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Crystal packing in *vicinal* diols $C_nH_m(OH)_2$

Carolyn Pratt Brock

Department of Chemistry, University of Kentucky, Lexington, KY 40506-0055, USA

Correspondence e-mail: cpbrock@uky.edu

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The O—H···O bonds in *vic*-diols $C_nH_m(OH)_2$ have been studied using data retrieved from the Cambridge Structural Database. About half of these diols form complete, or almost complete, sets of intermolecular O—H···O bonds (*i.e.* two satisfied donors per molecule). For this half of the structures the frequencies of high-symmetry space groups and of structures with $Z' > 1$ (more than one molecule in the asymmetric unit) are substantially elevated. The most common motif among fully bonded structures is an $R_2^2(10)$ dimer, which can be linked in a variety of ways to form one-, two- or even three-dimensional patterns. Most of the other half of the *vic*-diols form simple O—H···O chains in which each OH group participates in only one intermolecular hydrogen bond. The space-group frequencies for this second group of structures are unexceptional. The most important factor determining the extent of O—H···O bond formation is the degree of substitution of the *vic*-diol. The spatial segregation of OH groups that is necessary for the formation of O—H···O bonds is found to make the dense filling of space more difficult because the intermolecular spacings that are appropriate for the O—H···O bonds may be inappropriate for the rest of the molecule.

1. Introduction

The steric problems that are associated with the formation of a full set of O—H···O bonds in monoalcohols C_nH_mOH (*i.e.* one O—H donor per molecule; each O atom acts as both a donor and an acceptor) are important enough that the space-group frequencies are affected; structures in high-symmetry space groups and structures with $Z' \geq 2$ (two or more molecules in the asymmetric unit) are surprisingly common (Brock & Duncan, 1994). The steric problems that are associated with the formation of a full set of O—H···O bonds in *vic*-diols $C_nH_m(OH)_2$ (two O—H donors per molecule) are even more severe because the two O atoms of a molecule are separated by only three covalent bonds and because intramolecular O—H···O bonds are unfavorable.[1]

Small discrete aggregates (*i.e.* rings) are common for monoalcohols C_nH_mOH but are less likely for *vic*-diols $C_nH_m(OH)_2$ because half of the O—H···O bonds would have to be intramolecular and therefore weak. Rings of *vic*-diols (other than dimers) would also surround substantial regions of empty space. Fully connected three-dimensional nets also seem unlikely because there is not room for large numbers of C atoms in the volumes enclosed by the O—H···O bonds. These intermolecular hydrogen bonds can be more easily

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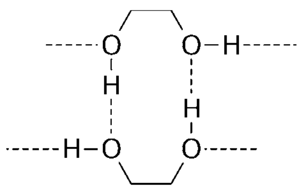
[1] Jeffrey (1997) concluded that for adjacent hydroxyl groups in carbohydrates 'vicinal intramolecular bonding is rare except as a minor component of a three-center bond because the angular geometry is unfavorable with O—H···O < 120°'.

stretched or compressed than covalent bonds, but the O···O distance cannot vary by much more than 0.5 Å. Most *vic*-diols $C_nH_m(OH)_2$ may therefore be expected to aggregate into two-dimensional layers or one-dimensional chains.

If a full set of O—H···O bonds is formed it seems likely that the pattern will include the following $R_2^2(10)$ dimer motif:[2]



This motif, if linked to form chains or layers, satisfies all donors, and extended patterns can be formed in a number of different ways (see Figs. 1 and 2). The motif can be located on an inversion center or on a twofold axis; if the hydroxyl proton positions are disordered the motif can also lie on the twofold axes that bisect the pairs of inter- or intramolecular O···O vectors.

It seems that one-dimensional chains of O—H···O bonds should be more common than two-dimensional layers because the matching of the spacings appropriate for the OH groups with the spacings appropriate for the rest of the molecule can be a problem. This matching requirement affects only one direction if the O—H···O bonds form a one-dimensional chain but affects a whole set of directions if the hydrogen bonds form a two-dimensional layer. Matching of spacings is more difficult if the molecule is very rigid or very large.

This study then addresses the following questions. How often do *vic*-diols $C_nH_m(OH)_2$ manage to satisfy both hydroxyl donors to form a full set of O—H···O bonds? Are the space-group frequencies anomalous? How robust is the dimer motif? How does the requirement for the matching of spacings affect the O—H···O patterns?

