

## A comparative study of the crystal structures of tetrahalogenated hydroquinones and $\gamma$ -hydroquinone

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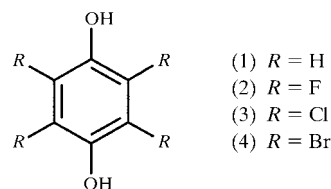
### Abstract

$\gamma$ -Hydroquinone (1) and its tetrafluoro, tetrachloro and tetrabromo derivatives (2), (3) and (4) adopt crystal structures that have an almost invariant system of O—H...O hydrogen bonds. However, within this O—H...O framework, the four structures display variations that are characteristic of the C—H, C—F, C—Cl and C—Br groups. In the parent compound (1) aromatic rings are packed with a herringbone geometry, whilst in the halogenated derivatives (3) and (4), polarization-type halogen...halogen contacts are optimized. The fluoro derivative (2) is exceptional in that neither of the above possibilities is adopted, even though the O—H...O scaffolding does not *per se* prohibit either of them geometrically.

### 1. Introduction

There has been much recent interest in the intermolecular binding ability of the C—F group, the so-called 'organic' fluorine. Curiously, the C—F group has been compared not only to the C—H and C—Cl groups, but also to the chemically rather different C—OH group and this in itself indicates that the behaviour of this group is quite variable (Hayashi *et al.*, 1998; O'Hagan & Rzepa, 1997; Larsen & Marthi, 1997; Fei *et al.*, 1997; Lommerse *et al.*, 1996; Shimoni *et al.*, 1994; Kumar *et al.*, 1993; Kumar & Venkatesan, 1993; Desiraju & Parthasarathy, 1989; Murray-Rust *et al.*, 1983). Interest in the C—F group is, in part, motivated by concerns in bioorganic and medicinal chemistry in that some control is sought in enzyme–substrate recognition (Silverman *et al.*, 1996; Choe *et al.*, 1995; Nangia & Chandrakala, 1995; Seebach, 1990). Crystal packing is governed by the same principles that apply when a ligand binds to a macromolecular receptor (Glusker, 1995). Thus, an understanding of the packing of small molecules containing the C—F group is expected to be of utility. In general, however, our understanding of the supramolecular behaviour of the C—F group is much poorer than say, for the C—Cl and C—Br groups (Dunitz & Taylor, 1997; Howard *et al.*, 1996; Shimoni & Glusker, 1994). We have recently shown, in the crystal structures of some fluoro-

benzenes, that the C—F group accepts C—H...F interactions in the absence of other strong acceptors such as O and N atoms (Thalladi *et al.*, 1998). During these studies we also determined the crystal structure of tetrafluorohydroquinone (2) and observed a certain similarity to the structure of  $\gamma$ -hydroquinone (1) (Maartmann-Moe, 1966) and tetrachlorohydroquinone (3) (Sikka & Chidambaram, 1967). Further, we noted that the crystal structure determination of tetrabromohydroquinone (4) had not been carried out previously. We report here the crystal structures of (2) and (4) and discuss the role of the C—F group in crystal packing with a comparative analysis of the four structures and related compounds.



### 2. Experimental

Single crystals of (2) suitable for X-ray diffraction were selected from the Aldrich sample as received. The crystallization of (2) from a number of solvents (MeOH, EtOH, CHCl<sub>3</sub>, CH<sub>2</sub>Cl<sub>2</sub> and C<sub>6</sub>H<sub>6</sub>) yielded crystals of a quality poorer than those found in the commercial sample. Single crystals of (4) grown from CHCl<sub>3</sub> were chosen for X-ray diffraction. Details of cell data, data collection and refinement are given in Table 1. In contrast to (2), where the H atom could be located and refined without constraints, the H atoms in (4) had to be treated as rigid groups because of the high absorption of the Br atoms. Final fractional atomic coordinates and isotropic displacement parameters are given in Table 2.†

† Supplementary data for this paper are available from the IUCr electronic archives (Reference: AN0560). Services for accessing these data are described at the back of the journal.

