Acta Crystallographica Section B
Structural Science
ISSN 0108-7681

Crystal engineering in the *gem*-alkynol family: the key role of water in the structure of 2,3,5,6-tetrabromo-*trans*-1,4-diethynyl-cyclohexa-2,5-diene-1,4-diol dihydrate determined by X-ray and neutron diffraction at 150 K

Clair Bilton,[a] Judith A. K. Howard,[a] N. N. L. Madhavi,[b] Gautam R. Desiraju,[b] Frank H. Allen[c]* and Chick C. Wilson[d]

[a]Department of Chemistry, University of Durham, South Road, Durham DH1 3LE, England, [b]School of Chemistry, University of Hyderabad, Hyderabad 500 046, India, [c]Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, England, and [d]ISIS Facility, Rutherford Appleton Laboratory, Chilton, Didcot, Oxon OX11 0QX, England

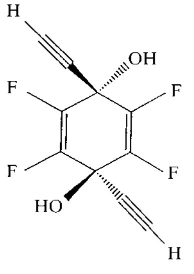
Correspondence e-mail: allen@ccdc.cam.ac.uk

Received 3 January 2001
Accepted 18 May 2001

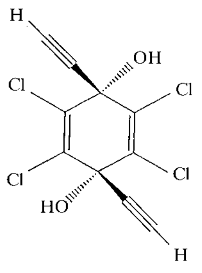
The structure of the title compound has been determined using low-temperature (150 K) single-crystal X-ray and neutron diffraction data. Crystals adopt the uncommon space group $P4_2/ncm$ and display a complex set of intermolecular interactions in which the water molecules play the crucial role: the water O-atom [O2(*w*)] accepts two hydrogen bonds and both water H atoms act as bifurcated donors. A set of O—H···O hydrogen bonds is formed around the 4_2 axis comprising (*a*) a cyclic tetrameric synthon involving four donor-H from two water molecules and two O(hydroxy) acceptors from two parent molecules, and (*b*) short discrete O(hydroxy)—H···O2(*w*) hydrogen bonds which link these tetramers along the *c* axis. Four Br···Br interactions [3.708 (1) Å] form cyclic Br_4 tetramers around the $\bar{4}$ axis and are linked to the O—H···O system *via* O2(*w*)—H···Br bonds with H···Br = 2.995 (2) Å. Finally, the O—H···O system is further linked to the parent molecules *via* C≡C···H···O2(*w*) bonds of 2.354 (3) Å. The supramolecular structure of the title hydrate is compared with that of the non-hydrated parent molecule, which also forms cyclic O—H···O bonded tetrameric synthons, and with its (non-hydrated) tetrachloro analogue, which forms cyclic tetrameric Cl_4 synthons [Madhavi, Desiraju *et al.* (2000*b*). *Acta Cryst.* B**56**, 1063–1070].

1. Introduction

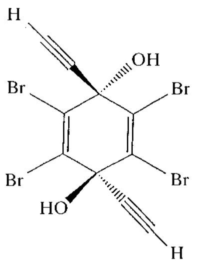
We have recently synthesized a variety of compounds containing the *gem* alkynol functionality. Such structures were considered likely to contain both strong O—H···O bonds and weaker interactions involving the acidic proton and π-system of the C≡C—H group, thus providing an opportunity to characterize the latter and study their competition with the former. A Cambridge Structural Database (CSD: Allen & Kennard, 1993) study of the 94 published structures of *gem*-alkynols has shown that they do indeed exhibit a bewildering variety of interaction patterns involving O—H···O, C—H···O, O—H···π and C—H···π contacts (Madhavi, Bilton *et al.*, 2000). However, more than half of that sample contained other functional groups which are capable of acting as strong hydrogen-bond donors or acceptors, or both. To avoid this unneccesary complication, our syntheses of novel *gem*-alkynols have varied the additional substituents in a controlled manner, so as to study the mutual interplay of strong and weak interactions (see, *e.g.*, Desiraju, 1997; Nangia & Desiraju, 1998), and to characterize the similarities and differences between the supramolecular synthons (Desiraju, 1995) which form in the crystal structures of this series of closely related molecules.



(1)



(2)



(3)

The structures of five compounds (Bilton *et al.*, 1999; Madhavi, Bilton *et al.*, 2000; Madhavi, Desiraju *et al.*, 2000*a*) that contain only the *gem*-alkynol functionality together with C—H groups of differing H-acidity are dominated by the expected O—H···O hydrogen bonds, together with a variety of weaker interactions involving the ethynyl group and other C—H donors. By contrast, a series of four substituted diphenylethynylmethanols (Bilton, Howard, Madhavi, Nangia *et al.*, 2000) all display the complete lack of O—H···O hydrogen bonds exhibited by the parent compound (Garcia *et al.*, 1995), relying entirely on weaker interactions for their supramolecular organization. Finally, we have studied a pair of compounds in which the keto-functionality has been introduced, resulting in structures (Bilton, Howard, Madhavi, Desiraju & Allen, 2000) which are dominated by O—H···O═C hydrogen bonds.