Two other studies of crystal packing of diols have appeared recently; both considered all diols $C_nH_m(OH)_2$ rather than just the more sterically constrained *vic*-diols. Taylor & Macrae (2001) found no anomalies in the space-group frequencies. Nguyen *et al.* (2001) focused on the identification of ladder-like patterns of O—H···O bonds.

2. Methodology

The final searches were performed on version 5.23 (April 2002) of the Cambridge Structural Database (CSD; Allen, 2002). Separate searches were performed for each of the substitution patterns shown in Table 1. The search questions also specified that the atom types C, H and O be the only kinds present, that exactly two O atoms be present, that coordinates be archived, and that the *R* factor be less than 0.10. Structures with *R* factors between 0.06 and 0.10 were evaluated individually; the structure was retained if it appeared to be correct

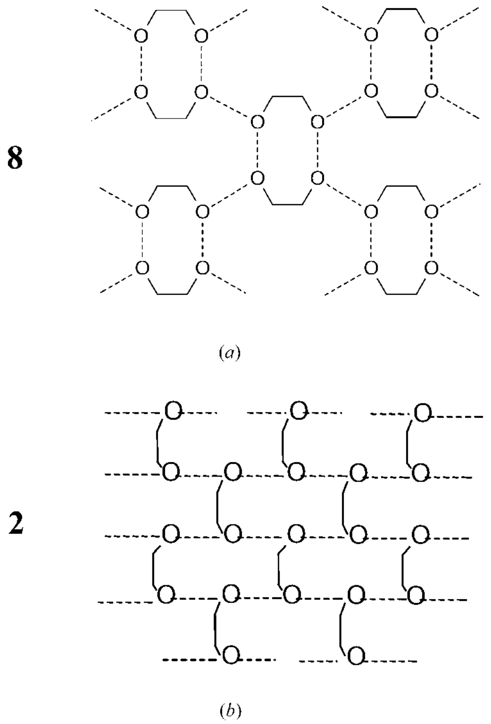


Figure 1
Two-dimensional patterns of O—H···O bonding found for *vicinal* diols $C_nH_m(OH)_2$. The number of times each pattern was found is shown. Two other two-dimensional patterns are too complicated to diagram.

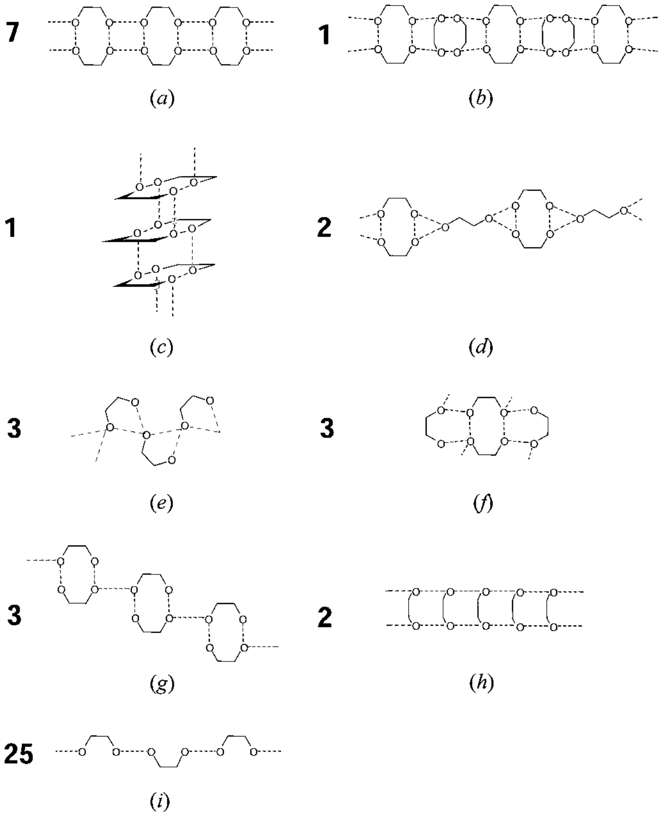


Figure 2
One-dimensional patterns of O—H···O bonding found for *vicinal* diols $C_nH_m(OH)_2$. The number of times each pattern was found is shown. One other one-dimensional patterns is too complicated to diagram.

