

### **Analysis of structures with saturated hydrogen bonding. Corrigendum**

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Corrected space groups for the paper by Loehlin & Okasako (2007), *Acta Cryst.* **B63**, 132–141 are given.

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Some of the space groups given in Table 5 of the paper by Loehlin & Okasako (2007), *Acta Cryst.* **B63**, 132–141 are incorrect. The correct space group for MORFCL, MORPHI and PDA10D is  $P2_1/c$ , while PDA8DO should have the space group  $C2/c$ .

#### **References**

Loehlin, J. H. & Okasako, E. L. N. (2007). *Acta Cryst.* **B63**, 132–141.

# Analysis of structures with saturated hydrogen bonding

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All simple structures with saturated hydrogen bonding (SHB) are classified into eight categories on the basis of the donor and acceptor numbers on the atoms at each end of the hydrogen bonds. Examples from the literature are included where known, along with seven structures investigated as part of this study (five have SHB). Graph-set descriptions of the hydrogen-bond patterns are given for each of these structures and for some selected literature examples. The structures presented are: piperazine (I), morpholinium chloride (II) and iodide (III) [(II) and (III) are not SHB], three 1:1 cocrystals of diols with 1,4-phenylenediamine (PDA) – PDA·1,8-octane diol (IV), PDA·1,10-decane diol (V), and PDA·1,12-dodecane diol (VI) and 6-amino-1-hexanol (VII). This study discusses some structures that show limitations of the graph-set model, along with possible suggestions to cover these limitations. The cocrystalline PDA·aliphatic diol structures may provide details applicable to the structure of self-assembled monolayers of aliphatic thiol molecules on Au(111) surfaces.

## 1. Introduction

Hydrogen bonds form whenever the donor H atom can get close to an electron-rich region of an acceptor atom in an approximately linear arrangement,  $D-H \cdots A$ . The geometry about the donor and acceptor atoms is usually consistent with the Lewis-atom/valence-bond model where bonds and valence lone pairs of electrons are pictured in a tetrahedral arrangement around each atom. The angles around the hydrogen-bonded atoms are similar whether determined from the 'heavy atom' positions or from experimentally determined H-atom positions. In cases where the donor or acceptor participates in double or triple bonds, its geometry will be trigonal or linear, respectively. When more than one hydrogen bond is possible for a molecule, especially stable complexes may form when complementary participants are available. The well known base-pairing in DNA is an example of this. Another is the network structure in ice, where the self-complementarity of the water molecules for hydrogen bonding is the best known example of the structures in this study.

In the past decade, Ermer & Eling (1994), ourselves (Loehlin *et al.*, 1998) and a few others have studied the complementary 1:1 alcohol/primary amine compounds in which the total number of donor H atoms exactly matches the number of acceptor lone pairs. Ermer and Eling introduced the idea of saturated hydrogen bonding (SHB) to refer to this situation, including the self-complementary water molecule in ice. Systematically extending this SHB concept to other complementary donor/acceptor arrangements has led to the

**Table 1**

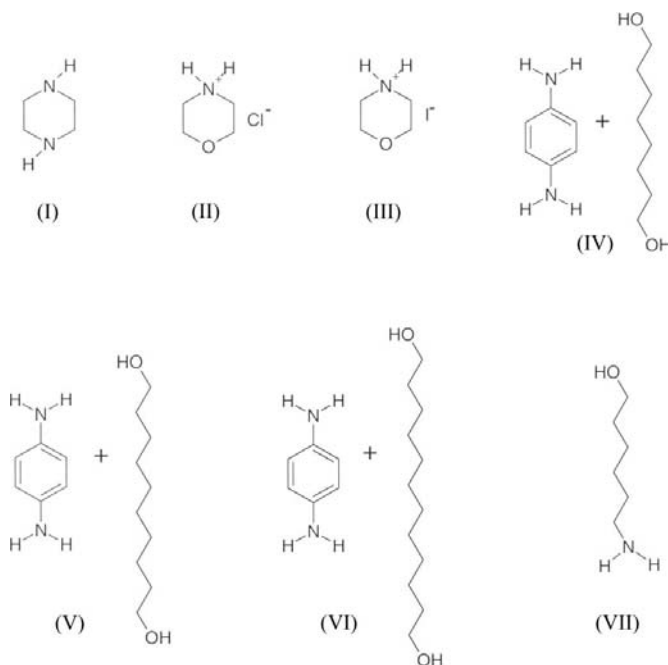
Categories of complementary SHB patterns.

The numbers of donor H atoms and acceptor lone pairs on atoms at each end of each hydrogen bond are shown.

Monohydrant <b>10 01</b>	1 hydrogen bond per atom	
Dihydrant <b>11 11</b>	2 hydrogen bonds per atom	<b>20 02</b>
Trihydrant <b>21 12</b>	3 hydrogen bonds per atom	<b>30 03</b>
Tetrahydrant <b>22 22</b>	4 hydrogen bonds per atom	<b>31 13</b> <b>40 04</b>

investigation of several new structural patterns in our own research, and to the search for other structures in the literature. The initial presentation of this work at IUCr XIX (Loehlin, 2002) included the basic outline and the structures of (I) and (VII).

The stabilization increase resulting from maximizing the number of hydrogen bonds would by itself make this an important field of study. When one adds to that the possibility of complementarity between unlike functional groups, a vast number of new possibilities opens up. We are proposing a systematization of this complementarity at the level of individual donor and acceptor atoms. We anticipate that it will be useful in understanding and creating new hydrogen-bonded materials.



## 2. Categorizing SHB structures

There are varieties of possible SHB patterns. In order to classify them we shall focus on the donor and acceptor atoms,

which may be in the same molecule, or as separate parts of binary systems. Since an atom may have both lone pairs and attached H atoms, in addition to covalent bonds to the remainder of the molecule, several hydrogen bonds may emanate from it. For convenience here we introduce the term *hydrancy* to refer to the number of hydrogen bonds participated in by a single atom. This term is analogous to the use of *valency* for covalent bonds. Thus, the SHB alcohol/amines are each trihydrant, where each O atom and each N atom participates in three separate hydrogen bonds. (There is the potential danger of confusing *hydrant* with *hydrate*, so that widespread usage of this term may not be ideal, but it is very useful in this analysis.) Finally, we look at a given hydrogen bond and specify the number of H atoms **d** and acceptor lone pairs **a** on the atoms at each end, giving a **da** designation to both the donor and likewise to the acceptor. For SHB, the **da** designation on the donor end of the hydrogen bond will usually complement the **da** on the acceptor end. The sum **d + a** at each end will equal that atom's hydrancy. Using this terminology, we find that there are just four possible hydrancies for tetravalent atoms and a total of only eight categories of SHB, when the donors and acceptors are complementary.