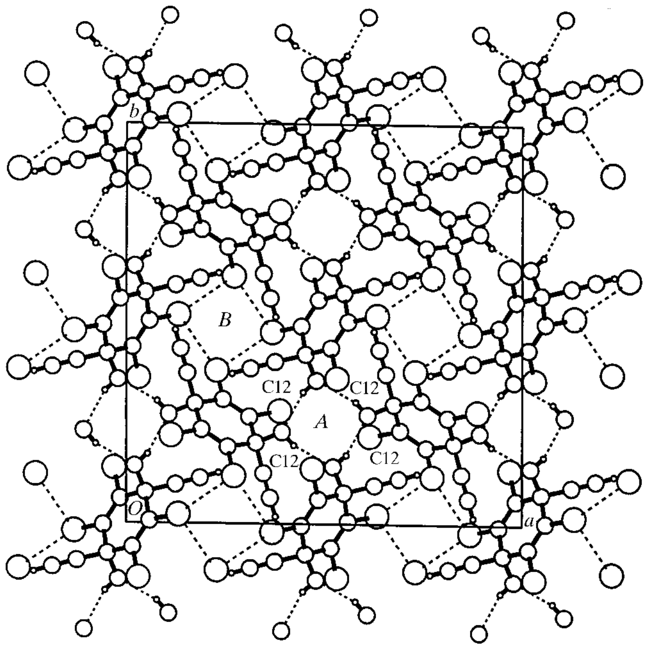


Figure 1
Structure of the Cl compound (2) viewed along the tetragonal *c* axis, showing *A* the tetrameric O—H···O synthon that forms about the $\bar{4}$ axes, and *B* the helical arrangement of Cl···Cl interactions around the 4_1 axes. The Cl(2) atoms labelled (and their symmetry-related sets) form a cyclic tetrameric unit that interleaves with synthon *A* along the $\bar{4}$ axis. These Cl···Cl links are omitted for clarity.

Of key relevance to the present work is a series of three 2,3,5,6-tetrahalo[F,Cl,Br]-*trans*-1,4-diethynyl-cyclohexa-2,5-dienes (1)–(3). Their structures (Madhavi, Desiraju *et al.*, 2000*b*) are dominated by strong O—H···O hydrogen bonds, which form a closed hexameric synthon in the F compound, reinforced by much weaker C≡C—H···F interactions. In the tetragonal Cl compound [(2), space group $I4_1/a$], illustrated in Fig. 1, the O—H···O synthon (*A*) is tetrameric and forms around the $\bar{4}$ axes. This O—H···O architecture is supported by two discrete sets of Cl···Cl interactions. The shorter interaction [Cl···Cl = 3.605 (1) Å] forms helical arrangements (*B*) around the 4_1 axes, while the longer one [Cl···Cl = 3.731 (2) Å] forms cyclic Cl_4 tetramers, involving the Cl2 atoms shown in Fig. 1, which alternate with the O—H···O synthon along the $\bar{4}$ axes.

The triclinic ($P\bar{1}$) Br compound [(3), Fig. 2] forms a pseudo-tetragonal structure which is again dominated by a tetrameric O—H···O synthon (*A*), supported by Br···Br interactions (not shown in Fig. 2). Here, however, the five shorter Br···Br interactions [3.421 (7)–3.680 (6) Å] simply provide cross-links between the stacks of hydrogen-bonded tetramers, although two longer interactions [Br···Br = 3.839 (5), 3.882 (7) Å] combine with one of the shorter interactions to form cyclic Br_3 trimers. The ethynyl groups in both (2) and (3) are involved in weak C≡C—H···Cl,Br hydrogen bonds (see, *e.g.*, area *B* in Fig. 2), together with C≡C—H···π(ethynyl) bonds in (3), at point *C* in Fig. 2.

Very recently, we have isolated large high-quality crystals of a compound that proved to be the dihydrate of the Br compound (3), hereinafter denoted as (3*w*), and have determined its structure using low-temperature (150 K) X-ray and neutron diffraction data. In this paper, we report the results of those experiments, and compare and contrast the highly complex pattern of intermolecular interactions in (3*w*), engendered by the presence of the water solvate, with those in the unsolvated parent compound (3) and its chloro analogue (2).

2. Experimental

2.1. Crystal structure determination

X-ray diffraction intensities for (3*w*) were collected at 150 K (Oxford Cryosystems cryostat) on a Bruker SMART CCD diffractometer using Mo *Kα* X-radiation. Data were processed using the Bruker *SAINT* package (Bruker Systems Inc., 1999), with structure solution and refinement using *SHELXL*97 (Sheldrick, 1997). H atoms were located in difference maps and refined freely with isotropic displacement parameters to yield a final *R* of 0.020. Full details and results of the X-ray experiment have been deposited.[1]

---

[1] Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM0041). Services for accessing these data are described at the back of the journal.

Table 1
Experimental details.