Table 1. *Experimental details*

	(2)	(4)
Crystal data		
Chemical formula	C <sub>6</sub> H <sub>2</sub> F <sub>4</sub> O <sub>2</sub>	C <sub>6</sub> H <sub>2</sub> Br <sub>4</sub> O <sub>2</sub>
Chemical formula weight	182.08	425.72
Cell setting	Monoclinic	Monoclinic
Space group	<i>P</i> 2 <sub>1</sub> / <i>n</i>	<i>P</i> 2 <sub>1</sub> / <i>n</i>
<i>a</i> (Å)	6.5533 (10)	8.8907 (2)
<i>b</i> (Å)	4.8848 (10)	4.7316 (1)
<i>c</i> (Å)	10.148 (2)	11.0612 (3)
$\beta$ (°)	107.990 (11)	92.167 (1)
<i>V</i> (Å <sup>3</sup> )	308.97 (9)	464.98 (2)
<i>Z</i>	2	2
<i>D</i> <sub>x</sub> (Mg m <sup>-3</sup> )	1.957	3.041
Radiation type	Mo <i>K</i> $\alpha$	Mo <i>K</i> $\alpha$
Wavelength (Å)	0.71073	0.71073
No. of reflections for cell parameters	50	2859
$\theta$ range (°)	10–12.5	2.89–28.18
$\mu$ (mm <sup>-1</sup> )	0.221	17.263
Temperature (K)	298 (2)	303 (2)
Crystal form	Block	Block
Crystal size (mm)	0.25 × 0.21 × 0.13	0.58 × 0.46 × 0.32
Crystal colour	Colourless	Colourless
Data collection		
Diffractometer	Siemens P4 four circle	Siemens SMART
Data collection method	Adaptive $\omega$ scans	$\omega$ scans with different $\phi$ settings
Absorption correction	None	Empirical ( <i>SADABS</i> ; Blessing, 1995)
<i>T</i> <sub>min</sub>	—	0.16
<i>T</i> <sub>max</sub>	—	1.00
No. of measured reflections	2177	4829
No. of independent reflections	901	1130
No. of observed reflections	664	709
Criterion for observed reflections	<i>I</i> > 2 $\sigma$ ( <i>I</i> )	<i>I</i> > 2 $\sigma$ ( <i>I</i> )
<i>R</i> <sub>int</sub>	0.0263	0.1501
$\theta$ <sub>max</sub> (°)	29.97	28.18
Range of <i>h, k, l</i>	–9 → <i>h</i> → 9 –1 → <i>k</i> → 6 –14 → <i>l</i> → 13	–11 → <i>h</i> → 11 –6 → <i>k</i> → 6 –14 → <i>l</i> → 14
No. of standard reflections	3	0
Frequency of standard reflections	Every 100 reflections	—
Intensity decay (%)	None	Not applicable
Refinement		
Refinement on	<i>F</i> <sup>2</sup>	<i>F</i> <sup>2</sup>
<i>R</i> [ <i>F</i> <sup>2</sup> > 2 $\sigma$ ( <i>F</i> <sup>2</sup> )]	0.0405	0.0665
<i>wR</i> ( <i>F</i> <sup>2</sup> )	0.1143	0.1431
<i>S</i>	1.080	1.160
No. of reflections used in refinement	901	1130
No. of parameters used	60	56
H-atom treatment	All H-atom parameters refined	Riding
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0709P)^2 + 0.0239P]$ , where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[\sigma^2(F_o^2) + (0.0448P)^2 + 0.0000P]$ , where $P = (F_o^2 + 2F_c^2)/3$
( $\Delta/\sigma$ ) <sub>max</sub>	0.001	0.001
$\Delta\rho$ <sub>max</sub> (e Å <sup>-3</sup> )	0.225	2.035
$\Delta\rho$ <sub>min</sub> (e Å <sup>-3</sup> )	–0.163	–1.923
Extinction method	<i>SHELXL93</i> (Sheldrick, 1993)	<i>SHELXL93</i> (Sheldrick, 1993)
Extinction coefficient	0.025 (20)	0.0017 (14)
Source of atomic scattering factors	<i>International Tables for Crystallography</i> (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)	<i>International Tables for Crystallography</i> (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)
Computer programs		
Data collection	<i>XSCANS</i> V.2.10 <i>b</i> (Siemens, 1994 <i>a</i> )	<i>SMART</i> V.4.209 (Siemens, 1995)
Cell refinement	<i>XSCANS</i> V.2.10 <i>b</i> (Siemens, 1994 <i>a</i> )	<i>SAINT</i> V.4.050 (Siemens, 1995)
Data reduction	<i>XSCANS</i> V.2.10 <i>b</i> (Siemens, 1994 <i>a</i> )	<i>SAINT</i> V.4.050 (Siemens, 1995)
Structure solution	<i>SHELXTL</i> V.5.03 (Siemens, 1994 <i>b</i> )	<i>SHELXTL</i> V.5.03 (Siemens, 1994 <i>b</i> )
Structure refinement	<i>SHELXTL</i> V.5.03 (Siemens, 1994 <i>b</i> )	<i>SHELXTL</i> V.5.03 (Siemens, 1994 <i>b</i> )
Preparation of material for publication	<i>SHELXTL</i> V.5.03 (Siemens, 1994 <i>b</i> )	<i>SHELXTL</i> V.5.03 (Siemens, 1994 <i>b</i> )

Table 2. Fractional atomic coordinates and equivalent isotropic displacement parameters ( $\text{\AA}^2$ )

