Acta Crystallographica Section B
**Structural
Science**
ISSN 0108-7681

Crystal engineering in the *gem*-alkynol family: interplay between strong and weak interactions in structures of 2,3,5,6-tetrahalo[F,Cl,Br]-*trans*-1,4-diethynylcyclohexa-2,5-diene-1,4-diols

N. N. L. Madhavi,[a] Gautam R. Desiraju,[a] Claire Bilton,[b] Judith A. K. Howard[b] and Frank H. Allen[c]*

[a]School of Chemistry, University of Hyderabad, Hyderabad 500 046, India, [b]Department of Chemistry, University of Durham, South Road, Durham DH1 3LE, England, and [c]Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, England

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

Received 31 May 2000
Accepted 22 August 2000

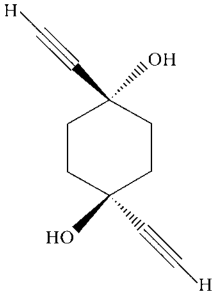
Structures of the title compounds are all mediated by strong cooperative arrangements of O—H···O hydrogen bonds, supported by a variety of weaker interactions which affect the type of O—H···O synthon that is formed. The tetrafluoro compound contains hexameric O—H···O synthons in a supramolecular chair conformation, together with C≡C—H···F interactions. However, the tetrachloro and tetrabromo compounds both form tetrameric O—H···O synthons. This dominant pattern is supported by halogen···halogen interactions having one C—Cl[Br]···Cl[Br] angle close to 180° and the other close to 90°, and by C≡C—H···Cl[Br] interactions.

1. Introduction

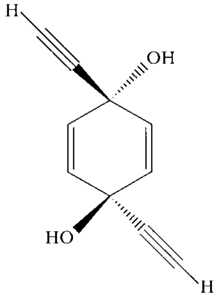
Crystal engineering methodologies attempt to identify common patterns in series of crystal structures of related molecules in order to understand these patterns in terms of the mutual interplay between particular types of intermolecular interactions (see *e.g.* Nangia & Desiraju, 1998; Desiraju, 1997). The identification of robust and reproducible interaction patterns or supramolecular synthons (Desiraju, 1995) is a major aim of these studies, so as to establish correspondences between molecular and crystal structures (see *e.g.* Ermer & Eling, 1994; Allen *et al.*, 1997).

Supramolecular synthons based on strong hydrogen bonds have been well documented (Desiraju, 1995) and the most common patterns formed by such bonds have been characterized (Allen *et al.*, 1999) using the Cambridge Structural Database (CSD; Allen & Kennard, 1993). The involvement of weaker interactions, *e.g.* C—H···O bonds, has also attracted significant attention (see *e.g.* Desiraju, 1991; Desiraju & Steiner, 1999), but others such as C—H···π(arene) (Malone *et al.*, 1997; Madhavi *et al.*, 1997) and C≡C—H···π(C≡C) (Steiner *et al.*, 1996; Nishio *et al.*, 1998) are less well understood. A particular difficulty arises when two or more interactions, strong or weak, are in competition (interaction interference) and in such cases predicting the likely interaction patterns in crystal structures becomes a highly complex task.

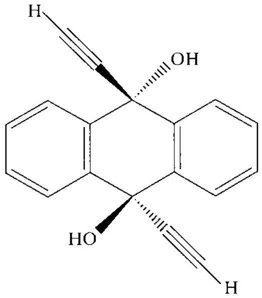
Recently, we have synthesized a variety of compounds containing the *gem*-alkynol functionality. Such structures are likely to contain both strong O—H···O bonds and weaker interactions involving the acidic proton and the π-system of the C≡C—H group, thus providing an opportunity to characterize the latter and study their competition with the former. A CSD study (Madhavi *et al.*, 2000) has shown that the 94 published structures of *gem*-alkynols exhibit a bewildering variety of interaction patterns, involving O—H···O, C—H···O, O—H···π and C—H···π contacts. However, the molecules within this sample are chemically diverse and sometimes complex. More than half of the sample contain other functional groups which are capable of acting as strong hydrogen-bond donors or acceptors (or both), and this introduces a wholly avoidable complication into the study of a chemical system in which strong and weak interactions are in a delicate balance.



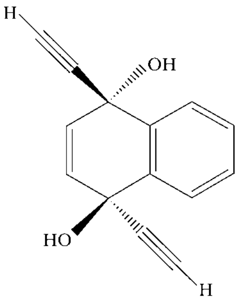
(1)



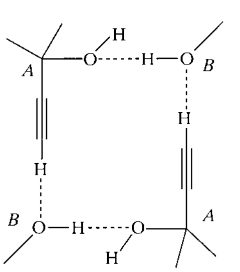
(2)

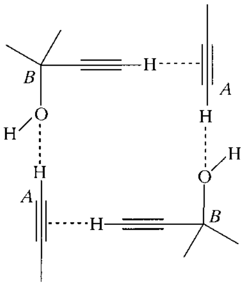


(3)



(4)

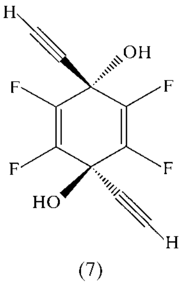




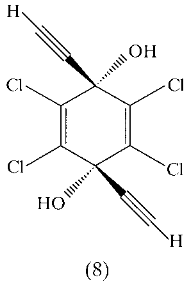
A and *B* refer to symmetry-independent molecules

(5)

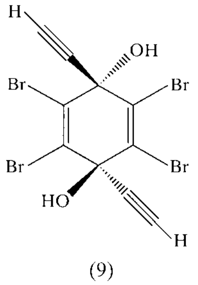
(6)



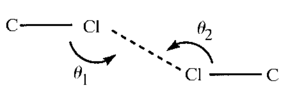
(7)



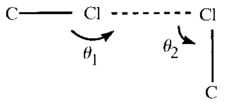
(8)



(9)



