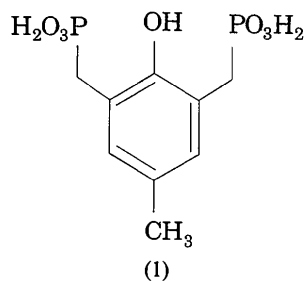


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or bromomethyl-substituted phenols with phosphorous acid trialkyl esters and subsequent hydrolysis; the pK_a values of the resulting compounds are strongly dependent on the nature and electronegativity of the ring substituents (Ageeva & Ivanov, 1967, 1968; Vogt, 1978; Kaiser, Schied, Trautmann & Vogt, 1993). The structure determination of the dihydrate of (1) was undertaken to establish the nature of the O—H...O hydrogen-bond interactions of the bis(phosphonic acid) derivative in the solid state.



Acta Cryst. (1993). **C49**, 1024–1026

4-Methyl-2,6-bis(phosphonomethyl)phenol Dihydrate

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(Received 12 June 1992; accepted 3 November 1992)

Abstract

The 4-methyl-2,6-bis(phosphonomethyl)phenol molecule, which crystallizes with two water molecules per asymmetric unit, has approximate twofold symmetry and is involved in extensive three-dimensional hydrogen bonding in which every available OH group participates. The principal dimensions include P=O 1.4981 (13) and 1.5015 (14) Å, four P—OH distances in the range 1.5395 (14) to 1.5688 (13) Å, P—C 1.7857 (17) and 1.7893 (17) Å, and O...O intramolecular and intermolecular hydrogen-bond distances in the range 2.458 (2) to 2.866 (2) Å.

Comment

Substituted 2,6-bis(methanephosphonic acid)phenols are obtained by reaction of the appropriate hydroxymethyl-

Fig. 1 shows that, if the H atoms are neglected, the diacid has approximate twofold symmetry with the twofold axis through atoms O(7), C(1), C(4) and C(8) [C(2)—C(7)—P(1)—O(1) —62.1 (1), C(6)—C(9)—P(2)—O(4) —65.1 (1)°]. The P(1)=O(1) and P(2)=O(6) bond lengths are 1.5015 (14) and 1.4981 (13) Å, respectively, while the four P—O distances are in the range 1.5395 (14) [P(2)—O(5)] to 1.5688 (13) Å [P(2)—O(4)] with an average value of 1.5507 (14) Å. A search of the January 1992 release of the Cambridge Structural Database (Allen, Kennard & Taylor, 1983) for structures containing the C—P=O(OH)₂ fragment revealed only two aliphatic diphosphonic acids and none with aromatic rings. Bond lengths in (1) are similar within experimental error to those measured in 1,2-ethanediphosphonic acid (Peterson *et al.*, 1977) and 1,3-propanediphosphonic acid (Gebert *et al.*, 1977). The P(1)—C(7) and P(2)—C(9) distances are 1.7857 (17) and 1.7893 (17) Å, while the C—C aromatic ring bond lengths are in the range 1.387 (2)–1.397 (2) Å with an average value of 1.393 (2) Å. The phosphonate groups are essentially fully staggered [C(2)—C(7)—P(1)—O(3) 174.4 (2), C(6)—C(9)—P(2)—O(5) —178.7 (2)°], with the orientation of the P=O and two P—OH groups (determined by the hydrogen-bonding process) different at each P atom. There are two intramolecular O—H...O hydrogen bonds [O(7)...O(1) 2.753 (2), HO(7)...O(1) 1.92 (3) Å, O(7)—HO(7)...O(1) 173 (3)°; O(4)...O(7) 2.640 (2), HO(4)...O(7) 1.88 (3) Å, O(4)—HO(4)...O(7) 164 (3)°] (Fig. 1) which control the molecular conformation.

