, respectively. The dimensionalities of the networks formed by hydrogen bonds have been determined by the *ADS* program of the *TOPOS* package. As a result, three-periodic hydrogen-bonded single networks have been found in 1777 homomolecular organic crystals. Out of them, 1546 crystal structures contain only symmetrically equivalent molecules and the other 231 consist of two or more non-equivalent molecules.

The topological classification of hydrogen-bonded three-periodic networks has been performed with the *ADS* and *IsoTest* programs of the *TOPOS* package according to algorithms described by Blatov (2006*a*). For this purpose, we simplified all the initial crystal structures by replacing molecules with their centroids (graph nodes), keeping the connectivity determined by hydrogen bonds (graph edges). A single graph edge was matched to hydrogen bonding between a pair of molecules even if they were connected by more than one hydrogen bond. Each graph edge corresponds to all hydrogen bonds between a pair of molecules (*cf.* Kuleshova & Zorky, 1980). The resulting graph is *simple* (*i.e.* it has no loops, directed or multiple edges) and represents a three-periodic *net* (*cf.* Delgado Friedrichs & O’Keeffe, 2005). When considering an *embedding* of the net into three-dimensional space we shall call it a *hydrogen-bonded net*. The degree of a node in the net equals the number of molecules connected to a given one by hydrogen bonds. To perform the topological classification, the topological indices – *vertex* symbols and coordination sequences (up to the 10th shell) – have been computed and compared with the indices of reference topological types included in the *TTD* collection (Blatov, 2006*a*) comprising the information from the *RCSR* (Reticular Chemistry Structure Resource, http://rcsr.anu.edu.au/) and *EPINET* (Euclidean Patterns in Non-Euclidean Tilings, http://epinet.anu.edu.au/) databases. Hydrogen-bonded nets have been assigned to the

Table 1
Topological types of hydrogen-bonded frameworks in crystals with crystallographically equivalent molecules.

Node degree	Topological type	No. of structures	Transitivity *pq*†
3	**ths**	8	12
	srs	7	11
	bto	3	12
	pcu-h	3	12
	dia-f	2	12
	etb	1	12
	lig	1	12
4	**dia**	352	11
	cds	28	12
	dmp	17	12
	qtz	10	11
	lvt	7	11
	neb	5	12
	qzd	5	12
	tcb	5	12
	uoc	5	12
	gis	4	12
	nbo	4	11
	snw-4-$I4_122$‡	3	12
	crb	2	12
	hxg-d-4-*Cccm*‡	2	13
	irl	2	13
	unj	2	12
	4/4/*t*16§	1	12
	hxg-d-4-*I*4/*mcm*‡	1	13
	lcv	1	11
	lon	1	12
	sra	1	13
	svi-x-4-$P4_2/nbc$‡	1	12
	unc	1	12
	unh	1	12
	unn	1	12
	usf	1	12
5	**bnn**	45	12
	sqp	25	12
	nov	19	13
	noz	3	13
	5/4/*t*5§	2	12
	acs-5-$P2_1/c$‡	2	14
	sxa-5-*Cmce*‡	2	13
	fob	1	13
	ftb	1	13
	ncd-5-$P4_22_12$‡	1	12
	svg-5-*I*422‡	1	13
	sxa-5-*Cmmm*‡	1	13
6	**pcu**	160	11
	sxd	98	13
	acs	68	11
	lcy	56	11
	bsn	30	12
	sma	5	12
	sxa	5	13
	ecu-6-$P2_1/c$-2‡	4	14
	msw	4	12
	rob	4	12
	ecu-6-$P2_1/c$-1‡	3	14
	bcs	2	11
	eca-6-*Pnna*‡	2	13
	hxg-d-6-*Cmmm*‡	2	13
	smi	2	12
	sxb	2	13
	tcc-6-$P6_4$‡	2	12
	bct-6-$I4_1cd$‡	1	13
	cco-6-*Pbcm*‡	1	13
	ecu-6-*Pnna*‡	1	13
	hxg-d-6-$P4_222$‡	1	12
	nce-6-*C*2/*c*‡	1	14
	sda	1	12
	sne	1	12
	snm	1	13
	svi-x-6-$P4_2/mcm$‡	1	12
	sxc	1	12
7	**ose**	7	13
	tsi-7-$P2_1/c$‡	7	14
	bcu-7-$P2_1/c$‡	4	14
	svk	4	14
	hxg-d-7-*Fddd*‡	3	13
	vcm	3	14
	vcn	3	14
	sev	2	13
	sve	2	13
	7/3/*t*27§	1	14
	bcu-7-*Cmce*‡	1	14
	bcu-7-*Ibam*‡	1	14
	bcu-7-*Pnnm*‡	1	14
	cco-7-$P2_1/c$‡	1	15
	nci-7-*Cccm*‡	1	14
	ncj-7-*C*2‡	1	14
8	**hex**	77	12
	ecu	36	13
	bcu	35	11
	vcs	34	13
	eci	23	13
	eca	22	12
	tsi	11	12
	hxg-d-8-*Pbcm*‡	3	14
	bct-8-*Cccm*‡	2	13
	8/3/*m*1§	1	14
	8/3/*m*2§	1	14
	10/3/*h*4-8-*C*2‡	1	15
	10/3/*h*4-8-$P2_1/c$‡	1	15
	bct-8-*Ibam*‡	1	15
	cco-8-*Pbcm*‡	1	14
	ecv	1	14
	fcu-8-$P3_221$‡	1	13
	*sqc*166¶	1	12
9	**ela**-9-$P2_12_12$‡	4	15
	nce	2	13
	bct-9-*Cmce*‡	1	15
	fcu-9-$P2_1/c$‡	1	16
	gpu-9-$P2_1/c$‡	1	15
	ncd	1	12
	vcy	1	15
10	**bct**	17	12
	cco	11	13
	feb	9	14
	chb	6	14
	tcg	5	14
11	**ela**	2	13
12	**fcu**	7	11
	hcp	2	12
14	W_2††	1	13

† *p* and *q* are the numbers of different kinds of topologically non-equivalent nodes and edges in the hydrogen-bonded net (*cf.* Ockwig *et al.*, 2005). ‡ The symbols proposed by Blatov (2007) are used. § The symbols proposed by Fischer (1971) are used. ¶ The *EPINET* nomenclature is used. †† The symbol proposed by O'Keeffe (1998) is used.

same topological type if they share the same vertex symbol and coordination sequence (O'Keeffe & Hyde, 1996). The distribution of hydrogen-bonded nets into the *RCSR* and *EPINET* topological types as well as net *transitivities* (Ockwig *et al.*, 2005) are given in Tables 1 and 2.

We have also analyzed the topologies of *molecular packings*, *i.e.* the networks of all intermolecular contacts (including hydrogen bonds, secondary, and van der Waals interactions) in the crystal structures with three-dimensional hydrogen-

Table 2
Topological types of hydrogen-bonded frameworks in crystals with crystallographically non-equivalent molecules.

