Anomalous Space-Group Frequencies for Monoalcohols C_nH_mOH[1]

Carolyn Pratt Brock[*] and Laura L. Duncan

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

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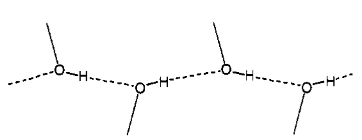
Consideration of the spatial requirements of OH···O bonds suggests that the frequencies of high-symmetry space groups, which are more likely than low-symmetry groups to be chiral or noncentrosymmetric, should be disproportionately high for structures of monoalcohols C_nH_mOH. Structures having more than one molecule in the asymmetric unit should also occur much more frequently for monoalcohols than for molecular crystals in general. These predictions have been confirmed using crystallographic information retrieved from the Cambridge Structural Database. Data for monoamines $C_nH_mNH_2$ are much more limited, but these molecules appear to follow the same crystallization pattern.

Introduction

Although the principles of molecular association via hydrogen bonding have been well documented,[2,3] the consequences of these rules for the overall packing of molecules into crystals have not. There are few relationships between molecular structure and molecular packing that have real predictive power.[4,5] This paper reports a new such generalization.

The genesis of this work was the determination of a crystal structure of a dinosterol steroid derivative, $C_{30}H_{53}$-OH, having a hydroxyl substituent as its lone functional group.[6] The space group, $P2_12_12_1$, was unremarkable, but the presence in the asymmetric unit of three independent molecules ($Z' = 3$)[7] was very unusual.[8] Cholesterol molecules are also known[10] to crystallize with large values of Z';[11] Craven[10] has pointed out that the conflict between the packing requirements of the relatively large, rigid, and hydrophobic steroid-ring structure and the small, hydrogen-bonding hydroxyl group must be responsible for the large Z' values. The three independent molecules in the dinostererol structure form a pseudo-3_1 helix., which led us to realize that high-symmetry space groups might occur more frequently in alcohols than in molecular crystals generally.

a) chain:



b) ring: c) dimer:

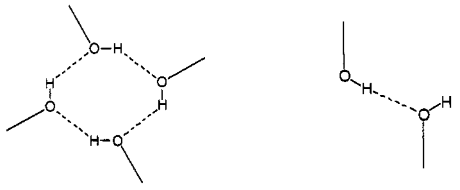


Figure 1. Types of OH···O aggregates: (a) chain; (b) ring; (c) dimer.

Hydroxyl groups are unique in being approximately equally good hydrogen-bond donors and hydrogen-bond acceptors. In the solid state –OH groups both donate and accept a proton unless hindered by nearby bulky substituents, or unless there is some stronger intermolecular interaction that takes precedence. H-bonded aggregates are therefore mostly rings and chains (Figure 1). Closed dimers, although occasionally proposed in the literature, are highly improbable;[2,12] rather, –OH dimers have one dangling H atom and one free acceptor (Figure 1c). Dimers occur only if the formation of an extended H-bonded structure is precluded.

If fully H-bonded aggregates of –OH groups are to be formed, two O atoms must be brought to within ca. 2.8 Å of a third. If the hydroxyl-containing molecules are relatively "thin", they can be related by 2_1 screw axes or by glide planes (Figure 2), or if very thin, by pure translation. If the molecules are bulkier, three O atoms related by 2_1 screw axes or by glide planes cannot get close enough to form hydrogen bonds (Figure 3). The same steric constraint is encountered if –OH groups are related by a row of 2-fold axes or a row of inversion centers. Two solutions to this crystal-packing problem can be imagined: either the asymmetric unit can contain more than

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(1) Dedicated to the memory of Margaret C. Etter, who pioneered the use of hydrogen bonding to drive the formation of designed cocrystals. After this project was underway we discovered that one of Etter's students, Andrea M. Cicero, had also started to investigate hydrogen-bonding patterns in alcohols.

(2) Jeffrey, G. A.; Saenger, W. *Hydrogen Bonding in Biological Structures*; Springer-Verlag: Berlin, 1991.

(3) Etter, M. C. *J. Phys. Chem.* **1991,** *95,* 4601–4618.