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[2] No attempt has been made to determine complete graph-set symbols (Etter *et al.*, 1990; Bernstein *et al.*, 1995) for all patterns but the terminology has been used to describe some aspects of the patterns.

Table 1
Summary of *vic*-diol structures.

						Number of patterns				
Class	Structure	Number of structures	% Cyclic	% Full O—H···O bonding	Average number of O—H···O bonds per O atom	3D	2D	1D	0D	None
0	$H_2C(OH)C(OH)H_2$	1	–	100	2	1	0	0	0	0
1	$HRC(OH)C(OH)H_2$	0	–	–	–	–	–	–	–	–
2_1	$RR'C(OH)C(OH)H_2$	0	–	–	–	–	–	–	–	–
2_2	$RHC(OH)C(OH)HR'$	21	86	86	1.9 (1)	1	9	10	0	1
3	$RR'C(OH)C(OH)HR''$	17	53	29	1.3 (1)	0	0	12	4	1
4	$RR'C(OH)C(OH)R''R'''$	29	52	24	1.2 (1)	0	2	24	1	2
A	$RC(OH)C(OH)R'$ (C—C bond not single)	3	100	67	1.8 (2)	0	1	2	0	0

and if there was a plausible reason for the higher agreement factor (*e.g.* a pseudosymmetric structure having a large value of Z' or unmodeled disorder). Structures that included solvent molecules or obvious voids were rejected. A separate search was made for molecules that included D atoms but none was found.

No structure of any primary alcohol other than ethylene glycol was found. Since there is no exceptional chemical instability associated with class 1 or 2_1 (see Table 1) it must be that structures of molecules of this type have not been considered interesting or important or that such molecules crystallize poorly. Another example of bias in the database is the high fraction of cyclic diols in class 2_2 (see Table 1). The three *vic*-diols that have non-single C—C bonds are all aromatic.

Of the 71 structures that are included in the final tabulation, 39 have $R \leq 0.050$ and three have $R \geq 0.075$. Only a few of the structures (10) were determined at low temperature, but 36 have OH proton positions that appeared to be both refined (O—H bond lengths not equal to standard values or to each other) and chemically reasonable.

No polymorphic structures were found.

Analyses of the individual structures were made first with the program *XP* in Sheldrick's (1990) package *SHELXTL/PC* and later with the *CCDC* program *Mercury* (Bruno *et al.*, 2002). In the absence of reliable hydroxyl proton positions O—H···O bonds had to be inferred from the O···O distances. The only ambiguities that were encountered were associated with the several cases of possible bifurcated hydrogen bonds and with the identification of possible intramolecular O—H···O bonds.

Contacts out to 3.60 Å were investigated because Steiner & Saenger (1994) concluded that longer O···O distances do not correspond to O—H···O bonds. All contacts with $3.22 < d(\text{O}\cdots\text{O}) \leq 3.60$ Å, as well as some shorter O···O contacts, were identified as nonbonding interactions [*e.g.* O···O contacts across the diagonals of $R_4^4(8)$ rings and $R_2^2(10)$ dimers].

All but 10 of the 67 *vic*-diols that form intermolecular O—H···O bonds have one of the hydrogen-bonding patterns shown in Figs. 1 and 2. Two of the 10 form three-dimensional patterns, three form unlinked $R_2^2(10)$ dimers, one forms a trimer and one forms a tetramer. Two of the other three *vic*-diols have unusual two-dimensional patterns and the last has a complicated one-dimensional pattern.

For each structure the average number of intermolecular O—H···O bonds per molecule was determined. This number is two for a full pattern in which each O atom donates one proton and accepts another. The number is also two for an unbalanced pattern in which one O atom accepts two protons and the other O atom accepts none. The number is one for a simple chain in which each O atom is either a donor or an acceptor in an intermolecular O—H···O bond but is not both. Non-integral values are possible; if one O atom participates in two intermolecular O—H···O bonds and the other O atom participates in one then the average number of intermolecular bonds per O atom is 1.5. Note that a complete pattern of intermolecular O—H···O bonds requires four different O—H···O interactions unless there are special symmetry relationships.

Searches that allowed the presence of F, S, Si and Ge atoms were also made, but only a few additional structures (3, 4, 3 and 0) were found. They were not included in the compilation.