	$U_{\text{eq}} = (1/3)\sum_i \sum_j U^{ij} a^i a^j \mathbf{a}_i \cdot \mathbf{a}_j$			
	x	y	z	$U_{\text{eq}}$
(2)				
O	0.7357 (2)	0.0043 (3)	0.8162 (2)	0.0636 (4)
C1	0.6196 (3)	0.0083 (3)	0.9067 (2)	0.0469 (4)
C2	0.6619 (2)	-0.1834 (3)	1.0113 (2)	0.0480 (4)
C3	0.5445 (2)	-0.1912 (3)	1.10273 (15)	0.0472 (4)
F1	0.8189 (2)	-0.3666 (2)	1.02410 (14)	0.0700 (4)
F2	0.5912 (2)	-0.3787 (2)	1.20450 (12)	0.0657 (4)
(4)				
O	0.2092 (6)	0.5559 (14)	-0.1783 (6)	0.031 (2)
Br1	0.32011 (10)	0.1586 (3)	0.01217 (10)	0.0367 (4)
Br2	0.07172 (10)	0.0776 (2)	0.22943 (9)	0.0316 (4)
C1	0.1052 (9)	0.5344 (18)	-0.0910 (8)	0.022 (2)
C2	0.1356 (8)	0.354 (2)	0.0062 (8)	0.021 (2)
C3	0.0310 (9)	0.3210 (19)	0.0963 (8)	0.021 (2)

### 3. Results and discussion

#### 3.1. Structural description

3.1.1. *Tetrafluorohydroquinone* (2). In the crystal structure of (2) (space group  $P2_1/n$ ,  $Z = 2$ ), the molecules lie on inversion centres. The  $-\text{OH}$  groups of adjacent  $2_1$ -related molecules form  $\text{O}-\text{H}\cdots\text{O}$  hydrogen bonds (Table 3) that link the molecules in chains parallel to [010]. In each chain, any  $-\text{OH}$  group participates in two hydrogen bonds, one as a donor and one as an acceptor. This is a common pattern in the crystal structures of phenols (Zorky & Zorkaya, 1997; Ahn *et al.*, 1996; Brock & Duncan, 1994). Adjacent chains may be said to form layers parallel to (202), these layers being defined as the mean planes of the O atoms (Fig. 1). The aromatic rings are inclined to the layers at an angle of  $39^\circ$ . The perpendicular distance between layers or the interlayer separation is 3.85 Å (Fig. 2). The nearest aromatic rings

Table 3. Some important geometrical parameters in the structures (1)–(4)

	(1)	(2)	(3)	(4)
$\text{O}\cdots\text{O}$ (Å)	2.84, 2.83	2.82	2.92	2.95
Inclination ( $^\circ$ )	33, 35	39	46	50
Interlayer separation (Å)	3.86	3.85	6.05	7.68
Layer offset (Å)	2.86	3.29	2.83	2.78
Layer plane†	(100)	(202)	(10)	(101)

† Defined as the plane in which  $\text{O}-\text{H}\cdots\text{O}$  hydrogen-bonded layers are present. The deviation of the O atoms from the mean plane lie in the range 0.17–0.24 Å.

in adjacent layers are not parallel. Additionally they are offset by 3.29 Å (Fig. 1). The layer offset is defined in terms of the distance between the projections of centroids of non-parallel aromatic rings in adjacent layers on the mean plane. The description of ring inclination and interlayer separation is shown in Fig. 2.

3.1.2.  *$\gamma$ -Hydroquinone* (1). There are two symmetry-independent molecules. Each forms hydrogen-bonded layers as described above for (2) and the structure consists of alternating symmetry-independent layers, within each of which is found a hydrogen-bond network that is topologically identical to that found in (2) (Fig. 3). The ring inclination and the layer offset are slightly less than those found in (2) (Table 3). The interlayer packing is governed by herringbone/ $\text{C}-\text{H}\cdots\pi$  interactions (Fig. 4; Nishio *et al.*, 1998; Madhavi *et al.*, 1997). The  $\text{C}-\text{H}$  groups point towards the midpoint of a  $\text{HC}=\text{CH}$  bond rather than towards the ring centroid.

3.1.3. *Tetrachlorohydroquinone* (3). Continuing further, tetrachlorohydroquinone (3) was also found to be structurally similar to (1) and (2) (Fig. 5). Topologically similar  $\text{O}-\text{H}\cdots\text{O}$  hydrogen-bonded layers may