Node degree	Topological type	No. of structures	Transitivity *pq*†
3	**srs**	7	11
	ths	7	12
	nod	1	23
4	**dia**	14	11
	cds	10	12
	sra	7	13
	lvt	4	11
	nbo	4	11
	crb	3	12
	uoc	3	12
	dmp	2	12
	hxg-d-4-$P6_222$‡	1	12
	lon	2	12
	qtz	2	11
	unc	2	12
	irl	1	13
	sev-4-*Cccm*‡	1	13
	uoo	1	12
	uox	1	13
	thj	2	23
	bbe	1	23
	mog	1	22
	pts	1	21
5	**bnn**	5	12
	nov	2	13
	sqp	2	12
	hxg-d-5-*C*2/*c*‡	1	13
	sev-5-*Cccm*‡	1	13
	*sqc*492§	1	14
	sxa-5-*Cmce*‡	1	13
	zft	1	13
6	**pcu**	11	11
	bsn	2	12
	bcu-6-$I4_1/amd$‡	1	12
	ecu-6-*Pnna*‡	1	13
	msw	1	12
	sev-6-$C222_1$‡	1	15
	sev-6-*C*2/*c*‡	1	15
	*sqc*24§	1	14
	sxd	1	13
	wht	1	14
	*sqc*25§	1	23
7	**hex**-7-*C*2/*c*‡	2	15
	svk	1	14
	swc	1	14
	ose	1	13
	vcn	1	14
8	**bcu**	2	11
	tcg-8-$Pna2_1$‡	2	14
	tsi	1	12
9	**nci**	1	14
	vcx	1	14
(*n*,*m*)-coordinated¶	**fsg** (*4*,*6*)	2	24
	*sqc*74§ (*3*,*4*)	2	23
	ins (*3*,*4*)	1	23
	gra (*3*,*5*)	1	22
	mcf (*3*,*5*)	1	24
	fsc (*4*,*6*)	1	22
	*sqc*135§ (*5*,*6*)	1	25

† See footnote to Table 1. ‡ The symbols proposed by Blatov (2007) are used. § The *EPINET* nomenclature is used. ¶ Nets with a mixed coordination of nodes. Coordination numbers are given in parentheses.

Table 3
Topologies of molecular packings in crystals with crystallographically equivalent molecules.

The topological types with occurrence > 1.0% are given.

Hydrogen-bonded frameworks			Crystals without hydrogen bonds		
Node degree	Topology	Occurrence (%)	Node degree	Topology	Occurrence (%)
Before clustering					
14	**bcu-x**	22.4	14	**bcu-x**	22.3
	O†	19.6		*O*†	8.1
	W_2†	8.4		W_2†	7.7
12	**fcu**	6.9		K'_D†	7.7
	hcp	4.9	16	16, 58, 128, 226	3.6
14	K'_D†	2.5	12	**fcu**	3.3
16	16, 60, 132, 234‡	2.4	14	14, 54, 126, 226	2.2
	16, 58, 128, 226	2.3	13	13, 47, 103, 182	1.7
	16, 60, 134, 236	1.7	14	14, 53, 122, 218	1.6
14	14, 54, 126, 226	1.4	16	16, 60, 134, 238	1.6
	14, 53, 122, 218	1.0	14	14, 53, 120, 212	1.2
			12	**hcp**	1.1
Close packings after clustering					
12	**fcu**	31.0	12	**fcu**	26.2
12	**hcp**	20.5	12	**hcp**	11.6

† The symbols proposed by O'Keeffe (1998) are used. ‡ If there are no conventional symbols for some packings, the first four terms of the coordination sequence are given.

bonded frameworks, and in 42 270 molecular crystals without hydrogen bonds (even intramolecular). To classify the molecular packings, we have used a procedure completely analogous to that applied to hydrogen-bonded networks; namely, any molecular packing has been reduced to a *packing graph* (Fischer & Koch, 1979; *cf.* Peresypkina & Blatov, 2000), the node degree of which equals the number of molecules linked to a given one by all intermolecular bonds. In addition, we applied the clustering algorithm (Blatov, 2006*b*) to all packing graphs to find the *underlying* topological motifs (*cf.* Ockwig *et al.*, 2005), *i.e.* the networks of molecules held together by the strongest intermolecular interactions. This algorithm allows one to discard the weakest interactions and, hence, to ignore the slight deformations of molecular packings and to determine the underlying topology of the packing. When applying the clustering algorithm, we have used *molecular solid angles* (*cf.* Peresypkina & Blatov, 2000) as the weights of edges in the packing graphs. The topologies of the initial hydrogen-bonded nets and the corresponding *underlying* topological motifs are compared in Table 3.

The most symmetrical embedding of a net (Delgado Friedrichs & O'Keeffe, 2003) and the corresponding space group *G* were either taken from the *RCSR* database or calculated with the *Gavrog Systre* program (http://gavrog.org). Space-group and site-symmetry relations for the nets of various topologies were found with a specially designed *TOPOS* subroutine (Blatov, 2007) to generate all the low-symmetrical net representations using group–subgroup relations for space groups (*International Tables for Crystallography*, 2004, Vol. A1). To look for correlations between the crystal symmetry and the symmetry of a molecule on the one hand and the type of hydrogen-bonded framework on the other hand we considered space groups and site-symmetry groups of nodes

Table 4
Space groups of hydrogen-bonded uninodal nets and site-symmetry groups of molecular centroids occurring in the most frequent topological types.

After the three-letter symbol of a topological type the space group of the most symmetrical embedding (G), the Wyckoff position as well as the site-symmetry group of a node are given. The occurrences of space groups and site-symmetry groups (as a percentage of the total number of compounds with a given topology) are indicated after their symbols in parentheses.

Space groups	Site-symmetry groups
dia $Fd\bar{3}m$ 8(a) ($\bar{4}3m$)	
$P2_12_12_1$ (81.5), $P2_1/c$ (5.4), Cc (2.8), $Pnma$ (2.0), $Pna2_1$ (1.7), $P4_12_12$ (1.7), $C2/c$ (1.1), $P4_32_12$ (0.9), $P4_3$ (0.9), $I4_1/a$ (0.9), $P4_1$ (0.6), $Fdd2$ (0.6)	1 (93.5), 2 (3.7), m (2.0), $\bar{4}$ (0.8)
pcu $Pm\bar{3}m$ 1(a) ($m\bar{3}m$)	
$P2_1$ (35.9), $P2_1/c$ (20.8), $P2_12_12_1$ (14.5), $C2/c$ (4.4), $P\bar{1}$ (4.4), $P1$ (3.8), Pc (3.8), $Pbca$ (2.5), Cc (1.9), $P\bar{4}2_1m$ (1.3), $R3c$ (1.3), $R3$ (1.3), $Pca2_1$ (1.3), $Pbcn$ (0.6), $P2_1/m$ (1.3), $Pna2_1$ (1.3), $I4_1/a$ (1.3), $P4_3$ (1.3)	1 (86.2), 2 (5.0), $\bar{1}$ (4.4), 3 (2.5), m (1.3), $mm2$ (0.6)
sxd $Imma$ 4(e) ($mm2$)	
$P2_12_12_1$ (93.9), $P2_1/c$ (3.1), $P\bar{1}$ (1.0), $C2/c$ (1.0), $C2$ (1.0)	1
hex $P6/mmm$ 1(a) ($6/mmm$)	
$P2_12_12_1$ (37.7), $P2_1$ (32.5), $P2_1/c$ (6.5), $P6_122$ (5.2), $P1$ (3.9), $Pbca$ (3.9), $P\bar{1}$ (2.6), $P6_1$ (2.6), $C2$ (2.6), $C2/c$ (1.3), $Pna2_1$ (1.3)	1 (88.3), 2 (9.1), $\bar{1}$ (2.6)
acs $P6_3/mmc$ 2(c) ($\bar{6}m2$)	
$P2_12_12_1$ (50.0), $P2_1$ (29.4), $Pna2_1$ (10.3), $P2_1/c$ (2.9), $Pnma$ (2.9), Cc (1.5), $Pbca$ (1.5), $Pca2_1$ (1.5)	1 (97.1), m (2.9)
lcy $P4_132$ 4(a) (32)	
$P2_12_12_1$	1
bnn $P6/mmm$ 2(c) ($\bar{6}m2$)	
$P2_1/c$ (77.8), $P\bar{1}$ (13.3), $C2/c$ (6.7), $Pbcn$ (2.2)	1
ecu $Cmcm$ 4c ($mm2$)	
$P2_1$ (50.0), $P2_12_12_1$ (41.7), $P2_1/c$ (5.6), $C2$ (2.8)	1
bcu $Im\bar{3}m$ 2a ($m\bar{3}m$)	
$P2_1/c$ (37.1), $P2_1$ (37.1), $P2_12_12_1$ (11.4), $Pbcn$ (2.9), $P4_32_12$ (2.9), $C2/c$ (2.9), $C2$ (2.9), $P1$ (2.9)	1 (68.6), $\bar{1}$ (20.0), 2 (11.4)
vcs $Pnma$ 4(c) (m)	
$P2_12_12_1$ (97.1), $P2_1/c$ (2.9)	1

occurring in the hydrogen-bonded nets belonging to the ten most frequent topological types (Table 4). The space-group distribution for the crystals with symmetrically equivalent molecules is given in Table 5.

