

4-Methoxyphenylphosphonic acid:  
reactivity of Lawesson's reagentM. Carla Aragoni,<sup>a</sup> Massimiliano Arca,<sup>a</sup> Alexander J. Blake,<sup>b\*</sup> Vito Lippolis,<sup>a</sup> Martin Schröder<sup>b</sup> and Claire Wilson<sup>b</sup><sup>a</sup>Dipartimento di Chimica Inorganica ed Analitica, Complesso Universitario di Monserrato, SS 554 Bivio per Sestu, 09042 Monserrato (CA), Italy, and <sup>b</sup>School of Chemistry, The University of Nottingham, University Park, Nottingham NG7 2RD, England

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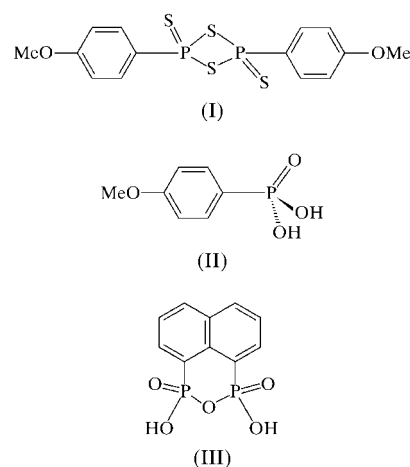
The title compound, C<sub>7</sub>H<sub>9</sub>O<sub>4</sub>P, obtained as a by-product of the reaction between Lawesson's reagent, (I), and CH<sub>3</sub>I, can be recognized as the final product of the S/O interchange reaction at the P atom of (I). Hydrogen bonds of type P—O—H···O=P link molecules into helical chains and form ten-membered hydrogen-bonded rings with the graph-set notation *R*<sub>3</sub><sup>2</sup>(10). Weaker intermolecular contacts between P—O and a phenyl H atom link the chains into a three-dimensional lattice. The parent benzenephosphonic acid [Weakley (1976). *Acta Cryst.* **B32**, 2889–2890] does not adopt an analogous structure, but its arsenic analogue [Shimada (1960). *Bull. Chem. Soc. Jpn.*, **33**, 301–304] does and can be regarded as isostructural. We rationalize these three structures in terms of their significant intermolecular interactions.

## Comment

It is widely recognized that 2,4-bis(4-methoxyphenyl)-2,4-dithio-1,3,2,4-dithiadiphosphetane [Lawesson's reagent, (I); Yde *et al.*, 1984; Scheibye *et al.*, 1978*a,b*, 1982; Shabana *et al.*, 1980; Pedersen *et al.*, 1978] is among the most effective thionating agents for organic molecules and plays a crucial role in the synthesis of phosphorus-containing rings (Cherkasov *et al.*, 1985; Foreman & Woollins, 2000). The wide range of applications, along with the variety of transformations and new products that can be made using it, make it one of the most widely used and versatile reagents. Recently, while exploring the high reactivity of (I) towards nucleophilic reagents, which is one of its most characteristic features, we obtained new phosphonodithioates and amidophosphonodithioates, and their metal complexes (Arca *et al.*, 1997; Aragoni *et al.*, 2000).

In an attempt to explore further the reactivity of Lawesson's reagent, 4-methoxyphenylphosphonic acid, (II), has been obtained as a by-product from the reaction of (I) with methyl iodide. Interestingly, a similar reaction between a structural analogue of (I) (*i.e.* 2,4-diphenyl-2,4-dithio-1,3,2,4-

dithiadiphosphetane) and methyl bromide in a sealed tube gives methyl phenylphosphonobromodithioate in almost quantitative yield (Von Fluk & Binder, 1967). Compound (II) can be considered the final desulfurated product in the S/O interchange reaction taking place at the P atom of (I) during thionation reactions. In this case, the O atoms probably come from traces of water in the solvent and/or from air during crystallization. A compound similar to (II) [structure (III) in the *Scheme*] was obtained from the reaction of 2,4-(naphthalene-1,8-diyl)-2,4-dithio-1,3,2,4-dithiadiphosphetane with ethylene glycol at 413 K (Kilian *et al.*, 1999). As in the structure of (II), the two P atoms are coordinated to four O atoms which come from ethylene glycol, but a P—O—P bridge is built into a six-membered C<sub>3</sub>P<sub>2</sub>O heterocycle due to the rigidity of the organyl backbone.