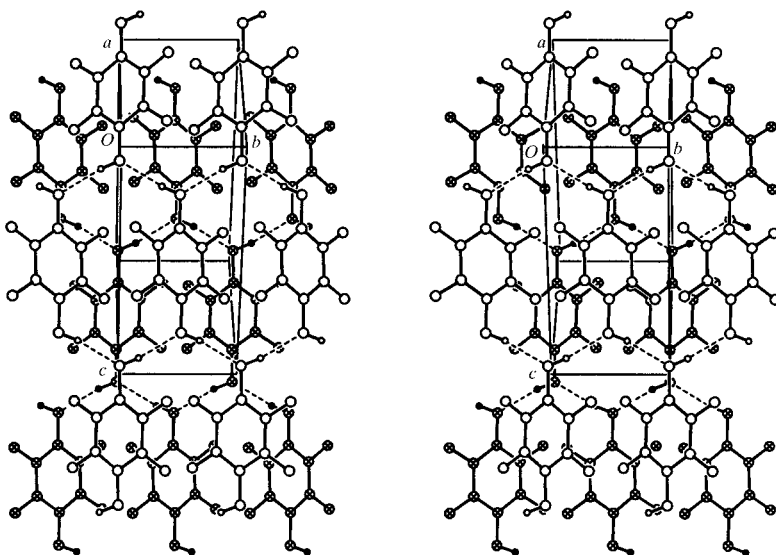


Fig. 1. Stereoview of the two consecutive  $\text{O}-\text{H}\cdots\text{O}$  hydrogen-bonded layers in the structure of (2). Note the ring inclination and layer offset. Molecular components in one layer are shown as open circles and in the other they are shaded in this figure and in Figs. 3, 5 and 7.

again be identified. The aromatic rings are also inclined, but at a steeper angle with respect to the layers and the layer offset is small (Table 2). Adjacent layers are interconnected with Cl $\cdots$ Cl interactions (Fig. 6) of both type I (Cl $\cdots$ Cl 3.39 Å;  $\theta_1 = \theta_2 = 167^\circ$ ) and type II geometries (Cl $\cdots$ Cl 3.44 Å;  $\theta_1 = 176^\circ$ ,  $\theta_2 = 81^\circ$ ). The halogen $\cdots$ halogen contact C—X $\cdots$ X—C is defined as type I if the C—X $\cdots$ X angle  $\theta_1$  is equal or nearly equal to the X $\cdots$ X—C angle  $\theta_2$ . If  $\theta_1 \simeq 180^\circ$  and  $\theta_2 \simeq 90^\circ$ , the contact is defined as type II (Ramasubbu *et al.*, 1986). A longer interlayer separation of 6.05 Å and a layer offset of 2.83 Å accommodate these Cl $\cdots$ Cl contacts. It may be noted at this point that tetramethylhydroquinone

(Pennington *et al.*, 1986) also contains the same O—H $\cdots$ O network, indicating the robustness of this pattern. However, in tetramethylhydroquinone the aromatic rings are inclined at a steeper angle ( $50^\circ$ ) with respect to the layers. The interlayer separation (6.51 Å) and the layer offset (3.00 Å) are also large and hence the methyl groups are well separated (shortest C $\cdots$ C and H $\cdots$ H distances between the methyl groups are 3.74, 3.77 and 2.25, 2.48 Å). Therefore, this is not a case of chloromethyl exchange (Desiraju & Sarma, 1986).

3.1.4. *Tetrabromohydroquinone (4)*. The structural similarities between (1), (2) and (3) prompted us to determine the crystal structure of (4), the details of

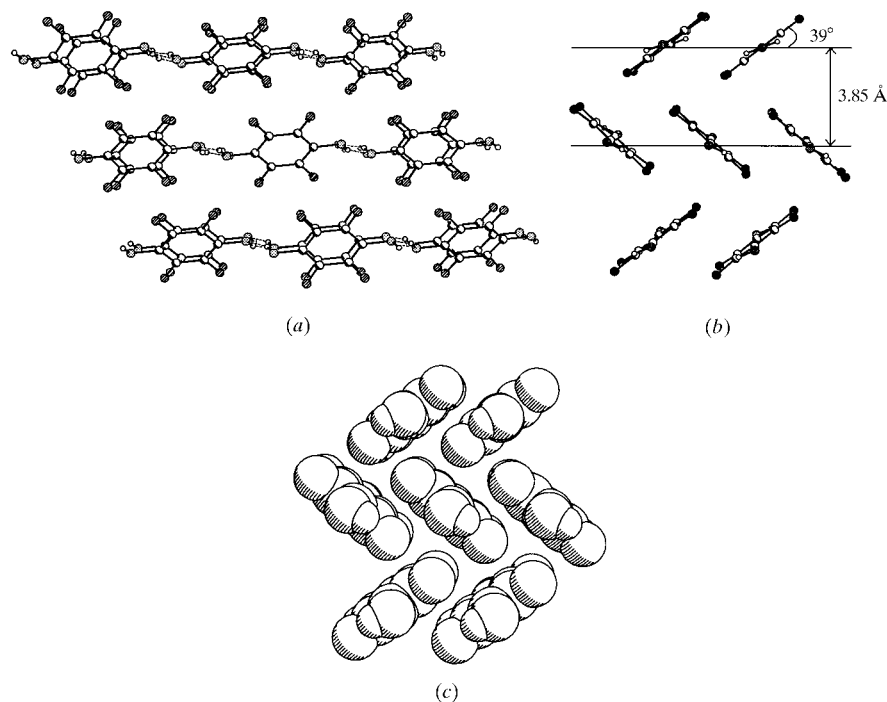


Fig. 2. Crystal structure of (2): (a) View down [010] showing parallel layers. (b) Lateral view of nearest interlayer molecules showing ring inclination and interlayer separation. The horizontal lines represent the mean planes of the layers. (c) Space-filling view of (b). Notice the loose packing of molecules.