A tabulation of the results has been deposited.[3]

3. Results

The 146 O···O distances that are identified as bonding in the 71 structures range from 2.66 to 3.22 Å. The average and median distances are 2.82 (1) and 2.80 Å; the variance of the distances is 0.11 Å. Nearly all (92%) of the distances are ≤ 3.00 Å.

3.1. *Gauche* conformers predominate

Quantum-mechanical calculations for the model systems ethane-1,2-diol (Yeh *et al.*, 1994) and pinacol (2,2-dimethylbutane-2,3-diol; Dahlqvist *et al.*, 1998) indicate that the best *gauche* conformer (O—C—C—O $\simeq 60^\circ$) is *ca.* 8 kJ mol^{-1} lower in energy than the best *trans* conformer (O—C—C—O $\simeq 180^\circ$) because of the weak intramolecular O—H···O bond that is possible in the former. If all O—H···O bonding is intermolecular then the two conformers are very similar in energy.

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[3] Supplementary data for this paper are available from the IUCr electronic archives (Reference: BS0017). Services for accessing these data are described at the back of the journal.

The *gauche* conformer is preferable if a full set of intermolecular O—H···O bonds cannot be formed because this conformer allows for intramolecular hydrogen bonding. The *gauche* conformer is also required for the dimer motif (see above). *Trans* conformers are therefore expected to occur infrequently.

Most of the structures do indeed contain *gauche* conformers; in 44 of the 68 non-aromatic diol structures some or all of the independent molecules[4] have O—C—C—O torsion angles in the range 40–80°. Only seven structures are built solely from *trans* conformers (O—C—C—O torsion angles in the range 160–180°) and only six more have O—C—C—O torsion angles in the range 80–160°. The O—C—C—O angle, however, is strongly influenced by nearby ring systems in many of the *gauche* molecules, in one of the *trans* molecules and in most of the remaining 17 molecules.

The molecules in seven of the 71 structures could lie on inversion centers, but just three of the structures contain $\bar{1}$-symmetric molecules only, and one of those structures (TITKIQ) has no O—H···O bonds at all. The molecule in one more structure (VEHGOE) has a conformation that is clearly *trans*. The other three molecules that could have $\bar{1}$ symmetry crystallize as *gauche* conformers even though molecules that can lie on inversion centers nearly always do (Yao *et al.*, 2002).

3.2. Most *vic*-diols form at least one intermolecular O—H···O bond

All but four (6%) of the molecules in the 71 *vic*-diol structures manage to form at least half of the two intermolecular O—H···O bonds that are possible. The percentage of monoalcohols C_nH_mOH that fail to form any O—H···O bonds (22%; Brock & Duncan, 1994) is much higher. On the other hand, only about half of the *vic*-diol molecules form a full, or almost full, set of intermolecular O—H···O bonds while 67% of the monoalcohols do so. The *vic*-diols are more likely to form some intermolecular O—H···O bonds than the monoalcohols but are less likely to form a complete set in which both donors are satisfied.

The *vic*-diols that form half of the possible intermolecular O—H···O bonds could do so by having each of the two OH groups involved in one bond or by having one OH group involved in two bonds. The latter arrangement was not found. It is likely that the important factor favoring the participation of both OH groups in the bonding is the spatial separation between the donor and the acceptor sites of the molecule. This separation also explains why *vic*-diols are more likely than monoalcohols to form at least one intermolecular O—H···O bond per hydroxyl group.[5]

Hydrogen bonds between symmetry-related hydroxyl groups are rare; they occur in only seven of the 67 O—H···O-bonded structures, and in one of those structures the diol lies on a symmetry element. Hydrogen bonds between independent hydroxyl groups are the rule, as was noted by Taylor & McCrae (2001).

The probability of forming a full set of O—H···O bonds falls as the number of C-atom substituents rises (see Table 1). Steric congestion around the attached C atoms hinders the close approach of the OH groups that is required for intermolecular hydrogen-bond formation. The preponderance of C_5 and C_6 rings in class 2_2 probably raises the probability of satisfying all donors because the rings 'tie back' the two substituents and leave the OH groups relatively unhindered.

3.3. Dimers and simple chains occur frequently

The two O—H···O bonding motifs that are most important among the *vic*-diols $C_nH_m(OH)_2$ are linked $R_2^2(10)$ dimers (found in 29 of the 71 structures) and simple $C(n)$ chains (found in 25 structures). The dimers usually occur in structures with complete, or almost complete, sets of O—H···O bonds; 29 of the 38 structures in which the average number of O—H···O bonds per O atom is greater than 1.5 include this dimer motif. Simple chains account for 25 of the 29 structures with intermolecular hydrogen-bonding patterns that are more incomplete. Only 13 of the 71 structures include neither a linked dimer nor a simple chain.

