duction: Xtal3.0 ADDREF and SORTRF (Hall & Stewart, 1990; Norrestam & Nielson, 1982). Program(s) used to solve structure: XRAY76 (Stewart et al., 1976). Program(s) used to refine structure: Xtal3.0 CRYLSQ. Software used to prepare material for publication: Xtal3.0 BONDLA and ATABLE.

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3,5-Difluorophenol

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Abstract

The X-ray crystallographic study of 3,5-difluorophenol, $C_6H_4F_2O$ (35-DFP), shows that the crystal structure has an amphiphilic layer-like arrangement. The hydrophilic contacts involve OH groups and H atoms; the hydrophobic contacts involve F atoms.

This unique arrangement is not observed in the crystal structure of phenol.

Comment

During the past few years special attention has been drawn to molecular assembly, with one of the major problems being the generation of an assembly with the desired architectural features. In crystal engineering one useful method of controlling the molecular arrangement is to add polar substituents to the starting component. 'Chlorosubstitution' has been established as an efficient method of controlling the arrangement (Sarma & Desiraju, 1986); in contrast, no systematic studies have been tried for fluorine although fluorine is also in Group 7. We have reported previously the crystal structure of phenyl 3-fluorobenzoate, indicating the effectiveness of 'fluorosubstitution' (Shibakami, Tamura, Arimura, Kurosawa & Sekiya, 1994). Here we report the crystal structure of 3,5-difluorophenol (35-DFP), demonstrating the unique layer-like arrangement which is not observed in the crystal structure of phenol.
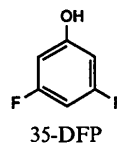
35-DFP

Colourless prismatic crystals of 35-DFP were purchased from Aldrich Co. and a well shaped crystal was mounted on an automated four-circle diffractometer. The crystal structure as drawn by ORTEPII (Johnson, 1976) is depicted in Fig. 1. As Table 2 shows, bond distances and angles are in the range of the normal values, within experimental error. The most striking feature is that molecules of 35-DFP form hydrophilic and hydrophobic contacts parallel to the crystallographic ac plane. The hydrophilic contacts involve the OH groups and the H(6) atoms; the hydrophobic contacts are formed by the F(1) atoms. Within the hydrophilic contacts, hydrogen bonds are formed between the OH groups with an O···O distance of 2.794 (3) Å. The O(1)—H(1) distance is 1.06 Å and the C(1)—O(1)—H(1) angle is 98.7°. Since the van der Waals radius of F is 1.47 Å and the shortest distance between the F atoms is 2.980 (2) Å in the hydrophobic contacts, it may indicate that a van der Waals contact occurs between two F atoms.

The crystal structure of phenol, which belongs to space group $P2_1$ with $a = 6.05$, $b = 9.24$, $c = 15.29$ Å, $\gamma = 90°$ (Scheringer, Wehrhahn & Stackelberg, 1960), shows that the molecules are linked by hydrogen bonds which result in the formation of a hydrogen-bond network. Contrary to the 35-DFP structure, the layer-like structure is not observed in

the phenol structure. In conclusion, we found that the substitution of two F atoms for two H atoms of phenol caused a drastic change in the crystal structure.
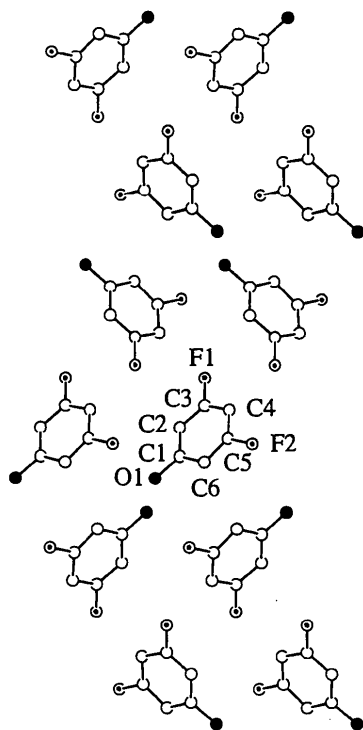

Fig. 1. *ORTEP*II drawing (Johnson, 1976) of the crystal structure of 35-DFP as viewed along the c axis. C, O and F atoms are drawn as open, solid and half-filled circles, respectively.