(10)



(11)

Our approach, therefore, has been to synthesize a series of *gem*-alkynols in which the substituents are varied in a controlled manner, beginning with compounds (1) (Bilton *et al.*, 1999), (2), (3) and (4) (Madhavi *et al.*, 2000) which contain only the *gem*-alkynol functionality (together with C—H groups of differing hydrogen acidity). Structure (1) (Bilton *et al.*, 1999) represents a unique example of the simultaneous occurrence of both conformational polymorphism and conformational isomorphism (Bernstein, 1987), and also forms a pseudopolymorphic monohydrate. All three forms of (1) aggregate through helical trimeric O—H···O synthons, with no interference from weaker interactions involving the C≡C—H groups. Structure (2) shows a simple infinite O—H···O cooperative chain, reinforced by C≡C—H···O and C(ring)—H···π interactions. In contrast, structures (3) and (4) both contain the cyclic synthons (5) and (6), each composed of alternating strong (O—H···O) and weak (C≡C—H···O or C≡C—H···π) hydrogen bonds.

Thus encouraged that structural repetitivity can be preserved in such a fragile system, we have now selectively embellished structure (2) with the tetrahalo functionality of (7) (F_4), (8) (Cl_4) and (9) (Br_4), whose structures are reported in this paper. Here the C(ring)—H donors are all replaced by halogens and the interest is to see how possible halogen···halogen and C—H···halogen interactions might interfere with, or reinforce, the O—H···O bonds observed in (2) (Madhavi *et al.*, 2000). Further, it is of interest to see if structural repetitivity is preserved in two or more structures of this series and to compare any synthons which may occur with those [(5) and (6)] which were observed in structures (3) and (4).

The role of halogen atoms in weak interactions is a matter of long-standing interest (see Desiraju & Steiner, 1999) and the nature of halogen···halogen interactions, particularly C—Cl···Cl—C, has been the subject of considerable debate over the past decade. Desiraju & Parthasarathy (1989) and Pedireddi *et al.* (1994) used the CSD to identify the occurrence of two interaction types. If we denote the larger of the two C—Cl···Cl angles as θ_1, and the smaller as θ_2, then type I interactions (10) have $\theta_1 = \theta_2$ and type II have $\theta_1 = 180^\circ$ and $\theta_2 = 90^\circ$. Linear C—Cl···Cl—C systems, $\theta_1 = \theta_2 = 180^\circ$, are seldom observed. The vast majority of type I examples arise from interactions across a crystallographic centre of symmetry, while type II interactions (11) were deemed to arise due to the increasing polarizability of the halogen (F < Cl < Br < I).

Calculations of interaction energies using intermolecular perturbation theory (Hayes & Stone, 1984) have been carried out for C—Cl···Cl—C interactions (Price *et al.*, 1994) and C—Cl···O interactions (Lommerse *et al.*, 1996). In broad terms, these authors agree 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 ($\theta_1 = 180^\circ$), and δ^- perpendicular to the bond vector ($\theta_2 = 90^\circ$). In these cases, stabilizing interaction energies of up to 10 kJ mol^{-1} can be attained for linear C—Cl···O interactions, about one-third of the interaction energy for a strong hydrogen bond (Lommerse *et al.*, 1996). These authors also provide computational evidence that the interactions become stronger for the more readily polarisable halogens, Br and I, but are not exhibited by F.

2. Experimental

2.1. Syntheses

Compounds (7), (8) and (9) were synthesized from the appropriate diketone, 2,3,5,6-tetrahalo[X]-cyclohexa-2,5-diene-1,4-dione, using a two-step procedure. All operations were carried out in a dry nitrogen atmosphere using standard syringe-septum techniques.

(i) A solution of trimethylsilylacetylene (4.4 mmol) in thf (15 ml) was mixed with *n*-butyllithium (4.2 mmol) at 195 K. After stirring for 15 min a solution of the appropriate ketone, X = F, Cl or Br, was added dropwise and stirring was continued for 30 min at 195 K and for a further 1 h at room temperature. Brine was added to the reaction mixture and the products were extracted with diethylether. The organic phase was dried over magnesium sulfate, filtered and the ether removed.

(ii) The solid product from step (i) was dissolved in methanol and methanolic KOH was added slowly and stirred for 1 h at room temperature. Water was added to the reaction mixture and the product was extracted with ethylacetate. The product was dried over magnesium sulfate and the solvent removed. Crystals were obtained by purification of the crude material (column chromatography) followed by recrystallization.

Melting points: (7) 405–406 K; (8) 478–479 K (with sublimation); (9) 493 K (with decomposition). Spectroscopic data have been deposited.[1]

2.2. Crystal structure analyses

X-ray diffraction intensities for (7), (8) and (9) were collected at 150 K (Oxford Cryosystems cryostat) on a Bruker SMART CCD diffractometer (Bruker Systems Inc., 1999*a*) using Mo $K\alpha$ X-radiation. Data were processed using the Bruker *SAINT* package (Bruker Systems Inc., 1999*b*), with structure solution and refinement using *SHELX*97 (Sheldrick, 1997). Data for (9) were corrected for absorption using *SADABS* (Sheldrick, 1996). H atoms were located in all three structures and refined freely with isotropic displacement parameters. Crystal data and details of data collections, structure solutions and refinements are given in Table 1. Atomic coordinates for non-H atoms are given in Table 2.