Many, perhaps even most, of the simple-chain structures probably contain weak intramolecular O—H···O bonds.

The two most common patterns for linked $R_2^2(10)$ dimers are the two-dimensional net of interlocking dimers [2*a* in Fig. 1(*a*)] and the one-dimensional dimer ribbon [1*a* in Fig. 2(*a*); called step-ladders by Nguyen *et al.* (2001)]. So many other patterns occur, however, that these two patterns cannot really be viewed as dominant. Isolated (unlinked) dimers are found in three structures.

3.4. Dimers usually lie on inversion centers

The $R_2^2(10)$ dimer motif is very likely (in 24 of the 32 structures in which it occurs) to lie on an inversion center.[6] In three structures the dimers are located on twofold axes; in five more the dimers have no symmetry, which means that Z' must be greater than 1. Enantiomerically pure crystals are less likely than racemic crystals to contain dimers; dimers occur in only four of the 25 enantiomerically pure crystals but in 28 of the 46 achiral or racemic crystals.

3.5. Smaller substituents favor O—H···O patterns of higher dimensionality

Patterns of higher dimensionality, if they do not require too many structural compromises, may promote crystal nucleation and growth because the greater connectivity increases

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[4] In 18 of these 68 structures there are two independent molecules, in three structures there are three molecules and in one structure there are six molecules. In 18 of the 22 $Z' > 1$ structures the independent O—C—C—O angles vary by 8° (average variation is 3°), but in the other four structures two conformers (one *trans*, one *gauche*) are present.

[5] It may also matter that one of the OH groups in a nonsymmetric *vic*-diol is at least very slightly more acidic than the other and that an OH group that forms two intermolecular O—H···O bonds is a less good acceptor for an intramolecular O—H···O bond.

[6] In two of these 24 structures (FILJIT and ZIWVEG) there is also at least one dimer in a general position.

Table 2
Space-group frequencies for *vic*-diols $C_nH_m(OH)_2$.

Group	Total	$Z' > 1$	Space group number > 74
All structures in the CSD		8%	4%
Vic-diols $C_nH_m(OH)_2$; ≥ 1.5 O—H···O bonds per O atom	38 (54%)	45%	21%
Vic-diols $C_nH_m(OH)_2$; ≤ 1.0 O—H···O bond per O atom	33 (46%)	18%	6%
All *vic*-diols $C_nH_m(OH)_2$	71	33%	14%

mechanical stability. The higher the dimensionality, however, the greater the packing problems.

3.5.1. Three-dimensional patterns. Only two structures with three-dimensional patterns were found. One contains the simplest *vic*-diol, ethylene glycol (NOZKES)[7], which has a complicated pattern of O—H···O bonds that does not include any dimers. The other structure is that of enantiomerically pure *trans*-*S*,*S*-1,2-cyclohexanediol (ZZZKPE03), which crystallizes in $P3_121$ with a dimer located on a twofold axis ($Z' = 1$). The related molecule (4*R*,5*R*)-1,2-dithiane-4,5-diol (DTHDOM) has the same structure.

3.5.2. Two-dimensional patterns. 12 of the 71 structures include two-dimensional layers of O—H···O bonds. Dimer nets (see Fig. 1*a*) are found in eight of the 12; linked chains (Fig. 1*b*) are found in two others.

The two-dimensional (and three-dimensional) patterns are far more probable for molecules with substituents that are small and/or few in number (see Table 1) than for more crowded diols; only two of the 12 two-dimensional examples come from groups 3 and 4 (Table 1), and one of those examples is pinacol, which has four methyl substituents. The two-dimensional patterns are especially likely for the *trans*-cyclic molecules of class 2_2 (seven of 12; all C_5 and C_6 rings) but are unlikely for the *cis*-cyclic molecules (none of six).