Experimental

Crystal data

$C_6H_4F_2O$
$M_r = 130.09$
Orthorhombic
$P2_12_12_1$
$a = 5.717$ (1) Å
$b = 20.077$ (5) Å
$c = 4.806$ (1) Å
$V = 551.6$ (2) Å^3
$Z = 4$
$D_x = 1.566$ Mg m^{-3}

Cu $K\alpha$ radiation
$\lambda = 1.5418$ Å
Cell parameters from 12 reflections
$\theta = 22.55-23.97°$
$\mu = 1.31$ mm^{-1}
$T = 298$ K
Prismatic
$0.30 \times 0.30 \times 0.10$ mm
Colourless

Data collection

Rigaku AFC-5R diffractometer
$\omega/2\theta$ scans
Absorption correction: empirical (*DIFABS*; Walker & Stuart, 1983)
$T_{min} = 0.76$, $T_{max} = 1.23$
540 measured reflections
540 independent reflections
419 observed reflections
 $[I > 3.0\sigma(I)]$

$\theta_{max} = 60.0°$
$h = 0 \rightarrow 6$
$k = 0 \rightarrow 22$
$l = 0 \rightarrow 5$
2 standard reflections monitored every 150 reflections
intensity variation: -3.7% (corrected)

Refinement

Refinement on F
$R = 0.040$
$wR = 0.055$
$S = 1.44$
419 reflections
83 parameters
H-atom parameters not refined
$w = 1/\sigma^2(F_o)$
$(\Delta/\sigma)_{max} = 0.01$

$\Delta\rho_{max} = 0.12$ e Å^{-3}
$\Delta\rho_{min} = -0.20$ e Å^{-3}
Extinction correction: secondary
Extinction coefficient: 0.11839×10^{-4}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, Table 2.2A)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$B_{eq} = (8\pi^2/3)\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}
F(1)	0.1354 (4)	0.2368 (1)	0.0683 (7)	6.9 (2)
F(2)	0.4714 (5)	0.1050 (1)	0.7611 (7)	6.9 (1)
O(1)	−0.2213 (5)	0.0346 (1)	0.3085 (6)	4.8 (1)
C(1)	−0.0424 (7)	0.0793 (2)	0.3500 (9)	3.7 (2)
C(2)	−0.0432 (7)	0.1364 (2)	0.1896 (9)	4.2 (2)
C(3)	0.1350 (7)	0.1807 (2)	0.225 (1)	4.5 (2)
C(4)	0.3097 (8)	0.1723 (2)	0.413 (1)	4.8 (2)
C(5)	0.2994 (8)	0.1155 (2)	0.571 (1)	4.7 (2)
C(6)	0.1313 (7)	0.0680 (2)	0.542 (1)	4.1 (2)

Table 2. *Selected geometric parameters* (Å, °)

F(1)—C(3)	1.356 (5)	C(2)—C(3)	1.363 (5)
F(2)—C(5)	1.358 (5)	C(3)—C(4)	1.356 (6)
O(1)—C(1)	1.376 (5)	C(4)—C(5)	1.373 (6)
C(1)—C(2)	1.381 (6)	C(5)—C(6)	1.361 (6)
C(1)—C(6)	1.375 (6)		
O(1)—C(1)—C(2)	117.2 (4)	C(2)—C(3)—C(4)	123.6 (4)
O(1)—C(1)—C(6)	121.8 (4)	C(3)—C(4)—C(5)	116.1 (4)
C(2)—C(1)—C(6)	120.9 (4)	F(2)—C(5)—C(4)	118.1 (4)
C(1)—C(2)—C(3)	118.0 (4)	F(2)—C(5)—C(6)	118.1 (4)
F(1)—C(3)—C(2)	118.3 (4)	C(4)—C(5)—C(6)	123.7 (4)
F(1)—C(3)—C(4)	118.1 (4)	C(1)—C(6)—C(5)	117.6 (4)

The structure was solved by direct methods using *MITHRIL* (Gilmore, 1984) and expanded using *DIRDIF* (Beurskens *et al.*, 1992). The non-H atoms were refined anisotropically; H atoms were found from a difference Fourier map, but were not refined. All calculations were performed using the *TEXSAN* crystallographic software package of the Molecular Structure Corporation (1985).