There are very restrictive steric and packing constraints, which limit the molecules that form SHB in crystals. As a result there are relatively few structures which are rigorously SHB ones. Owing to these constraints, and hence a lack of ideal examples, we have included some that have donors or acceptors (usually the latter) which are not utilized at other sites in the structure. Here we will restrict our analysis to hydrogen bonds that have SHB at both ends of the bond being considered.

In cocrystal systems it is possible to have different hydrancies in the same material. (Note the analysis of SHB in piperazine hexahydrate later in this report.) The simple **da da** designations for the various SHB categories are shown in Table 1.

In order to analyze the hydrogen-bonding patterns in SHB structures, we will use the graph set (GS) approach introduced by the late Margaret C. Etter (Etter, 1990; Etter *et al.*, 1990) and further developed by Bernstein *et al.* (1995). When hydrogen bonds are not equivalent, we will rank them by increasing length (presumably corresponding to decreasing strength). Each identical type of hydrogen bond forms a pattern, whose GS descriptor is referred to as its *motif*. The collected motifs form the first level or unitary GS, designated  $N_1$ . With more than one type of hydrogen bond, upper-level graph sets, binary ( $N_2$ ), ternary ( $N_3$ ) *etc.* can also be specified. For details of the types of patterns, symbols and terminology refer to Bernstein *et al.* (1995).

Since we are proposing a new model, we sought examples that are as clear as possible. If the concept is useful, others will adapt it in various ways to include additional structures. For simplicity, we first attempted to limit our examples to those where the positions of the electrons are localized on donor and acceptor atoms. In some cases, however, examples have donors or acceptors that participate in delocalized bonding so

**Table 2**  
CSD refcodes in this report.

Refcode	Relevant fragment	Reference
ACEMID05	Acetamide	Zobel <i>et al.</i> (1992)
ACEMID06	Acetamide	Bats <i>et al.</i> (2003)
BETLER	2-Methylpiperazine	Okamoto <i>et al.</i> (1982)
EBIFOL	Linked aniline phenol	Bhogala <i>et al.</i> (2004)
FORMAM02	Formamide	Stevens (1978)
FUXKEO	Diborane linked pyrazolium	Brock <i>et al.</i> (1988)
GAZNIE	Bicyclic piperazine	Böttcher <i>et al.</i> (1987)
GAZNIE01	Bicyclic piperazine	Sänger <i>et al.</i> (2004)
JAKPER	4-Aminothiophenol	Jetti <i>et al.</i> (2004)
JOFDEN	Linked <i>tert</i> -amine/onium <sup>+</sup>	Brzezinski <i>et al.</i> (1991)
LULWEO	<i>tert</i> -Amine/onium borate	Betley & Peters (2002)
NABWAP	(Diazabicyclooctane)H <sup>+</sup>	Braga <i>et al.</i> (2004)
NEBPUF	Aziridene	Mitzel <i>et al.</i> (1997)
PIPERH	Piperazine hydrate	Schwarzenbach (1968)
RUYSUZ	2-Ammoniummethanethiolate	Fleischer <i>et al.</i> (2005)
SARJUQ	Phenylenediamine-hexanediol	Loehlin <i>et al.</i> (1998)
SEGCOW	<i>tert</i> -Ammonium tetrazole	Chertanova <i>et al.</i> (1988)
YERLUC	Trimethylamine/onium <sup>+</sup>	Bock <i>et al.</i> (1994)

that counting the number of acceptor sites is a little ambiguous. We have tried to be clear when this is the case.

### 3. Analysis of published structures

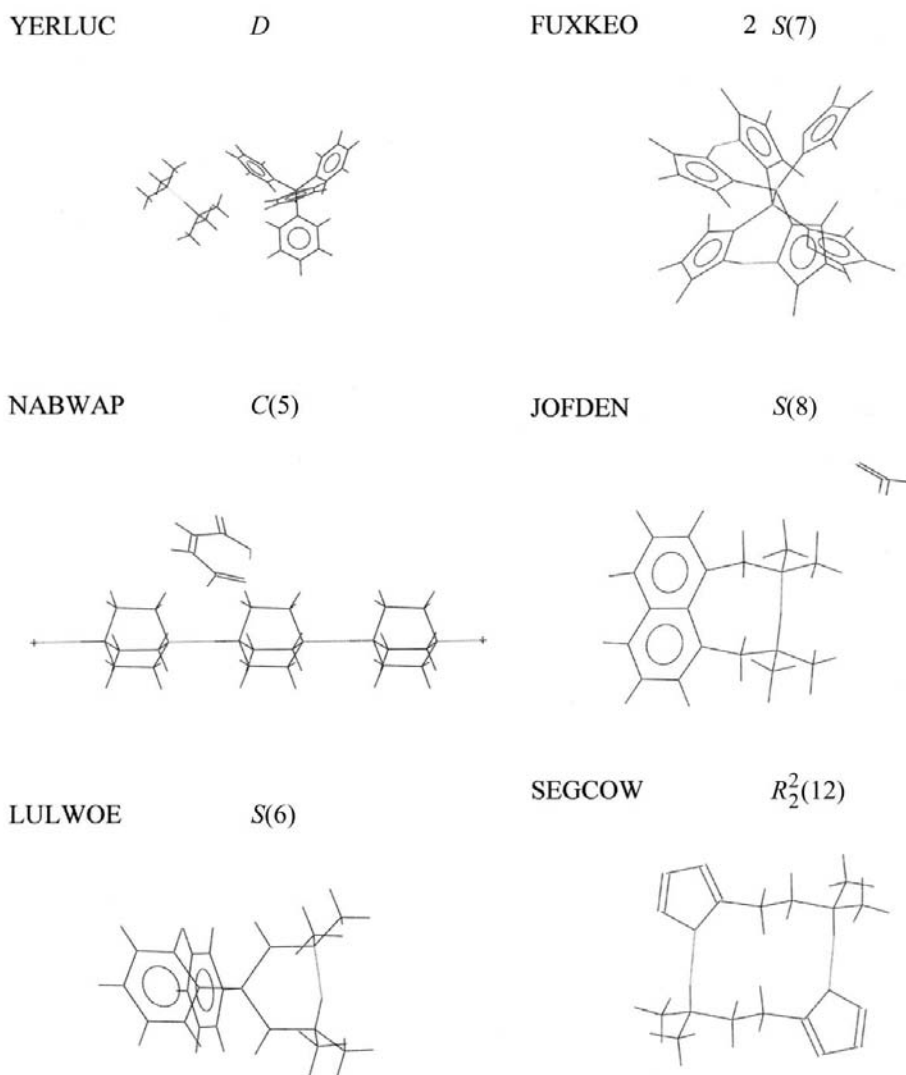
Most of the structures in this study were found in the Cambridge Structural Database, Version 5.27 (2005; Allen, 2002). The majority of searches were based on separate donor and acceptor fragments with **d**–**a** distances in the 2.0–3.5 Å range. The resulting hit list was then examined in *Mercury* (Bruno *et al.*, 2002). Table 2 gives an alphabetical list of the CSD refcodes referred to in this report. It includes the reference and the molecular fragments relevant to this work.

