Crystals of 4-chloro-2′-biphenyloxol grown at 263 K and studied at both 293 and 142 K are loosely packed and contain OH⋯O bonded tetramers composed of four crystallographically independent molecules ($Z' = 4$). Approximate symmetry relationships between independent molecules are apparent in many, perhaps even most, structures with $Z' > 1$, but are not obvious in this structure. The inefficient crystal packing, the surprisingly large value of $Z'$ and the absence of pseudosymmetry reflect the difficulty of finding a dense molecular arrangement that also allows for hydrogen-bond formation. Impediments to good packing are the steric congestion around the ortho hydroxyl groups and the difficulty in filling space with significantly twisted biphenyl fragments. The packing arrangement adopted is strongly reminiscent of the structure type found for eight simple 4,4′-biphenyl derivatives, but one of the four independent 4-chloro-2′-biphenyloxol molecules has an orientation that is significantly different from the orientations of the other three and that does not fit the 4,4′-XPhPhY pattern. It is suggested that molecules that crystallize with $Z' > 1$ are good candidates for solid-state compound formation.

1. Introduction

The structure of 4-chloro-2′-biphenyloxol (hereafter referred to as 4CL2′OH) was determined as part of a study of the toxicity of chlorinated biphenyls and, especially, of chlorinated biphenols (Robertson & Hansen, 2001). The structure proved to be very unusual because of the large number of independent molecules ($Z' = 4$) in the asymmetric unit (Brock & Dunitz, 1994) and because of the lack of approximate symmetry operations relating the independent molecules. When we first started looking at packing diagrams the structure seemed to be just a jumble of molecules, but eventually we saw an analogy with a structure type common for simple 4,4′-disubstituted biphenyls. Three of the independent molecules of 4CL2′OH are arranged in a variant of that structure type; the fourth independent molecule has a quite different orientation. The structural peculiarities (large $Z'$; lack of pseudosymmetry) appear to result from conflicts between the drive to form OH⋯O hydrogen bonds and the steric constraints associated with the ortho location of the hydroxyl group, and from the problems associated with filling space densely with twisted biphenyl fragments.
2. Experimental

2.1. Synthesis

The compound was synthesized by palladium-catalyzed cross-coupling of 4-chlorobenzene boronic acid and 2-bromoanisole followed by demethylation with boron tribromide (Bauer et al., 1995). Crystals grown at 263 K by slow evaporation of chloroform/n-hexane solutions are thin laths with pointed ends. Crystals are thinnest along a* and are elongated along b. The crystals are colorless initially, but develop a bluish-gray cast over a period of weeks. Oxidation of phenol groups very near the surface of the crystals probably accounts for the color change.

2.2. Structure determination

Structure determination at 142 K and then at 293 K was routine. Two different crystals were used. Hydroxyl protons were located in difference maps; there was no indication of any disorder. The coordinates and $U_{iso}$ values for the four OH protons at 142 K were refined \[ R_{O-H} = 0.79-0.84 (2) \AA; \] $U_{iso} = 0.027 (8)-0.074 (11) \AA^2$; all other protons were constrained to ride on the attached C atom \( r_{C-H} 0.95 \AA at 142 K and 0.93 \AA at 293 K; \( U_{iso} 1.2U_{eq} for the corresponding C atom \). The bond lengths and angles for the OH protons at 293 K were fixed \( (0.82 \AA, 109.5^\circ) \) and the $U_{iso}$ values determined as for the CH protons, but the four torsion angles \( (Hn-OH-C8n-C7n) \) were varied. Experimental details can be found in Table 1.\footnote{Supplementary data for this paper are available from the IUCr electronic archives (Reference: NS0006). Services for accessing these data are described at the back of the journal.}

Ellipsoid plots of the asymmetric units are shown in Fig. 1 and the crystal packing is illustrated in Fig. 2. All bond lengths and angles are normal; s.u.s at 142 K are 0.003 \AA and 0.2\textdegree. The change with temperature of the average $U_{eq}$ values is also normal (Dunitz et al., 1988); the values increase by an average factor of 2.1 (1) when the temperature is changed from 142 to 293 K (ratio 2.06).

2.3. Database searches

All searches were run on the April 2001 version (5.21) of the Cambridge Structural Database (Allen & Kennard, 1993; hereafter the CSD).