(4) The best-known example of a predictive rule is the observation by Schmidt and Green that halogen substitution in aromatic molecules often gives crystals with a 4-Å axis (see discussion on p 186 of ref 5).

(5) Desiraju, G. R. *Crystal Engineering: The Design of Organic Solids*; Elsevier: Amsterdam, 1989, and references therein.

(6) Brock, C. P.; Stoilov, I.; Watt, D. S. *Acta Crystallogr.* **1994,** *C50,* 434–438.

(7) $Z' = Z/n$, where Z is the number of molecules in the unit cell and n is the order of the group.

(8) Only about 0.4% of the structures in the CSD have three or more molecules in the asymmetric unit ($Z' \geq 3$).[9]

(9) (a) Brock, C. P.; Dunitz, J. D. *Mol. Cryst. Liq. Cryst.* **1994,** *242,* 329–337. (b) Brock, C. P.; Dunitz, J. D. *Chem. Mater.*, **1994,** *6,* 1118–1127.

(10) Craven, B. M. In *The Physical Chemistry of Lipids*; Small, D. M., Ed.; Plenum Press: New York, 1986; pp 149–182.

(11) Up to 8: Shieh, H.-S.; Hoard, L. G.; Nordman, C. E. *Nature (London)* **1977,** *267,* 287–289. Shieh, H.-S.; Hoard, L. G.; Nordman, C. E. *Acta Crystallogr.* **1981,** *B37,* 1538–1543.

(12) See, e.g.: Schweizer, W. B.; Dunitz, J. D.; Pfund, R. A.; Tombo, G. M. R.; Ganter, C. *Helv. Chim. Acta* **1981,** *64,* 2738–2740.

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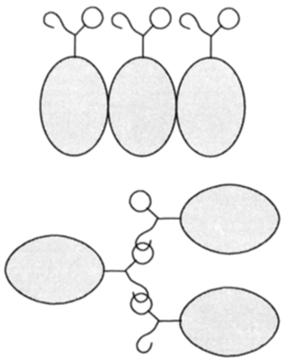

Figure 2. Schematic drawing of possible arrangements of molecules with a single functional group that acts as both a donor and an acceptor: the thickness of the molecule is small enough that adjacent molecules can be related by glide or 2_1 screw operations, but is too large to allow molecules to be related by a pure translation.

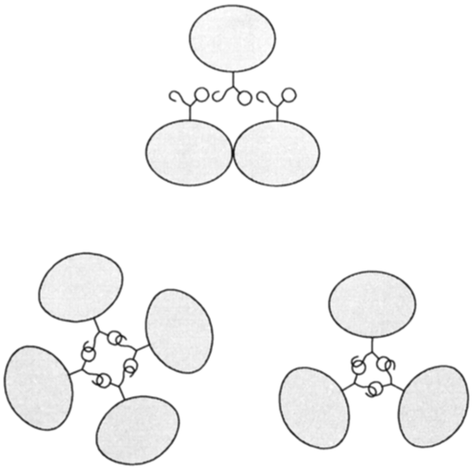

Figure 3. Schematic drawing of possible arrangements of molecules with a single functional group that acts as both a donor and an acceptor: the thickness of the molecule is too large to allow adjacent molecules to be related by glide or 2_1 screw operations, but aggregation around 4- and 3-fold axes is possible.

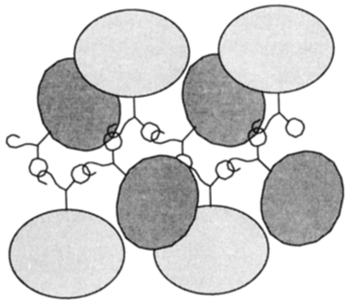

Figure 4. Schematic drawing of possible arrangements of molecules with a single functional group that acts as both a donor and an acceptor: thick molecules can be related by glide or 2_1 screw operations if there is more than one molecule in the asymmetric unit.