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The structures of only two 3,3,6,6-tetramethoxy-cyclohexa-1,4-dienes have been reported, the unsubstituted parent compound (IV) (Liebich, Yvon & Margaretha, 1976) and the tetramethyl derivative (V) (Nørskov-Lauritsen, Larsen, Ettlinger & Jaroszewski, 1982). These two compounds and the derivatives (I), (II) and (III) (Fig. 1) lie on a crystallographic centre of symmetry.

Three Tetramethylketals of 2,5-Distyryl-[1,4]benzoquinones

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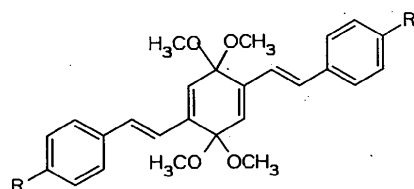
Abstract

The methoxy groups of the title compounds 3,3,6,6-tetramethoxy-1,4-distyrylcyclohexa-1,4-diene, $C_{26}H_{28}O_4$ (I), 1,4-bis[2-(4-chlorophenyl)vinyl]-3,3,-6,6-tetramethoxycyclohexa-1,4-diene, $C_{26}H_{26}Cl_2O_4$ (II), and 3,3,6,6-tetramethoxy-1,4-bis[2-(4-methyl-phenyl)vinyl]cyclohexa-1,4-diene, $C_{28}H_{32}O_4$ (III), adopt either an *anti–anti* or a *gauche–anti* orientation. In the *anti–anti* conformation the O—C—O bond angle is reduced to 99.2–99.3° because of intramolecular repulsive interactions between the methyl groups. The stacking of the molecules in the crystal is defined by an interlocking pattern.

Comment

In the course of topochemical studies of 2,5-distyryl-[1,4]benzoquinones we synthesized their corresponding ketals 3,3,6,6-tetramethoxy-1,4-distyrylcyclohexa-1,4-diene (I), 1,4-bis[2-(4-chlorophenyl)vinyl]-3,3,6,6-tetramethoxycyclohexa-1,4-diene (II) and 3,3,6,6-tetramethoxy-1,4-bis[2-(4-methylphenyl)-vinyl)cyclohexa-1,4-diene (III) (Irngartinger, Lichtenthäler, Fenske & Baum, 1993).
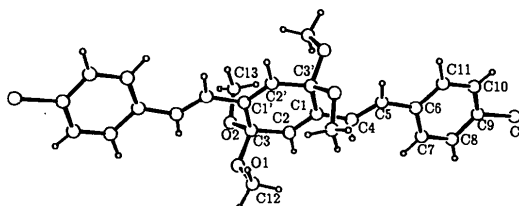

(I) R = H

(II) R = Cl

(III) R = CH_3

Fig. 1. View of (II) showing the atom labelling.

The cyclohexadiene rings are planar. The methoxy groups show two kinds of conformation. In the derivatives (I), (II) and (V) the methoxy groups adopt an *anti–anti* orientation and in compounds (III) and (IV) a *gauche–anti* conformation (Fig. 2). The *gauche* orientation is defined by the torsion angle O2—C3—O1—C12 of −63.1° in (III). For the *anti* orientation the corresponding torsion angles are in the region of 180° [177.4 (1) in (I), 173.9 (2)° in (II)].
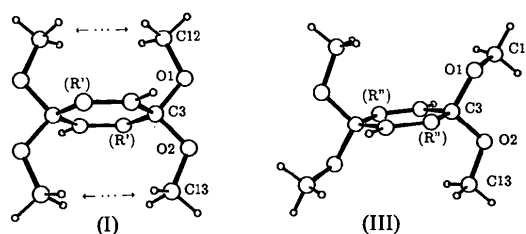

Fig. 2. The orientation of the methoxy groups [R' = styryl, R'' = 2-(4-methylphenyl)vinyl].

The repulsion between the methyl groups [along the double arrow in Fig. 2; 1⋯8 (C12⋯C13′) distances 3.718 (2) in (I), 3.731 (4) Å in (II)] generates a reduction of the angle O1—C3—O2 [99.2 (1) in (I), 99.3 (1)° in (II)]. Similar molecular geometry was found in (V) (Nørskov-Lauritsen *et al.*, 1982). In the case of the *gauche–anti* conformation, however, this angle is not affected [106.1 (2)° in (III)], as was also found for (IV) (Liebich *et al.*, 1976). The remaining molecular dimensions (Table 2) are similar to those of related molecules. The stacking and interlocking of the molecules in the packing arrangement are comparable for all the three compounds and are illustrated in Fig. 3 for compound (I).