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### Table 1. Experimental details.

<table>
<thead>
<tr>
<th></th>
<th>209 K</th>
<th>210 K</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crystal data</td>
<td></td>
<td></td>
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<tr>
<td>Chemical formula</td>
<td>C$_{12}$H$_9$ClO</td>
<td>C$_{12}$H$_9$ClO</td>
</tr>
<tr>
<td>Chemical formula weight</td>
<td>204.64</td>
<td>204.64</td>
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<td>Cell setting, space group</td>
<td>Monoclinic, $P2_1/c$</td>
<td>Monoclinic, $P2_1/c$</td>
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<td>$a$, $b$, $c$ (Å)</td>
<td>17.418 (3), 12.015 (2), 19.841 (3)</td>
<td>17.211 (3), 11.962 (2), 19.621 (3)</td>
</tr>
<tr>
<td>$\beta$ (°)</td>
<td>95.95 (2)</td>
<td>95.95 (2)</td>
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<tr>
<td>$V$ (Å$^3$)</td>
<td>4132.5 (12)</td>
<td>4017.8 (11)</td>
</tr>
<tr>
<td>$Z$</td>
<td>16</td>
<td>16</td>
</tr>
<tr>
<td>$D_\lambda$ (Mg m$^{-3}$)</td>
<td>1.316</td>
<td>1.353</td>
</tr>
<tr>
<td>Radiation type</td>
<td>Mo Ka</td>
<td>Mo Ka</td>
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<tr>
<td>No. of reflections for cell refinement</td>
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<td>20 387</td>
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<td>$I &gt; 2\sigma(I)$</td>
</tr>
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<td>1.0-25.0</td>
</tr>
<tr>
<td>$\mu$ (mm$^{-1}$)</td>
<td>0.33</td>
<td>0.34</td>
</tr>
<tr>
<td>Temperature (K)</td>
<td>293 (1)</td>
<td>142 (1)</td>
</tr>
<tr>
<td>Crystal form, color</td>
<td>Pointed laths, colorless</td>
<td>Pointed laths, colorless</td>
</tr>
<tr>
<td>Crystal size (mm)</td>
<td>0.26 x 0.25 x 0.05</td>
<td>0.41 x 0.25 x 0.05</td>
</tr>
</tbody>
</table>

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Computer programs used: COLLECT (Nonius, 1999), DENZO-SMN, SCALEPACK (Otwinowski & Minor, 1997), SHELXS97 (Sheldrick, 1997), SHELXL (Sheldrick, 1997), SHELXL/PC (Sheldrick, 1990).
however, is not especially favorable. The OH· · · O bonds at 293 K seem to be a little weaker than at 142 K.

Molecules A and B are conformational enantiomers of molecules C and D, i.e. the senses of the twists in two of the molecules of the tetramer (A and B) are opposite from those in the two other molecules (C and D). The magnitudes of the twists in the four molecules can be described by the dihedral angles between the planes of atoms C1n±C6n and C7n±C12n; at 142 K these angles are 48.0, 51.3, 50.6 and 59.5° (s.u.s < 0.1°). Another measure of the twist is the average torsion angle ψ around the central C–C bond (i.e. the average of the four angles C2n/C6n–C1n–C7n–C8n/C12n); the ψ values at 142 K for molecules A–D are −48.0 (8), −51.1 (5), 50.6 (5) and 59.2 (3). The similarities of the dihedral and torsion angles indicates there is little bending at C1n or C7n. The twist of molecule D is a little larger than the twists of molecules A, B and C, which are nearly the same. There is no important conformational change between 142 and 293 K.

The tetramer in the 4CL20H structure is not very pseudosymmetric (see Figs. 1 and 2). While the long axes of molecules A, B and D (the axes defined by atoms C1n, C4n, C1n, C7n and C10n) are roughly parallel (angles 18, −7 and −14° for vectors C04–C10 in molecule pairs A–B, A–D and B–D), the long axis of molecule C has a very different orientation (angles −32, −48 and 39° for molecule pairs A–C, B–C and C–D; all s.u.s < 1°).