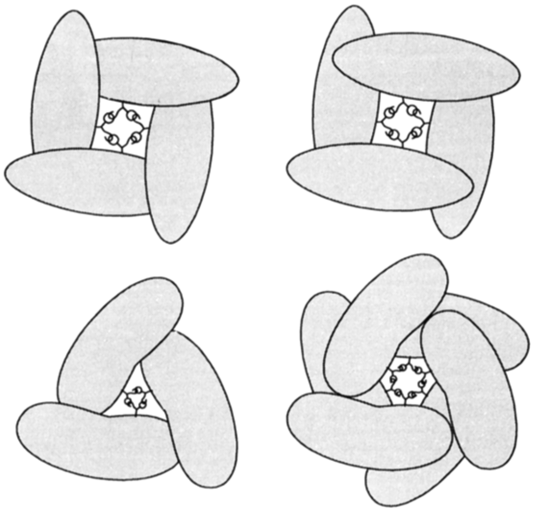

Figure 5. Schematic drawing of possible arrangements of molecules with a single functional group that acts as both a donor and an acceptor: the functional group in very large molecules can be arranged around 4_1, $\bar{4}$, 3_1, or $\bar{3}$ axes.

one molecule (Figure 4), or the molecules can aggregate around screw or rotation–inversion axes of order 3, 4, or 6 (Figures 3 and 5). The latter possibility is especially interesting because noncentrosymmetric[13] and chiral[14] space groups occur much more frequently among high-symmetry structures than among triclinic and monoclinic structures.[9] Both possible solutions to the packing problem violate the general rule that molecules of arbitrary shape usually crystallize in low-symmetry space groups with $Z' = 1$.[9,15]

This study examines the crystal packing of monoalcohols C_nH_mOH. We conclude that crystallization with more than one molecule in the asymmetric unit, or in tetragonal and trigonal space groups, is to be expected.

Methodology

Searches of the October 1992 (MDAT 920701) version of the Cambridge Structural Database[16] (hereafter, the CSD) required that the overall chemical formula be of the type C_nH_mOH and that there be only one type of molecule in the unit cell. The following criteria were added to guarantee that the structure was determined well and that no solvent molecule had been overlooked: RFAC 0.010–0.070; SIGF 1–2 (average standard deviation for a C–C bond ≤0.010 Å); coordinates present. The SIGF criterion is quite strict, but we discovered that a substantial number of questionable structures were retrieved if the SIGF criterion was relaxed. An unfortunate consequence of this choice was the elimination of a number of very interesting structures, like the cholesterol structure,[11] that could not be determined precisely because of large Z' values.

A separate search located molecules $C_nH_mNH_2$ that met the same NRES, RFAC, SIGF, and COOR criteria.

The hydrogen bonding schemes for each of the retrieved structures were elucidated with the help of the CSD program GSTAT and with reference to the original literature. Graph-set symbols[17] were assigned. An O···O distance less than ca. 3.0 Å was considered evidence of an OH···O bond. No O···O distance longer than 3.05 Å and shorter than 3.92 Å was found.

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[13] Noncentrosymmetric space groups are required for nonlinear optical (i.e., NLO) materials.

[14] Chiral space groups are required for spontaneous resolution.

[15] Kitaigorodskii, A. I. *Organic Chemical Crystallography*; Consultant's Bureau: New York, 1961.

[16] Allen, F. H.; Kennard, O.; Taylor, R. *Acc. Chem. Res.* **1983**, *16*, 146–153.

[17] (a) Etter, M. C. *Acc. Chem. Res.* **1990**, *23*, 120–126. (b) Etter, M. C.; MacDonald, J. C.; Bernstein, J. *Acta Crystallogr.* **1990**, *B46*, 256–262.