### 4. Monohydrant patterns

There is only a single class of monohydrant SHB materials, **10 01**, where the donor atom has just one hydrogen attached and no lone pairs, while the acceptor has no H atoms and one lone pair. The donor might be a tertiary ammonium ion and the acceptor a tertiary amine.

Several different patterns are shown in Fig. 1.

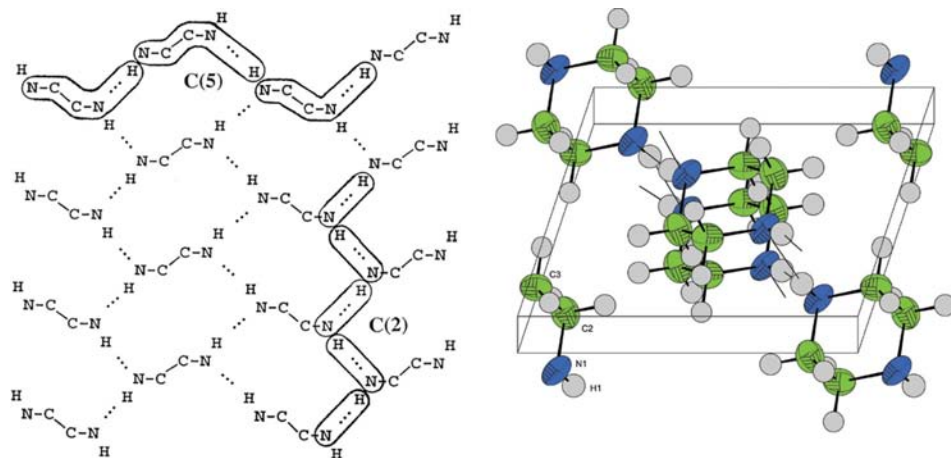
All of these structures have a substituted ammonium ion as a donor and an uncharged amine as an acceptor. Thus, true SHB requires that the charge-balancing moiety does not offer additional hydrogen-bonding sites. YERLUC, LULWEO and FUXKEO accomplish this with borate groups. The first two of these are the best examples of true SHB. All of the others have potential hydrogen-bonding sites elsewhere in the structure. All four GS descriptors are represented in these examples. FUXKEO has two *S*(7) rings which share a common B–B bond. The two *S*(7) rings are not equivalent (and in fact are different from the analogous ones in the second molecule of the asymmetric unit). The GS first level for each molecule is  $N_1 = S(7)S(7)$  and binary  $N_2 = S_2^2(12)$ . It is unusual to have *S* patterns with more than a single hydrogen bond. Note that the degree, 12, in the binary ring is less than the sum of the motif degrees, which can only happen when the rings share a common covalent link.



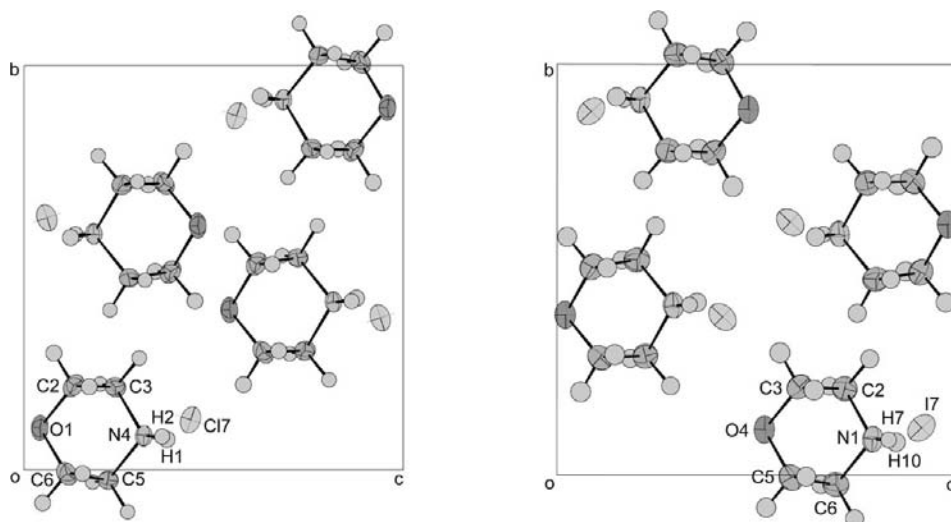
**Figure 1**  
Some representative **10 01** structures from the CSD showing the refcode and GS descriptors for each. Only YERLUC and LULWEO are fully SHB. The other structures have potential acceptor sites on anions or heterocyclic N atoms.

## 5. Dihydrant patterns

Dihydrant SHB materials fall into two possible classes, **11 11** and **20 02**, with simple tetrahedral structures only in the former category. When we originally searched for dihydrant SHB structures in the CSD, we searched for secondary amines, but missed BETLER. We decided to look for crystals of solid amines and tried first to determine the structure of diphenylamine. The crystals we obtained were only good enough to show that the average nitrogen–nitrogen distance was much too great to accommodate the hydrogen-bonded SHB chain we were looking for. Our next try was piperazine, (I), which yielded nice crystals by sublimation. The specimen used for data collection had to be sealed in a capillary, as the crystals are extremely hygroscopic and dissolve rapidly in moisture from the air. The molecules are in the chair configuration with



**Figure 2**  
The SHB pattern and packing diagram for piperazine (I). Note that all hydrogen bonds are identical.

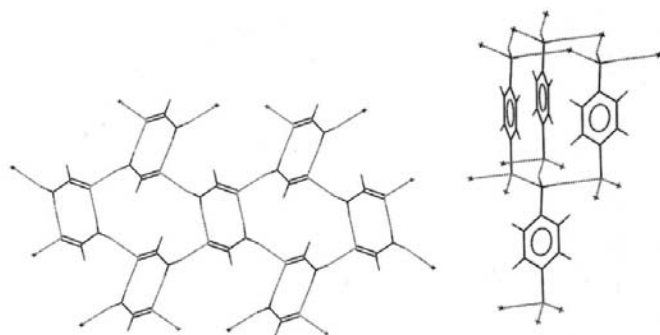


**Figure 3**  
Projections along the *a* axis for the morpholinium salts (II) and (III), showing the absence of hydrogen bonding to the O atoms.