In nearly all (ten) of the 12 two-dimensional structures each O atom acts as both a donor and an acceptor; the two exceptions are both enantiomerically pure. In TETRDO01 (OH proton positions refined) the pattern is unbalanced; in one of the two independent molecules one O atom accepts no protons and the other O atom accepts two. In CSNRLA, an unusual hexagonal structure, one OH group of a bulky polycyclic molecule participates in an $R_3^3(6)$ ring while the other has a rather long contact (3.15 Å) to the next layer. The O atoms that are involved in these interlayer contacts either donate or accept a proton but cannot do both.

3.5.3. One-dimensional patterns. Most of the *vic*-diol structures (48 of 71) have one-dimensional O—H···O patterns. The patterns in about half (20) of those structures have two O—H···O bonds per molecule; another three structures have 1.5 or 1.75 bonds per molecule. In the other 25 one-dimensional structures each O atom participates in one intermolecular O—H···O bond rather than two.

The most common one-dimensional pattern with full O—H···O bonding is the dimer ribbon (Fig. 2*a*). The ribbon is not necessarily flat; alternating $R_2^2(10)$ and $R_4^4(8)$ rings may be approximately coplanar or nearly perpendicular. In five of the seven examples at least one of the rings lies on an inversion center.

3.5.4. Patterns composed of discrete aggregates. Five compounds form discrete O—H···O-bonded units. One (HOMQOP) is a rigid-cage compound that forms a linear trimer. Three of the other four compounds, all of which have the general formula $Ar_2C(OH)C(OH)(H)R$, form discrete dimers around inversion centers. The fourth compound, which is resolved, forms an unusual tetramer around a twofold rotation axis. Four of the five compounds that form discrete aggregates are in group 3; one is in group 4.

Three other compounds $Ar_2C(OH)C(OH)(H)R$ occur in the full list. One forms simple chains (Fig. 2*i*); a second forms a simple-chain variant in which $Z' = 2$ and one OH group forms no O—H···O bonds; and a third (YUYXEV) forms no O—H···O bonds at all (see below). These six $Ar_2C(OH)$-$C(OH)(H)R$ structures suggest that efficient packing of the Ar_2C fragment competes with the formation of an extended pattern of hydrogen bonds.

3.5.5. Structures with no O—H···O bonding. Four compounds form no intermolecular O—H···O bonds at all. The molecules of TITKIQ and FUTZOJ are very hindered; the latter is also enantiopure. The packing in YUYXEV appears to be determined by the interactions of the naphthyl groups, which form polar stacks. In enantiopure BHPHOL the filling of space by the $(C_{14}H_{14})$—$(C_{14}H_{14})$ unit seems to be structure determining.

3.6. Space-group frequencies for *vic*-diols with complete O—H···O patterns are anomalous

While the space-group statistics for the *vic*-diols that have less than one intermolecular O—H···O bond per O atom are unremarkable (see Table 2) the statistics for the *vic*-diols with complete, or almost complete, sets of intermolecular O—H···O bonds are anomalous. Structures in high-symmetry space groups and structures with more than one molecule in the asymmetric unit are unusually likely, almost certainly for the same reasons as described for the monoalcohols C_nH_mOH (Brock & Duncan, 1994).

Of the 38 *vic*-diol structures $C_nH_m(OH)_2$ that have at least 1.5 intermolecular O—H···O bonds per molecule, 25 (66%) crystallize either in a high-symmetry space group or with $Z' > 1$. This percentage is a little lower than that for the monoalcohols C_nH_mOH (79%) but it is still strikingly high. The drive for complete O—H···O bonding produces many unusual structures. Especially notable are the structures in which the independent molecules have very different conformations and the structures in which $Z' \geq 3$.

Four of the 23 structures with $Z' > 1$ contain both *gauche* and *trans* conformers [*e.g.* the pattern in Fig. 2(*d*), which is found for two of the four]. These four structures (DIJWUO10, FUJREH, PINCOL and ZOTBUF) are unusual because the

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[7] Although the text for this structure (Boese & Weiss, 1998) describes it as having ‘catamer-like two-dimensional networks with hydrogen bridges parallel to the [100] plane’ the hydrogen-bonding pattern is actually three-dimensional.

independent molecules in most $Z' > 1$ structures have similar shapes and orientations. While these four structures cannot be called compounds, they are similar to compounds in being formed from two units of different shape. An analogy could be made to the rare compounds of stereoisomers.

3.7. Some O—H···O patterns are exceptionally complex

Four structures have at least three independent molecules, or molecule halves, in the asymmetric unit. All four have full sets of intermolecular O—H···O bonds.