Table 5
Space-group distribution for crystals with crystallographically equivalent molecules.

Space groups with occurrence > 1.0% are given.

Space group	Occurrence (%)
$P2_12_12_1$	45.0
$P2_1/c$	15.6
$P2_1$	12.6
$Pna2_1$	3.4
$P4_12_12$ ($P4_32_12$)	2.8
$C2/c$	2.6
Cc	1.9
$Pbca$	1.8
$P\bar{1}$	1.2

3. Results and discussion

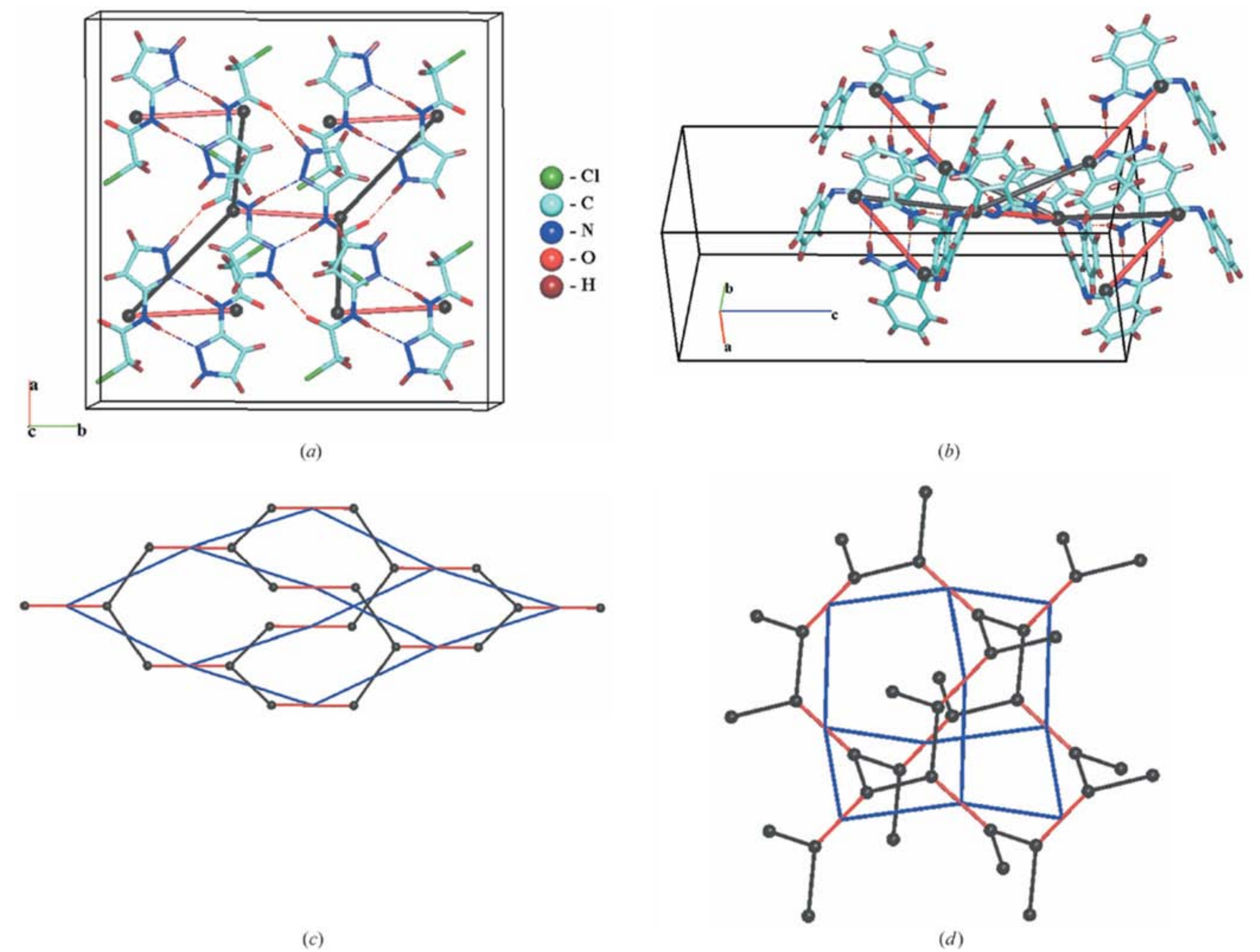
3.1. Different representations of hydrogen-bonded frameworks

The assignment of topology to a hydrogen-bonded framework can be carried out in different ways depending on the choice of nodes in the corresponding hydrogen-bonded net. The most straightforward possibility, used in this paper and in previous graph-theoretical studies (Kuleshova & Zorky, 1980; Grell *et al.*, 2002), is to associate molecular centroids with the nodes of hydrogen-bonded nets; we shall call this representation *standard*. In this representation, hydrogen-bonded nets in 1415 crystals (91.5%) with symmetrically equivalent molecules and in 136 (58.9%) crystals with two or more non-equivalent molecules have been found to form 122 and 59 familiar topological types, respectively (Tables 1 and 2). Only 26 topological types of the latter group do not occur in the former, thus 1551 crystals (87.3%) can be related to the 148 topological types stored in *RCSR*, *EPINET* and *TTD*. Hydrogen-bonded frameworks in the remaining 226 compounds belong to topological types not described earlier.

Another way is to consider molecules in more detail, for instance, to distinguish hydrogen-bond donors/acceptors (Etter, 1990; Grell *et al.*, 2002). Finally, one may look either for molecular associates such as dimers *etc.* or synthons (Desiraju, 1995) formed by hydrogen bonds and assume them to be nodes. Let us emphasize that all these possible topologies to be assigned to a hydrogen-bonded crystal structure are interdependent and related to each other with varying complexity. Often such relations may be described using the notions *edge net* and *ring net* to be discussed in detail below.

Edge nets: Starting from a particular net one may construct a corresponding edge net by placing new nodes in the middle of the edges, connecting new nodes by new edges and removing old nodes and edges. We shall call the edge net *complete* if all the edges in the initial net are centered by new nodes and all old nodes and edges are removed. If only some edges are centered and only the old nodes incident with these edges are removed, the edge net is *partial.* The topology of the edge net, both complete and partial, is determined by the mode of connecting new nodes. Following the definitions of *line graph* (*edge graph*) in graph theory (*cf.* Harary, 1969, ch. 8; Delgado Friedrichs *et al.*, 2003*a*) we retain all links between edge centers passing through the adjacent old nodes. Another approach to the edge net (Delgado Friedrichs *et al.*, 2003*a*) keeps links only between the geometrically nearest nodes, *i.e.* leads to a subnet of the edge net defined above.