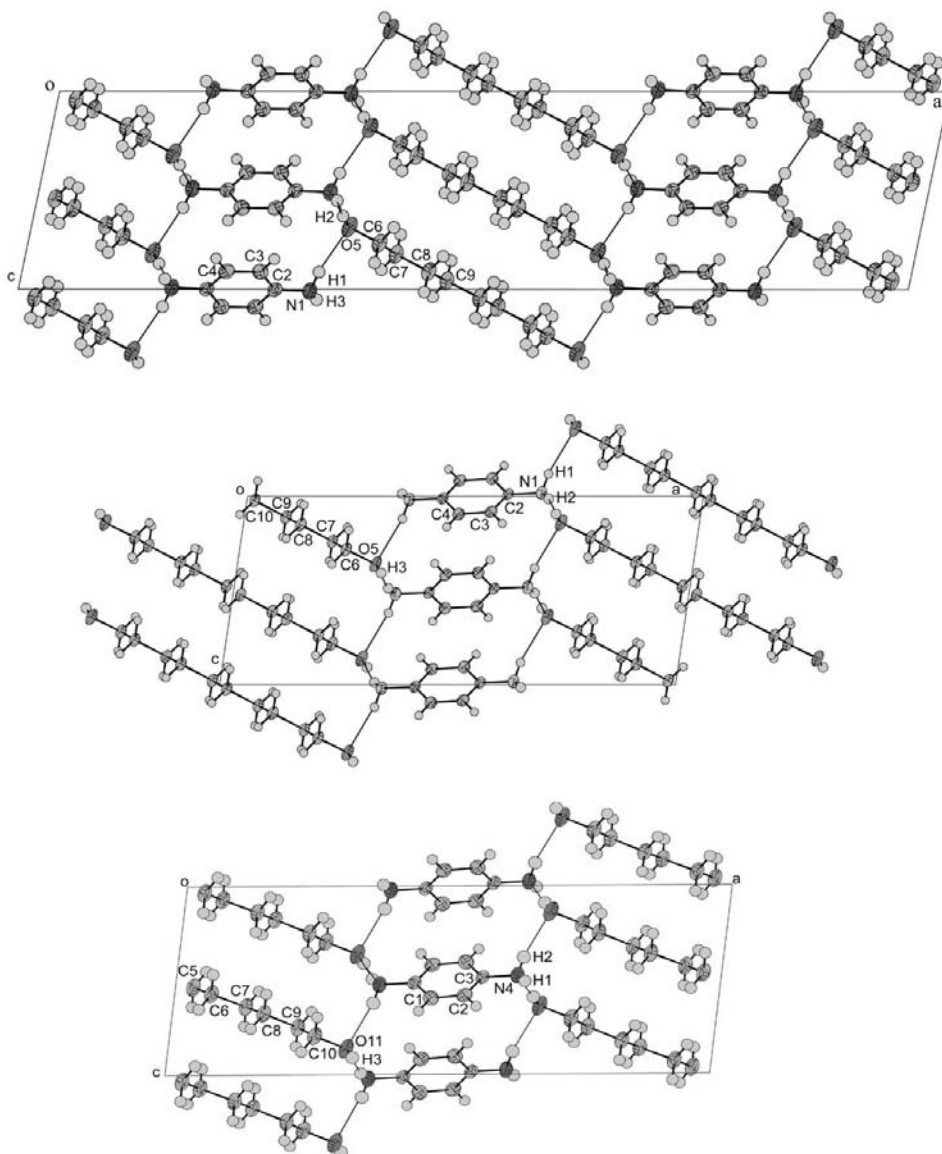
the amine H atoms in an equatorial orientation. They crystallize in a zigzag arrangement forming sheets linked by  $C(2)$  chains along  $2_1$  axes of the crystal, with  $C(5)$  chains through the molecules cross-linking the adjacent  $C(2)$  chains, as illustrated in Fig. 2, which also shows the crystal packing. All hydrogen bonds are identical so the entire sheet forms the GS motif,  $N_1 = [C(5)C(2)]$ . Recently, piperazine's structure, at a lower temperature, as well as that of piperidine, which is also **11 11**, have been published by Parkin *et al.* (2004). Piperidine lacks the molecular cross-linking and thus has a simple  $N_1 = C(2)$  graph set, but it too is SHB. The four-membered analog, azetidine (Bond *et al.*, 2007), is likewise **11 11** SHB, but has a different GS pattern as the result of  $Z' = 2$  and thus molecules linked by non-equivalent hydrogen bonds. The motifs are thus both  $D (N_1 = D D)$ , with the second level GS,  $N_2 = C_2^2(4)$ . The three-atom ring, NEBPUF (azeridene), is also **11 11**, but with  $Z' = 3$ ,  $N_1 = D D D$  and  $N_3 = C_3^3(6)$ .

After determining the structure of piperazine, we did a more careful CSD search for dihydrant structures and found both BETLER (with SHB pattern identical to piperazine) and also GAZNIE, which is essentially two fused piperazines. [In GAZNIE, N–N distances and angles strongly suggest **11 11** SHB, but require adjacent amines along the SHB  $C(2)$  chains to alternate from equatorial to axial. GAZNIE places all H atoms equatorial which is not reasonable. GAZNIE01 reports disordered H atoms, although there are several plausible ordered structures with reduced symmetry which differ only in the pattern of hydrogen conformations.]

In our search of the CSD for dihydrant SHB structures belonging to the **20 02** category, we looked first, but did not find structures with a secondary ammonium ion and an ether oxygen. An obvious candidate, which has the appropriate donors and acceptors, as well as being somewhat analogous to piperazine, is the morpholinium ion. We have tried to grow crystals of morpholinium with several anions. Morpholinium chloride (II) is readily crystallized and we have determined its structure. In this case the chloride, rather than



**Figure 4**  
**20 02** structure of FORMAM02 on the left with the  $C(4)$  ladder rails horizontal and the rings acting as rungs. The **30 03** structure of JAKPER on the right has the three  $C(7)$  motifs through the molecules with the  $\beta$ -As pattern horizontal.



**Figure 5**  
 Packing diagrams projected along **b** for cocrystal structures (IV), (V) and (VI) (top to bottom), showing the  $\beta$ -As pattern in the  $bc$  planes and the numbering systems used.

the oxygen, acts as the hydrogen-bond acceptor, with non-SHB  $\text{NH}\cdots\text{Cl}$  hydrogen bonds with GS  $N_1 = D D$  and  $N_2 = C_2^1(4)$ . We have also determined the structure of the less electronegative iodide, **III** (see Fig. 3 for both structures). The primary hydrogen bonding of the iodide is similar to the chloride, although distance criteria suggest the possibility of bifurcated interactions to adjacent iodides. Anions that might be used to balance the ionic charges but not have hydrogen-bonding acceptor sites are tetra-substituted boranes. We are investigating some of these to see if they crystallize with morpholinium ions as SHB materials.