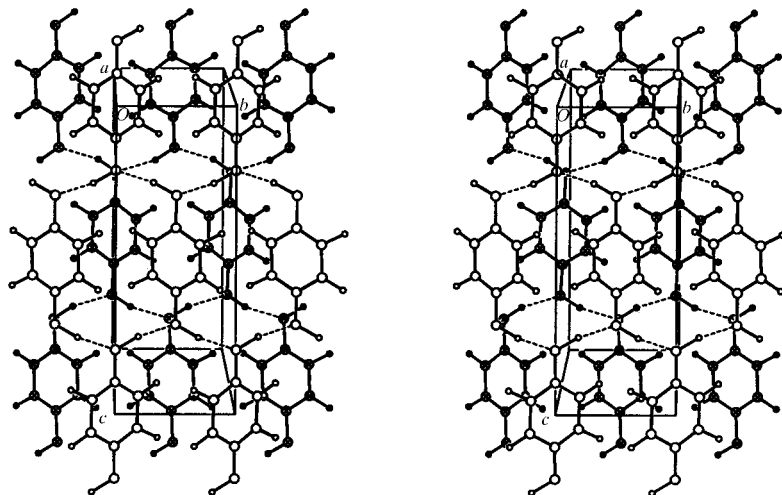


Fig. 3. Stereoview of the two consecutive O—H $\cdots$ O hydrogen-bonded layers in the structure of (1). Note the decrease in layer offset compared with Fig. 1.

which are given in Table 1 and Figs. 7 and 8. Chains of O—H...O hydrogen bonds parallel to [010] are found. The chain and layer structure is as described previously for (1)–(3) with type I (Br...Br 3.55 Å;  $\theta_1 = \theta_2 = 172^\circ$ ) and type II (Br...Br 3.58 Å;  $\theta_1 = 175^\circ$ ,  $\theta_2 = 88^\circ$ ) Br...Br interactions in the interlayer region.

### 3.2. Structural discrimination between hydroquinones (1)–(4)

It may be noted that it is very unusual to find a group of crystal structures wherein replacement of a majority of the H atoms in a molecule by F, Cl and Br successively causes no major changes in the gross structure, crystal symmetry and network features. For example, replacement of either a single H atom, as in the case of ethynylbenzene and 4-haloethynylbenzenes (Weiss, Bläser *et*

*al.*, 1997; Weiss, Boese *et al.*, 1997), or all H atoms, as in the case of benzoquinone and tetrahalobenzoquinones (van Bolhuis & Kiers, 1978; Ueda, 1961; Baudour *et al.*, 1981; Hagen *et al.*, 1987; Kobayashi *et al.*, 1974), led to different structures. For this reason, a more detailed comparison of the structures (1)–(4) was deemed worthwhile.

3.2.1. *Herringbone interactions in (1) and halogen...halogen interactions in (3) and (4).* The invariant feature in the four structures in this study is the O—H...O hydrogen-bonded network with O...O distances lying within a narrow range of 0.13 Å. The variable features are the interlayer separation, the aromatic ring inclination and the layer offset (Table 3). These three parameters are geometrically interrelated. Some ring inclination is necessary given the O—H...O geometry. Consider the inclinations of 33 and 35° in (1). A steeper

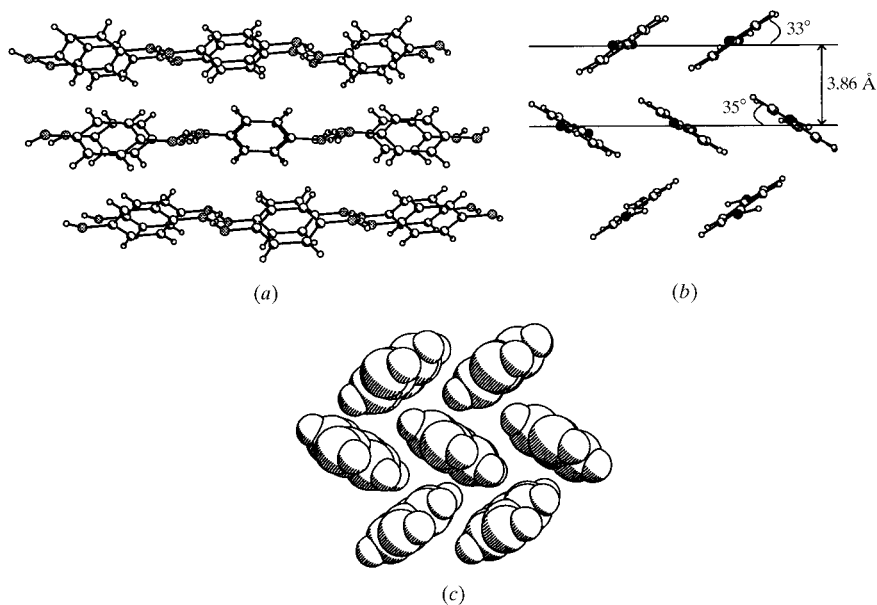


Fig. 4. Crystal structure of (1): (a) View down [010] showing parallel layers. (b) Lateral view of the nearest interlayer molecules showing ring inclination and interlayer separation. The horizontal lines represent the mean planes of the layers. (c) Space-filling view of (b). Notice that the C—H groups approach the midpoint of the HC=CH bond and not the ring centroid. Compare this with Fig. 2(c).