For instance, the net, whose nodes correspond to dimers, is an edge net with respect to the standard representation;



(a)

(b)

(c)

(d)

Figure 1
Hydrogen bonding in the crystal structures of (*a*) 3-(chloroacetamido)pyrazole (SAYNAI) and (*b*) *anti*-1-amino-3-(phenylimino)isoindole-3-(chloroacetamido)pyrazole (NAJDIM; hydrogen bonds are shown as dash–dotted lines): each molecule is hydrogen bonded to three others; molecules are linked into four-connected dimers (red lines) *via* synthons $R_2^2(8)$ (for the nomenclature see *e.g.* Etter, 1990). Molecular centroids are shown as black spheres; (*c*) **ths** and (*d*) **srs** nets (red and black lines) together with the corresponding partial edge nets with **dia** topology (blue lines); the **ths** and **srs** edges matched with the dimers are red.

moreover, the edge net is always partial; only one edge per node is centered. As was shown by Kuleshova & Zorky (1980), in the crystals built up only from symmetrically equivalent molecules, each molecule forms an even number of hydrogen bonds. One may expect that the number of molecules hydrogen-bonded to a given one is also even, as a rule. Indeed, odd-coordinated nets account for about 13% of all the crystal structures considered (Table 1). A close inspection shows that any odd-coordinated net may be related to an even-coordinated net by taking dimers as nodes in the resulting hydrogen-bonded net. Thus, in the crystal structure of 3-(chloroacetamido)pyrazole (Kaftory *et al.*, 2005; SAYNAI[1]), whose topology in the standard representation corresponds to a three-coordinated **ths**[2] net, one may select dimers (Fig. 1*a*) and obtain a partial edge net with diamond (**dia**) topology (Fig. 1*c*). Analogously, in the crystal structure of *anti*-1-amino-3-(phenylimino)isoindole (Zhang *et al.*, 2004; NAJDIM) having **srs** topology in the standard description, dimers (Fig. 1*b*) also give rise to the **dia** net (Fig. 1*d*). Note that the relationship between **dia** and **ths** nets was recognized long ago by Wells (1977). The correspondence of **srs** and **dia** nets is not so clear; this would require the space-group symmetry of the ideal **srs** net ($I4_132$) to decrease down to the maximal translation-equivalent subgroup $I4_122$, *i.e.* to the maximal space-group symmetry of the net array in Fig. 1(*d*).

Strictly speaking, to derive all the possible partial edge nets, one has to consider all the low-symmetrical embeddings of the initial net together with all different ways of centering the old edges. However, for the purpose of crystal design it is most interesting to discover the relations encountered in real crystal structures. All such relations between the hydrogen-bonded frameworks in an odd-coordinated standard representation and the corresponding even-coordinated partial edge nets are collected in Table 6.

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[1] Hereafter the codes of compounds in the Cambridge Structural Database (CSD) are given in brackets.
[2] Hereafter the RCSR three-letter symbols are used to designate topological types.

In turn, the standard representation is an edge net with respect to the net where each molecule is represented by a pair of donor/acceptor centers. Let us consider as an example the crystal structures of *p*-aminophenol (AMPHOL01) and 4,4′-hydroxyaminobiphenyl (PITZAT), to which the authors (Ermer & Eling, 1994) assigned the wurtzite topology (**lon-b**) by considering the donor N and acceptor O atoms as nodes, and phenyls as edges of a wurtzite net (Figs. 2*a* and *b*). If the N and O nodes could not be distinguished the wurtzite topology is then reduced to a lonsdaleite-type net (**lon**). However, if the nodes are ascribed to molecular centroids, both AMPHOL01 and PITZAT are related to a six-coordinated **acs** net (Figs. 2*a* and *b*).

If molecules are linked to dimers *via* synthons, then a partial edge net describes the arrangement of the synthons; in this case the nodes of this net correspond to the synthon centers (Fig. 1).

Ring nets: If a synthon consists of more than two molecules joined in a ring, then we may introduce a new net whose nodes coincide with the centers of the rings, a *ring net*. Similarly to the edge net, the ring net may be *complete*, if all rings in the initial net are centered with the new nodes, and *partial*, if some rings remain empty. The nodes of the initial net belonging to the centered rings are removed in the ring net, and the links between these nodes are transformed into edges of the ring net. Obviously, the ring net describing synthons is partial, as a rule. Let us consider the crystal structure of 2,3,5,6-tetrachloro-*trans*-1,4-diethynylcyclohexa-2,5-diene-1,4-diol (Madhavi *et al.*, 2000; XEHKIE; space group $I4_1/a$) having **lvt** topology in the standard representation. However, there are synthons $(O—H)_4$ with $\bar{4}$ symmetry (Fig. 3*a*). Assuming the centers of synthons to be the nodes of a hydrogen-bonded net, we obtain a partial ring net with diamondoid topology (Fig. 3*c*). Note that the relationship between **dia** and **lvt** has already been discussed by Delgado Friedrichs *et al.* (2003*b*).

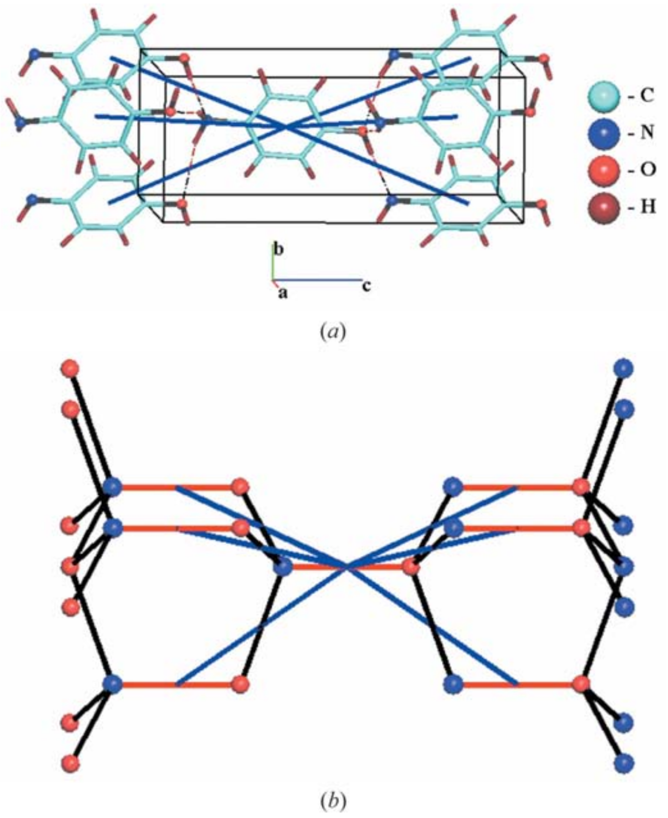
Table 6
Net relationships between odd-coordinated nets and the corresponding even-coordinated edge nets.

Odd-coordinated net	Even-coordinated edge net
bto	**qtz**
ths; **srs**	**dia**
dia-f; **lig**	**lvt**
etb; **pcu-h**	**nbo**
bnn; **sve**	**pcu**
sqp; **nov**; 5/4/*t*5; **ftb**; **sev**; **ncd**	**bcu**
noz	**bcu**; **hex**
fob	**tsi**; *sqc*117†
ose; **ela**	**bct**
svk	**hex**
7/3/*t*27	$4^{22}6$‡
nce	**fcu**

† The *EPINET* nomenclature is used. ‡ This eight-coordinated net has never been described; the Schläfli symbol for the shortest circuits is given in the table. Vertex symbol: $4.4.4.4.4.4.4.4.4_2.4_2.4_2.4_2.4_2.4_2.4_3.4_3.4_3.4_3.4_3.4_3.4_3.4_3.6_4.6_4.6_4.6_4.8_8.8_8$. Coordination sequence: 8 28 68 126 204 298 412 542 692 858.

Another example is the crystal structure of 5-hydroxy-4a-methyl-*trans*-decahydroquinoline (Gladii *et al.*, 1991; SOXVEG; space group $I4_1/a$) with centrosymmetric synthons $(N—H\cdots O—H)_2$ (Fig. 3*b*). The molecules form a net with the topology of zeolite gismondine (**gis**), whereas synthons form an **lvt** partial ring net (Fig. 3*d*).