3. Results and discussion

3.1. 2,3,5,6-Tetrafluoro-*trans*-1,4-diethynylcyclohexa-2,5-diene-1,4-diol (7)

Compound (7) crystallizes in space group $P\bar{1}$ with three symmetry-independent molecules occupying distinct inversion centres at 0, 0.5, 0; 0.5, 0, 0.5 and 0.5, 0.5, 0.5, as illustrated in Fig. 1. The dominant interaction pattern is formed by six O—H···O hydrogen bonds in a supramolecular chair conformation (Fig. 2*a*). All hydroxy groups are involved in forming this synthon, which is located on the inversion centre at 0, 0.5, 0.5. The hydrogen-bond geometry (Table 3) describes three strong O—H···O bonds, which deviate by a maximum of 19° from linearity at H. The three independent molecules each contribute two OH groups to synthon formation and the molecules of each independent pair are located at 1,4 positions (numbering only O atoms in the synthon ring) relative to one another, such that they adopt an antiparallel disposition (Fig. 2*a*). Each hexameric synthon is therefore connected to six others through molecular spacers, and acts as an octahedral supramolecular node, which extends the network in three dimensions.

Two of the three independent ethynyl groups form three C—H···F—C interactions (Table 3) within a van der Waals radius sum of 2.67 Å [v(F) = 1.47 Å (Bondi, 1964); v(H) = 1.20 Å (Rowland & Taylor, 1996)]. The shortest of these has a hydrogen-normalized H···F distance of only 2.34 Å, with directionality angles θ(H) and θ(F) of 171 and 142°, respectively. One of the C—H···F bonds forms a dimeric motif between molecules related by an *a*-translation, and this dimer and the O—H···O hexamer alternate along the *b* axis. Other C—H···F interactions link translation-related molecules along the *b* axis. There are two F···F contacts (Table 3) which are respectively just below and just above the van der Waals sum of 2.94 Å. The shortest of these [2.86 (2) Å] has θ_1, θ_2 = 173.72 (7) and 90.58 (6)°, respectively, which is very close to

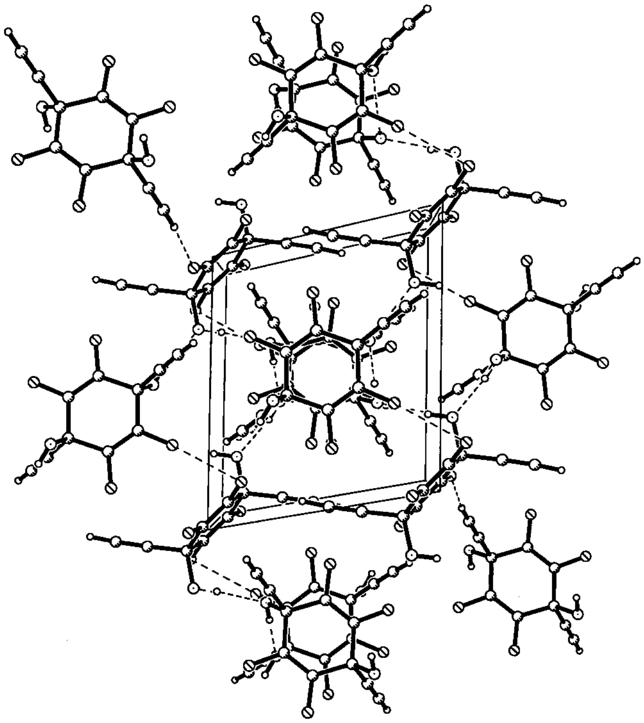


Figure 1
Packing diagram of trimeric (7), viewed down the *c* axis and with the *b* axis vertical

---

[1] Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM0033). Services for accessing these data are described at the back of the journal.

Table 1
Experimental details.

	(7)	(8)	(9)
Crystal data			
Chemical formula	$C_{10}H_4F_4O_2$	$C_{10}H_4Cl_4O_2$	$C_{10}H_4Br_4O_2$
Chemical formula weight	232.13	297.93	475.77
Cell setting	Triclinic	Tetragonal	Triclinic
Space group	$P\overline{1}$	$I4_1/a$	$P\overline{1}$
a (Å)	8.9002 (18)	16.758 (2)	8.9147 (3)
b (Å)	9.2388 (18)	16.758 (2)	12.6402 (5)
c (Å)	9.6721 (19)	8.865 (2)	12.6547 (5)
α (°)	93.73 (3)	90	85.738 (1)
β (°)	98.73 (3)	90	69.625 (1)
γ (°)	114.46 (3)	90	72.72 (1)
V (Å^3)	708.3 (2)	2489.6 (7)	1275.76 (8)
Z	3	8	4
D_x (Mg m^{-3})	1.633	1.590	2.477
Radiation type	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$
Wavelength (Å)	0.71073	0.71073	0.71073
No. of reflections for cell parameters	999	505	510
θ range (°)	0.16–30.57	5.26–25.31	5.10–23.72
μ (mm^{-1})	0.165	0.930	12.599
Temperature (K)	150	150	150
Crystal form	Block	Block	Block
Crystal size (mm)	0.7 × 0.3 × 0.2	0.3 × 0.3 × 0.2	0.3 × 0.2 × 0.2
Crystal colour	Colourless	Colourless	Colourless
Data collection			
Diffractometer	Bruker SMART CCD	Bruker SMART CCD	Bruker SMART CCD
Data collection method	ω scans	ω scans	ω scans
Absorption correction	Empirical	Multi-scan	Multi-scan
$T_{\min}$	0.289	0.665	0.0180
$T_{\max}$	0.382	0.830	0.0737
No. of measured reflections	8674	8404	14 367
No. of independent reflections	3722	1421	5818
No. of observed reflections	3376	1202	4966
Criterion for observed reflections	$I > 2\sigma(I)$	$I > 2\sigma(I)$	$I > 2\sigma(I)$
$R_{\rm int}$	0.0288	0.0432	0.0431
$\theta_{\max}$ (°)	29.88	27.39	27.48
Range of h, k, l	$-12 \rightarrow h \rightarrow 12$ $-12 \rightarrow k \rightarrow 12$ $-13 \rightarrow l \rightarrow 13$	$-21 \rightarrow h \rightarrow 20$ $-21 \rightarrow k \rightarrow 19$ $-9 \rightarrow l \rightarrow 11$	$-11 \rightarrow h \rightarrow 11$ $-16 \rightarrow k \rightarrow 16$ $-16 \rightarrow l \rightarrow 16$
Refinement			
Refinement on	F^2	F^2	F^2
$R[F^2>2\sigma(F^2)]$	0.0336	0.0489	0.0336
$wR(F^2)$	0.0928	0.1245	0.0781
S	1.031	1.091	1.148
No. of reflections used in refinement	3722	1421	5818
No. of parameters used	242	82	321
H-atom treatment	All H-atom parameters refined	All H-atom parameters refined	All H-atom parameters refined
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0484P)^2 + 0.2454P]$, where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0383P)^2 + 5.8833P]$, where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0218P)^2 + 4.0324P]$, where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max}$	0.001	0.001	0.005
$\Delta\rho_{\max}$ (e Å^{-3})	0.456	0.589	0.797
$\Delta\rho_{\min}$ (e Å^{-3})	−0.239	−0.437	−1.052
Extinction method	*SHELXL* (Sheldrick, 1997)	*SHELXL* (Sheldrick, 1997)	None
Extinction coefficient	0.080 (5)	0.0178 (11)	–
Source of atomic scattering factors	*International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)	*International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)	*International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)
Computer programs			
Data collection	*SMART* (Bruker Systems Inc., 1999*a*)	*SMART* (Bruker Systems Inc., 1999*a*)	*SMART* (Bruker Systems Inc., 1999*a*)
Cell refinement	*SMART* (Bruker Systems Inc., 1999*a*)	*SMART* (Bruker Systems Inc., 1999*a*)	*SMART* (Bruker Systems Inc., 1999*a*)
Data reduction	*SAINT* (Bruker Systems Inc., 1999*b*)	*SAINT* (Bruker Systems Inc., 1999*b*)	*SAINT* (Bruker Systems Inc., 1999*b*)
Structure solution	*SHELXS*97 (Sheldrick, 1997)	*SHELXS*97 (Sheldrick, 1997)	*SHELXS*97 (Sheldrick, 1997)
Structure refinement	*SHELXL*97 (Sheldrick, 1997)	*SHELXL*97 (Sheldrick, 1997)	*SHELXL*97 (Sheldrick, 1997)
Preparation of material for publication	*SHELXL*97 (Sheldrick, 1997)	*SHELXL*97 (Sheldrick, 1997)	*SHELXL*97 (Sheldrick, 1997)