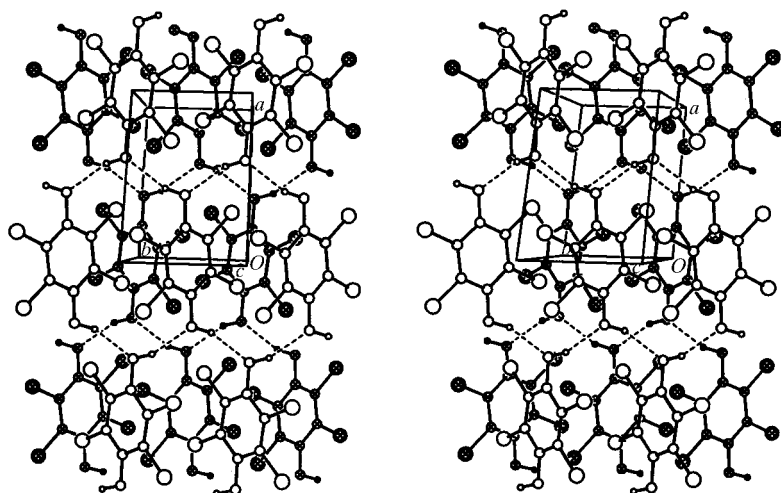


Fig. 5. Stereoview of the two consecutive O—H...O hydrogen-bonded layers in the structure of (3). Note the decrease in layer offset compared with Fig. 1.

inclination results in a greater interlayer separation, as in (3) and (4), or in a longer offset, as in (2). The structure of (1) is archetypal of the herringbone packing between layers. The combination of a shallow inclination and small offset enables optimal C—H $\cdots\pi$  contacts and Figs. 3(b) and (c) highlight the resemblance

of this structure to the classic herringbone structure of naphthalene (Desiraju & Gavezzotti, 1989). Indeed, it is known that such herringbone packing is compatible with the demands of O—H $\cdots$ O hydrogen bonding in the crystal structures of other phenols (Zorky & Zorkaya, 1997). Now let us consider the chloro and bromo deri-

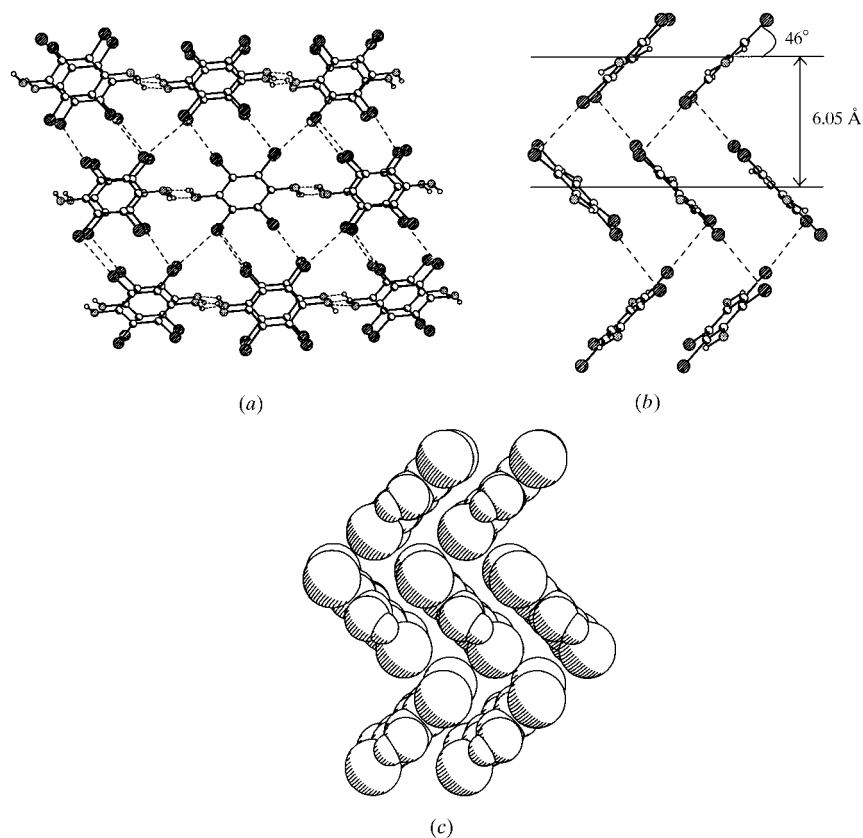


Fig. 6. Crystal structure of (3): (a) View down [010] showing parallel layers. (b) Lateral view of the nearest interlayer molecules showing ring inclination and interlayer separation. The horizontal lines represent the mean planes of the layers. Notice the type II Cl $\cdots$ Cl interactions between the layers. Compare this with Fig. 2(b). (c) Space-filling view of (b). Note the close approaches of Cl groups. Compare this with Fig. 2(c).

