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Key indicators

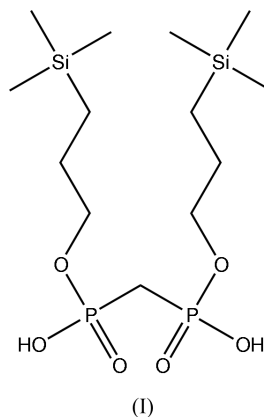
Single-crystal X-ray study
 $T = 100$ K
Mean $\sigma(\text{C}-\text{C}) = 0.005$ Å
 R factor = 0.061
 wR factor = 0.178
Data-to-parameter ratio = 23.2For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

Bis[3-(trimethylsilyl)propyl] methylenebisphosphonate

The title compound, also known as *P,P'*-di[3-(trimethylsilyl)-1-propyl] methylenebisphosphonic acid, $\text{H}_2\text{DTMSP}[\text{MBP}]$, $\text{C}_{13}\text{H}_{34}\text{O}_6\text{P}_2\text{Si}_2$, was crystallized from a neat oil. The compound exists in the solid state as a hydrogen-bonded infinite chain along the *a* axis.

Comment

Symmetrically substituted dialkyl esters of methylenebisphosphonic acid are effective solvent extraction reagents for the removal of actinide ions from acidic aqueous solutions into conventional organic solvents (Chiarizia *et al.*, 1996; Chiarizia & Herlinger, 2004). The aggregation and solvent-extraction behavior of the silyl-substituted partial esters closely mimics that of the analogous alkyl-substituted extractants, with the silyl-substituted compounds typically extracting metal ions two to three times more efficiently (McAlister *et al.*, 2001). Interestingly, the supercritical carbon dioxide (SCCO_2) solubility of $\text{H}_2\text{DTMSP}[\text{MBP}]$ is also significantly higher than that of the di-2-ethylhexyl extractant $\text{H}_2\text{DEH}[\text{MBP}]$, suggesting that the incorporation of silyl functionalities could be a useful method for increasing the SCCO_2 solubility of compounds (Herlinger *et al.*, 2003).



Recently, a high-yield synthetic route to symmetric dialkyl-substituted methylenebisphosphonic acids was reported (Stepinski & Herlinger, 2002). Owing to their low melting points, it has been difficult to obtain X-ray diffraction quality single crystals of these compounds, despite numerous attempts (Chiarizia *et al.*, 1996; Griffith-Dzielawa *et al.*, 2000; Stepinski & Herlinger, 2002). We report here the crystal structure of one of those esters, namely bis[3-(trimethylsilyl)propyl] methylenebisphosphonate, $\text{H}_2\text{DTMSP}[\text{MBP}]$, (I). The compound crystallizes with a single molecule in the asymmetric unit (Fig. 1). In the solid state, the molecules are linked together by

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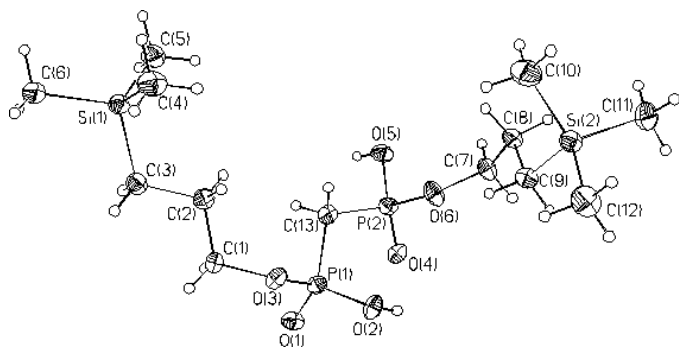


Figure 1
Displacement ellipsoid plot (50%) of the molecule of H₂DTMSP[MBP].

hydrogen bonds to form an infinite chain along the *a* axis (Fig. 2). Each molecule of H₂DTMSP[MBP] is bound to each of two neighboring molecules by two hydrogen bonds, with an average donor–acceptor distance of 2.506 Å (Fig. 3). In contrast, in the solution phase (toluene), H₂DTMSP[MBP] is found by vapor phase osmometry to exist primarily as a strongly hydrogen-bonded dimer (Herlinger *et al.*, 2003). Two of the possible proposed structures of this dimer (Barrans *et al.*, 1999) are shown in Fig. 4.