It should be emphasized that all the different kinds of nets discussed above are the representations of the same crystal structure considered from different points of view. It seems to be meaningless to decide which of them is the 'best'; they are all closely interrelated and to choose any of them depends on the matter in hand. In this study we are interested in the topology of hydrogen-bonded nets and molecular packings that justifies applying the standard representation.



(*a*)

(*b*)

Figure 2
(*a*) Hydrogen bonding in the crystal structure of *p*-aminophenol (AMPHOL01). Each molecule is hydrogen bonded to six others; (*b*) four-coordinated **lon-b** net; blue and red spheres respresent N and O atoms, respectively, red edges correspond to phenyls. The hydrogen-bonded net of molecular centroids (*a*) and the corresponding partial edge net (*b*), both with **acs** topology, are shown as blue lines.

3.2. Crystals with symmetrically equivalent molecules

As can be seen from Table 1, the most frequent topological types of hydrogen-bonded nets are **dia** (22.8%), **pcu** (10.3%), **sxd** (6.3%), **hex** (5.0%). Six-coordinated topologies are the most numerous (32.5%) followed by four-coordinated (30.2%) and eight-coordinated (19.4%) ones. Comparing these statistics with those of MOFs (Ockwig *et al.*, 2005) it is easy to see that **dia** and **pcu** are the most frequent topologies in both samples. This coincidence could be explained by the fact that hydrogen bonds have a partial directional character resembling covalent bonds in MOFs. Nevertheless, there are some important differences. Firstly, the majority of MOFs

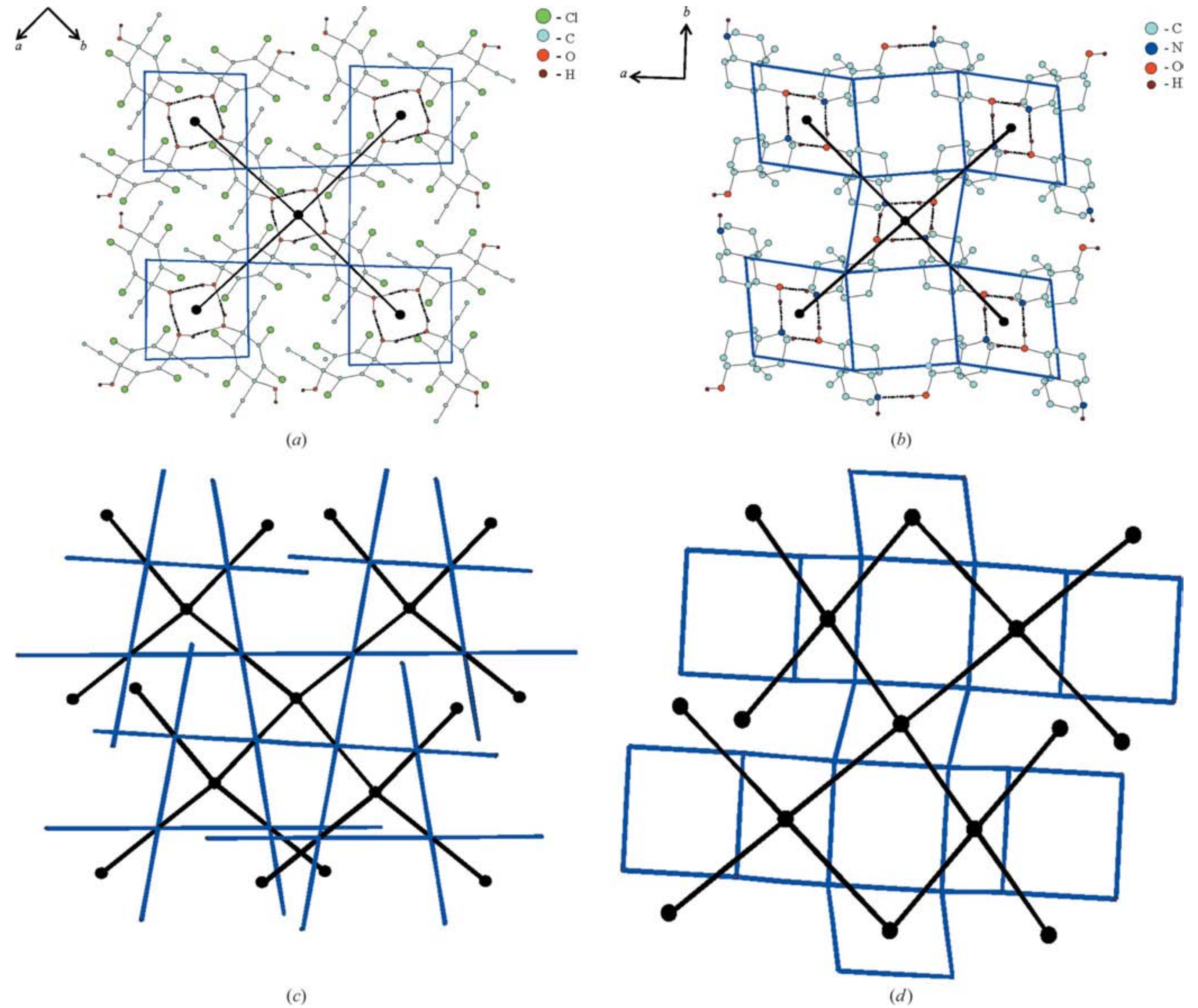


Figure 3
Hydrogen bonding in the crystal structures of (*a*) 2,3,5,6-tetrachloro-*trans*-1,4-diethynylcyclohexa-2,5-diene-1,4-diol (XEHKIE) and (*b*) 5-hydroxy-4a-methyl-*trans*-decahydroquinoline (SOXVEG) with $R_4^4(8)$ synthons; (*c*) relationship between **lvt** net and a partial ring net with **dia** topology; (*d*) relationship between **gis** net and a partial ring net with **lvt** topology. In all cases the initial net and the corresponding partial ring net are shown as blue and black lines, respectively.

have four-coordinated topologies followed by six-coordinated and three-coordinated ones. Although four- and six-coordinated topologies are also typical for hydrogen-bonded frameworks, three-coordinated (and other odd-coordinated) topologies are rare (*cf.* §3.1). Secondly, eight-coordinated topologies rarely encountered in MOFs are common to hydrogen-bonded frameworks. Thirdly, some six-coordinated nets frequently observed in hydrogen-bonded frameworks (**bsn**,[3] **lcy** and **sxd**) have never been found in MOFs. Further we discuss some general correspondence between geometrical features of initial structures and geometrical-topological properties of hydrogen-bonded nets.

The data on net transitivities generally confirm the conclusion of Ockwig *et al.* (2005) about the preference of high-symmetrical nets with small numbers of different kinds of topologically non-equivalent nodes and edges. Indeed, for the hydrogen-bonded nets with occurrences of more than ten the smallest transitivities of 11 and 12 are typical.

3.2.1. Symmetry of molecules *versus* topology of hydrogen-bonded nets

In general, the site-symmetry group of a molecule in a crystal is a subgroup of the symmetry group of an isolated molecule[4] (Vainshtein *et al.*, 1982). However, when forming a crystal, molecules lose their intrinsic symmetry as a rule. Inversion centers, twofold axes and mirror

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[3] The **bsn** topology was found only in the MOF structure (XULDIR) composed of three interpenetrating **bsn** nets (Blatov *et al.*, 2004).