	Neutron	X-ray
Crystal data		
Chemical formula	$C_{10}H_4Br_4O_2{\cdot}2H_2O$	$C_{10}H_4Br_4O_2{\cdot}2H_2O$
Chemical formula weight	511.8	511.8
Cell setting, space group	Tetragonal, $P4(2)/ncm$	Tetragonal, $P4(2)/ncm$
a, b, c (Å)	12.6551 (18), 12.6551 (18), 8.7340 (17)	12.6551 (18), 12.6551 (18), 8.7340 (17)
V (Å^3)	1398.8 (4)	1398.8 (4)
Z	4	4
D_x (Mg m^{-3})	2.429	2.430
Radiation type	Neutron	Mo $K\alpha$
No. of reflections for cell parameters	From X-ray	999
θ range (°)	–	2.28–23.25
μ (mm^{-1})	0.000	11.510
Temperature (K)	150	150
Crystal form, colour	Block, colourless	Block, colourless
Crystal size (mm)	3 × 2 × 2	0.4 × 0.3 × 0.3
Data collection		
Diffractometer	SXD	Bruker SMART CCD
Data collection method	Time-of-flight LAUE diffraction	ω scans
Absorption correction	None	Multi-scan
$T_{\min}$	–	0.644
$T_{\max}$	–	1.000
No. of measured, independent and observed parameters	1654, 1654, 1654	6046, 539, 501
Criterion for observed reflections	$I > 2\sigma(I)$	$I > 2\sigma(I)$
$R_{\rm int}$	0.0000	0.0302
$\theta_{\max}$ (°)	62.64	23.25
Range of h, k, l	$0 \rightarrow h \rightarrow 28$ $0 \rightarrow k \rightarrow 18$ $0 \rightarrow l \rightarrow 21$	$-13 \rightarrow h \rightarrow 14$ $-14 \rightarrow k \rightarrow 13$ $-8 \rightarrow l \rightarrow 9$
Refinement		
Refinement on	F^2	F^2
$R[F^2>2\sigma(F^2)]$, $wR(F^2)$, S	0.0607, 0.0819, 6.188	0.0201, 0.0532, 1.224
No. of reflections and parameters used in refinement	1654, 70	539, 58
H-atom treatment	All H-atom parameters refined	Mixed
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0000P)^2 + 0.0000P]$, where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0231P)^2 + 2.4727P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max}$	0.000	0.000
$\Delta\rho_{\max}$, $\Delta\rho_{\min}$ (e Å^{-3})	2.284, −1.399	0.441, −0.298
Extinction method	Becker–Coppens Lorentzian model	*SHELXL*97 (Sheldrick, 1997)
Extinction coefficient	–	0.0039 (3)

Computer programs used: *SHELXL*97 (Sheldrick, 1997), *SAINT* (Bruker Systems Inc., 1999).

A large (3 × 2.5 × 2 mm^3) crystal of (3*w*) was selected for the neutron experiment. Diffraction data were collected at 150 K on the SXD diffractometer (Keen & Wilson, 1996) at the ISIS spallation source, Rutherford Appleton Laboratory, Chilton, England. Data were processed using *SXD*97 (Wilson, 1997), and coordinates for Br, C and O atoms from the X-ray refinement were used as the starting model for neutron refinement. H atoms were located from the resulting difference map and included in the neutron refinement model. Crystal data and details of the neutron data collection, structure solution and refinement are given in Table 1. Atomic coordinates for all atoms from the neutron refinement have been deposited. Other results from the neutron study have also been deposited.

2.2. Analysis of intermolecular interaction patterns

While it is relatively trivial to identify the strong intermolecular interactions that are crucial to the supramolecular organization of crystal structures, it is often much more difficult to identify and describe the networks and synthons that they generate *via* space-group symmetry. This is particularly true when these networks are three-dimensional and/or are comprised of several different types of interactions, often of different strengths. Here, visual perception can be time-consuming, even using the typical rotation and zoom facilities of modern graphics systems. Since its inception (Motherwell, 1972), the crystal structure visualization program *PLUTO* has been upgraded over time, particularly to provide for the generation of the discrete packing motifs that arise from specific intermolecular contacts. More recently, the program has been further upgraded to generate graph-set descriptors (Etter, 1990; Bernstein *et al.*, 1995) for hydrogen-bonded patterns, involving the location and characterization of discrete hydrogen bonds (*D*), and of hydrogen-bonded chains (*C*) and rings (*R*) (Motherwell *et al.*, 1999, 2000). More recently, we have been working on the detection and display of molecular symmetry within the program. These recent extensions, together with developments to other parts of the code, have been made freely available within a research version of the program, denoted *RPLUTO* (Motherwell & Shields, 2001).[2] A number of the features of *RPLUTO* have proved invaluable in the analysis of intermolecular interactions in the present study and all of the figures presented in this paper have been generated using *RPLUTO*.

---

[2] The *RPLUTO* program is available free of charge for non-commercial use and may be downloaded from the CCDC website: http://www.ccdc.cam.ac.uk/prods/rpluto.

3. Results and discussion

3.1. Molecular structure and symmetry

Crystals of (3*w*) adopt the uncommon space group $P4_2/ncm$ (No. 138) with $Z = 4$ and the coordinates deposited are referred to the origin at the centre of symmetry. Using the chemical atom numbering of dialkynol (3), the molecules have $2/m$ symmetry with the twofold axis bisecting the 2–3 and 5–6 bonds, so that ring C atoms 1 and 4, together with the ethynyl and hydroxy groups and the water oxygen, lie in the mirror plane [molecular centres of (3) at Wyckoff position 4(*c*), *International Tables for X-ray Crystallography*, 1965].