Although unambiguous tetravalent examples of the **20 02** group have not been identified, a family of structures with delocalized bonding which can place it into this SHB group was noted during the editorial process. These are the amides, where delocalization of the electrons on the primary amine

makes the nitrogen lone pair unavailable as an acceptor. Three structures of simple amides illustrate the variety of patterns that may be obtained. Each molecule has just two distinguishable hydrogen bonds that differ in length only slightly. FORMAM02 (See Fig. 4a) crystallizes with its longer bonds linking adjacent molecules to form a centrosymmetric dimer. The other motif is a chain forming ladder rails with the cyclic dimers being the rungs. In this case, alternate rungs are on opposite sides of the rail, so that the structure consists of a two-dimensional sheet with the rails and rungs in a pattern similar to mortar lines in a brick wall,  $N_1 = R_4^2(8) C(4)$ . In ACEMID05 the adjacent amide groups are not coplanar and form a second chain connecting adjacent layers into a three-dimensional structure,  $N_1 = C(4) C(4)$ ,  $N_2 = R_6^3(12)$ . The structure of ACEMID06 is similar to FORMAM02, except that four ladder rails form a one-dimensional tube linked by the alternating amide dimer rings,  $N_1 = C(4)R_4^2(8)$ .

## 6. Trihydrant patterns

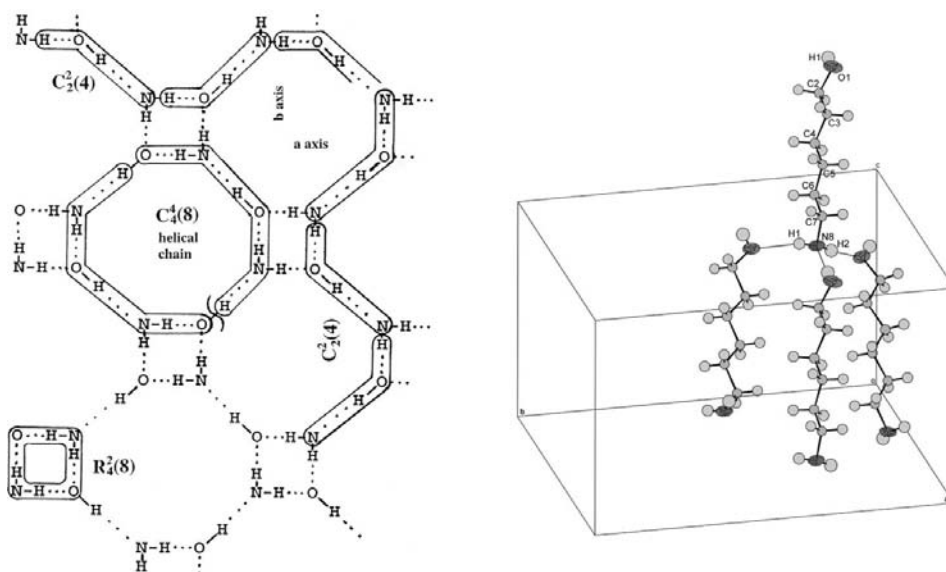
Alcohol/amine SHB structures and their hydrogen-bond patterns have been an important focus of our work for a number of years and were analyzed in an earlier paper (Loehlin *et al.*, 1998). These are all

**Table 3**  
Graph set for 6-amino-1-hexanol.

	Length (Å)	<i>a</i>	<i>b</i>	<i>c</i>
O—H...N <i>a</i>	2.794	$C(9)$		
N—H...O <i>b</i>	3.209	$C_2^2(4)$	$C(9)$	
N—H...O <i>c</i>	3.406	$C_2^2(4)$	$R_2^2(8)$	$C(9)$

$N_3 = C_4^4(8)$  helical chain.

in the **21 12** group. We present here four new structures. Three of these are (1:1) cocrystals of PDA with aliphatic primary diols: (IV) is PDA·1,8-octanediol; (V) is PDA·1,10-decanediol; (VI) is PDA·1,12-dodecane diol (see Fig. 5). These three have hydrogen-bond patterns analogous to our previously determined PDA·1,6-hexanediol structure SARJUQ (Loehlin *et al.*, 1998). (VII) is 6-amino-1-hexanol and has a pattern distinct from those previously observed. The most common hexagonal ‘chicken-wire’ SHB pattern seen in earlier alcohol-amine structures is also referred to as a  $\beta$ -As pattern. Another recent report (Vangala *et al.*, 2003) of aminophenol structures adds half a dozen examples to the **21 12**  $\beta$ -As class. (VII) forms a different pattern where the aminohexanol molecules are all oriented in a polar direction with the covalent chains having the same projection as the O—H...N hydrogen bonds in Fig. 6. The **a** motif thus forms a zigzag chain parallel to the *c* axis, while the projections of the **b** and **c** motifs are the same as the projections of the vertical and horizontal  $C_2^2(4)$  chains in Fig. 6. The hydrogen-bond graph set is shown in Table 3 in matrix form, where the diagonals are the motifs and the off-diagonal elements are the graphs of the binary patterns. Perhaps the most striking feature of the structure are the  $R_4^2(8)$  rings which are joined by third-level  $C_4^4(8)$  helical chains, forming a series of interlinked spiral staircase steps connecting the entire structure into a single hydrogen-bonded unit. Bhogala *et al.*



**Figure 6**  
The SHB pattern and a partial packing diagram for (VII). Only four adjacent molecules are shown for clarity of the hydrogen-bonded motifs and the numbering scheme.

(2004) report two structures in this class with a novel twisted ladder or tube variation where  $C_2^2(4)$  chains are crosslinked into similar  $R_4^2(8)$  rings forming the SHB tubes. [The GS pattern of EBIFOL is identical at the second level with (VII), but with  $N_1 = C(12)C(12)R_2^2(24)$  and a suggested  $N_3$  designation  $2C_2^2(4)[R_4^2(8)]$ ].

We searched for  $R-NH_3^+ \cdots O-R$  without success, in looking for examples of the other trihydrant SHB group **30 03**. During the review process, two recently reported structures, JAKPER and RUYSUZ, were suggested. These structures are aminothiols, where the proton from the thiol, which is a stronger acid than the alcohol, is lost to form an ammonium ion. Both are **30 03** SHB structures with hydrogen bonds from the ammonium ion to thiolate ions which are chemically identical, thus differentiating them from the analogous trihydrant alcoholamines. JAKPER forms a  $\beta$ -As-type SHB pattern, with GS  $N_1 = C(7)C(7)C(7)$ ,  $N_2 = C_2^1(4)C_2^1(4)C_2^1(4)$  and  $N_3 = R_6^3(12)$  (Fig. 4*b*). RUYSUZ with its shorter molecular length has  $C(5)$  motifs rather than  $C(7)$ , otherwise its GS at the basic level is identical to JAKPER, although complex graph sets and crystal packing show that it is not a  $\beta$ -As pattern.