[4] We disregard the cases when the 'averaged' symmetry of a molecule can be higher than that of an isolated molecule because of disordering.

planes are the symmetry elements often retained by molecules in the crystal structure (Pidcock *et al.*, 2003). Thus, the symmetry of a molecule predetermines to some extent its nearest environment and influences the net topology as a whole. On the other hand, the global topology of the hydrogen-bonded net determines the allowable site symmetry of a molecule. Let us consider, following Delgado Friedrichs & O'Keeffe (2003), the most symmetrical embedding of a hydrogen-bonded net into Euclidean space. Let G be the space group of such an embedding. If a net is crystallographic, *i.e.* G is isomorphic to its automorphism group (Klee, 2004), then G may be found uniquely. As expected, the site-symmetry group of a molecule in the crystal structure is a subgroup of the site-symmetry group of a node in the hydrogen-bonded net of maximal symmetry (Table 4). Let us consider a diamond net as an example. It is well known that its spatial embedding has the highest symmetry $Fd\bar{3}m$ with the nodes in positions 8(a) or 8(b) (site symmetry $\bar{4}3m$). In all, 352 cases of *uninodal* (with one crystallographic kind of node) hydrogen-bonded nets with **dia** topology molecules are allowed to occupy the sites whose point-symmetry groups are subgroups of $\bar{4}3m$ (1, 2, m or $\bar{4}$; more complex subgroups are not found as molecules generally have trivial symmetry). This means that a diamondoid hydrogen-bonded net, even arbitrarily distorted, cannot be built up from molecules having inversion symmetry in a crystal. One may expect that centrosymmetric molecules can hardly form such a net because they have to lose the center of symmetry in this case.

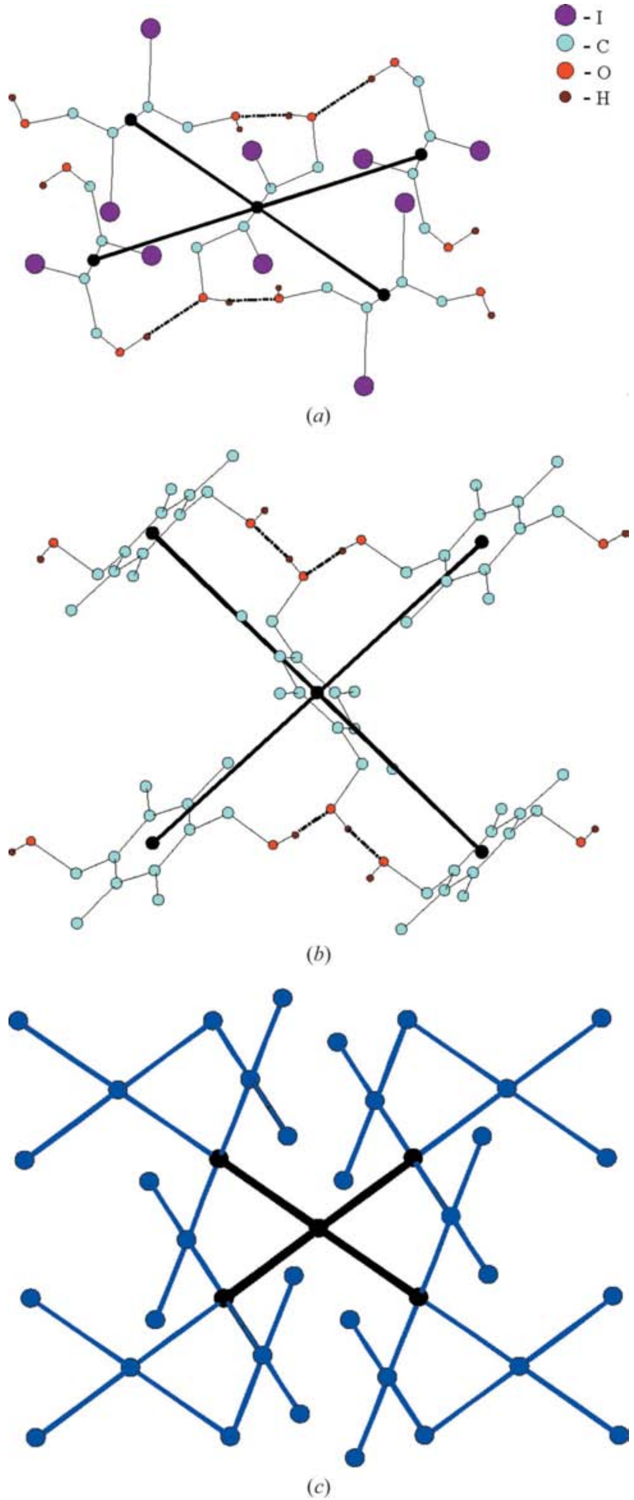

Figure 4
Hydrogen bonding in the crystal structures of (a) *trans*-2,3-diiodo-2-butene-1,4-diol (NIMGOF) and (b) 1,4-bis(hydroxymethyl)-2,3,5,6-tetramethylbenzene (OJEZUY); (c) a fragment of **lvt** net. In all cases square-like coordination figures are shown as black lines and spheres.

Another example demonstrating the use of group–subgroup relations is the cubic ($Pa\bar{3}$) crystal structure of hexaaminobenzene (Dixon *et al.*, 1989; ZZZWOU01), where each molecule is hydrogen-bonded to 12 others forming a framework with the **fcu** (face-centered cubic) topology and occupies 4(b) positions with the site symmetry $\bar{3}$. *Ab initio* calculations showed that hexaaminobenzene exists in the two conformations with $\bar{3}m$ or $\bar{3}$ symmetry (Dixon *et al.*, 1989), *i.e.* has a center of symmetry in any case. One may consider why the molecules do not form a hexagonal close packing (**hcp**) that occurs with maximal symmetry in $P6_3/mmc$ 2c (site symmetry $\bar{6}m2$). As the $\bar{6}m2$ group has no $\bar{1}$ subgroup, all low-symmetrical embeddings of **hcp** topology, unlike **fcu**, require hexaaminobenzene molecules to lose the center of symmetry. This is probably why the **hcp** motif is less favourable in the arrangement of hexaaminobenzene molecules.

3.2.2. Hydrogen-bonded net space-group symmetry *versus* topology

Table 4 also demonstrates relations between the space-group symmetry of a crystal structure and the possible topology of the corresponding hydrogen-bonded net. Namely, in all cases the space group of the initial hydrogen-bonded molecular framework is a subgroup of G for the corresponding hydrogen-bonded net. Since we consider only crystallographic nets, this observation confirms the results of Klee (1974) who showed the space group of a net embedding to be a subgroup of the automorphism group of a net. For instance, all the crystals where molecules are linked into diamondoid hydrogen-bonded frameworks belong to the space groups that are subgroups of $Fd\bar{3}m$. Analogously, the symmetry $P2_1/c$ cannot appear at the **lcy** topology because in this case $G = P4_132$ is noncentrosymmetric. The net topology also imposes a restriction on the possible number of inequivalent molecules in the unit cell. As was described in §2, *TOPOS* applies group–subgroup relations to derive all low-symmetrical embeddings

Table 7
All space groups compatible with some widespread uninodal hydrogen-bonded nets.