3.2. Intermolecular interaction geometry

Geometrical details of the four unique intermolecular hydrogen bonds in the structure of (3*w*) are given in Table 2 [here, and in the ensuing discussion, the water oxygen (O2 in deposited coordinates) and the hydroxy-O ring substituent (O1 in deposited coordinates) are denoted as O2(*w*) and O1(*r*) for ease of reading]. All of the hydrogen bonds involve the water molecule as either donor or acceptor, but the two O—H···O bonds differ in length, the O2(*w*)—H···O1(*r*) bond being significantly (0.441 Å) longer than the O1(*r*)—H···O2(*w*) bond. The two weaker hydrogen bonds, C≡C—H···O2(*w*) and O2(*w*)—H···Br, are still shorter than the relevant sums of van der Waals radii [$\nu_{\rm Br} = 1.85$ Å, $\nu_{\rm O} = 1.55$ Å (Bondi, 1964) and $\nu_{\rm H} = 1.20$ Å (Rowland & Taylor, 1996)], with the C≡C—H···O bond being significantly shorter (by nearly 0.4 Å) than the van der Waals criterion, a reflection of the significant acidity of the ethynyl C—H group relative to alkyl or alkenyl C—H.

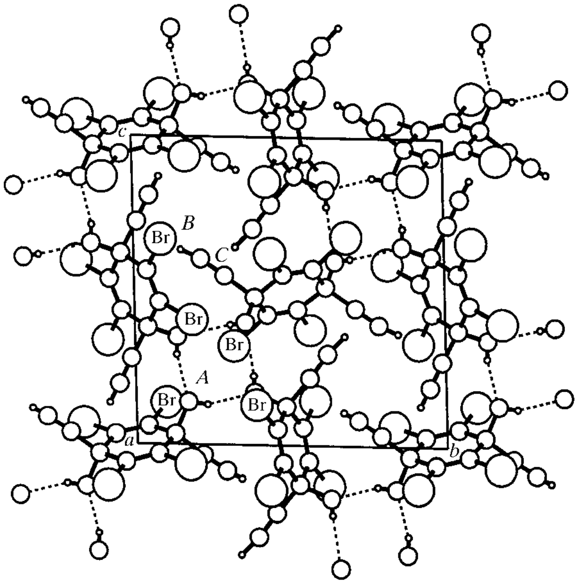


Figure 2
Structure of the Br compound (3) viewed along the pseudotetragonal *a* axis, showing *A* the tetrameric O—H···O synthon, *B* the C≡C—H···Br hydrogen bond, and *C* the interaction of the C≡C—H donor with ethynyl π-density.

Table 2
Intermolecular interaction geometries.

Hydrogen-bond parameters are *d*, the H···O or H···Br distance, and θ, the angle at the donor hydrogen. O*r* is the hydroxy oxygen, O*w* is the water oxygen. The C—Br···Br—C interactions are characterized by the interatomic distance, *d*, and the two C—Br···Br angles, ordered as θ_1 and θ_2, and discussed in the text.

Interaction type	*d* (Å)	θ (°)
O1(*r*)—H···O2(*w*)	1.700 (2)	179.4 (2)
O2(*w*)—H···O1(*r*)	2.141 (2)	159.7 (2)
C≡C—H···O2(*w*)	2.354 (3)	150.4 (3)
O2(*w*)—H···Br	2.995 (2)	121.2 (2)
Br···Br	3.708 (1)	155.26 (4) 88.37 (4)
	3.847 (1)	122.19 (4) 122.19 (4)†

† $\theta_1 = \theta_2$ by symmetry.

Also included in Table 2 are geometrical details of the two shortest C—Br···Br—C interactions. The strongest of these [3.708 (1) Å] is within 0.01 Å of $2\nu_{\rm Br}$, and has C—Br···Br angles of $\theta_1 = 155.26$ (4)° and $\theta_2 = 88.37$ (4)°. High-level *ab initio* calculations of interaction energies for Cl···Cl, Cl···O and Br···O interactions (Price *et al.*, 1994; Lommerse *et al.*, 1996) have been performed using intermolecular perturbation theory (Hayes & Stone, 1984). These studies show that carbon-bound halogens in sufficiently electron-withdrawing environments present an anisotropic charge distribution, δ^+ forward of the halogen along the C–halogen bond vector, the so-called polar direction, and δ^-perpendicular to this vector, *i.e.* in the equatorial direction. Further, these authors have shown that the attractive nature and directionality of these soft interactions persist beyond the conventional limits imposed by van der Waals radii considerations, although of course the attractive interaction energies fall off with increasing interatomic distance. While the softer interactions in this structure are at or slightly above van der Waals criteria, we consider that so long as their directional properties are acceptable, it is valid to include them in a discussion of supramolecular organization (see *e.g.* Steiner, 2000).