The intramolecular geometry of (II) is unexceptional and we note only the distinction between the two equivalent P—O single bonds of 1.552 (2) and 1.557 (2) Å and the P=O distance of 1.511 (2) Å (Fig. 1 and Table 1), and the typical coplanarity of the anisole methoxy substituent at C4 with its phenyl ring [*e.g.* C3—C4—O4—C4M −8.8 (5)°]. However, there are two unique, but geometrically similar, hydrogen bonds of type P—O—H···O=P (Fig. 2 and Table 2), which result in the formation of ten-membered hydrogen-bonded rings, each containing three P—OH donors and two P=O acceptors, giving a graph-set notation *R*<sub>3</sub><sup>2</sup>(10) (Bernstein *et al.*, 1995). Successive molecules are related by the operation of a 2<sub>1</sub> screw axis parallel to *a*. The overall helical structure along *a* is generated by repetition of these rings in that direction. In addition, there is a weak interaction between an H atom on the phenyl ring and the P—O related by the screw axis parallel to *b*, which links the chains into a three-dimensional lattice

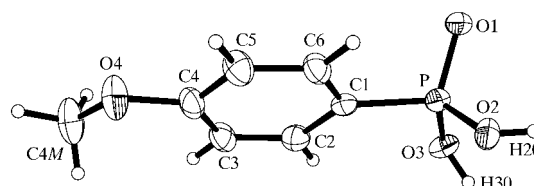


Figure 1

A view of the title molecule showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

[C3—H3 $\cdots$ O2( $-x$ ,  $-\frac{1}{2}+y$ ,  $\frac{3}{2}-z$ ): H $\cdots$ O 2.56 Å, C $\cdots$ O 3.465 (4) Å and C—H $\cdots$ O 159°].

There are very few structures of arylphosphonic acids in the literature; in fact, we have identified only three, two of which (Nieger *et al.*, 1999*a,b*) are dimethyl sulfoxide solvates, where the solvent molecules are involved in the hydrogen bonding, and which are, therefore, not comparable with the title compound. The only immediate comparison is with the parent benzenephosphonic acid, PhP(O)(OH)<sub>2</sub> (Weakley, 1976), in which hydrogen bonding produces puckered layers of molecules with only weak contacts between these layers. Each P—OH group participates in one hydrogen bond, but the O atom of the P=O group accepts two hydrogen bonds. In contrast to the title compound, the layers in PhP(O)(OH)<sub>2</sub> contain centrosymmetric pairs of molecules. The chains observed in the title compound are, therefore, more analogous to the structure of PhAs(O)(OH)<sub>2</sub> (Shimada, 1960) than to that of PhP(O)(OH)<sub>2</sub> (Weakley, 1976). Allowing for an extension of the *c* axis caused by the addition of the 4-methoxy substituent, the unit-cell dimensions are comparable [*a* = 4.70, *b* = 10.42 and *c* = 14.92 Å for PhAs(O)(OH)<sub>2</sub>] and the compounds adopt the same space group, *P*2<sub>1</sub>2<sub>1</sub>2<sub>1</sub>, and the same packing motif *via* hydrogen bonding. They can, therefore, be regarded as isostructural.

We have attempted to rationalize the relationship of the structures of (II), PhAs(O)(OH)<sub>2</sub> and PhP(O)(OH)<sub>2</sub>. In the last of these, any extension to the length of the molecule, whether by substitution at the 4-position of the phenyl ring or by exchanging As for P, would push the layers further apart, thereby destabilizing the structure. In contrast, the motif assumed by (II) and PhAs(O)(OH)<sub>2</sub> depends on strong hydrogen bonding along the *a* direction and weaker interac-

tions along *b*, but is rather tolerant of extension in the *c* direction as there are no important interactions along that axis. It would be interesting to explore the limits of this tolerance by increasing the length of the substituent on C4.

## Experimental

Lawesson's reagent, (I) (0.50 g, 1.2 mmol), was dissolved in toluene (60 ml, dried over molecular sieves) under a dinitrogen atmosphere, and then a fourfold stoichiometric excess of CH<sub>3</sub>I was added. The reaction mixture was refluxed for 5 h and the resulting solid was then filtered off. Compound (II) separated from the filtrate as white needles after two weeks standing in the open atmosphere. Elemental analysis (%), found (calculated for C<sub>7</sub>H<sub>9</sub>O<sub>4</sub>P): C 44.53 (44.69), H 4.71 (4.82).

### Crystal data

C <sub>7</sub> H <sub>9</sub> O <sub>4</sub> P	Mo K $\alpha$ radiation
<i>M</i> <sub>r</sub> = 188.11	Cell parameters from 1415 reflections
Orthorhombic, <i>P</i> 2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>	$\theta$ = 2.3–26.4°
<i>a</i> = 4.5819 (6) Å	$\mu$ = 0.30 mm <sup>−1</sup>
<i>b</i> = 10.0867 (13) Å	<i>T</i> = 150 (2) K
<i>c</i> = 18.087 (2) Å	Lath, colourless
<i>V</i> = 835.91 (18) Å <sup>3</sup>	0.31 × 0.07 × 0.04 mm
<i>Z</i> = 4	
<i>D</i> <sub>x</sub> = 1.495 Mg m <sup>−3</sup>	