Molecule (1) crystallizes with two molecules of water which are involved in extensive three-dimensional hy-

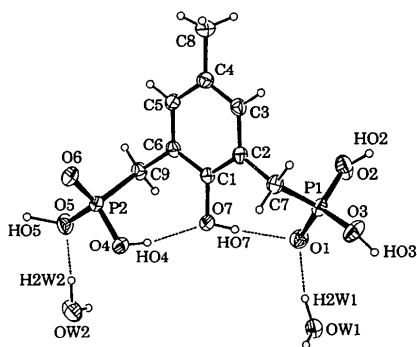


Fig. 1. An ORTEP view of the title compound. Thermal ellipsoids are drawn at the 50% probability level with H atoms shown as spheres of an arbitrary size. The two intramolecular hydrogen bonds and two of the intermolecular hydrogen bonds linking the molecule to the two water molecules are also shown.

drogen bonding in which all available OH groups in the diacid and in the water molecules participate (as depicted in the stereoview in Fig. 2; details in Table 2), forming hydrogen-bonded rings and leading to a very rigid framework. There are three short O—H...O hydrogen bonds [O(2)...OW(2) 2.522 (2), O(3)...O(6) 2.529 (2), O(5)...OW(1) 2.458 (2) Å]. The other, slightly longer O—H...O hydrogen bonds involve the water molecules acting as donors [OW(1)...O(1) 2.688 (2), OW(1)...O(6) 2.693 (2), OW(2)...O(1) 2.866 (2), OW(2)...O(5) 2.801 (2) Å]. A complete listing of all of the O—H...O intra- and intermolecular hydrogen-bond distances and angles is given in Table 2. The three-dimensional structure has phenyl rings stacked about inversion centres with plane-to-plane separations of 3.506 (3) and 3.563 (3) Å.

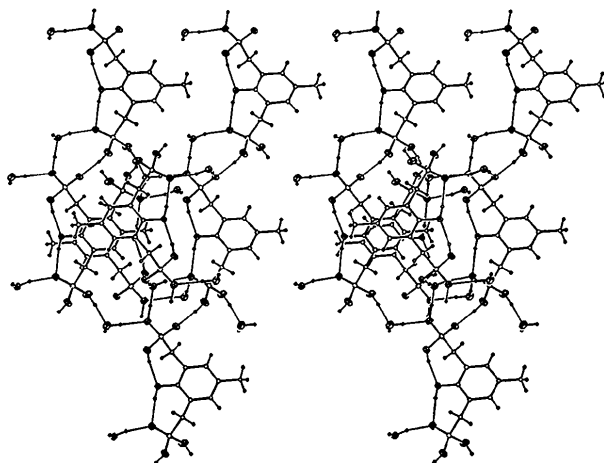


Fig. 2. A stereoview of part of the structure of the title compound showing the extensive three-dimensional hydrogen-bonding network. The thermal ellipsoids for the O atoms are drawn at the 35% probability level and those for the P, C and H atoms as spheres of arbitrary size.

Experimental

Crystal data

$C_9H_{14}O_7P_2 \cdot 2H_2O$
 $M_r = 332.18$
 Triclinic
 $P\bar{1}$
 $a = 7.7744$ (6) Å
 $b = 9.1759$ (6) Å
 $c = 10.4290$ (13) Å
 $\alpha = 74.986$ (8)°
 $\beta = 81.999$ (8)°
 $\gamma = 77.091$ (6)°
 $V = 697.8$ (1) Å³
 $Z = 2$

$D_x = 1.581$ Mg m⁻³

Mo $K\alpha$ radiation

$\lambda = 0.70930$ Å

Cell parameters from 25 reflections

$\theta = 5.50$ – 26.00°

$\mu = 0.34$ mm⁻¹

$T = 293$ K

Block

$0.45 \times 0.55 \times 0.60$ mm

Colourless

Data collection

Nonius CAD-4 diffractometer
 $\omega/2\theta$ scans
 Absorption correction: empirical (ψ scans)
 $T_{min} = 0.8461$, $T_{max} = 0.9226$
 3276 measured reflections
 3044 independent reflections

2823 observed reflections

$[I_{net} > 2.5\sigma(I_{net})]$

$R_{int} = 0.015$

$\theta_{max} = 26.93^\circ$

$h = -9 \rightarrow 9$

$k = 0 \rightarrow 11$

$l = -12 \rightarrow 13$

3 standard reflections

frequency: 120 min

intensity variation: < 2%

Refinement

Refinement on F
 Final $R = 0.045$
 $wR = 0.067$
 $S = 1.78$
 2823 reflections
 217 parameters
 $w = 1/[\sigma^2(F) + 0.0012F^2]$
 $(\Delta/\sigma)_{max} = 0.008$