## 7. Tetrahydrant patterns

The tetrahydrant SHBs fall into three possible categories, **22 22**, **31 13** and **40 04**. Various structures of ice fit the **22 22** system, which is probably the best-known hydrogen-bonded material (Eisenberg & Kauzmann, 1969). Its structure, though, presents a problem. There are six possible orientations of each molecule in the lattice, with adjacent hydrogen-bonded molecules each having three distinguishable orientations. It appears unlikely that a completely ordered structure will be found in the near future. What is clear is that each O atom acts

twice as a donor and twice as an acceptor, when participating in four hydrogen bonds. Each hydrogen bond is assumed to have twofold disorder, so the model has each hydrogen bond appear symmetric as a result. Normal hexagonal ice,  $I_h$ , has two crystallographically distinct hydrogen bonds: the slightly shorter bonds along the hexagonal axis and the set of three equivalent hydrogen bonds in the other directions. Using GS notation, the molecules connected by a bond along the unique axis form a *D* motif. The second motif in

**Table 4**  
Aliphatic chain angles ( $^{\circ}$ ) in PDA-aliphatic diol cocrystals.

Substance	1 Angle of stacking plane with <i>c</i>	2 Average angle of molecule with <i>b</i>	3 Crossing angle of adjacent chains
PDA-hexanediol SARJUQ	73.1	61.6	56.7
PDA-octanediol (IV)	74.6	66.9	46.3
PDA-decanediol (V)	72.7	60.9	58.1
PDA-dodecanediol (VI)	75.0	64.8	50.2

the unitary graph set,  $N_1$ , does not conform to any of the GS descriptors, as the model is currently set up. Perpendicular to the principal axis is a network of molecules in a hexagonal pattern, all with *indistinguishable* hydrogen bonds linking the O atoms together. Thus, the entire two-dimensional network forms the motif. The problem here is analogous to defining the molecular unit in a graphitic sheet (or in the case of ice  $I_c$ , below, to defining the molecule in diamond). We suggest not abandoning the GS model in the infrequent cases of this type which may be encountered, but rather merely supplementing strict GS notation by putting the entire motif in brackets [] and preceding the GS notation for an  $\text{OH}\cdots\text{OH}\cdots$  chain, *i.e.*  $C(2)$  in this case, with a number indicating how many of them there are from each atom in this set. Thus, we would refer to this motif as  $[3C(2)]$ . The unitary graph set would then be  $N_1 = [3C(2)] D$ . The corresponding binary graph set is  $N_2 = 4C(2)$ . In cubic ice,  $I_c$ , all hydrogen bonds are identical and the entire crystal is, strictly, the motif. Using the above logical extension of strict GS usage, we refer to the unitary graph set as  $N_1 = [4C(2)]$ . We used similar notation for the GS description of (I), where there is only a single type of hydrogen bond connecting the molecules into sheets *via*  $C(2)$  and  $C(5)$  chains.

We are not aware of any structures in the **31 13** category. Two simple hypothetical structures that would have the appropriate numbers of donors and acceptors are hydronium hydroxide,  $\text{H}_3\text{O}^+\cdot\text{OH}^-$ , and ammonia chlorohydride,  $\text{NH}_3\cdot\text{ClH}$ . Perhaps other researchers with a different perspective might suggest other possibilities.

The ammonium halides (Wyckoff, 1968) fit the **40 04** category. Ammonium fluoride has the ZnO structure and is analogous to ice  $I_h$ . Here, however, the unique axis hydrogen bond is longer than the others and in addition the hydrogen-bond chains include both an N and an F atom, and two hydrogen bonds so that the GS unitary set  $N_1 = D [3C_2^1(4)]$  and the binary set  $N_2 = 4C_2^1(4)$ . Ammonium chloride, bromide and iodide have the cubic CsCl structure and corresponding unitary set  $N_1 = [4C_2^1(4)]$ .

## 8. Related observations

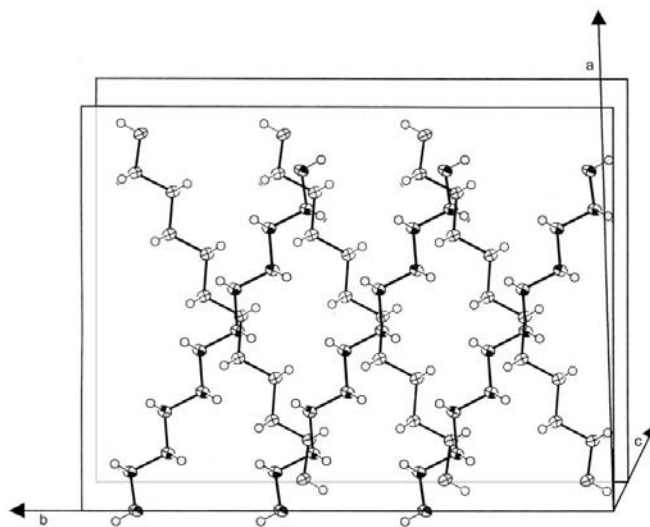
### 8.1. Mixed hydrancy SHB

Piperazine hexahydrate, PIPERH, is a mixed hydrancy structure and does not fall neatly into one of the above categories. A careful study of the hydrogen-bond pattern,

however, shows that it is an SHB material with a more complex arrangement **11 22 22 22 11**. In this structure the piperazine molecules hydrogen bond only to water molecules two thirds of the water molecules are hydrogen bonded to piperazine and three other water molecules, while the other third have all four hydrogen bonds only to water. The piperazine molecules form motifs  $D_2^2(6)$  and  $D_2^2(8)$  with an interesting second-level descriptor  $D_4^4(10)$ . We have not searched for mixed-hydrancy SHB structures, but feel that many other examples might be found among the large number of possible combinations using the eight classes we have identified.

### 8.2. SAMs and diol structures

An interesting feature of the aliphatic diol·PDA structures is that they may provide information relevant to the structure of self-assembled monolayers (SAMs) of alkyl thiol molecules on Au(111) surfaces (Dubois & Nuzzo, 1992). We have noted that the distances and arrangement of the alcohol groups in our structures are almost identical to those of the S atoms in SAMs, which surface scientists refer to as a  $((\sqrt{3} \times \sqrt{3})R30^{\circ})$  structure, where each group of three adjacent Au atoms has one S atom attached. The reported inclination angle of the aliphatic carbon chains to the Au surface also appears to be similar to the chain angle we observe relative to the plane formed by the diol O atoms. The structures usually pictured for SAMs indicate linear, parallel chains and imply that adjacent rows of molecules are also parallel with these. In our structures the molecular chains, rather than being parallel, cross each other at angles of the order of  $50^{\circ}$ . See Fig. 7, which shows the diol chains in two of the stacked planes of (VI). The aliphatic diols in our crystals are centrosymmetric, which might force an orientation that would not occur in the absence of this symmetry. We are attempting to obtain structural information for cocrystals of PDA·bis(aliphatic monol) to



**Figure 7**  
Two adjacent planes of stacked diol molecules of (VI) showing the large crossing angles of adjacent aliphatic chains.



