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) [P–O(5)] to 1.5688(13) Å [P–O(4)] with an average value of 1.5507(14) Å. 

Comment

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

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-ethanedi phosphonic acid (Peterson et al., 1977) and 1,3-propanedi phosphonic 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-
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(1)···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. 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.

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.
Table 2. Geometric parameters (Å, °)

<table>
<thead>
<tr>
<th>Bond</th>
<th>Length (Å)</th>
<th>Angle (°)</th>
</tr>
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<tbody>
<tr>
<td>O(1)...H(1W2)</td>
<td>1.93 (1)</td>
<td>112.2 (1)</td>
</tr>
<tr>
<td>O(1)...H(2W1)</td>
<td>2.02 (1)</td>
<td>114.0 (1)</td>
</tr>
<tr>
<td>O(1)...H(1W1)</td>
<td>1.99 (1)</td>
<td>110.4 (1)</td>
</tr>
<tr>
<td>O(1)...H(2W1)</td>
<td>2.02 (1)</td>
<td>114.0 (1)</td>
</tr>
</tbody>
</table>

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

The data were collected using a θ-scan width of (0.8 + 0.35tanθ)° and a θ-scan rate of 5.49° min⁻¹ with background counts for 5 s on each side of every scan. The absorption correction used nine strong low-angle (x 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 Å) and included as riding atoms in the structure-factor calculations.

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References


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

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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.

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