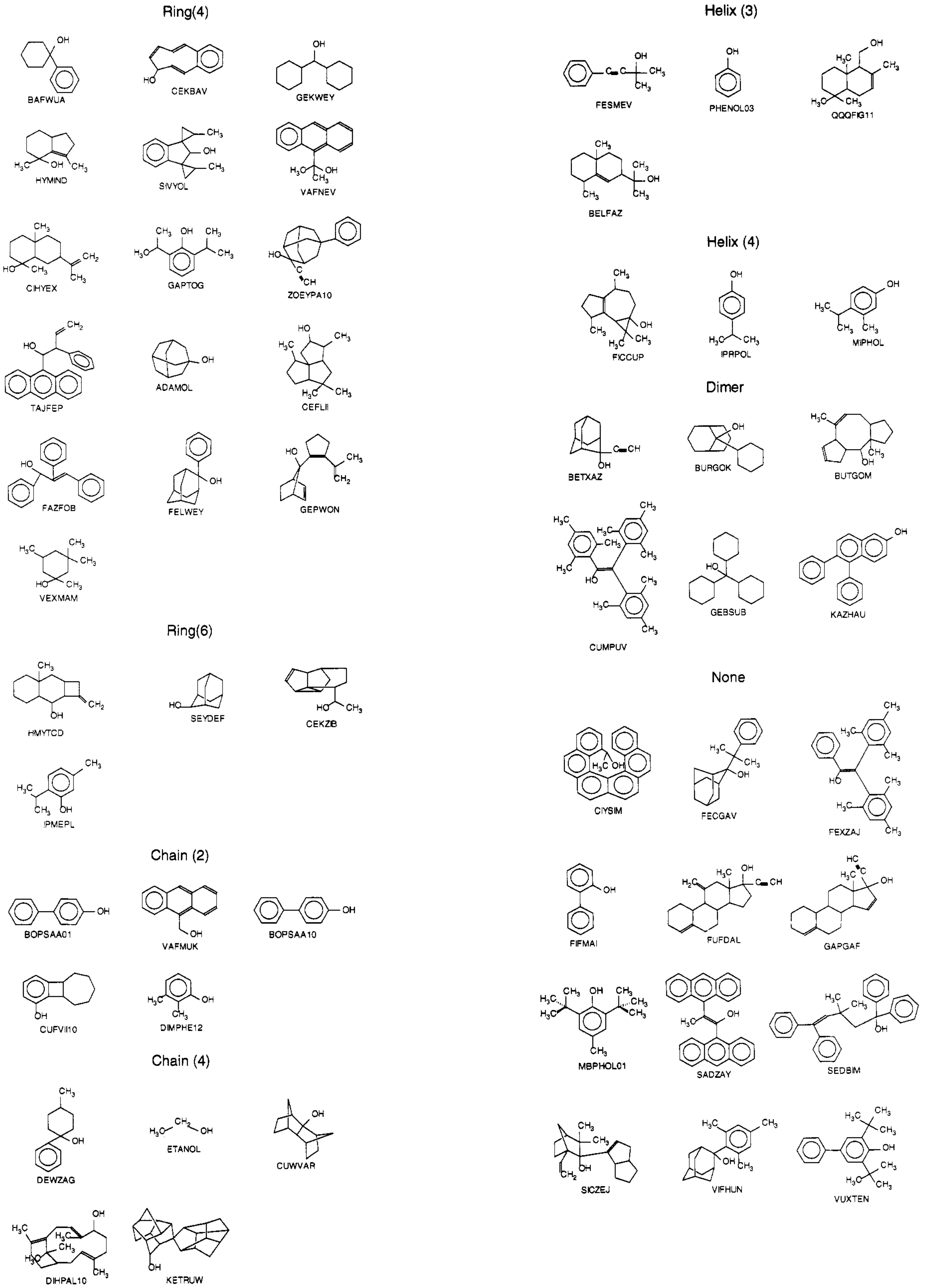

Figure 6. Line drawings and REFCODEs for the retrieved C_nH_mOH structures sorted by type of hydrogen-bonding arrangement.

Results

Fifty-five C_nH_mOH structures were retrieved; line drawings are shown in Figure 6 and full references are given in the supplementary material (see paragraph at end of paper). The molecules in about a third of the structures fail to participate fully in a hydrogen-bonding scheme. In about a quarter of the structures (see Table 1) there are no OH···O bonds at all because the molecules are too sterically hindered. Typical examples are 2,6-di-*tert*-butyl-4-methylphenol (MBPHOL01) and 1,1,5,5-tetraphenyl-3,3-dimethyl-1-penten-5-ol (SEDBIM). Many of the molecules in this group contain aromatic rings; some OH···π interactions are documented in the original papers, but such interactions are much weaker than OH···O bonds

Table 1. Summary of Hydrogen-Bonding Patterns in Structures of Monoalcohols C_nH_mOH

full OH···O bonding	37 (67%)	20 rings (16 tetramers; 4 hexamers) 17 chains (including 7 helices)
partial OH···O bonding	6 (11%)	(some OH···π bonds documented)
no OH···O bonding	12 (22%)	(some OH···π bonds documented)

and cannot be classified as structure determining.[2] A second, smaller, group of molecules forms dimers in which at least one O atom fails to act as both a hydrogen-bond acceptor and a hydrogen-bond donor.