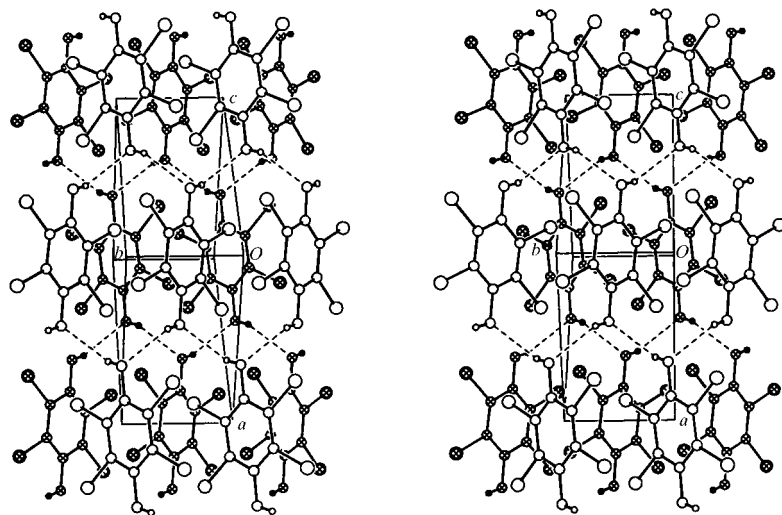


Fig. 7. Stereoview of the two consecutive O—H $\cdots$ O hydrogen-bonded layers in the structure of (4). Note the smaller layer offset and longer interlayer separation.

vatives (3) and (4). Given the invariant O—H···O network, these compounds opt for a steep increase in the inclination with little change in the layer offset so that halogen···halogen interactions of type II geometry are manifested (Figs. 6*b, c* and 8*b, c*). It is well known that the type II contacts are polarization-induced and contribute actively to crystal structure stabilization (Pedireddi *et al.*, 1994), while type I contacts (which could be repulsive) arise due to close-packing about an inversion centre. The structures of (3) and (4) are almosty isostructural and show the close similarity of the Cl and Br groups in forming such polarization-induced halogen···halogen interactions. In terms of interaction insulation, one could state that the O—H···O hydrogen-bonded network is effectively insulated from the herringbone interactions in (1) as well as from the halogen···halogen interactions in (3) and (4). These situations in effect represent two distinct structural possibilities for this family of compounds.

3.2.2. *Indecisive C—F groups in the interlayer packing of (2)*. Given the above background, it is now instructive to analyse the structure of the tetrafluoro derivative (2)

with respect to (1), (3) and (4). Given the fixed geometry of the O—H···O network, the only element of variability in these structures is the mutual accommodation between the ring inclination, the interlayer separation and the layer offset. The ring inclination in (2) is only slightly more than in (1), but this is accompanied by an increase in the offset to 3.29 Å. Consideration of only inclinations in (1)–(4) might lead to the conclusion that there is a smooth structural transition in this series. However, a consideration of the offsets and interlayer separations clearly shows that this is not the case. In particular, the increase in the offset in structure (2) [much greater than in (1), (3) or (4)] indicates that herringbone-type interactions, say of the C( $\delta^+$ )···F( $\delta^-$ ) type, are precluded (Fig. 2; Alkorta *et al.*, 1997). Again, large interlayer separations accompanied by large inclinations are required for effective halogen···halogen interactions as in (3) and (4). The fact that the interlayer separation in (2) is only 3.85 Å [even smaller than in (1)] shows, therefore, that F···F interactions are not feasible. In effect, two structure types, exemplified by (1) on the one hand and by (3) and (4) on