Topology	Space groups
dia	$Fd\bar{3}m$, $P4_132$†, $F4_132$, $Fd\bar{3}$, $R\bar{3}c$, $R\bar{3}m$, $R32$, $P3_121$†, $R\bar{3}$, $I4_1/amd$, $I\bar{4}2d$, $I4_1md$, $I4_122$, $P4_12_12$†, $P4_122$†, $I4_1/a$, $I4_1$, $P4_1$†, $Imma$, $Fddd$, $Pnma$, $Pbcn$, $Pmna$, $Pnna$, $Ima2$, $Fdd2$, $Pna2_1$, $Pnc2$, $I2_12_12_1$, $P2_12_12_1$, $P222_1$, $C2/c$, $P2_1/c$, $P2/c$, $C2/m$, Cc, $C2$, $P\bar{1}$
sxd	$Imma$, $Pnma$, $Pbcn$, $Pmna$, $Pnna$, $Ima2$, $Pna2_1$, $Pnc2$, $I2_12_12_1$, $P2_12_12_1$, $P222_1$, $C2/c$, $P2_1/c$, $P2/c$, $C2/m$, Cc, $C2$, $P\bar{1}$
acs	$P6_3/mmc$, $P6_3/mcm$, $P\bar{6}2c$, $P\bar{6}c2$, $P6_3mc$, $P6_3cm$, $P6_322$, $P6_122$†, $P6_3/m$, $P6_3$, $P6_1$†, $R\bar{3}c$, $P\bar{3}c1$, $P\bar{3}m1$, $P\bar{3}1c$, $P\bar{3}1m$, $R3c$, $P31c$, $P3c1$, $P3_121$†, $P321$, $P312$, $R\bar{3}$, $P\bar{3}$, $Cmcm$, $Pnma$, $Pbca$, $Pbcn$, $Pnnm$, $Pbcm$, $Pnna$, $Ama2$, $Cmc2_1$, $Pnn2$, $Pna2_1$, $C222_1$, $P2_12_12_1$, $C2/c$, $P2_1/c$, $P2/c$, $C2/m$, $P2_1/m$, Cc, $C2$, $P2_1$, $P\bar{1}$
lcy	$P4_132$†, $P2_13$, $P4_12_12$†, $P4_1$†, $P2_12_12_1$
bnn	$P6/mmm$, $P6_3/mmc$, $P6_3/mcm$, $P6/mcc$, $P\bar{6}2c$, $P\bar{6}2m$, $P\bar{6}c2$, $P\bar{6}m2$, $P6_3mc$, $P6_3cm$, $P6cc$, $P6mm$, $P6_322$, $P6_122$†, $P6_222$†, $P622$, $P6_3/m$, $P6/m$, $P6_1$†, $P6_2$†, $P6$, $R\bar{3}c$, $R\bar{3}m$, $P\bar{3}c1$, $P\bar{3}m1$, $P\bar{3}1c$, $P\bar{3}1m$, $R3m$, $P31m$, $P3m1$, $P3_121$†, $P321$, $P312$, $R\bar{3}$, $P\bar{3}$, $Imma$, $Ibam$, $Immm$, $Cccm$, $Cmmm$, $Cmce$, $Cmcm$, $Pnma$, $Pbcn$, $Pmmn$, $Pnnm$, $Pbcm$, $Pccn$, $Pbam$, $Pcca$, $Pmna$, $Pnna$, $Pmma$, $Pban$, $Pnnn$, $Ima2$, $Iba2$, $Imm2$, $Ama2$, $Amm2$, $Ccc2$, $Cmc2_1$, $Cmm2$, $Pba2$, $Pmn2_1$, $Pnc2$, $Pma2$, $I2_12_12_1$, $I222$, $C222$, $C222_1$, $P2_12_12$, $P222_1$, $C2/c$, $P2_1/c$, $P2/c$, $C2/m$, $P2_1/m$, $P2/m$, Cm, $C2$, $P2$, $P\bar{1}$
ecu	$Cmcm$, $Pnma$, $Pbca$, $Pbcn$, $Pnnm$, $Pbcm$, $Pnna$, $Ama2$, $Cmc2_1$, $Pnn2$, $Pna2_1$, $Pca2_1$, $C222_1$, $P2_12_12_1$, $C2/c$, $P2_1/c$, $P2/c$, $C2/m$, $P2_1/m$, Cc, $C2$, $P2_1$, $P\bar{1}$
vcs	$Pnma$, $Pna2_1$, $P2_12_12_1$, $P2_1/c$

† Only one group of the enantiomorphic pair is given.

of the net with a given topology; this capability was used to find all possible combinations of the net topology and space-group symmetry at a given number of inequivalent molecules. For instance, a uninodal diamond net is forbidden in the $P2_1$ group because low symmetry gives rise to at least two inequivalent nodes (molecular centers) in the unit cell. Resting upon the results of Fischer & Koch (1978), it could be concluded that a uninodal net of a given topology can be embedded into some space group G' (that is a subgroup of its automorphism group G) if and only if the index of G' in G is a divisor of the order of the site-symmetry group of a node in the embedding with the highest symmetry G. In the case of diamond we have $G' = P2_1$, $G = Fd\bar{3}m$, the minimal index of G' in G is 48. The order of the site-symmetry group of a node in the embedding with the highest symmetry is 24 ($\bar{4}3m$). As 48 is not a divisor of 24, the uninodal **dia** net is forbidden in $P2_1$ symmetry, but there can be a binodal $P2_1$ **dia** net.

The space-group distribution (Table 5) shows that the most frequent space groups for hydrogen-bonded frameworks are $P2_12_12_1$, $P2_1/c$ and $P2_1$. It is known (*cf.* Pidcock *et al.*, 2003) that these space groups frequently occur in organic substances irrespective of the presence or absence of hydrogen bonds. Table 4 shows that nearly all widespread topological types are compatible with the space groups $P2_12_12_1$ and $P2_1/c$. Note that in the popular space groups ($P2_12_12_1$, $P2_1$, $Pna2_1$ and Cc) odd-coordinated uninodal nets are forbidden (*cf.* Fischer & Koch, 1979), which correlates with the preference of even-coordinated topologies among hydrogen-bonded nets (*cf.* §3.1). The relations between topology and space-group symmetry, most common to hydrogen-bonded frameworks, are collected in Tables 7 and 8.

3.2.3. Local arrangement of molecules *versus* hydrogen-bonded net topology

Ockwig *et al.* (2005) found correlations between the geometries of coordination figures formed by secondary building units, and the underlying topologies of valence-bonded MOFs. In our case, building units are molecules and the links correspond to hydrogen bonds, but the underlying topologies are similar to MOFs to some extent (*cf.* §3.2). Therefore, it is reasonable to consider the relationships between the local arrangement of molecules and the resulting type of hydrogen-bonded net. To elucidate these relationships we studied in detail some four-coordinated hydrogen-bonded nets having rather common **cds**, **dmp**, **qtz** and **lvt** topologies. It turned out that the coordination figures of nodes in the **cds**, **dmp** and **qtz** hydrogen-bonded nets are strongly distorted tetrahedra in 53.6, 76.5 and 50.0% of cases, respectively. In all other cases square-like (**cds**) and tetrahedron-like (**dmp** and **qtz**) coordination figures are realised. Note that this result is unexpected only for the **cds** topology considered as an arrangement of square building units by Ockwig *et al.* (2005), whereas the other two topologies (**dmp** and **qtz**) are characterized by tetrahedron-like coordination figures in the most symmetrical embedding. Note that a single example of the coordination figure as a distorted tetrahedron has also been found in the hydrogen-bonded net with **lvt** (3-methyl-3-pyrazolin-5-one; MPYAZO11) topology, whereas square-like coordination dominates in this case. Sometimes (especially in high-symmetrical crystal structures) the arrangement of molecules is clearly predetermined by the geometry of hydrogen bonds. For example, in the crystal structures of *trans*-2,3-di-iodo-2-butene-1,4-diol (NIMGOF) and 1,4-bis(hydroxymethyl)-2,3,5,6-tetramethylbenzene (OJEZUY) hydrogen bonds lie in the plane almost perpendicular to the r.m.s. plane of the molecule (Figs. 4*a* and *b*) and form a square-like arrangement, thus predetermining the square-like **lvt** topology of hydrogen-bonded nets (Fig. 4*c*). This result correlates with the square coordination of the nodes in the most symmetrical embeddings of the hydrogen-bonded net.