The 4CL20H structure is very loosely packed. The VOID instruction in PLATON (Spek, 2001) gives packing coefficients of 0.65 (Kitaigorodskii, 1961) at 295 K (just 20 K below the melting point) and 0.68 at 142 K; these coefficients are at the low end of the expected range (0.65–0.80; Kitaigorodskii, 1961; Dunitz et al., 2000). At 295 K the average $U_{eq}$ value is 0.068 Å² for the C atoms and 0.113 Å² for the Cl atoms; the corresponding r.m.s. displacements are 0.26 and 0.34 Å. The large $U$ values are consistent with the melting point (314–316 K; this work), which is ca 30 K lower than the melting point of the tetramer.
Table 3
Melting points (K) for some biphenyl derivatives with simple ortho and para substituents.

<table>
<thead>
<tr>
<th>Substituent at 2- or 4-position</th>
<th>Other substituents</th>
<th>T_{fus} (K) for 2-substituted isomer</th>
<th>T_{fus} (K) for 4-substituted isomer</th>
<th>Approximate difference</th>
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<tbody>
<tr>
<td>---</td>
<td></td>
<td>---</td>
<td>---</td>
<td>---</td>
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<tr>
<td>F</td>
<td></td>
<td>344±348</td>
<td>344±348</td>
<td>0</td>
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<tr>
<td>Cl</td>
<td></td>
<td>302±307</td>
<td>349±351</td>
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<tr>
<td>Br</td>
<td></td>
<td>274±275</td>
<td>360±365</td>
<td>90</td>
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<tr>
<td>I</td>
<td></td>
<td>&lt;298</td>
<td>382±387</td>
<td>120</td>
</tr>
<tr>
<td>CH₂</td>
<td></td>
<td>273</td>
<td>318±324</td>
<td>50</td>
</tr>
<tr>
<td>OCH₃</td>
<td></td>
<td>303±304</td>
<td>359±365</td>
<td>60</td>
</tr>
<tr>
<td>OH</td>
<td></td>
<td>329±334</td>
<td>437±443</td>
<td>110</td>
</tr>
<tr>
<td>CH₂OH</td>
<td></td>
<td>322±324</td>
<td>371±375</td>
<td>50</td>
</tr>
<tr>
<td>NH₂</td>
<td></td>
<td>319±323</td>
<td>323±328</td>
<td>5</td>
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<tr>
<td>NO₂</td>
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<td>307±311</td>
<td>386±391</td>
<td>80</td>
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<td>CN</td>
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<td>308±314</td>
<td>357±361</td>
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<td>OH 4'-Cl</td>
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<td>OH 4'-Br</td>
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<td>OH 4'-I</td>
<td></td>
<td>346±347</td>
<td>466±467</td>
<td>120</td>
</tr>
</tbody>
</table>

Melting point ranges taken from the data in the Beilstein Database (2001). The corresponding range for unsubstituted biphenyl is 339–346 K.

4. Discussion

4.1. Packing of 4CL2'OH

The 4CL2'OH molecule, which is both a monovalent and a simple biphenyl, has three important packing problems. The first is the steric congestion around the OH groups; the second problem is the difficulty of filling space densely with twisted biphenyl fragments. Biphenyls often crystallize with a more planar and (higher-energy) conformation than they would have in the gas phase (Brock & Minton, 1989) because flatter molecules can usually fill space more densely than more twisted molecules (see e.g. Gavezzotti, 1990). This space-filling problem is exacerbated when there are ortho substituents, because the molecular twist must then be greater than is found for any biphenyl molecules without ortho substituents (Brock & Minton, 1989). It is no accident that biphenyl fragments are important building blocks of many liquid crystals (see e.g. Baker et al., 1993; see also the comments by Rajnikant et al., 1995, on the crystallization of biphenyls). The third problem is the rigidity of the molecule; there is only a single low-energy degree of freedom that can be varied to optimize intermolecular contacts.

The observed 4CL2'OH structure can be seen as a compromise arrangement that allows a set of contacts which correspond to rather weak OH···O bonds and that gives acceptably dense packing. The overall arrangement, however, is not very satisfactory, at least as measured by the melting point. The comparison with T_{fus} for unsubstituted biphenyl has already been made; consider also 2-biphenylol, for which the T_{fus} is 15 K higher (see Table 3), even though the structure allows for little OH···O bonding and even though the absence of the Cl atom would be expected to lower the melting point. Note also that there is only one Cl···Cl contact shorter than 4.4 Å [Cl···Cl = 3.808 (1) Å at 142 K] in this structure. The Cl···Cl contacts with lengths < 3.6 Å that might be expected to be present (Desiraju & Parthasarathy, 1989; see also Boese et al., 2001) are missing.