Of the two-thirds of the structures with fully elaborated H-bonding networks, about a half (see Tables 2 and 3) are in "normal"[18] space groups with two or more independent molecules ($Z' \geq 2$) in the asymmetric unit, and another third are in trigonal and tetragonal groups. Only 16% crystallize in low-symmetry groups with a single molecule in the asymmetric unit. In the high-symmetry groups, aggregation around a $\bar{4}$ axis is common, and aggregation around 3_1 (or 3_2),[19] 4_1 (or 4_3), and $\bar{3}$ axes, and around a 222 site, occurs at least once (see Table 3).

The average O···O distance is 2.79(1) Å, the range is 2.55–3.05 Å, and the median is 2.77 Å; these values agree with those given by Jeffrey and Saenger.[2] Types of aggregates showing the greatest deviations from the mean are the hexameric rings [2.70(1) Å], the simple chains [2.86(3) Å], and the dimers [2.86(3) Å], but the differences are barely significant.

Four $C_nH_mNH_2$ structures were retrieved; line drawings are shown in Figure 7 and full references are given in the supplementary material (see paragraph at end of paper). Data for these structures are found in Table 4.

Discussion

The space-group statistics for C_nH_mOH molecules confirm the predictions made by considering the general features of OH···O hydrogen bonds: C_nH_mOH molecules with fully elaborated H-bond networks are *much* more likely to crystallize with $Z' > 1$ (51% vs 8%) or in high-symmetry space groups (32% vs 1%) than would be expected based on statistics determined for the CSD as a whole.[9] Nine of the high-symmetry structures are in tetragonal groups and three are in trigonal groups; no hexagonal or cubic group is represented.

The study also provides data about the types of aggregates formed. Rings and chains are equally probable. About three-fourths of the rings are tetrameric (hence the relatively large number of tetragonal groups), while the rest are hexameric. About half of the chains are either strictly helical or are approximate helices formed from several independent molecules (FESMEV, PHENOL03, QQQFIG11, and FICCUP). These results are similar to those reported in the MS Thesis of Andrea M. Cicero.[20]

Of the six molecules that crystallize in triclinic, monoclinic, or orthorhombic space groups with $Z' = 1$, three [BOPSAA10 ($P2_1/a$), CUFVII10 ($P2_12_12_1$), and DIMPHE12 ($P2_12_12_1$)] are thin in one direction and so are examples of the packing arrangement depicted in Figure 2. The other three molecules (CUWVAR, DIHPAL10, and KETRUW, all in $C2/c$) are, however, bulky. The alternation in $C2/c$ of inversion centers, which require corresponding bonds of related molecules to be parallel, and 2-fold rotation axes, which do not, allows bulky C_nH_mOH molecules to form extended chains. Of the space groups in which this arrangement is possible (e.g., $P2/c$, $Pccn$, $Pbcn$), $C2/c$ is by far the most common.[9]

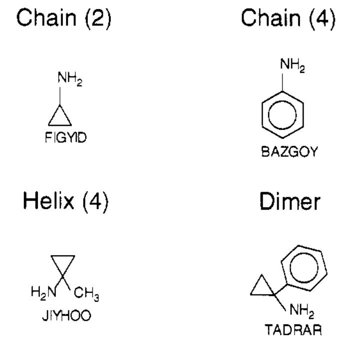

Figure 7. Line drawings and REFCODEs for the retrieved C_nH_m-NH_2 structures sorted by type of hydrogen-bonding arrangement.

Only 5 of the 37 structures with full H bonding have symmetry elements that require the H atoms to be disordered over two sets of sites, *i.e.*, that require a disorder of the direction of the donor–acceptor interaction. These five structures include the three in $C2/c$ described above, DEWZAG, and TAJFEP. The last is the only structure in which a ring is formed around perpendicular 2-fold axes.