### Data collection

Bruker SMART1000 CCD area-detector diffractometer	<i>R</i> <sub>int</sub> = 0.090
$\omega$ scans	$\theta_{\max}$ = 28.8°
5423 measured reflections	<i>h</i> = −5 → 6
1210 independent reflections	<i>k</i> = −11 → 13
939 reflections with <i>I</i> > 2 $\sigma$ ( <i>I</i> )	<i>l</i> = −24 → 22

### Refinement

Refinement on <i>F</i> <sup>2</sup>	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.042$	$w = 1/[\sigma^2(F_o^2) + (0.050P)^2]$
$wR(F^2) = 0.094$	where $P = (F_o^2 + 2F_c^2)/3$
<i>S</i> = 0.94	( $\Delta/\sigma$ ) <sub>max</sub> = 0.001
1210 reflections	$\Delta\rho_{\max} = 0.30 \text{ e \AA}^{-3}$
112 parameters	$\Delta\rho_{\min} = -0.31 \text{ e \AA}^{-3}$

**Table 1**

Selected geometric parameters (Å, °).

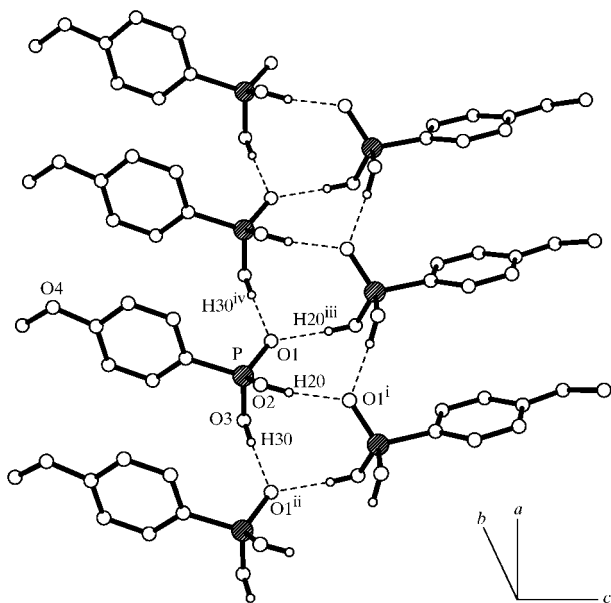
P—O1	1.511 (2)	P—O3	1.552 (2)
P—O2	1.557 (2)	P—C1	1.771 (3)
O1—P—O2	112.03 (13)	O1—P—C1	110.97 (14)
O1—P—O3	109.88 (13)	O2—P—C1	105.96 (14)
O2—P—O3	110.12 (12)	O3—P—C1	107.73 (15)
C3—C4—O4—C4 <i>M</i>	−8.8 (5)	C5—C4—O4—C4 <i>M</i>	171.2 (3)

**Table 2**

Hydrogen-bonding geometry (Å, °).

<i>D</i> —H $\cdots$ <i>A</i>	<i>D</i> —H	H $\cdots$ <i>A</i>	<i>D</i> $\cdots$ <i>A</i>	<i>D</i> —H $\cdots$ <i>A</i>
O2—H2O $\cdots$ O1 <sup>i</sup>	0.84	1.75	2.580 (3)	169
O3—H3O $\cdots$ O1 <sup>ii</sup>	0.84	1.72	2.550 (3)	169

Symmetry codes: (i)  $x - \frac{1}{2}, \frac{3}{2} - y, 2 - z$ ; (ii)  $x - 1, y, z$ .



**Figure 2**

A view of part of a helix of molecules in the title structure linked by hydrogen bonding. The helices run parallel to the crystallographic *a* axis. [Symmetry codes: (i)  $x - \frac{1}{2}, \frac{3}{2} - y, 2 - z$ ; (ii)  $x - 1, y, z$ ; (iii)  $x + \frac{1}{2}, \frac{3}{2} - y, 2 - z$ ; (iv)  $x + 1, y, z$ .]

A meaningful Flack (1983) parameter could not be determined; it refined to a value of 0.4 (2) and so Friedel opposites were merged for the final stages of the refinement. Hydroxyl and methyl H atoms were located from  $\Delta F$  syntheses and thereafter refined as part of rigid rotating groups, with  $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{O,C})$ ; aromatic H atoms were placed geometrically and then allowed to refine riding on their parent atoms, with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ . The following distance constraints were applied: O—H = 0.84, methyl C—H = 0.98 and aromatic C—H = 0.95 Å.

Data collection: *SMART* (Bruker, 1998); cell refinement: *SAINT* (Bruker, 1998); data reduction: *SAINT* and *SHELXTL* (Bruker, 1997); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXL97* and *PLATON* (Spek, 2001).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: NA1560). Services for accessing these data are described at the back of the journal.

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