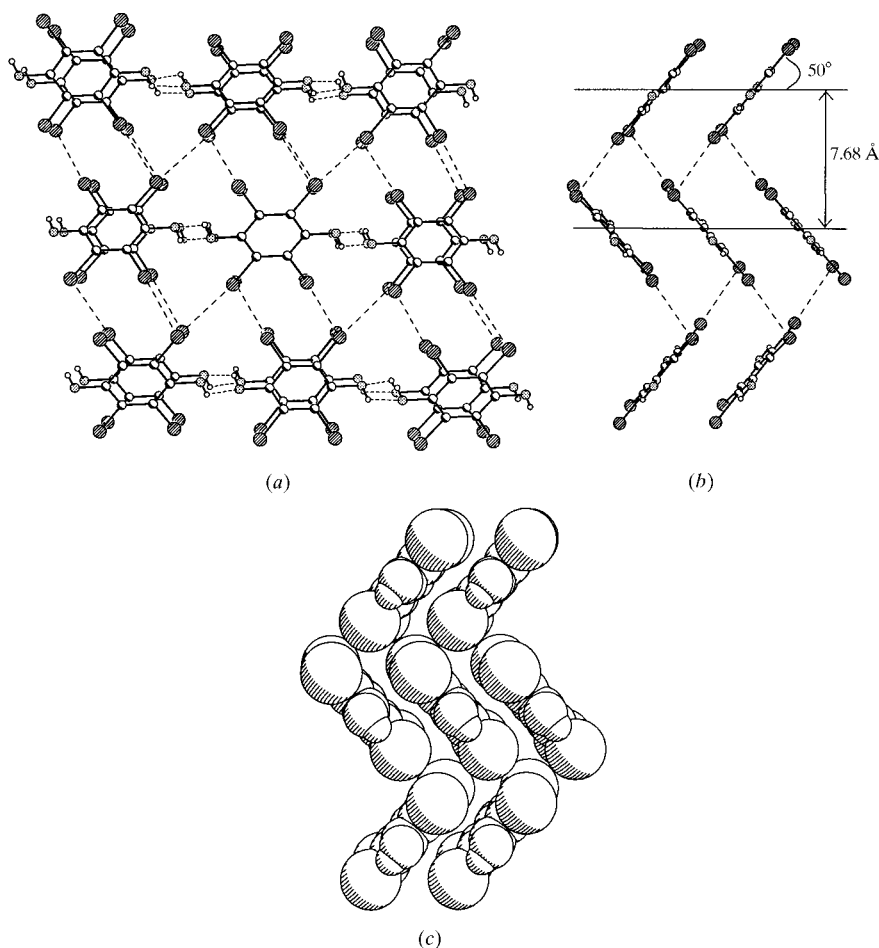


Fig. 8. Crystal structure of (4): (a) View down [010] showing parallel layers. (b) Lateral view of the nearest interlayer molecules showing ring inclination and interlayer separation. The horizontal lines represent the mean planes of the layers. Notice the type II Br···Br interactions between the layers. Compare this with Fig. 2(b). (c) Space-filling view of (b). Notice the close approach of the Br groups. Compare this with Fig. 2(c).

the other, are ideal. However, the tetrafluoro derivative (2) adopts neither possibility and its structure is poised uneasily between the two optimal situations. The layer structure and interlayer geometry are such that the F atoms are as distant from one another or from any other group (shortest F...F 2.88 Å; shortest F...C 3.00 Å).

There has been some discussion on the existence of attractive F...F contacts (Kumar *et al.*, 1993; Kumar & Venkatesan, 1993). Retrieval of F...F distances from the Cambridge Structural Database (CSD; Allen *et al.*, 1991) in a recent study reveals many geometries in the 2.40–3.50 Å range (Fernández-Castaño *et al.*, 1997). Assuming a van der Waals radius of 1.47 Å for the F atom (Bondi, 1964), many of these contacts could be described as short. However, most of these have the type I geometry like the contact in (2), with the two F atoms being related by an inversion centre. A search for F...F contacts in the CSD (April 1997 release, version 5.16, 190 307 entries) reveals that out of a total of 1627 C—F...F—C contacts retrieved (F...F distance in the range 2.4–3.0 Å with no constraints on C—F...F—C angles, only non-organometallic compounds, error-free and disorder-free structures with  $R < 0.075$ ) only 67 contacts (4%) have the type II geometry,  $150 < \theta_1 < 180^\circ$  and  $80 < \theta_2 < 100^\circ$  ( $\theta_1$  and  $\theta_2$  are the C—F...F—C angles;  $\theta_1 > \theta_2$ ). 24 of these 67 contacts are longer than the van der Waals sum and the rest are found either in perfluoro or polyfluoro compounds, wherein a short contact could well arise from statistical rather than chemical factors (Price *et al.*, 1994). What is significant in (2) is that while the aromatic rings should be fully able to optimize their inclination, layer separation and offset within the constraints of the O—H...O hydrogen bonding to achieve an optimal F...F type II geometry, they fail to do so. This more than any other reason indicates that the F atom does not tend to form a polarization-induced F...F contact, like Cl and Br.

#### 4. Conclusions

A detailed comparison of the crystal structures of hydroquinones (1)–(4) is only possible because the dominant interactions, namely the O—H...O hydrogen bonds, form a rigid and invariant scaffolding within which the differences in the molecular structures have some limited scope to manifest their supramolecular variability. An analysis of these four crystal structures reveals that the C—F group resembles neither the C—H group nor the C—Cl and C—Br groups in its packing characteristics and that it disfavours the structural alternatives adopted by the three latter groups. Neither herringbone-type interactions, say of the C( $\delta^+$ )...F( $\delta^-$ ) type, nor halogen...halogen interactions of the F...F type are realistic because if they were, (2) would resemble (1) or (3) and (4) more closely. The C—F group is also unable to adopt a distinctively stabilizing packing of its own, say with a change in the O—H...O

pattern (Zorky & Zorkaya, 1997; Brock & Duncan, 1994).

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