There are relatively few structures of primary amines $C_nH_mNH_2$.[21] The amine group is a good H-bond acceptor but it not a particularly good donor.[2] The greater importance of hydrogen bonding in the monoalcohols is reflected in their generally higher melting points relative to the monoamines. All $C_nH_mNH_2$ structures retrieved for this study were determined below 260 K. Nevertheless, the four structures follow the predictions made for C_nH_mOH molecules (see Table 4): two of the structures are in normal space groups with $Z' > 1$, and two are in high-symmetry space groups.

Other classes of molecules might be expected to follow the same rules for crystal packing if there exist relatively strong intermolecular interactions that require a small region of a molecule be brought within ca. 3 Å of the corresponding regions of two like molecules. The existence of surprisingly large numbers of structures having $Z' > 1$ or in high-symmetry groups would then constitute evidence for a structure-determining intermolecular interaction.[22] The criterion that the region of interaction be small is, however, quite strict. A search for $C_nH_m(OH)_2$ molecules with the two –OH groups bonded to adjacent C atoms showed that 68% of the structures are in "normal" space

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[18] Here taken to be the triclinic, monoclinic, and orthorhombic space groups.

[19] For the purposes of this tally no distinction has been made between 3_1 and 3_2 axes or between 4_1 and 4_3 axes.

[20] Cicero, A. M. M.S. Thesis, University of Minnesota, 1991. Cicero's list of 44 structures included molecules with ≤20 C atoms only, and her criteria for structure quality were less stringent than ours. The proportion of phenols, which she found to be much more likely to form chains than rings, was higher in her sample (43%) than in ours (24%). Overall she found that 27% of the structure contained H-bonded rings, 52% contained H-bonded chains, and 20% had no OH···O hydrogen bonds at all.

[21] Twenty-four structures of secondary amines C_nH_mNH were located, but only three had significant – NH···N– interactions (N···N distance <3.70 Å), and all of these were dimers with incomplete hydrogen-bonding networks.

[22] Structural data and space-group statistics for molecules containing the 1,2,3,5-dithiadiazole ring system suggest the presence of such interactions. The rings, which have seven electrons in the aromatic system, usually form dimers, and the dimers often form stacks that are related by S···S interactions to two other stacks.[23]

[23] Cordes, A. W., personal communication. See also: Cordes, A. W.; Bryan, C. D.; Davis, W. M.; de Laat, R. H.; Glarum, S. H.; Goddard, J. D.; Haddon, R. C.; Hicks, R. G.; Kennepohl, D. K.; Oakley, R. T.; Scott, S. R.; Westwood, N. P. C. *J. Am. Chem. Soc.* **1993**, *115*, 7232–7239.

Table 2. Summary of Space-Group Distributions in Structures of Monoalcohols C_nH_mOH

	total	"normal" space groups; $Z' \leq 1$	"normal" space groups; $Z' > 1$	high-symmetry groups; $Z' = 1$
full OH···O bonding	37	6 (16%)	19 (51%)	12 (32%)
partial OH···H bonding	6	3 (50%)	3 (50%)	0
no OH···O bonding	12	12 (100%)	0	0
overall	55	21 (38%)	22 (40%)	12 (12%)
all structures in CSD[9] (same RFAC, SIGF criteria, but no NRES criterion)	31770	91%	8%	1%

Table 3. Space Groups and Hydrogen-Bonding Patterns for Structures of Monoalcohols C_nH_mOH