Thus, the *ab initio* results indicate that electrostatic interactions C—Br(δ^+)···Br(δ^-)—C will have one C—Br···Br angle (θ_1) approaching 180° and the other (θ_2) approaching 90°, as observed here for the shorter Br···Br interaction in the structure of (3*w*). This is the type II geometry identified by Desiraju & Parthasarathy (1989) and Pedireddi *et al.* (1994). A similar geometry is also observed in the structures of (2) and (3) (Madhavi, Desiraju *et al.*, 2000*b*). These same principles are also reflected in the geometry of the O2(*w*)—H···Br hydrogen bond, where the angle of approach of O—H(δ^+) to Br is in the nucleophilic trajectory, perpendicular [88.1 (2)°] to the C—Br bond vector. The longer and much weaker C—Br···Br—C interaction in (3*w*) [3.847 (1) Å] forms about a centre of symmetry and has both C—Br···Br angles at 122.19 (4)°, a situation previously documented by Desiraju & Parthasarathy (1989) and Pedireddi *et al.* (1994) using CSD analysis.

3.3. Supramolecular organization

3.3.1. Overview. The supramolecular architecture generated by the six independent interactions of Table 2 is viewed along the tetragonal *c* axis in Fig. 3. There are two principal features: (*A*) an O—H···O hydrogen-bonded network around the 4_2 axes involving molecules of (3) and the water molecules, and (*B*) a network of Br···Br interactions around the $\bar{4}$ axes. These major features are supported by (*C*) the O2(*w*)—H···Br hydrogen bonds along the *a* and *b* axes and which connect the two major features, and also by the C≡C—H···O2(*w*) bonds that provide further links, this time along the *c* axis (hence not visible in Fig. 3), between molecules of (3) and the O—H···O network *via* the water molecules. This complex three-dimensional architecture is difficult to dissect into its component parts, the supramolecular synthons, by visual inspection of simple rotations of Fig. 3. Hence, the program *RPLUTO* (see §2) has been used to isolate and visualize the extended motifs formed by the individual interactions of Table 2.

3.3.2. The O—H···O hydrogen-bonded network (Fig. 4). By symmetry, the longer O—H···O bond [O2(*w*)—H···O1(*r*) 2.141 (2) Å] forms a boat-like eight-membered ring [graph set[3] *R*(2,4)8] in which four of these (water-donor) hydrogen bonds connect two water molecules and two molecules of (3). Each hydroxy O1(*r*) atom is thus coordinated by its covalent bonds to C and H, and by two O2(*w*)—H donors in an approximately tetrahedral geometry which has three angles of 110°, two of 125°, and one [O2(*w*)—H···O1(*r*)···H—O2(*w*)] of 74°.

The shorter of the two O—H···O hydrogen bonds [O1(*r*)—H···O2(*w*), d = 1.700 (2) Å] binds water molecules very tightly to molecules of (3), as expected. Each molecule of (3) forms two bonds of this type and, in graph-set terminology (Bernstein *et al.* 1995), these bonds are discrete (*D*) at the first level. Pairs of these short O1(*r*)—H···O2(*w*) bonds therefore connect the tetrameric O2(*w*)—H···O1(*r*) rings along **c** to form stacks about the crystallographic 4_2 axis, as depicted in Fig. 4.

3.3.3. The C≡C—H···O2(*w*) hydrogen bonds and the O2(*w*) coordination sphere (Fig. 5). The O—H···O network described above generates an O2(*w*) atom which is coordinated by its two bonded H atoms and by the O1(*r*)—H donor (Fig. 4). This is extended to a four-coordinate arrangement by the C≡C—H···O2(*w*) hydrogen bond along the *c* direction, yielding a distorted tetrahedron about O2(*w*) (Fig. 5) which has two angles of 117°, two of 84°, the H—O—H angle of 105°, and the C≡C—H···O2(*w*)···H—O1(*r*) angle of 142°. The C≡C—H···O2(*w*) bonds are again discrete (*D*) as first-level graph sets and serve to further bind molecules of (3) to water molecules in their eight-membered ring environments, thus reinforcing the stacking about the 4_2 axis.

3.3.4. Br···Br interactions (Fig. 6). The shorter Br···Br contact [3.708 (1) Å] forms a cyclic tetrameric Br_4 synthon (*A* in Fig. 6) around the $\bar{4}$ axis, a pattern which is identical to that of the cyclic tetrameric Cl_4 synthon of (2) (see Fig. 1). In (3*w*) the four-membered ring has a buckled conformation with Br···Br···Br angles of 68° and a buckling angle about the ring diagonals of 84°. In the Cl compound (2) these angles are 64 and 77°, respectively. Each Br atom in (3*w*) acts as a node in a Br_4 synthon, which stack around the $\bar{4}$ axis. Each Br atom also forms one longer contact [3.847 (1) Å] to a centrosymmetrically related Br atom, the so-called Type I geometry, thus