$\Delta\rho_{max} = 0.45$ e Å⁻³

$\Delta\rho_{min} = -0.81$ e Å⁻³

Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, Table 2.2B)

Data collection: Enraf-Nonius CAD-4 software. Cell refinement: Enraf-Nonius CAD-4 software. Data reduction: NRC-VAX DATRD2 (Gabe, Le Page, Charland, Lee & White, 1989). Program(s) used to solve structure: NRCVAX SOLVER. Program(s) used to refine structure: NRCVAX LSTSQ. Molecular graphics: NRCVAX; ORTEPII (Johnson, 1976); PLUTON (Spek, 1990). Software used to prepare material for publication: NRC-VAX TABLES.

Table 1. Fractional atomic coordinates and isotropic or equivalent isotropic thermal parameters (Å²)

Hydroxyl H atoms HO(2)–HO(7) were refined isotropically. For non-H,
 $U_{eq} = (1/3)\sum_i\sum_j U_{ij}a_i^*a_j^*a_i \cdot a_j$.

| | <i>x</i> | <i>y</i> | <i>z</i> | U_{iso}/U_{eq} |
|-------|--------------|--------------|--------------|------------------|
| P(1) | 0.29342 (6) | 0.86084 (5) | 0.64081 (4) | 0.0243 (2) |
| P(2) | 0.28297 (5) | 0.60926 (5) | 1.29958 (4) | 0.0215 (2) |
| O(1) | 0.20324 (18) | 0.72921 (15) | 0.70960 (13) | 0.0318 (7) |
| O(2) | 0.14988 (20) | 1.00681 (18) | 0.60052 (14) | 0.0409 (7) |
| O(3) | 0.42084 (20) | 0.83429 (18) | 0.51722 (14) | 0.0386 (8) |
| O(4) | 0.38845 (20) | 0.51164 (16) | 1.20037 (14) | 0.0354 (7) |
| O(5) | 0.18930 (20) | 0.49778 (15) | 1.40866 (13) | 0.0337 (7) |
| O(6) | 0.40761 (16) | 0.67649 (14) | 1.35406 (12) | 0.0285 (6) |
| O(7) | 0.27791 (20) | 0.67981 (14) | 0.96962 (13) | 0.0305 (7) |
| OW(1) | 0.24738 (19) | 0.45878 (16) | 0.64213 (13) | 0.0312 (7) |
| OW(2) | 0.13954 (22) | 0.21257 (17) | 1.38623 (16) | 0.0404 (8) |

| | | | | |
|-------|--------------|--------------|--------------|-------------|
| C(1) | 0.26630 (21) | 0.83009 (17) | 0.97825 (16) | 0.0216 (7) |
| C(2) | 0.33520 (21) | 0.93646 (19) | 0.87369 (16) | 0.0222 (7) |
| C(3) | 0.31755 (22) | 1.08584 (19) | 0.88933 (16) | 0.0248 (8) |
| C(4) | 0.23836 (23) | 1.12924 (19) | 1.00489 (18) | 0.0262 (8) |
| C(5) | 0.17739 (22) | 1.01860 (19) | 1.10861 (16) | 0.0243 (7) |
| C(6) | 0.18936 (21) | 0.86878 (19) | 1.09728 (16) | 0.0220 (7) |
| C(7) | 0.43206 (22) | 0.89243 (20) | 0.74979 (16) | 0.0252 (8) |
| C(8) | 0.2195 (3) | 1.29339 (23) | 1.01610 (21) | 0.0374 (10) |
| C(9) | 0.11680 (22) | 0.75239 (19) | 1.21043 (16) | 0.0243 (7) |
| HO(2) | 0.166 (4) | 1.080 (3) | 0.527 (3) | 0.065 (9) |
| HO(3) | 0.407 (3) | 0.788 (3) | 0.456 (3) | 0.039 (6) |
| HO(4) | 0.371 (4) | 0.553 (3) | 1.125 (3) | 0.051 (8) |
| HO(5) | 0.226 (5) | 0.479 (4) | 1.515 (4) | 0.090 (12) |
| HO(7) | 0.251 (4) | 0.689 (3) | 0.891 (3) | 0.046 (7) |