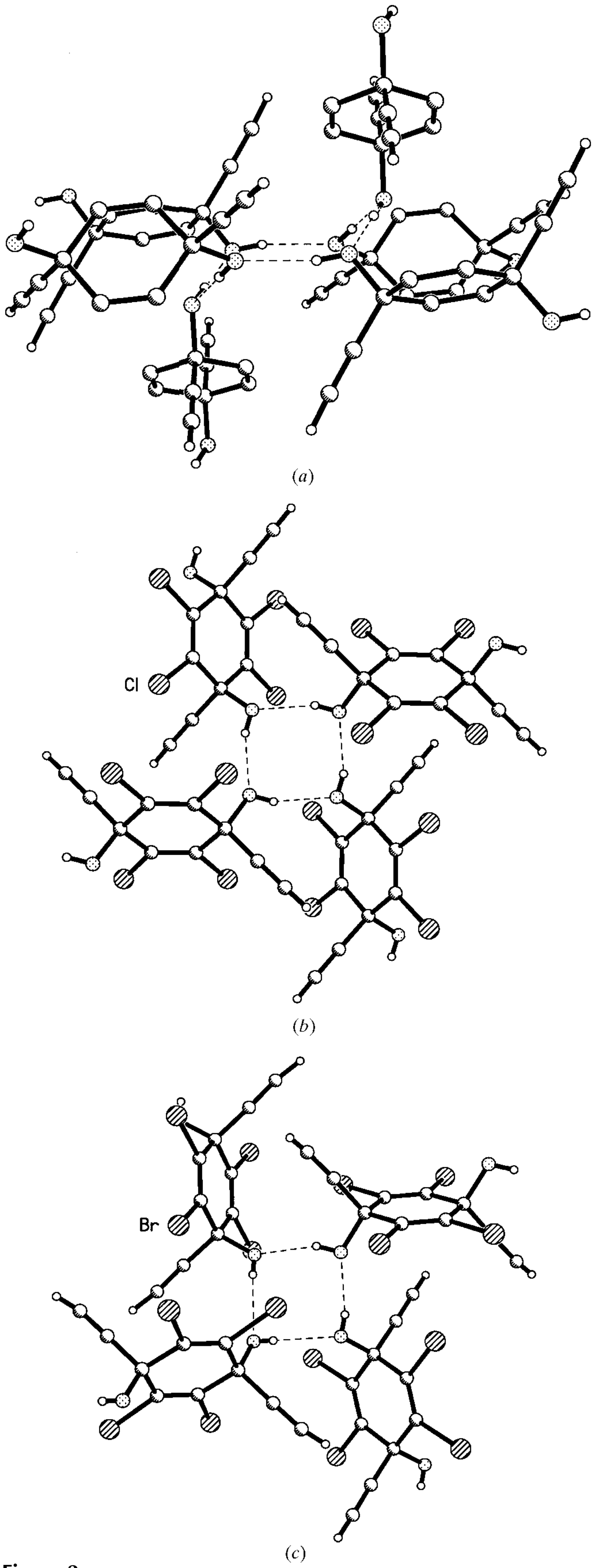


Figure 2
(*a*) Hexameric O—H⋯O synthon in (7); (*b*) tetrameric O—H⋯O synthon in (8); (*c*) tetrameric O—H⋯O synthon in (9).

the geometry (11) expected for type II halogen⋯halogen interactions. Given the hardness of F coupled with existing computational evidence, we regard this geometry as arising from crystal packing effects rather than from any specific attractive forces.