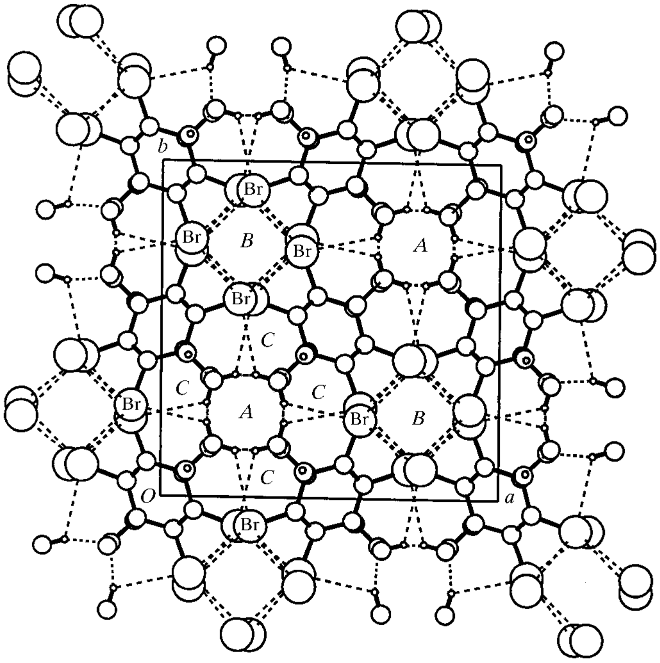


Figure 3
Structure of (3*w*) viewed along the tetragonal *c*-axis showing: *A* the O—H···O hydrogen-bonded network about the 4_2 axes, *B* the Br···Br interaction network about the $\bar{4}$ axes, and *C* the O2(*w*)—H···Br hydrogen bonds along the *a* and *b* axes. The C≡C—H···O2(*w*) hydrogen bonds run parallel to the *c* axis, hence cannot be seen in this orientation.

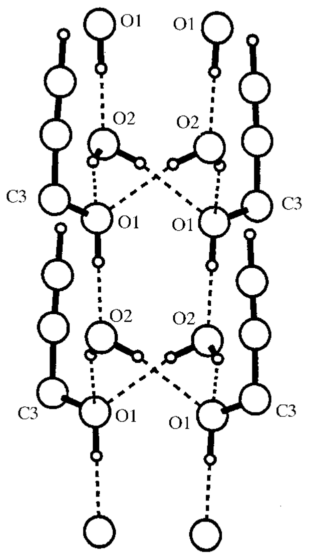


Figure 4
The water-mediated O—H···O hydrogen-bonded network about the 4_2 axes in the structure of (3*w*).

---

[3] Graph-set descriptors cited in this paper use the *RPLUTO* linear notation, *e.g.* [*R*(*a*,*d*)*n*] indicating a ring of size *n* comprising *a* acceptors and *d* donors.

linking the cyclic synthons along the *c* axis (*B* in Fig. 6). There is a considerable degree of structural mimicry between the Br···Br network in (3*w*) and the Cl···Cl networks in (2), with the discrete open and closed tetrachloro synthons of (2) (Fig. 1) being effectively superimposed within the Br interaction network of (3*w*) (Fig. 6).

3.3.5. O2(*w*)—H···Br hydrogen bonds (Fig. 7). These weak bonds in (3*w*) link molecules located at different inversion centres, *e.g.* the molecule centred at 0,0,0 with the molecule centred at 0.5,0.5,0, through the intermediacy of the water molecule. The pattern formed by these bonds alone is depicted in Fig. 7, which shows the 16-membered ring [graph set *R*(4,4)16] formed by two molecules of (3) and two water molecules. These bonds also serve to link the stacks of Br···Br interactions around the $\bar{4}$ axis with the O—H···O network around the 4_2 axis. The formation of the O2(*w*)—H···Br bonds means that each water-H atom is bifurcated (Fig. 5), the angle subtended at H by the two acceptors [Br and O1(*r*)] being 75°.

3.4. Pseudopolymorphism and the role of water in the structure of 3*w*

The interaction analysis shows that the solvent water plays *the* crucial role in the supramolecular organization of (3*w*), forming hydrogen bonds in a maximally effective manner (Fig. 5). The water O atom accepts two hydrogen bonds [from O1(*r*)—H and C≡C—H] which are approximately aligned with its lone-pair directions, while both water H atoms are bifurcated, each donating to O1(*r*) and to Br. The water molecule therefore acts as a tetrahedral spacer between the individual molecules of (3) in the structure of (3*w*), interacting with all possible hydrogen-bonding partners. Nangia & Desiraju (1999) have recently studied the relative occurrences of hydrogen-bonding organic solvents in molecular crystals and have observed that multipoint recognition of a solvent *via* both strong and weak hydrogen bonds is a vital factor in solvent retention. The tight coordination of water in the structure of (3*w*) is a further manifestation of this observation.