**Table 5**  
Experimental data.

	PZ	MORFCL	MORPHI	PDA8DO	PDA10D	PDA12D	AMHXOL
Crystal data							
Chemical formula	C <sub>4</sub> H <sub>10</sub> N <sub>2</sub>	C <sub>4</sub> H <sub>10</sub> ClNO	C <sub>4</sub> H <sub>10</sub> INO	C <sub>6</sub> H <sub>8</sub> N <sub>2</sub> ·C <sub>8</sub> H <sub>18</sub> O <sub>2</sub>	C <sub>6</sub> H <sub>8</sub> N <sub>2</sub> ·C <sub>10</sub> H <sub>22</sub> O <sub>2</sub>	C <sub>6</sub> H <sub>8</sub> N <sub>2</sub> ·C <sub>12</sub> H <sub>26</sub> O <sub>2</sub>	C <sub>6</sub> H <sub>15</sub> NO
<i>M<sub>r</sub></i>	86.14	123.58	215.03	254.37	282.43	310.48	117.19
Cell setting, space group	Monoclinic, <i>P</i> <sub>2</sub> <sub>1</sub> / <i>n</i>	Monoclinic, <i>P</i> <sub>2</sub> <sub>1</sub> / <i>n</i>	Monoclinic, <i>P</i> <sub>2</sub> <sub>1</sub> / <i>n</i>	Monoclinic, <i>C</i> <sub>2</sub> <sub>1</sub> / <i>c</i>	Monoclinic, <i>P</i> <sub>2</sub> <sub>1</sub> / <i>n</i>	Monoclinic, <i>P</i> <sub>2</sub> <sub>1</sub> / <i>c</i>	Orthorhombic, <i>Fdd</i> 2
Temperature (K)	293	213	294	293	293	293	293
<i>a</i> , <i>b</i> , <i>c</i> (Å)	6.0817 (12), 5.2501 (4), 8.4646 (14)	5.7360 (16), 10.618 (3), 10.142 (3)	6.6521 (3), 10.4682 (8), 10.2590 (4)	36.190 (6), 5.1258 (8), 8.2222 (13)	19.453 (2), 5.1589 (6), 8.180 (1)	22.2081 (14), 5.1843 (9), 8.217 (4)	15.4577 (12), 17.5074 (12), 10.9970 (7)
$\beta$ (°)	108.207 (14)	101.197 (5)	98.703 (4)	101.773 (5)	98.398 (3)	96.818 (3)	90
<i>V</i> (Å <sup>3</sup> )	256.74 (7)	605.9 (3)	706.17 (7)	1493.2 (4)	812.08 (17)	939.4 (5)	2976.1 (4)
<i>Z</i>	2	4	4	4	2	2	16
<i>D<sub>x</sub></i> (Mg m <sup>-3</sup> )	1.114	1.355	2.022	1.131	1.155	1.098	1.046
Radiation type	Cu <i>K</i> $\alpha$	Mo <i>K</i> $\alpha$	Mo <i>K</i> $\alpha$	Mo <i>K</i> $\alpha$	Mo <i>K</i> $\alpha$	Mo <i>K</i> $\alpha$	Mo <i>K</i> $\alpha$
$\mu$ (mm <sup>-1</sup> )	0.55	0.52	4.44	0.08	0.08	0.07	0.07
Crystal form, color	Prism, colorless	Plate, colorless	Plate, colorless	Prism, colorless	Prism, colorless	Prism, colorless	Prism, colorless
Crystal size (mm)	0.60 × 0.35 × 0.25	0.12 × 0.10 × 0.08	0.66 × 0.26 × 0.08	0.75 × 0.30 × 0.25	0.35 × 0.30 × 0.05	0.26 × 0.18 × 0.08	0.40 × 0.40 × 0.38
Data collection							
Diffractometer	CAD-4	Bruker SMART CCD	Enraf–Nonius CAD-4	Bruker CCD	Bruker CCD	Bruker CCD	Siemens P4
Data collection method	$\omega$ scan	$\omega/2\theta$	$\omega/2\theta$	$\omega/2\theta$	$\omega/2\theta$	$\omega/2\theta$	$\omega/2\theta$
Absorption correction	For a cylinder mounted on the $\varphi$ axis	None	$\psi$ scan	None	None	None	None
<i>T<sub>min</sub></i>	0.77	–	0.39	–	–	–	–
<i>T<sub>max</sub></i>	0.87	–	0.70	–	–	–	–
No. of measured, independent and observed reflections	535, 453, 424	4061, 1463, 1152	1600, 1519, 1323	5234, 1776, 1087	5982, 2017, 1051	6256, 2260, 1143	17 546, 1323, 560
Criterion for observed reflections	<i>I</i> > 2.00 $\sigma$ ( <i>I</i> )	<i>I</i> > 3.00 $\sigma$ ( <i>I</i> )	<i>I</i> > 2.00 $\sigma$ ( <i>I</i> )	<i>I</i> > 3.00 $\sigma$ ( <i>I</i> )	<i>I</i> > 3.00 $\sigma$ ( <i>I</i> )	<i>I</i> > 3.00 $\sigma$ ( <i>I</i> )	<i>I</i> > 2.00 $\sigma$ ( <i>I</i> )
<i>R<sub>int</sub></i>	0.02	0.06	0.01	0.02	0.03	0.08	0.08
$\theta_{\max}$	76.7	28.3	26.3	27.9	28.3	28.3	26.6
No. and frequency of standard reflections	3 every 120 min	–	3 every 120 min	–	–	–	–
Intensity decay (%)	0.2	–	0.0	–	–	–	–
Refinement							
Refinement on <i>R</i> [ <i>F</i> <sup>2</sup> > 2 $\sigma$ ( <i>F</i> <sup>2</sup> )], <i>wR</i> ( <i>F</i> <sup>2</sup> ), <i>S</i>	<i>F</i> <sup>2</sup> 0.046, 0.111, 1.04	<i>F</i> <sup>2</sup> 0.036, 0.083, 0.96	<i>F</i> 0.018, 0.019, 1.11	<i>F</i> <sup>2</sup> 0.038, 0.094, 1.03	<i>F</i> <sup>2</sup> 0.035, 0.090, 0.94	<i>F</i> <sup>2</sup> 0.037, 0.090, 0.96	<i>F</i> <sup>2</sup> 0.085, 0.226, 1.06
No. of reflections	424	1152	1323	1087	1051	1143	560
No. of parameters	33	70	73	95	103	113	56
H-atom treatment	Mixture of independent and constrained refinement	Mixture of independent and constrained refinement	Mixture of independent and constrained refinement	Mixture of independent and constrained refinement	Mixture of independent and constrained refinement	Mixture of independent and constrained refinement	Mixture of independent and constrained refinement
Weighting scheme	Calculated method = Prince modified Chebyshev polynomial (Watkin, 1994); <i>W</i> = [weight]*[1 – ( $\delta F/6*\sigma F$ ) <sup>2</sup> ] <sup>2</sup> ; 0.140 <i>E</i> + 04 0.222 <i>E</i> + 04 0.125 <i>E</i> + 04 385	Calculated method = Prince modified Chebyshev polynomial (Watkin, 1994); <i>W</i> = [weight]*[1 – ( $\delta F/6*\sigma F$ ) <sup>2</sup> ] <sup>2</sup> ; 26.1 38.6 20.8 4.87	Calculated method = Prince modified Chebyshev polynomial (Watkin, 1994); <i>W</i> = [weight]*[1 – ( $\delta F/6*\sigma F$ ) <sup>2</sup> ] <sup>2</sup> ; 0.710 –0.154 0.397 –0.143 0.253 <i>E</i> -01	Calculated method = Prince modified Chebyshev polynomial (Watkin, 1994); <i>W</i> = [weight]*[1 – ( $\delta F/6*\sigma F$ ) <sup>2</sup> ] <sup>2</sup> ; 6.89 9.46 3.19	Calculated method = Prince modified Chebyshev polynomial (Watkin, 1994); <i>W</i> = [weight]*[1 – ( $\delta F/6*\sigma F$ ) <sup>2</sup> ] <sup>2</sup> ; 94.7 149. 108. 43.5 17.7	Calculated method = Prince modified Chebyshev polynomial (Watkin, 1994); <i>W</i> = [weight]*[1 – ( $\delta F/6*\sigma F$ ) <sup>2</sup> ] <sup>2</sup> ; 5.77 7.86 2.57	Calculated method = Prince modified Chebyshev polynomial (Watkin, 1994); <i>W</i> = [weight]*[1 – ( $\delta F/6*\sigma F$ ) <sup>2</sup> ] <sup>2</sup> ; 80.9 127. 62.7 15.1