3.2. 2,3,5,6-Tetrachloro-*trans*-1,4-diethynylcyclohexa-2,5-diene-1,4-diol (8)

Compound (8) crystallizes in the high-symmetry space group $I4_1/a$, with the molecules located on inversion centres ($Z = 8$), as illustrated in Fig. 3. Once again, the dominant interaction pattern is formed by O—H⋯O hydrogen bonds, but here the synthon is tetrameric and arranged about a $\bar{4}$ axis (Fig. 2*b*). The hydrogen-bond geometry is reported in Table 3. Each molecule of (8) connects two tetramer units, such that each synthon is connected to four others through molecular spacers which extend the network to three dimensions.

The fundamental O—H⋯O architecture is supported by a number of weaker interactions described in Table 3. Both symmetry-independent Cl atoms are involved in type II Cl⋯Cl interactions (11), *i.e.* four such interactions per molecule, at contact distances that are slightly more than twice the isotropic van der Waals radius of Cl (1.75 Å; Bondi, 1964), but within the ranges discussed by Price *et al.* (1994) and Lommerse *et al.* (1996). The shorter of these interactions [3.605 (1) Å] forms a helical arrangement about a 4_1 axis, while the longer interaction [3.731 (2) Å] forms a closed tetrameric Cl_4 synthon, which alternates with the O—H⋯O tetramer along a $\bar{4}$ axis. This halogen arrangement is reminiscent of the recently reported *triangulo*-trichloro and *triangulo*-tribromo synthons (Anthony *et al.*, 1998; Thalladi *et al.*, 1998; Jetti *et al.*, 1999; Broder *et al.*, 2000). Table 3 also reports a long C≡C—H⋯Cl contact.

3.3. 2,3,5,6-Tetrabromo-*trans*-1,4-diethynylcyclohexa-2,5-diene-1,4-diol (9)

Compound (9) crystallizes with each of the four symmetry-independent molecules located on distinct inversion centres, as illustrated in Fig. 4. The dominant interaction pattern is again formed by O—H⋯O hydrogen bonds (see Table 3 for geometrical details). Each independent molecule contributes one OH group to the formation of a tetrameric synthon (Fig. 2*c*) and links adjacent tetramers into a three-dimensional network that is topologically analogous to that observed in the chloro compound (8).

The four symmetry-independent molecules are cross-linked by six different Br⋯Br interactions. Four of these are shorter than 3.70 Å [v(Br) = 1.85 Å; Bondi, 1964] and represent interpenetration of the van der Waals spheres, while the remaining two interactions are up to 0.20 Å longer than this comparator. All six interactions are clearly of type II (11), as shown by the geometrical data of Table 3. It is clear that the Br⋯Br interactions in (9) are shorter relative to van der Waals sums than the Cl⋯Cl interactions in (8), in line with the increased polarizability of Br, and in agreement with indications from the *ab initio* calculations of Price *et al.* (1994) and

Table 2
Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2).