Table 2. Geometric parameters (\AA , $^\circ$)

| | | | | |
|---|-------------|-----------------------------------|-------------|---------|
| P(1)—O(1) | 1.5015 (14) | C(1)—C(2) | 1.396 (2) | |
| P(1)—O(2) | 1.5450 (15) | C(1)—C(6) | 1.397 (2) | |
| P(1)—O(3) | 1.5496 (14) | C(2)—C(3) | 1.396 (2) | |
| P(1)—C(7) | 1.7857 (17) | C(2)—C(7) | 1.505 (2) | |
| P(2)—O(4) | 1.5688 (13) | C(3)—C(4) | 1.387 (2) | |
| P(2)—O(5) | 1.5395 (14) | C(4)—C(5) | 1.389 (3) | |
| P(2)—O(6) | 1.4981 (13) | C(4)—C(8) | 1.514 (3) | |
| P(2)—C(9) | 1.7893 (17) | C(5)—C(6) | 1.392 (2) | |
| O(7)—C(1) | 1.387 (2) | C(6)—C(9) | 1.511 (2) | |
| O(1)—P(1)—O(2) | 108.48 (8) | C(3)—C(4)—C(5) | 118.24 (15) | |
| O(1)—P(1)—O(3) | 114.68 (8) | C(4)—C(5)—C(6) | 121.71 (15) | |
| O(1)—P(1)—C(7) | 110.34 (8) | C(1)—C(6)—C(5) | 118.46 (15) | |
| O(2)—P(1)—O(3) | 109.81 (9) | C(1)—C(6)—C(9) | 121.11 (15) | |
| O(2)—P(1)—C(7) | 109.45 (9) | C(5)—C(6)—C(9) | 120.42 (15) | |
| O(3)—P(1)—C(7) | 103.96 (8) | P(1)—C(7)—C(2) | 114.48 (12) | |
| O(4)—P(2)—O(5) | 105.73 (8) | P(2)—C(9)—C(6) | 114.21 (11) | |
| O(4)—P(2)—O(6) | 109.86 (8) | P(1)—O(1)—HO(7) | 104.0 (8) | |
| O(4)—P(2)—C(9) | 107.22 (8) | P(1)—O(2)—HO(2) | 121.6 (19) | |
| O(5)—P(2)—O(6) | 112.57 (7) | P(1)—O(3)—HO(3) | 128.2 (17) | |
| O(5)—P(2)—C(9) | 108.10 (8) | P(2)—O(4)—HO(4) | 112.4 (19) | |
| O(6)—P(2)—C(9) | 112.98 (8) | P(2)—O(5)—HO(5) | 116.2 (18) | |
| O(7)—C(1)—C(2) | 121.04 (14) | P(2)—O(6)—HO(3) ⁱⁱ | 140.6 (9) | |
| O(7)—C(1)—C(6) | 117.43 (14) | C(1)—O(7)—HO(7) | 104.1 (18) | |
| C(2)—C(1)—C(6) | 121.49 (14) | C(1)—O(7)—HO(4) | 106.8 (9) | |
| C(1)—C(2)—C(3) | 117.75 (15) | HO(4)—O(7)—HO(7) | 148.5 (20) | |
| C(2)—C(3)—C(4) | 122.28 (15) | O(4)—P(2)—C(9)—C(6) | -65.1 (1) | |
| O(1)—P(1)—C(7)—C(2) | -62.1 (1) | O(5)—P(2)—C(9)—C(6) | -178.7 (2) | |
| O(3)—P(1)—C(7)—C(2) | 174.4 (2) | P(1)—O(1)—H(1W2) ⁱ | 107.3 (10) | |
| P(1)—O(1)—H(2W1) | 129.9 (8) | P(1)—O(1)—H(2W1) | 128.1 (12) | |
| HO(7)—O(1)—H(1W2) ⁱ | 104.7 (11) | HO(7)—O(1)—H(2W1) | 85.4 (13) | |
| H(1W2) ⁱ —O(1)—H(2W1) | 126.2 (9) | P(2)—O(5)—H(2W2) | 107.5 (20) | |
| P(2)—O(5)—H(2W2) | 122.0 (10) | HO(5)—O(5)—H(2W2) | 95.3 (13) | |
| P(2)—O(6)—H(1W1) ⁱⁱⁱ | 99.7 (25) | P(2)—O(6)—H(1W1) ⁱⁱⁱ | 118.8 (21) | |
| HO(3) ⁱⁱ —O(6)—H(1W1) ⁱⁱⁱ | 112.7 (25) | HO(5) ^{iv} —OW(1)—H(1W1) | 110.5 (22) | |
| HO(3) ⁱⁱ —O(6)—H(1W1) ⁱⁱⁱ | 110.5 (22) | HO(5) ^{iv} —OW(1)—H(2W1) | 114.5 (21) | |
| HO(5) ^{iv} —OW(1)—H(1W1) | 97 (3) | H(1W1)—OW(1)—H(2W1) | | |
| HO(5) ^{iv} —OW(1)—H(2W1) | | HO(2) ^v —OW(2)—H(1W2) | | |
| H(1W1)—OW(1)—H(2W1) | | HO(2) ^v —OW(2)—H(2W2) | | |
| HO(2) ^v —OW(2)—H(1W2) | | H(1W2)—OW(2)—H(2W2) | | |
| HO(2) ^v —OW(2)—H(2W2) | | | | |
| H(1W2)—OW(2)—H(2W2) | | | | |
| O—H...O | O—H | H...O | O...O | O—H...O |
| O(2)—HO(2)...OW(2) ^{vi} | 0.89 (3) | 1.65 (3) | 2.522 (2) | 164 (3) |
| O(3)—HO(3)...O(6) ^{iv} | 0.88 (3) | 1.66 (3) | 2.529 (2) | 170 (2) |
| O(4)—HO(4)...O(7) | 0.80 (3) | 1.88 (3) | 2.640 (2) | 164 (3) |
| O(5)—HO(5)...OW(1) ⁱⁱ | 1.14 (4) | 1.32 (4) | 2.458 (2) | 173 (3) |
| O(7)—HO(7)...O(1) | 0.85 (3) | 1.92 (3) | 2.753 (2) | 173 (3) |
| OW(1)—H(1W1)...O(6) ⁱⁱⁱ | 0.92 (3) | 1.77 (3) | 2.693 (2) | 172 (3) |
| OW(1)—H(2W1)...O(1) | 0.91 (3) | 1.79 (3) | 2.688 (2) | 168 (2) |
| OW(2)—H(1W2)...O(1) ⁱ | 0.93 (4) | 1.94 (4) | 2.866 (2) | 173 (3) |
| OW(2)—H(2W2)...O(5) | 0.95 (3) | 1.87 (3) | 2.801 (2) | 167 (3) |