4.2. Packing of some related biphenylols

Compared with 2-biphenylol, 4-biphenylol crystallizes ‘normally’ in two polymorphic forms (P_{2}1/a, Z = 1 and P_{2}1_22_1, Z = 2; Brock & Haller, 1984), both of which have a full set of OH···H bonds and allows the molecules to adopt a more planar conformation (ψ < 10º), which is better for crystal packing. The structure of 3-biphenylol, however, is another high Z' structure; Z' = 6, with two packing units each composed of OH···O bonded trimers (Watkin, 2000). The melting point of 3-biphenylol (349–351 K; Sigma-Aldrich Co., 2000) is intermediate between the melting points of 2- and 4-biphenylol (330–332 and 438–440 K; Sigma-Aldrich Co., 2000).

There are few other comparison structures available in the CSD. Notable is biphenyl-2-methanol (ZENVAP; Rajnikant & Watkin, 1995). ZENVAP differs from 2-biphenylol and 4CL2'OH by having a CH₂ spacer that separates the biphenyl and hydroxyl groups. The additional flexible link makes possible the formation of OH···O chains [basic graph-set symbol C(2)] with O···O distances in the range 2.72–2.78 Å. Still, Z' = 4, although the four independent molecules in each chain are related by a rather approximate translation and a fairly good screw axis that would be a 2₁ axis if the translation were exact. The important differences between the independent molecules are the molecular twists; absolute values of the torsion angles ψ (see above) are in the range 53.5–61.9 (1º).

In the CSD there are structures of several more complicated molecules that contain the 2-biphenylol fragment, but that have no other heteroatom that could act as a proton acceptor. None of these structures contain OH···O bonds.

Two other structures from the CSD merit comment. In 2,2'-biphenyldiol (NUTSUQ; P_{2}1_2/c, Z = 1; Byrne et al., 1998) intra-
and intermolecular OH···O bonds alternate to form chains parallel to b. The introduction of the second OH group allows intramolecular OH···O bonding and thus allows spatial separation of the proton donor and acceptor of the intermolecular OH···O bond. This spatial separation relieves the packing problem. Consider also trans-(2-p-tolyl)cyclohexanol (YELNEI; $P \bar{1}$, $Z' = 2$; Peters et al., 1994), in which the 4-Cl substituent of 4CL2OH is replaced by a methyl group and the phenol fragment is reduced to a cyclohexanol ring. YELNEI, like 4CL2OH, forms $R_1^2(8)$ tetramers, but in YELNEI the tetramers are located on inversion centers and the O···O distances (2.73 and 2.82 Å) are more favorable. It is not clear why the cyclohexanol can form more symmetric tetramers than the phenol. The greater thickness and flexibility of the cyclohexyl ring may play a role; examination of van der Waals surfaces of the 4CL2OH structure suggests that the region around the tetramer is not very densely packed.

4.3. Melting-point comparisons

Melting-point differences for pairs of isomers are good indicators of their relative packing energies. Gavezzotti (1995) has shown that the melting points of para-disubstituted benzenes (see also Boese et al., 2001) are systematically higher than the melting points of the corresponding ortho-substituted isomers. The differences range from −50 to 150 K, with an average a little above 50 K

Compiling a list of melting points is not so simple (see Gavezzotti, 1995). In the end we decided to use the range of values available in the Beilstein Database (2001) after removing the obvious outliers. The high end of each range is probably more reliable than the low because impurities affect the latter. The ranges are larger for compounds that have been studied by many authors than for compounds that have been mentioned in the literature only a few times.

Table 3 shows that moving a biphenyl substituent from an ortho to a para position nearly always raises the melting point very substantially, even if the substituent is not involved in OH···O bonding. Moving a fluoro substituent has no effect, but F and H atoms are nearly the same size and the fluoro-biphenyl isomers melt at nearly the same temperature as biphenyl itself (342–345 K). Moving an amino substituent has little effect either, but the melting points for both isomers are unexpectedly low.