Table 5 (continued)

	PZ	MORFCL	MORPHI	PDA8DO	PDA10D	PDA12D	AMHXOL
$(\Delta/\sigma)_{\max}$	< 0.0001	0.010	0.002	< 0.0001	0.007	< 0.0001	0.006
$\Delta\rho_{\max}, \Delta\rho_{\min}$ ( $e \text{ \AA}^{-3}$ )	0.17, -0.10	0.48, -0.25	0.70, -0.49	0.24, -0.27	0.24, -0.28	0.21, -0.20	0.39, -0.44
Extinction method	Larson (1970)	None	Larson (1970)	Larson (1970)	None	Larson (1970)	Larson (1970)
Extinction coefficient	68.7 (48)	–	80.2 (19)	190.0 (78)	–	95.4 (50)	242.4 (436)

Computer programs used: EXPRESS, SMART (Enraf-Nonius, 1993), SAINT, XSCANS (Siemens, 1993), SHELXS86 (Sheldrick, 1990), XTAL (Hall *et al.*, 1995), SIR97 (Altomare *et al.*, 1994), CRYSTALS (Watkin, 1994; Watkin *et al.*, 1996, 2001).

check the relative orientations when the opposite end of the aliphatic molecule is not constrained by symmetry.

In our structures the zigzag aliphatic chains stack in the *b* direction. The planes of the individual molecules are almost coincident with the plane of the stacking as shown in Fig. 5. The planes formed by these parallel chains are inclined at an angle of  $74 \pm 2^\circ$  to the plane of the end groups [the *bc* plane in these crystals, which is analogous to the surface Au(111) plane of the SAM]. Within each plane of stacked aliphatic molecules, the chains lie at an angle relative to the edge of the plane (the *b* axis), as shown in column 2 in Table 4. This chain angle and the  $2_1$  screw axis result in the molecules crossing those in the adjacent plane at significant angles (column 3, twice the complement of the angle in column 2).

The reported angles were calculated by determining the angles between pairs of even (and of odd) numbered chain atoms and the *b* or *c* axis directions. The tight clustering of all the pairs for each case confirm the almost linearity of the zigzag chains and, when averaged, result in estimated angular uncertainties of a few tenths of a degree.

## 9. Structural results

### 9.1. Piperazine (I)

Crystals were prepared by sublimation under reduced pressure at *ca* 343 K. The crystals rapidly accumulate water from the air, so were selected and transferred to a glass capillary under a dry  $N_2$  blanket and sealed. H atoms on C were treated as riding, while the amine H atom was found in a difference map and isotropically refined. Comparing the cell parameters of our 293 K structure to those of the 150 K determination of Parkin *et al.* (2004) shows an expansion of 0.7% for *c*, while *a* and *b* expand 1.1–1.3%, as does the N–N length of the hydrogen bond. Table 5 shows the experimental details for all the structures.<sup>1</sup>

### 9.2. Morpholinium chloride (II) and iodide (III)

Crystals were grown by evaporation of solutions of morpholine neutralized with aqueous HCl and HI, respectively. The numbering and packing are shown in Figs. 3(a) and

(b). H atoms on C were treated as riding, while the amine H atoms were isotropically refined.

### 9.3. Phenylene diamine-diols (IV), (V) and (VI)

These cocrystals were grown from 3:1 toluene:ethanol solutions and the selected crystal sealed in glass to prevent crystal degradation by slow loss of volatiles. The amine and hydroxy H atoms were found in difference maps and refined isotropically. The H atoms attached to carbon were placed at calculated positions and refined as riding atoms. Displacement ellipsoid plots showing atomic numbering are shown in Fig. 5.

### 9.4. Aminoalcohol (VII)

The crystal is polar with all the molecules in nearly the same orientation. Molecules and the  $OH \cdots N$  hydrogen bonds form a *C*(9) graph set along *c*. Owing to the limitations of the data set, only the N and O atoms were anisotropic in the final refinement. The C atoms and hydrogen-bonding H atoms were refined isotropically, with  $CH_2$  hydrogen atoms at calculated positions as riding atoms. A partial packing diagram showing four adjacent SHB molecules of the 16 in the cell and indicating the numbering used is shown in Fig. 6.

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<sup>1</sup> Supplementary data for this paper are available from the IUCr electronic archives (Reference: GP5014). Services for accessing these data are described at the back of the journal.

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