REFCODE	space group	space group no.	Z'	graph-set symbol	OH···O pattern	symmetry operations relating H-bonded molecules	O···O distance, Å
BAFWUA	$P2_1/c$	14	4	$R_4^4(8)$	ring (4)	1···2···3···4···1	2.73, 2.75 2.76, 2.77
CEKBAV	$P\bar{1}$	2	2	$R_4^4(8)$	ring (4)	1···2···1(i)···2(i)···1	2.71, 2.74
GEKWEY	$P\bar{1}$	2	2	$R_4^4(8)$	ring (4)	1···2···1(i)···2(i)···1	2.76, 2.77
HYMIND	$P\bar{1}$	2	2	$R_4^4(8)$	ring (4)	1···2···1(i)···2(i)···1	2.78, 2.82
SIVYOL	$P2_1/n$	14	2	$R_4^4(8)$	ring (4)	1···2···1(i)···2(i)···1	2.75, 2.76
VAFNEV	$P2_1/c$	14	2	$R_4^4(8)$	ring (4)	1···2···1(i)···2(i)···1	2.77, 2.79
CIHYEX	$A2$ ($C2$)	5	2	$R_4^4(8)$	ring (4)	1···2···1(2)···2(2)···1	2.83, 2.91
GAPTOG	$C2/c$	15	2	$R_4^4(8)$	ring (4)	1···2···1(2)···2(2)···1	2.73, 2.73
ZOEYPA10	$P2_12_12$	18	2	$R_4^4(8)$	ring (4)	1···2···2(2)···1(2)···1	2.78, 2.78, 2.81
TAJFEP	$P4_22_12$	94	1	$R_4^4(8)$	ring (4)	around 222 site	2.55, 2.90
ADAMOL	$P4_2/n$	86	1	$R_4^4(8)$	ring (4)	around $\bar{4}$ axis	2.81
CEFLII	$P4_2/n$	86	1	$R_4^4(8)$	ring (4)	around $\bar{4}$ axis	2.81
FAZFOB	$P\bar{4}2_1c$	114	1	$R_4^4(8)$	ring (4)	around $\bar{4}$ axis	2.76
FELWEY	$I4_1/a$	88	1	$R_4^4(8)$	ring (4)	around $\bar{4}$ axis	2.75
GEPWON	$I4_1/a$	88	1	$R_4^4(8)$	ring (4)	around $\bar{4}$ axis	2.86
VEXMAM	$I\bar{4}$	82	1	$R_4^4(8)$	ring (4)	around $\bar{4}$ axis	2.78
HMYTCD	$P\bar{1}$	2	3	$R_6^6(12)$	ring (6)	1···2···3···1(i)···2(i)···3(i)···1	2.74, 2.75, 2.76
SEYDEF	$P\bar{1}$	2	3	$R_6^6(12)$	ring (6)	1···2···3···1(i)···2(i)···3(i)···1	2.67, 2.67, 2.68
CEKZIB	$R\bar{3}$	148	1	$R_6^6(12)$	ring (6)	around $\bar{3}$ axis	2.67
IPMEPL	$R\bar{3}$	148	3	$R_6^6(12)$	ring (6)	around $\bar{3}$ axis	2.70
BOPSAA01	$P2_12_12_1$	19	2	C(2)	chain (2)	···1···2···1(t)···	2.94, 2.96
VAFMUK	Cc	9	2	C(2)	chain (2)	···1···2···1(t)···	2.92, 2.93
BOPSAA10	$P2_1/a$	14	1	C(2)	chain (2)	around 2_1 axis	2.93
CUFVII10	$P2_12_12_1$	19	1	C(2)	chain (2)	around 2_1 axis	2.81
DIMPHE12	$P2_12_12_1$	19	1	C(2)	chain (2)	around 2_1 axis	2.79
DEWZAG	$P\bar{1}$	2	2	C(2)	chain (4)	···1···1(i)···2···2(i)···1(t)···	2.87. 2.94, 3.05
ETANOL	Pc	7	2	C(2)	chain (4)	···1···2···1(g)···2(g)···1(t)···	2.72, 2.73
CUWVAR	$C2/c$	15	1	C(2)	chain (4)	···1···1(i)···1(2)···1(i′)···1(t)···	2.85, 2.88
DIHPAL10	$C2/c$	15	1	C(2)	chain (4)	···1···1(i)···1(2)···1(i′)···1(t)···	2.75, 2.77
KETRUW	$C2/c$	15	1	C(2)	chain (4)	···1···1(i)···1(2)···1(i′)···1(t)···	2.81, 2.86
FESMEV	$Pca2_1$	29	3	C(2) [3]	helix (3)	···1···2···3···1(t)···	2.75, 2.76, 2.80
PHENOL03	$P2_1$	4	3	C(2) [3]	helix (3)	···1···2···3···1(t)···	2.65, 2.66, 2.69
QQQFIG11	$P2_1$	4	3	C(2) [3]	helix (3)	···1···2···3···1(t)···	2.74, 2.76, 2.77
BELFAZ	$R3$	146	1	C(2) [3]	helix (3)	around 3_1 axis	2.74
FICCUP	$P2_12_12_1$	19	2	C(2) [4]	helix (4)	···1···2···1(2_1)···2(2_1)···1(t)···	2.92, 2.98
IPRPOL	$P4_1$	76	1	C(2) [4]	helix (4)	around 4_1 axis	2.81
MIPHOL	$P4_1$	76	1	C(2) [4]	helix (4)	around 4_1 axis	2.86
BETXAZ	$P2_1/c$	14	2	D	dimer	1···2 (+OH···π, intramolecular)	2.84
BURGOK	$P2_1/n$	14	1	D	dimer	1···1(i)	2.97
BUTGOM	$P2_1$	4	2	D	dimer	1···2	2.77
CUMPUV	$P\bar{1}$	2	2	D	dimer	1···2	2.80
GEBSUB	$P\bar{1}$	2	1	D	dimer	1···1(i)	2.95
KAZHAU	$P2_1/c$	14	1	D	dimer	1···1(i)	2.76
CIYSIM	$P2_12_12_1$	19	1		none	NA (OH···π, intramolecular)	>4.0
FECGAV	$P2_1/n$	14	1		none	NA	>4.0
FEXZAJ	$P\bar{1}$	2	1		none	NA	>4.0
FIFMAI	$Fdd2$	43	0.5		none	NA (OH···π, intramolecular)	>4.0
FUFDAL	$P2_1$	4	1		none	NA	>4.0
GAPGAF	$P2_1$	4	1		none	NA	>4.0
MBPHOL01	$C2/c$	15	1		none	NA	3.9
SADZAY	$P2_1/c$	14	0.5		none	NA	>4.0
SEDBIM	$P2_1/n$	14	1		none	NA	>4.0
SICZEJ	$P2_12_12_1$	19	1		none	NA	>4.0
VIFHUN	$C2/c$	15	1		none	NA [chain(2) of intermolecular OH···π bonds]	>4.0
VUXTEN	$P2_1/a$	14	1		none	NA	>4.0