The melting-point differences between the ortho- and para-substituted compounds are at least as large as those seen by Gavezzotti (1995). We believe the melting-point difference reflects the difficulty of filling space densely with molecules having $\psi$ values of 50° or more.

If the effect of hydrogen-bond formation is to be isolated, then pairs of isomers must be located that have an −OH group and a substituent of similar size at positions 2 and 4 of the same phenyl ring. Two pairs of such isomers were found (see Table 3). In both cases the compound with the −OH group in the para position has the higher melting point, presumably because that location allows the formation of more favorable OH···O bonds.

Density comparisons cannot be made for the molecules in Table 3, because structures have been determined for only a few of them. Simple biphenyl derivatives crystallize so poorly that systematic studies have been frustrated (Rajnikant & Watkin, 1995; this work).

4.4. Symmetry relationships in alcohol tetramers

In a survey of monoalcohol structures (Brock & Duncan, 1994) we found that many of the $R_1^2(8)$ tetramers were located on 4 sites and that the remainder were located at inversion centers or on a twofold axes. Since that survey, six monoalcohol structures with $R_1^2(8)$ motifs and $Z' = 4$ have been published, all of them in space group $P2_1/c$, $P2_1$, or $P1$. One structure (BAJMOO) has two sets of tetramers, each of which is located on an inversion center. The tetramers in three more of the structures show only small deviations from symmetry 4 (HEGJOS) or 4 (PEZQEO; SILQJE); another (YEKBAR) has approximate symmetry 222. The tetramer in the sixth structure (HAVGAM) has an approximate symmetry 2 and very approximate symmetry $2/m$. The tetramer in a seventh structure (WEYTA; $P1$, $Z' = Z = 6$) is nearly centrosymmetric; the other two molecules are disposed almost, but

Figure 3
Two projections of the structure of 4,4′-dichlorobiphenyl (Brock et al., 1978). In the upper drawing (projection down b) two unit cells are shown so that the projection may be more easily compared with the projection shown in Fig. 2. In the lower drawing (projection down −a*) a single slice centered around $x = 0.125$ is shown.
4.5. A conjecture about structures with $Z > 1^4$

It seems likely that structures with large $Z$ values are associated with packing conflicts, especially if the structures are not pseudosymmetric (see Desiraju et al., 1991). This conjecture grew out of the observations (Brock & Dunitz, 1994) that $Z > 1$ structures are unusual and that most molecules that can lie on inversion centers, do. Taken together these generalizations suggest that the size of the asymmetric unit should be minimized. Finally, consider glasses, which have infinite $Z$ values (or at least $Z$ values that are too large to measure) and which are often engineered by synthesizing compounds that can be expected to crystallize badly.

The molecule 4-chloro-2'-biphenyl belongs to two classes of compounds (monoalcohols and simple biphenyls with no ortho substituent) that have identifiable packing problems (Brock & Duncan, 1994; Brock & Minton, 1989) and that crystallize unusually frequently with $Z > 1$.

The tendency towards minimization of $Z$ values, and thus minimization of the volume of the asymmetric unit, may be related to the low incidence of solid-state compound (or co-crystal) formation. Co-crystal formation is rare unless the constituents are enantiomers (inversion symmetry being very favorable for crystal packing) or unless there is a strong donor–acceptor interaction between the two constituents.

4.6. Related structure type

The overall arrangement of molecules A, B and D, as seen in projection down b, is very reminiscent of the $P2_1/c$, $Z = 2$ pattern found for eight biphenyls$^5$ that have simple substituents (halo, cyano, methyl, methoxy) in the 4 and 4$'$. The structures of these eight 4,4'-disubstituted biphenyls are pseudohexagonal (see DCLBIQ10; Brock et al., 1978, which is illustrated in Fig. 3). Projections down b of the 4CL2'OH and

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$^4$ WEYTA V (Rieger et al., 1994) is not listed in Marsh's (1999) compilation of $P1$ structures that should probably be described in a higher-symmetry group.