$$U_{\rm eq} = (1/3)\Sigma_i \Sigma_j U^{ij} a^i a^j \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
(7)				
F1	0.13140 (9)	0.32812 (9)	0.85824 (8)	0.02992 (17)
F2	0.10278 (9)	0.82232 (8)	0.99013 (8)	0.02855 (17)
F11	0.54677 (9)	0.58373 (9)	1.23827 (7)	0.03106 (18)
F12	0.18252 (8)	0.32907 (9)	1.54950 (8)	0.03013 (17)
F21	−0.45397 (9)	−0.00542 (9)	0.78559 (7)	0.02882 (17)
F22	−0.18494 (8)	0.15228 (9)	0.66778 (7)	0.02902 (17)
O1	0.09274 (10)	0.60128 (10)	0.76376 (8)	0.02489 (18)
O11	0.24851 (10)	0.53620 (9)	1.34412 (8)	0.02313 (17)
O21	−0.70633 (11)	−0.25896 (9)	0.57778 (9)	0.02384 (17)
C1	0.46278 (16)	0.73049 (19)	0.99717 (14)	0.0373 (3)
C2	0.31531 (14)	0.66562 (14)	0.95594 (11)	0.0248 (2)
C3	0.13028 (13)	0.58530 (12)	0.91000 (10)	0.0196 (2)
C4	0.06470 (13)	0.40977 (13)	0.92853 (11)	0.0205 (2)
C5	0.05022 (13)	0.66421 (12)	0.99688 (11)	0.0204 (2)
C11	0.21624 (16)	0.17711 (15)	1.19891 (14)	0.0305 (2)
C12	0.27270 (14)	0.29858 (13)	1.27786 (12)	0.0235 (2)
C13	0.34702 (13)	0.44886 (12)	1.37978 (11)	0.0197 (2)
C14	0.52767 (13)	0.54587 (13)	1.36766 (11)	0.0212 (2)
C15	0.34023 (13)	0.40981 (12)	1.52821 (11)	0.0207 (2)
C21	−0.85068 (17)	0.02473 (16)	0.66346 (15)	0.0344 (3)
C22	−0.76156 (14)	−0.02754 (13)	0.62251 (12)	0.0246 (2)
C23	−0.65179 (13)	−0.09123 (12)	0.56684 (11)	0.0197 (2)
C24	−0.47257 (14)	−0.00009 (12)	0.64633 (10)	0.0204 (2)
C25	−0.34131 (13)	0.07603 (12)	0.58808 (11)	0.0205 (2)
(8)				
Cl1	0.77134 (5)	0.61807 (5)	−0.00252 (9)	0.0642 (3)
Cl2	0.61323 (6)	0.71900 (6)	−0.01517 (12)	0.0813 (4)
O1	0.89228 (11)	0.72875 (11)	−0.1540 (3)	0.0533 (6)
C1	0.8625 (2)	0.5634 (2)	−0.3678 (5)	0.0714 (10)
C2	0.84570 (16)	0.62493 (16)	−0.3155 (3)	0.0462 (6)
C3	0.82653 (13)	0.70177 (13)	−0.2419 (3)	0.0363 (6)
C4	0.75598 (14)	0.69120 (14)	−0.1362 (3)	0.0379 (6)
C5	0.68998 (14)	0.73415 (15)	−0.1411 (3)	0.0402 (6)
(9)				
Br1	0.79084 (7)	−0.18445 (4)	0.59429 (4)	0.03404 (12)
Br2	0.84216 (7)	−0.08758 (5)	0.33470 (4)	0.03575 (13)
Br11	0.78564 (6)	0.43745 (4)	0.62350 (4)	0.03124 (12)
Br12	0.48669 (6)	0.68322 (4)	0.67843 (4)	0.02516 (10)
Br21	0.26974 (6)	0.38542 (4)	1.13043 (4)	0.02820 (11)
Br22	0.40392 (6)	0.42595 (5)	0.85341 (4)	0.03255 (12)
Br31	0.40744 (6)	−0.09732 (4)	0.86395 (4)	0.02761 (11)
Br32	0.23387 (6)	0.17095 (4)	0.93445 (4)	0.02955 (11)
O1	1.0803 (5)	−0.1357 (3)	0.6498 (3)	0.0273 (7)
O2	0.7898 (4)	0.3546 (3)	0.3984 (3)	0.0202 (6)
O3	−0.0988 (4)	0.3802 (3)	1.1712 (3)	0.0233 (7)
O4	0.0960 (4)	−0.1677 (3)	0.8614 (2)	0.0207 (6)
C1	0.7190 (7)	0.0528 (5)	0.8056 (4)	0.0330 (11)
C2	0.8281 (6)	0.0123 (4)	0.7218 (4)	0.0240 (9)
C3	0.9714 (5)	−0.0412 (3)	0.6199 (3)	0.0185 (8)
C4	0.9092 (5)	−0.0793 (4)	0.5363 (4)	0.0218 (9)
C5	0.9306 (6)	−0.0423 (4)	0.4334 (4)	0.0215 (9)
C11	0.5609 (7)	0.2152 (5)	0.6053 (5)	0.0385 (13)
C12	0.5913 (6)	0.2906 (4)	0.5515 (4)	0.0233 (9)
C13	0.6262 (5)	0.3856 (3)	0.4816 (3)	0.0186 (8)
C14	0.6176 (5)	0.4770 (4)	0.5572 (3)	0.0178 (8)
C15	0.5043 (5)	0.5748 (4)	0.5760 (3)	0.0183 (8)
C21	−0.1280 (6)	0.6166 (4)	1.2985 (4)	0.0268 (10)
C22	−0.0946 (5)	0.5578 (3)	1.2199 (4)	0.0201 (8)
C23	−0.0620 (5)	0.4806 (3)	1.1266 (3)	0.0182 (8)
C24	0.1214 (5)	0.4505 (3)	1.0519 (3)	0.0187 (8)
C25	0.1746 (5)	0.4672 (3)	0.9417 (4)	0.0183 (8)
C31	0.2033 (8)	−0.2869 (5)	1.0836 (5)	0.0367 (13)
C32	0.1482 (6)	−0.2131 (4)	1.0344 (4)	0.0222 (9)
C33	0.0778 (5)	−0.1231 (3)	0.9671 (3)	0.0163 (8)
C34	0.1752 (5)	−0.0377 (3)	0.9406 (3)	0.0187 (8)
C35	0.1068 (5)	0.0694 (3)	0.9688 (3)	0.0187 (8)

Lommerse *et al.* (1996). However, in contrast to (8), the Br$\cdots$Br interactions do not form either closed or helical tetramers.

Three of the four independent ethynyl groups form C≡C—H$\cdots$Br contacts which, with normalized H-atom positions (Table 3), have H$\cdots$Br distances that are at or just below the sum of v(Br) and v(H) of 3.05 Å. The fourth ethynyl H atom is directed towards the π density of a C≡C bond (Table 3).

3.4. Structural relationships in the *trans*-1,4-diethynylcyclohexa-2,5-diene-1,4-diols (2), (7)–(9)

Strong cooperative arrangements of O—H$\cdots$O hydrogen bonds are fundamental to all four structures in this series. In all cases these arrangements are supported by a variety of weaker interactions that have significant effects on the type of O—H$\cdots$O synthon that is formed. Parent 2 (Madhavi *et al.*, 2000) is the most straightforward, comprising infinite cooperative O—H$\cdots$O chains, together with C≡C—H$\cdots$O and C(sp^2)—H$\cdots\pi$(ethynyl) hydrogen bonds.

The structure type observed for (2) is not available to (7), where the four C(sp^2)—H are replaced by fluorines. In accordance with recent work (Dunitz & Taylor, 1997), no O—H$\cdots$F bonds are formed. However, evidence from structures that contain only C, H and F would indicate that F atoms do participate in C—H$\cdots$F bonds (Suzuki *et al.*, 1992; Rodham *et al.*, 1993; Thalladi *et al.*, 1998). C≡C—H$\cdots$F interactions are indeed observed in (7), rather than the C≡C—H$\cdots$O bonds of (2), and the O—H$\cdots$O bonds now form the hexameric synthon of Fig. 2(*a*). We note that the fluoro compound (7) crystallizes in space group $P\overline{1}$ with Z = 3, a situation also

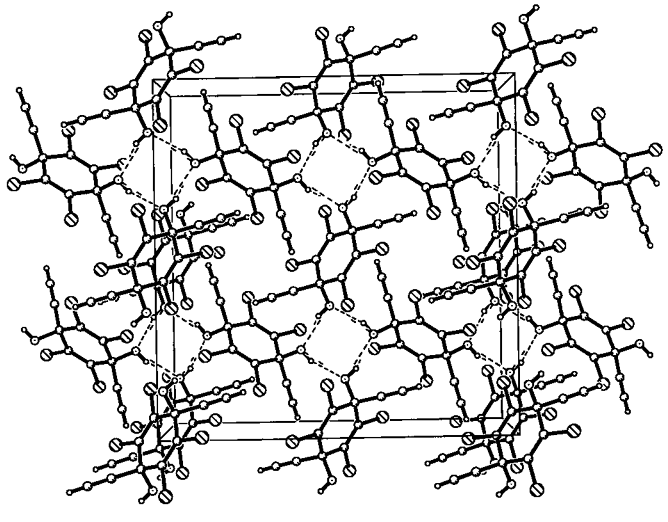
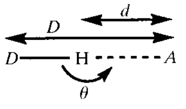


Figure 3
Packing diagram of tetragonal (8) viewed down the *c* axis.