Dimer ribbons are found in the structure of *cis*-1,5-dihydroxy-1,5-diphenylcyclopentane (ZIWVEG; *C*2/*c*, $Z' = 3$). Every third dimer is located on an inversion center; the other two are related by a twofold rotation in the $R_4^4(8)$ ring. The orientations of the three independent molecules are very different.

The dimer/trimer pattern shown in Fig. 2(*d*) is found in the structure of enantiopure (1*S*,3*R*)-1-[(1*S*)-1-hydroxy-3-methylcyclohexyl]-3-methyl-1-cyclohexanol (DIJWUO10; *P*1, $Z = Z' = 3$). There are local twofold axes through the two (HO)C—C(OH) bonds of the dimer and of the connecting molecule, but the triclinic stacking of the ribbons prevents the local axes from being crystallographic.

Layers of O—H···O bonds are found in 2,3-dimethyl-2,3-butanediol (PINCOL; *C*2/*c*, $Z' = 1 + \frac{1}{2} + \frac{1}{2}$). *Gauche* conformers lie on general positions and twofold axes; *trans* conformers lie on inversion centers. There is no obvious pseudosymmetry.

The asymmetric unit of 2-*tert*-butylcyclohexane-1,2-diol (FILJIT; $P\bar{1}$, $Z' = 6$) has no obvious pseudosymmetry either. The one-dimensional pattern contains ladders (Fig. 2*h*) and two independent dimers, but the overall pattern is too complex (24 independent O—H···O bonds) for a simple description. This structure must be one of the most complicated in the CSD.

4. Discussion

4.1. Packing conflicts

The existence of such a high proportion of *vic*-diol structures having $Z' > 1$ and having molecules in different orientations and/or different conformations hints at the packing compromises necessary if a full set of intermolecular O—H···O bonds is to be formed.

Structures cannot be observed unless they are energetically favorable. In the case of the *vic*-diol structures $C_nH_m(OH)_2$, space should be filled and a full set of intermolecular O—H···O bonds should be formed. The formation of such a set of bonds nearly always leads to the segregation of the hydroxyl groups into chains or layers; the crystals of *vic*-diols $C_nH_m(OH)_2$ can nearly always be partitioned into hydrophilic regions (ribbons or sheets) that contain the OH groups and hydrophobic regions that are filled with C and H atoms. The segregation of hydroxyl groups, however, often makes dense packing harder to achieve because the spacings that are appropriate for the regions containing the OH groups may not be appropriate for the rest of the crystal. The problem of matching the spacings is aggravated if the molecule is rigid [see discussion in Duncan *et al.* (2002)].

The layered structure of NADNIP (*S*,*S*-3,5-cyclohexadiene-1,2-diol) illustrates the conflict between forming O—H···O bonds and filling space. The hydroxyl groups, which are segregated in the middle of the layers, are connected in a variant of pattern 2*b*. Space-filling representations show clearly that there are empty spaces between the CH═CH—CH═CH regions of the molecules. The hydroxyl groups cannot move close enough together to allow dense packing of the C_4H_4 fragments and cannot move far enough apart to allow interleaving of adjacent layers. The structures of *cis*- and *rac*-*trans*-1,2-cyclohexanediol (ZZZKPE01 and ZZZPSA) are similar. These three structures are reminders that the observed crystal-packing arrangement does not have to be perfect; it just has to be better than the alternatives.

The difficulty of filling the space above and below a two-dimensional layer of hydroxyl groups with the 'rest' of the molecule results in two-dimensional patterns being less common than one-dimensional patterns (12 *versus* 23) even if there is more than one O—H···O bond per molecule. The steric constraints associated with molecule types 3 and 4 (Table 1) are an obvious hindrance to layer formation. Stereochemistry is also important; the data show that layers are much more likely to form if the OH groups on a five- or six-membered ring are *trans* than if they are *cis*.

The problems with forming a full set of intermolecular O—H···O bonds would be expected to be even greater for *gem*-diols, but there are no *gem*-diols $C_nH_m(OH)_2$ in the CSD. There are, however, two structures of simple boronic acids. Styrylboronic acid (ZILEB) forms dimer ribbons; phenylboronic acid [$PhB(OH)_2$; PHBORA; $Z' = 2$] forms a tightly linked one-dimensional chain in which the repeating unit is a pair of dimers. There are also eight structures $C_nH_mSi(OH)_2$ and one structure $C_nH_mGe(OH)_2$. Of these nine structures, four contain dimer ribbons, two are variants of dimer ribbons and one contains discrete dimers. One of the nine has a two-dimensional pattern of O—H···O bonds and one more has a one-dimensional pattern that is not seen among the *vic*-diols.