$^5$ We know of no systematic study of approximate symmetry, or pseudosymmetry, in all $Z > 1$ structures, but believe that $Z > 1$ structures that have identifiable pseudosymmetry occur more frequently than those that do not. The routine determination of structures at low temperatures accounts for some of the pseudosymmetric $Z > 1$ structures, because transitions with cooling to a larger or lower-symmetry unit cell are fairly common. Some other $Z > 1$ structures (ca 20% of the P1 entries in the October 1998 version of the CSD and ca 3% of the C2 entries in the October 200 release) should probably have been described in higher-symmetry space groups (Marsh, 1999; Marsh & Spek, 2001). Studies of pseudosymmetry in a restricted group of compounds (Britton, 2000) and in specific space groups (Desiraju et al., 1991; Kálmán & Argay, 1998; Marsh, 1999) have appeared.

$^6$ Refcodes BRCYBP, BTOLYL, DBRBI R, DCLBIQ10, FAZGES01, GAXWAD, JIXBEX and KUSVOJ.

$^7$ The long axes of molecules A and B are rotated ca $10^\circ$ about axes that are approximately parallel to c, while the rotation of the long axis of molecule D is around an axis that is roughly parallel to a.
For the eight 4,4′-disubstituted biphenyls the lengths of the c axes\(^7\) are in the range 9.42–9.85 Å (all measured at room temperature); in 4Cl\(_2\)OH the length of c is 2 × 9.92 Å at 293 K. The corresponding values for a are 15.56–16.11 and 17.42 Å. The tilting of molecule C causes a small (several %) expansion along c and a significant expansion (ca 10%) along a.

Projections down –a (Figs. 3 and 4) show that the patterns of molecular displacement along b are not the same for the two structures and show why c is ca twice as long in the 4Cl\(_2\)OH structure as in the DCLBIQ10 structure. Why are the patterns different? First, the formation of hydrogen-bonded tetramers imposes constraints on the \(y\) coordinates of the O atoms. Secondly, the 4Cl\(_2\)OH molecules, which have only one \textit{para} substituent, are ‘shorter’ than the 4,4′-XPhPhY molecules that crystallize in the pseudohexagonal pattern\(^8\) and so cannot fit together in quite the same way.

The 4Cl\(_2\)OH structure can be viewed as being formed of two sets of centrosymmetric double layers that are perpendicular to \(a^*\) (see Fig. 4 for pictures of one half of each double layer). The structural importance of those layers is demonstrated by the crystal morphology: growth is slowest along \(a^*\). The double layer at \(x = 0\) is composed of molecules \(A\) and \(B\), and is very similar to a fragment of the DCLBIQ10 structure (see Figs. 2 and 3). The double layer at \(x = 1/2\) is composed of molecules \(C\) and \(D\) and looks much less like a fragment of the DCLBIQ10 structure. The contacts at the centers of the two double layers (i.e. the contacts at \(x = 0\) and at \(x = 1/2\)) are very different (see Fig. 2).

4.7. Implications for formation of solid-state compounds (or Co crystals)

Co-crystallization is viewed as a route to new solids with potentially interesting properties,\(^9\) but co-crystal formation is uncommon unless the components are enantiomers or interact strongly.\(^10\) It is well known that molecules that crystallize poorly when pure are more likely to give solid-state compounds; this is the basic principle that underlies the field of host–guest chemistry and explains the formation of solvates.\(^11\) Molecules that crystallize poorly can be identified by their melting points and packing efficiencies. We suggest that looking at high-\(Z\) structures, particularly those in which there are no approximate symmetry relationships, might also be a good way of finding molecules that are likely to form solid-state compounds.

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References


\(^7\)All cells were transformed to the \(P2_1/n\) setting corresponding to that used for 4,4′-dichlorobiphenyl.
\(^8\)The 4,4′-dichlorobiphenyl structure has two sets of short (3.37, 3.38 Å) Cl–Cl interactions that stabilize the molecular columns parallel to b of the pseudohexagonal arrangement. There are no Cl–C contacts shorter than 3.80 Å in the 4Cl\(_2\)OH structure.
\(^9\)See e.g. Thaimattam \textit{et al.} (2001) and Desiraju (1989).
\(^{10}\)It is worth noting that negative deviations from Raoult’s Law are rare, even if one component is an organic acid and the other an amine. Segregation of unlike molecules is the rule, even in liquids.
\(^{11}\)Consider a two-component solid-liquid phase diagram. The lower the freezing point of one of the pure compounds the greater the likelihood of its freezing-point depression curve falling below the melting-point curve of one of the possible solid-state compounds.

Watkin, D. J. (2000). Personal communication.