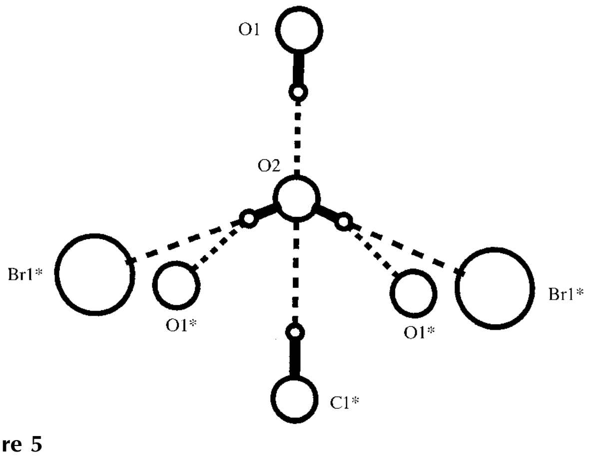


Figure 5
The hydrogen-bond coordination of the O and H atoms of the water molecule, including the C≡C(1*)—H···O2 [O2(*w*)] hydrogen bonds arising from an ethynyl group in a molecule that is symmetry-related (*) to that containing the O1 [O1(*r*)]—H donor.

The principal synthon in the parent compound (3) [and its chloro analogue (2)] is the cyclic O—H···O hydrogen-bonded tetramer, graph set *R*(4,4)8, involving the hydroxy groups of four symmetry-related molecules as both donors and acceptors. A cyclic tetrameric O—H···O arrangement is preserved in (3*w*), but with two of the molecules of (3) being replaced by water molecules which both contribute their two donor-H atoms to ring formation. The hydroxy-H donors in (3*w*) now form the hydrogen bonds that link molecules of (3) to the water molecule. Thus, by comparison with the $\bar{4}$-symmetric synthon in the structure of parent (unsolvated) (3), use of the 4_2-axis allows pairs of molecules of (3) to move apart in (3*w*), so as to allow the insertion of the tetrahedral water spacers. Indeed, in our original description of the structures of (2) and (3) (Madhavi, Desiraju *et al.*, 2000*b*), we noted that the molecules themselves acted as tetrahedral spacers, since they connect each tetrameric synthon to four others.

The substitution of water for a molecular hydroxy group in an O—H···O mediated synthon was also observed in the pseudopolymorphic structures of *trans*-1,4-diethynylcyclohexane-1,4-diol (Bilton *et al.*, 1999). Here, the parent molecule forms helical trimeric O—H···O synthons using the O—H groups of three symmetry-related molecules. This pattern is preserved in the monohydrate, but with one water O—H substituting for one molecular hydroxy group, while the second water O—H serves to link the trimers into an extended network. These structural changes on hydration are very similar to those observed in the case of (3) and (3*w*).

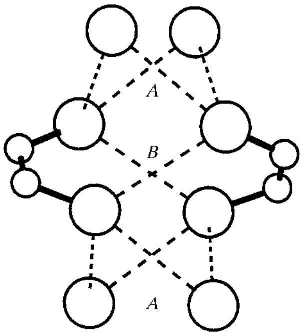


Figure 6
The Br···Br interactions in (3*w*). The stronger interactions of Table 2 form the cyclic tetramer motif (*A*) about the $\bar{4}$ axis. These tetramers are connected (*B*) by the weaker Br···Br interactions of Table 2.

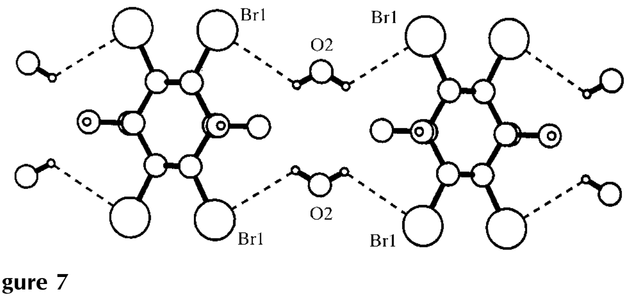


Figure 7
The 16-membered pattern, graph set [*R*(4,4)16], generated by the O2(*w*)—H···Br hydrogen bonds in (3*w*).

The expansion of the lattice of host molecules (3) in the structure of (3*w*) also appears crucial to the formation of a Br···Br interaction network in (3*w*) that mimics the Cl···Cl network in (2). Clearly, formation of the dominant O—H···O tetramers in (2) leads to an arrangement of host molecules that provides channels of suitable size to facilitate the observed Cl···Cl interaction patterns. However, formation of the analogous O—H···O tetramer in the parent (3) does not generate channels of sufficient size to accommodate the increased spatial requirements of Br. Hence, the Br···Br interactions in (3) are discrete rather than cooperative, and (2) and (3) are not isostructural. However, expansion of the host lattice of (3) to accommodate the solvent water molecules in (3*w*) now provides the extra space to permit the formation of cooperative Br···Br interactions and, indeed, leads to the overall structure of (3*w*) being even more symmetrical than that of (2).

4. Conclusions

Once again, a single-crystal neutron diffraction determination of a *gem*-alkynol structure has proved fertile ground for the study of the mutual interplay of strong and weak intermolecular interactions. The accurate hydrogen positions yielded by the analysis have enabled the complex hydrogen-bonding scheme to be characterized accurately, and the geometry of hydrogen-bond acceptance and donation at both O2(*w*) and O1(*r*) to be determined precisely. The analysis also reveals the importance of cooperative arrangements of halogen···halogen interactions in providing strong secondary stabilization of the assembly in the presence of the stronger fundamental synthon generated by hydrogen-bond formation about the water molecule. The chemical equivalence between O—H···O and Br···Br interactions is further brought out by the fact that both are similarly elaborated into tetrameric synthons. In many ways, there are several relationships between hydroxy, halogen and ethynyl groups, because all three functionalities donate and accept intermolecular interactions with themselves in a complementary manner, and some of these similarities emerge in the present study. A closer examination of the packing relationships between the structures of anhydrous and hydrated structures, possible through the use of the *RPLUTO* package, is now beginning and should shed further light on the effects of solvation, and their relevance in crystal engineering, drug development and delivery, and related areas.