4.2. Comparison with previous studies

Taylor & McCrae (2001) found a strong preference for O—H···O bonds between O atoms that are not symmetry related. The present study finds the same.

Nguyen *et al.* (2001) found 12 dimer ribbons (which they call step-ladders) among all diols $C_nH_m(OH)_2$. In 10 of these 12 structures the 'uprights' that connect the O—H···O 'rails' are enantiomerically pure. In six of the 12 both the $R_2^2(10)$ and $R_4^4(8)$ rings are located on inversion centers. The corresponding numbers for the seven dimer ribbons that are found in the present study are four and two.

Nguyen *et al.* (2001) also found 16 'staircase-ladder' patterns in which the 'uprights' are offset so that each diol in one chain is hydrogen bonded to two different diols in the other chain. This pattern was not found among the *vic*-diols even though the intra- and intermolecular O···O distances seem to be well matched. The staircase-ladder pattern does occur in KOMROT ($C_{15}H_{16}O_2Si$), which contains an HO—C—Si—OH grouping.

4.3. Enantiomerically pure compounds

For groups 2_2 and 3 the number of O—H···O bonds per O atom is the same for crystals that contain enantiomerically pure material and for crystals that contain achiral or racemic material. For group 4 there may be a small difference: for 12 crystals in proper space groups the average is 1.0 (2) O—H···O bonds per O atom; the corresponding average is 1.4 (1) for 17 crystals in groups that allow improper symmetry operations.

4.4. Is the dimer a 'supramolecular synthon'?

The $R_2^2(10)$ dimer motif, which appears in 76% of the structures that have more than one O—H···O bond per molecule, is robust and so may be termed a supramolecular synthon (Desiraju, 1995). Dimers, however, are found in only 45% of the structures of all *vic*-diols $C_nH_m(OH)_2$. In any event the dimers can be linked in so many different ways that the motif cannot be viewed as determining the overall packing arrangement.

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References

Allen, F. H. (2002). *Acta Cryst.* B**58**, 380–388.

Bernstein, J., Davis, R. E., Shimoni, L. & Chang, N.-L. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1555–1573.

Boese, R. & Weiss, H.-C. (1998). *Acta Cryst.* C**54**, IUC9800024.

Brock, C. P. & Duncan, L. L. (1994). *Chem. Mater.* **6**, 1307–1312.

Bruno, I. J., Cole, J. C., Edgington, P. R., Kessler, M., Macrae, C. F., McCabe, P., Pearson, J. & Taylor, R. (2002). *Acta Cryst.* B**58**, 389–397.

Dahlqvist, M., Hotokka, M. & Räsänen, M. (1998). *Chem. Phys.* **229**, 137–147.

Desiraju, G. R. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 2311–2327.

Duncan, L. L., Patrick, B. O. & Brock, C. P. (2002). *Acta Cryst.* B**58**, 502–511.

Etter, M. C., MacDonald, J. C. & Bernstein, J. (1990). *Acta Cryst.* B**46**, 256–262.

Jeffrey, G. A. (1997). *An Introduction to Hydrogen Bonding.* New York: Oxford University Press.

Nguyen, V. T., Ahn, P. D., Bishop, R., Scudder, M. L. & Craig, D. C. (2001). *Eur. J. Org. Chem.* **2001**, 4489–4499.

Sheldrick, G. M. (1990). *SHELXTL/PC.* Siemens Analytical Instruments, Inc., Madison, Wisconsin, USA.

Steiner, T. & Saenger, W. (1994). *J. Carbohydr. Res.* **259**, 1–12.

Taylor, R. & Macrae, C. F. (2001). *Acta Cryst.* B**57**, 815–827.

Yao, J. W., Cole, J. C., Pidcock, E., Allen, F. H., Howard, J. A. K. & Motherwell, W. D. S. (2002). *Acta Cryst.* B**58**, 640–646.

Yeh, T.-S., Chang, Y.-P., Su, T.-M. & Chao, I. (1994). *J. Phys. Chem.* **98**, 8921–8929.