groups with $Z' = 1$. While this percentage is substantially lower than for the CSD as a whole (Table 2), it is a great deal higher than the corresponding percentage (16%) for the monoalcohols.

Chiral and noncentrosymmetric space groups occur more frequently for monoalcohols than for all molecular crystals because such groups are more common in high-symmetry systems than in low.[9] Only 20% of the molecules in the

Table 4. Space Groups and Hydrogen-Bonding Patterns for Structures of Monoamines $C_nH_mNH_2$

REFCODE	space group	space group no.	Z'	graph-set symbol	NH···N pattern	symmetry operations relating H-bonded molecules	N···N distance, Å
FIGYID	$R3c$	161	1	C(2)	chain (2)	···1···1(g)···1(t)···	3.23
BAZGOY	$P2_1/c$	14	2	C(2)	chain (4)	···1···2···1(g)···2(g)···1(t)···	3.18, 3.37
JIYHOO	$I4_1/a$	88	1	C(2) [4]	helix (4)	around 4_1 axis	3.25
TADRAR	$P2_1/n$	14	4	C(2) [4]; D	helix (4); dimer	···1···2···1(2_1)···2(2_1)···1(t)···; 3···4	3.47, 3.61; 3.34

CSD are in chiral groups, but 32% (12) of the 37 C_nH_mOH structures with full hydrogen bonding are in chiral groups. The magnification appears even greater if a correction is made for resolved starting material. Crystals of 4 of the 12 alcohols were grown from resolved starting material, so the frequency of spontaneous resolution is 12 − 4 = 8 in 37 − 4 = 33 (24%), a frequency about 2.5 times higher than that estimated for all molecular crystals.[24,25] Seventeen of the 37 structures (46%) are in noncentrosymmetric space groups (vs 23% for the whole CSD); correction for resolved starting materials lowers the value for the monoalcohols to 39% but would lower the value for the whole CSD even more.

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Supplementary Material Available: Lists of REFCODES and associated literature references for monoalcohols C_nH_mOH and monoamines $C_nH_mNH_2$ (5 pages). Ordering information is given on any current masthead page.

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