Table 3
Intermolecular interaction geometries.



		Experimental			H-normalized	
		D (Å)	d (Å)	θ (°)	d (Å)	θ (°)
(7)	O—H···O	2.756 (2)	1.88 (2)	174 (2)	1.78	174
		2.718 (2)	1.87 (2)	179 (2)	1.74	179
		2.733 (1)	1.95 (2)	162 (2)	1.79	161
	F···F		2.86 (2)	173.72 (7), 90.58 (6)		
			2.95 (1)	134.52 (7), 122.52 (7)		
	C≡C—H···F	3.409 (2)	2.48 (2)	171 (1), 142.0 (4)	2.34	170.6, 142.2
		3.347 (2)	2.62 (2)	146.9 (5), 132 (1)	2.54	145.0, 130.9
		3.630 (2)	2.72 (2)	158 (1), 129.8 (4)	2.61	157.1, 130.6
(8)	O—H···O	2.653 (3)	1.93 (4)	160 (3)	1.716	157.97
	Cl···Cl		3.605 (1)	161.86 (9), 78.48 (9)		
			3.731 (2)	166.0 (1), 127.7 (6)		
	C≡C—H···Cl	3.695 (4)	3.14 (5)	123 (3), 126.8 (1)	3.025	120.5, 126.9
(9)	O—H···O	2.724 (5)	2.08 (7)	153 (7)	1.830	149.8
		2.688 (5)	2.13 (9)	145 (1)	1.862	139.9
		2.72 (5)	2.08 (6)	165 (7)	1.772	162.2
	Br···Br		3.421 (7)	163.0 (1), 116.1 (1)		
			3.661 (7)	157.8 (1), 75.5 (1)		
			3.515 (6)	172.9 (1), 110.8 (1)		
			3.680 (6)	167.2 (1), 120.6 (1)		
			3.882 (7)	166.8 (1), 68.1 (1)		
			3.899 (5)	152.3 (1), 116.6 (1)		
	C≡C—H···Br	3.900 (5)	3.20 (7)	134 (6), 120 (1)	3.074	133.6, 121.0
		3.751 (7)	3.23 (7)	134 (6), 138 (1)	2.974	128.9, 140.7
		3.720 (5)	3.02 (6)	129 (4), 113 (1)	2.951	128.2, 112.5
	C≡C—H···≡†	3.507	2.954	125.7	2.821	121.3

† Distances and angles measured to the mid-point of the triple bond.

observed for the more flexible saturated cyclohexane compound (1) (Bilton *et al.*, 1999). However, in (1) the dominant O—H···O bonds form a helical trimeric synthon in both of its polymorphs and in its pseudopolymorph.

The O—H···O network undergoes a further significant change to the tetrameric synthon (Figs. 2*b* and *c*) in structures (8) and (9), where the more polarisable Cl and Br now replace F. Whilst short F···F contacts do occur in (7), they do not make a systematic contribution to that structure. However, in (8) the Cl···Cl interactions form both closed and helical tetrameric units, which are important to structural integrity. These could not form within the framework adopted by the fluoro compound, hence there is a major change which results in the high-symmetry O—H···O and Cl···Cl synthons of (8). There is a reduction in symmetry in moving to the bromo compound (9), although the tetrameric O—H···O unit is preserved. This synthon repetitivity is reminiscent of structures (3) and (4) (Madhavi *et al.*, 2000), in which the synthons (5) and (6) have obvious topological relationships with the O—H···O tetramers (Figs. 2*b* and *c*) in (8) and (9), but are formed by cooperation between O—H···O and C≡C—H···O bonds.

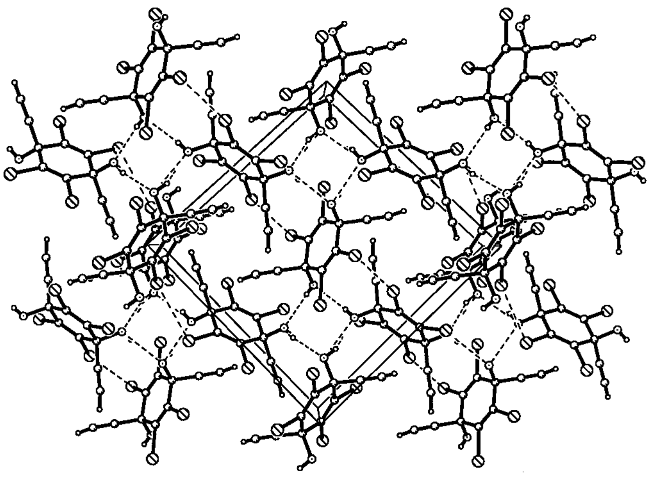


Figure 4
Packing diagram of triclinic (9) viewed down the pseudotetragonal *a* axis.

The topological similarities between the supramolecular structures of (8) and (9) are reflected in the relationship between their unit cells. The Niggli reduced cell of the tetragonal (8) has $a = 8.870$, $b = 12.654$, $c = 12.654$ Å, $\alpha = 82.94$, $\beta = 69.48$, $\gamma = 69.48°$, values which are very close to the triclinic cell dimensions of (9). Clearly, (9) is pseudo-tetragonal with its *a* axis unique in that symmetry, and with b,c (9) $\simeq 0.75$ a,b (8). The symmetry reduction allows the most polarizable halogen in this series (Br) to form a larger number [by comparison with (7) and (8)] of short halogen···halogen contacts which contribute significantly to structural stability, but which no longer form the higher-level tetrameric units seen in (8).