The EPSRC (UK) is thanked for financial support to CB and JAKH (Senior Research Fellowship) and the CSIR (India) is thanked for financial support to NNLM. This work has been conducted under the Indo-UK bilateral cooperation project No. INT/UK/P-15/99 of the Department of Science and Technology, Government of India and the British Council. We are also grateful to Dr W. D. S. Motherwell and Dr G. P. Shields (CCDC) for assistance in the application of *RPLUTO* to the present structure.

References

Allen, F. H. & Kennard, O. (1993). *Chem. Des. Autom. News*, **8**, 1, 31–37.
Bernstein, J., Davis, R. E., Shimoni, L. & Chang, N.-L. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1555–1573.
Bilton, C., Howard, J. A. K., Madhavi, N. N. L., Nangia, A., Desiraju, G. R., Allen, F. H. & Wilson, C. C. (1999). *J. Chem. Soc. Chem. Commun.* pp. 1675–1676.
Bilton, C., Howard, J. A. K., Madhavi, N. N. L., Nangia, A., Desiraju, G. R., Allen, F. H. & Wilson, C. C. (2000). *Acta Cryst.* B**56**, 1071–1079.
Bilton, C., Howard, J. A. K., Madhavi, N. N. L., Desiraju, G. R. & Allen, F. H. (2000). *Acta Cryst.* C**56**, 1356–1358.
Bondi, A. (1964). *J. Phys. Chem.* **68**, 441–451.
Bruker Systems Inc. (1999). *SAINT*, Version 6.0. Bruker Systems Inc., Madison, Wisconsin, USA.
Desiraju, G. R. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 270–276.
Desiraju, G. R. (1997). *Chem. Commun.* pp. 1475–1476.
Desiraju, G. R. & Parthasarathy, R. (1989). *J. Am. Chem. Soc.* **111**, 8725–8726.
Etter, M. C. (1990). *Acc. Chem. Res.* **23**, 120–126.
Garcia, J. G., Ramos, B. & Rodriguez, A. (1995). *Acta Cryst.* C**51**, 2674–2676.
Hayes, I. C. & Stone, A. J. (1984). *Mol. Phys.* **53**, 83–105.
Keen, D. A. & Wilson, C. C. (1996). *Single Crystal Diffraction at ISIS. User Guide for the SXD Instrument.* Technical Report RAL-TR-96-083. Rutherford Appleton Laboratory, Chilton, Oxford, England.
Lommerse, J. P. M., Stone, A. J., Taylor, R. & Allen, F. H. (1996). *J. Am. Chem. Soc.* **118**, 3108–3116.
Madhavi, N. N. L., Bilton, C., Howard, J. A. K., Allen, F. H., Nangia, A. & Desiraju, G. R. (2000). *New J. Chem.* **24**, 1–4.
Madhavi, N. N. L., Desiraju, G. R., Bilton, C., Howard, J. A. K. & Allen, F. H. (2000*a*). *Acta Cryst.* C**56**, 1359–1360.
Madhavi, N. N. L., Desiraju, G. R., Bilton, C., Howard, J. A. K. & Allen, F. H. (2000*b*). *Acta Cryst.* B**56**, 1063–1070.
Motherwell, W. D. S. (1972). *PLUTO.* University of Cambridge, England.
Motherwell, W. D. S. & Shields, G. P. (2001). In preparation.
Motherwell, W. D. S., Shields, G. P. & Allen, F. H. (1999). *Acta Cryst.* B**55**, 1044–1056.
Motherwell, W. D. S., Shields, G. P. & Allen, F. H. (2000). *Acta Cryst.* B**56**, 466–473.
Nangia, A. & Desiraju, G. R. (1998). *Top. Curr. Chem.* **198**, 57–95.
Nangia, A. & Desiraju, G. R. (1999). *J. Chem. Soc. Chem. Commun.* pp. 605–606.
Pedireddi, V. R., Reddy, D. S., Goud, B. S., Craig, D. C., Rae, A. D. & Desiraju, G. R. (1994). *J. Chem. Soc. Perkin Trans. 2*, pp. 2353–2360.
Price, S. L., Stone, A. J., Lucas, J., Rowland, R. S. & Thornley, A. E. (1994). *J. Am. Chem. Soc.* **116**, 4910–4918.
Rowland, R. S. & Taylor, R. (1996). *J. Phys. Chem.* **100**, 7384–7391.
Sheldrick, G. M. (1997). *SHELX*97. University of Göttingen, Germany.
Steiner, T. (2000). *IUCr Newsletter*, **8**, 19–20.
Wilson, C. C. (1997). *J. Mol. Struct.* **405**, 207–215.