Symmetry code: (i) $-x, 1-y, 2-z$; (ii) $x, y, 1+z$; (iii) $1-x, 1-y, 2-z$; (iv) $x, y, z-1$; (v) $x, y-1, 1+z$; (vi) $x, 1+y, z-1$.

The data were collected using a θ -scan width of $(0.8 + 0.35\tan\theta)^\circ$ and a θ -scan rate of $5.49^\circ \text{ min}^{-1}$ with background

counts for 5 s on each side of every scan. The absorption correction used nine strong low-angle (χ values close to 90°) reflections. All H atoms were visible in difference maps; the hydroxyl H atoms were refined isotropically while those attached to the C atoms were positioned geometrically (C—H 0.95 \AA) and included as riding atoms in the structure-factor calculations.

GF thanks NSERC Canada for Grants in Aid of Research.

Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55824 (22 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: BR1012]

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Acta Cryst. (1993). **C49**, 1026–1028

Structure of 4,6-Bis(trifluoromethyl)-2,2-bis[2,4,6-tris(trifluoromethyl)phenylthio]-1-thiabenzocyclobutene

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(Received 5 October 1992; accepted 26 November 1992)

Abstract

The structure of the title compound, 3,5-bis(trifluoromethyl)-8,8-bis[2,4,6-tris(trifluoromethyl)phenylthio]-7-thiabicyclo[4.2.0]octa-1,3,5-triene, is reported.