4. Conclusions

Crystal structures are the result of the interplay between intermolecular interactions of varying strengths, directionalities and distance dependence characteristics. The present structures typify this statement – the dominant tendency is to form O—H···O hydrogen bonds, but the particular arrangement of these bonds depends strongly on the nature of the weaker interactions, dictated in this case by the type of halogen present in the molecule. Thus, the structures of (2), (7), (8) and (9) illustrate the pitfalls of attempting to dissect crystal structures into modular units based on hierarchies of interactions. Rather, a crystal structure is a supramolecular entity in which any particular synthon results from a large number of concurring or competing forces. Another theme that develops here is the chemical similarity between O—H···O hydrogen bonds and type II halogen···halogen interactions. This has previously been noted by Robinson *et al.* (1998) and by Desiraju & Steiner (1999: p. 178). In a recent interesting example, Brehmer *et al.* (2000) show that hydrogen bonds and halogen···halogen interactions are actually mutually replaceable in tetrameric synthons, but the levels of interaction mimicry are not so high in the structures reported in the present paper.

The EPSRC (UK) are thanked for financial support to CB and JAKH (Senior Research Fellowship), and the CSIR (India) 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.

References

Allen, F. H., Hoy, V. J., Howard, J. A. K., Thalladi, V. R. & Desiraju, G. R. (1997). *J. Am. Chem. Soc.* **119**, 3477–3480.

Allen, F. H. & Kennard, O. (1993). *Chem. Des. Autom. News*, **8**, 1, 31–37.

Allen, F. H., Motherwell, W. D. S., Raithby, P. R., Shields, G. P. & Taylor, R. (1999). *New J. Chem.* pp. 25–34.

Anthony, A., Desiraju, G. R., Jetti, R. K. R., Kuduva, S. S., Madhavi, N. N. L., Nangia, A., Thaimattam, R. & Thalladi, V. R. (1998). *Cryst. Engng. 1, Mater. Res. Bull.* Suppl. S, 1–18.

Bernstein, J. (1987). *Organic Solid State Chemistry*, edited by G. R. Desiraju, pp. 471–518. London: Elsevier.

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.

Bondi, A. (1964). *J. Phys. Chem.* **68**, 441–451.

Brehmer, T. H., Weber, E. & Cano, F. H. (2000). *J. Phys. Org. Chem* **13**, 63–74.

Broder, C. K., Howard, J. A. K., Keen, D. A., Wilson, C. C., Allen, F. H., Jetti, R. K. R., Nangia, A. & Desiraju, G. R. (2000). *Acta Cryst.* B**56**, 1080–1084.

Bruker Systems Inc. (1999*a*). *SMART.* Bruker Systems Inc., Madison, Wisconsin, USA.

Bruker Systems Inc. (1999*b*). *SAINT.* Bruker Systems Inc., Madison, Wisconsin, USA.

Desiraju, G. R. (1991). *Acc. Chem. Res.* **24**, 270–276.

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

Desiraju, G. R. (1997). *Chem. Commun.* pp. 1475–1476.

Desiraju, G. R. & Parthasarathy, R. (1989). *J. Am. Chem. Soc.* **111**, 8725–8726.

Desiraju, G. R. & Steiner, T. (1999). *The Weak Hydrogen Bond in Structural Chemistry and Biology.* Oxford University Press.

Dunitz, J. D. & Taylor, R. (1997). *Chem. Eur. J.* **3**, 89–98.

Ermer, O. & Eling, A. (1994). *J. Chem. Soc. Perkin Trans. 2*, pp. 925–944.

Hayes, I. C. & Stone, A. J. (1984). *Mol. Phys.* **53**, 83–105.

Jetti, R. K. R., Xue, F., Mak, T. C. W. & Nangia, A. (1999). *Cryst. Engng*, **2**, 215–224.

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., Katz, A. K., Carrell, H. L., Nangia, A. & Desiraju, G. R. (1997). *J. Chem. Soc. Chem. Commun.* pp. 1953–1954.

Malone, J. F., Murray, C. M., Charlton, M. H., Docherty, R. & Lavery, A. (1997). *J. Chem. Soc. Faraday Trans.* **93**, 3429–3436.

Nangia, A. & Desiraju, G. R. (1998). *Top. Curr. Chem.* **198**, 57–95.

Nishio, M., Hirota, M. & Umezama, Y. (1998). *The CH/π Interaction, Evidence, Nature and Consequences.* New York: Wiley.

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.

Robinson, J. M. A., Kariuki, B. M., Harris, K. D. M. & Philp, D. (1998). *J. Chem. Soc. Perkin Trans. 2*, pp. 2459–2469.

Rodham, D. A., Suzuki, S., Suenram, R. D., Lovas, F. J., Dasgupta, S., Goddard III, W. A. & Blake, G. A. (1993). *Nature*, **362**, 735–737.

Rowland R. S. & Taylor, R. (1996). *J. Phys. Chem.* **100**, 7384–7391.

Sheldrick, G. M. (1996). *SADABS.* University of Göttingen, Germany.

Sheldrick, G. M. (1997). *SHELX*97. University of Göttingen, Germany.

Steiner, T., Tamm, M., Lutz, B. & van der Maas, J. (1996). *J. Chem. Soc. Chem. Commun.* pp. 1127–1128.

Suzuki, S., Green, P. G., Bumgarner, R. E., Dasgupta, S., Goddard III, W. A. & Blake, G. A. (1992). *Science*, **257**, 947–944.

Thalladi, V. R., Brasselet, S., Weiss, H.-C., Blaser, D., Katz, A. K., Carrell, H. L., Boese, R., Zyss, J., Nangia, A. & Desiraju, G. R. (1998). *J. Am. Chem. Soc.* **120**, 2563–2577.