3.2.4. Molecular packings *versus* hydrogen-bonded networks

Organic crystals with intermolecular hydrogen bonds are often assumed to have less 'dense' structures than those without hydrogen bonds (*cf. International Tables for Crystallography*, 2004, Vol. C, ch. 9). The open structures of ice, β-hydroquinone *etc.* are characteristic in this respect. However, Kitaigorodskii (1965) admitted that the trends to form a close packing and to saturate all hydrogen bonds act simultaneously; in crystals the latter trend conforms to Donohue's rule (Etter, 1991). Table 3 shows that the topologies of molecular packings realised in the organic crystals with hydrogen-bonded frameworks and in those without hydrogen bonds are essentially the same. Analysis of all intermolecular contacts confirms the conclusion of Peresypkina & Blatov (2000) regarding the preference of molecular coordination number 14. However, the underlying topologies found with

Table 8
Topological types that can be realised as uninodal nets in the most frequent space groups of hydrogen-bonded nets.

Space group	Node degree	Topologies
$P2_12_12_1$	4	**dia**
	6	**acs**, **bsn**, **lcy**, **pcu**, **sxd**
	8	**hex**, **bcu**, **eca**, **eci**, **ecu**, **tsi**, **vcs**
	10	**cco**, **chb**, **feb**, **tcg**, **bct**
	12	**fcu**, **hcp**
$P2_1/c$	4	**dia**, **cds**, **dmp**
	5	**bnn**, **fnu**, **nov**, **noz**, **sqp**
	6	**acs**, **bsn**, **msw**, **pcu**, **roa**, **rob**, **sxa**, **sxb**, **sxd**
	7	**ose**, **sev**, **sve**, **svk**
	8	**bcu**, **eca**, **ecu**, **hex**, **tsi**, **vcs**
	9	**ncd**, **nce**, **nci**, **ncj**
	10	**bct**, **cco**, **chb**, **feb**, **gpu**, **hxg-d**, **tcd**, **tcg**
	11	**ela**, **elb**, **elc**
	12	**fcu**, **hcp**
$P2_1$	6	**acs**, **pcu**
	8	**bcu**, **eca**, **ecu**, **hex**
	10	**bct**, **cco**, **chb**
	12	**fcu**, **hcp**

clustering contacts and discarding the weakest ones correspond to close packings in 51.5% of crystals with hydrogen-bonded frameworks and in 37.8% of crystals without hydrogen bonds (**fcu** is preferable in both cases), *i.e.* hydrogen bonding promotes the trend to form close-packed motifs.

The tendency to form a close packing can explain the high frequency of the hydrogen-bonded net topologies to be unusual for valence-bonded MOFs (*cf.* §3.2). Indeed, a reason for the frequent occurrence of eight-coordinated topologies in our sample is that most of them (**ecu**, **hex**, **vcs**) can be easily related to close packings (Figs. 5*a*–*f*). Similarly, one of the most common six-coordinated nets observed in hydrogen-bonded frameworks, **sxd**, is also related to close packings, either **fcu** or **hcp** (Figs. 5*a*, *b* and *f*).

3.3. Crystals with symmetrically non-equivalent molecules

The distribution of topological types for homomolecular crystals with crystallographically different molecules (Table 2) shows that there are no especially preferable types; for instance, only 6.1% of structures correspond to the **dia** net. However, it should be noted that more than half of hydrogen-bonded nets (53.2%) have one topological kind of node; the leading nets have small transitivities as for the uninodal hydrogen-bonded nets. This means that molecules not even related by symmetry tend to form the same hydrogen-bond pattern. One of the reasons for the presence of symmetrically non-equivalent molecules in crystals is that the low crystal symmetry does not allow uninodal hydrogen-bonded nets to be realised. For instance, out of 14 diamondoid hydrogen-bonded nets with non-equivalent molecules, there are nine crystal structures with symmetries $P2_1$ and $P1$, incompatible with a uninodal diamond net (*cf.* §3.2.2).

4. Conclusions

Our results show that hydrogen-bonded frameworks in organic crystals exhibit a great diversity of topological types, although most of them are known to crystal chemists and have been either observed before in crystals or derived theoretically. The most common types, **dia** and **pcu**, that are found for about one third of the compounds studied, are so-called regular nets (Delgado Friedrichs *et al.*, 2003*c*) which are highly symmetrical in the topological sense and have a great importance in crystal design. The grammar of crystal design (Ockwig *et al.*, 2005) can be extended with new rules confirmed by a large amount of crystal data. These rules relate the geometrical–topological features of the initial framework of hydrogen-bonded molecules, isolated molecules and the resulting hydrogen-bonded net.

(i) The point group of a molecule in the framework must be a common subgroup of the point group of the corresponding node in the most symmetrical (with the space group *G*) embedding of the hydrogen-bonded net and the point group of an isolated molecule.

(ii) The space group of any embedding of the hydrogen-

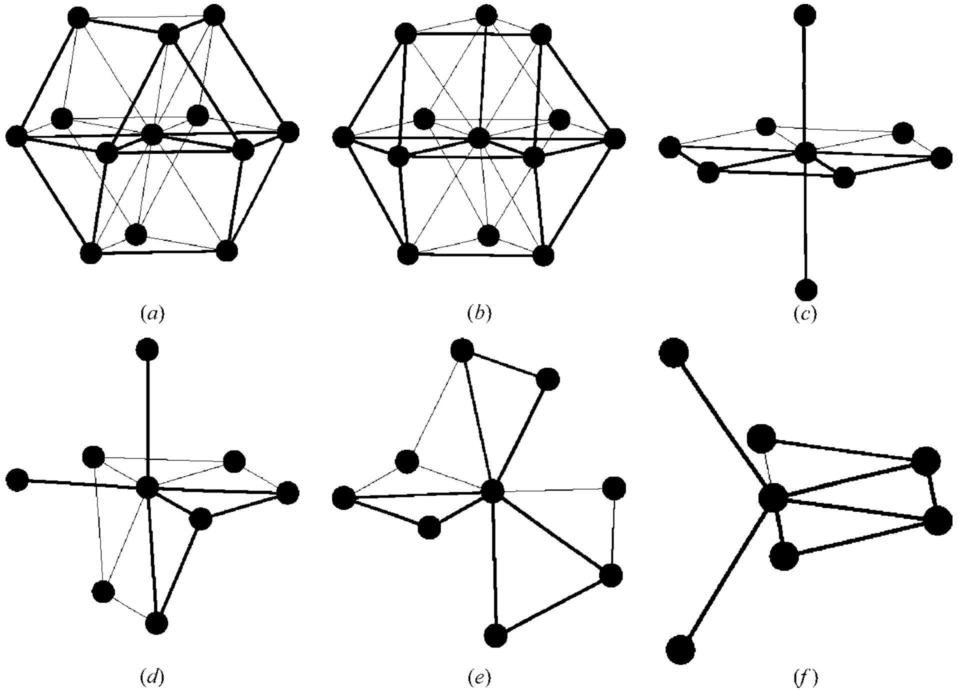
(*a*) (*b*) (*c*) (*d*) (*e*) (*f*)

Figure 5
Coordination figures for (*a*) a face-centered cubic lattice (**fcu**); (*b*) hexagonal close packing (**hcp**); (*c*) a hexagonal primitive lattice (**hex**); (*d*) the **ecu** net; (*e*) the **vcs** net; (*f*) the **sxd** net.

bonded net must be a subgroup of G (*cf.* Klee, 1974).

(iii) Some space groups obeying the previous rule are forbidden for a particular number of inequivalent molecules (Tables 7 and 8). A uninodal net of a given topology may be realised in some space-group symmetry G' if, and only if, the index of G' in G is a divisor of the order of the point group of the net node in the most symmetrical embedding (*cf.* Fischer & Koch, 1978).

(iv) Different topological representations of the initial framework are interrelated; the most important representations involve a 'standard' hydrogen-bonded net, whose nodes correspond to molecular centroids, and the corresponding edge and ring nets.

Obviously, these rules may be easily extended to the three-periodic nets with other types of bonding, and to low-dimensional (one-dimensional or two-dimensional) periodic nets. Their application in each of the cases is the subject of a further study.

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