Experimental

The title compound was prepared according to the procedure of Stepinski & Herlinger (2002). Crystals suitable for study (m.p. 312–314 K) were obtained by slow growth at room temperature from a H₂DTMSP[MBP] sample initially isolated as an oil. Melting point, equivalent weight by titration, ¹H NMR spectra, and ³¹P NMR spectra are consistent with those previously reported (Stepinski & Herlinger, 2002; McAlister *et al.*, 2002).

Crystal data

C ₁₃ H ₃₄ O ₆ P ₂ Si ₂	Z = 2
<i>M_r</i> = 404.52	<i>D_x</i> = 1.236 Mg m ⁻³
Triclinic, <i>P</i> $\bar{1}$	Mo <i>K</i> α radiation
<i>a</i> = 6.534 (2) Å	Cell parameters from 3959 reflections
<i>b</i> = 11.130 (2) Å	θ = 1.8–29.4°
<i>c</i> = 16.325 (2) Å	μ = 0.33 mm ⁻¹
α = 100.64 (1)°	<i>T</i> = 100 (2) K
β = 100.25 (1)°	Prism, colorless
γ = 106.23 (2)°	0.36 × 0.13 × 0.02 mm
<i>V</i> = 1086.6 (4) Å ³	

Data collection

Oxford Diffraction Xcalibur3 diffractometer equipped with a CCD detector	4971 independent reflections
φ and ω scans	3556 reflections with <i>I</i> > 2σ(<i>I</i>)
Absorption correction: numerical (Clark & Reid, 1995)	<i>R</i> _{int} = 0.046
<i>T</i> _{min} = 0.888, <i>T</i> _{max} = 0.983	θ _{max} = 27.5°
10 850 measured reflections	<i>h</i> = -8 → 7
	<i>k</i> = -14 → 14
	<i>l</i> = -21 → 21

Refinement

Refinement on <i>F</i> ²	H-atom parameters constrained
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)] = 0.061	$w = 1/[\sigma^2(F_o^2) + (0.1P)^2]$
<i>wR</i> (<i>F</i> ²) = 0.178	where $P = (F_o^2 + 2F_c^2)/3$
<i>S</i> = 1.15	(Δ/σ) _{max} < 0.001
4971 reflections	$\Delta\rho$ _{max} = 1.00 e Å ⁻³
214 parameters	$\Delta\rho$ _{min} = -0.57 e Å ⁻³

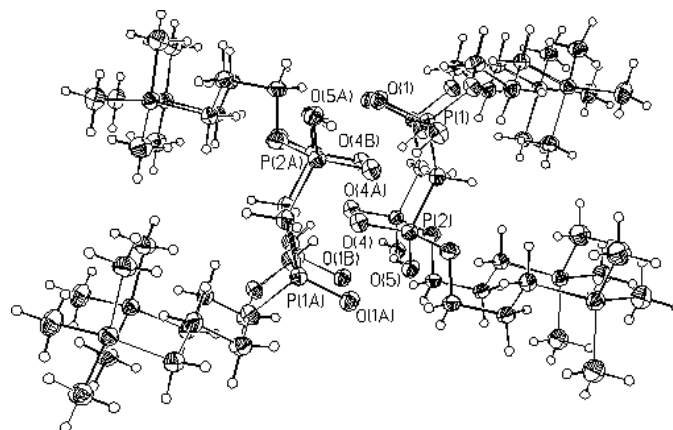


Figure 2
Extended structure of H₂DTMSP[MBP], viewed along the *a* axis.

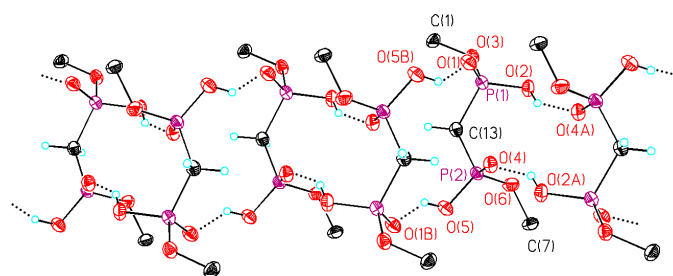


Figure 3
View of the extended structure of H₂DTMSP[MBP]. Each molecule is bound by four hydrogen bonds to two adjacent H₂DTMSP[MBP] molecules to form an infinite chain along the *a* axis. The bulk of the 3-(trimethylsilyl)propyl groups have been removed for clarity. Hydrogen bonds are shown as dashed lines. The view is approximately along [011].

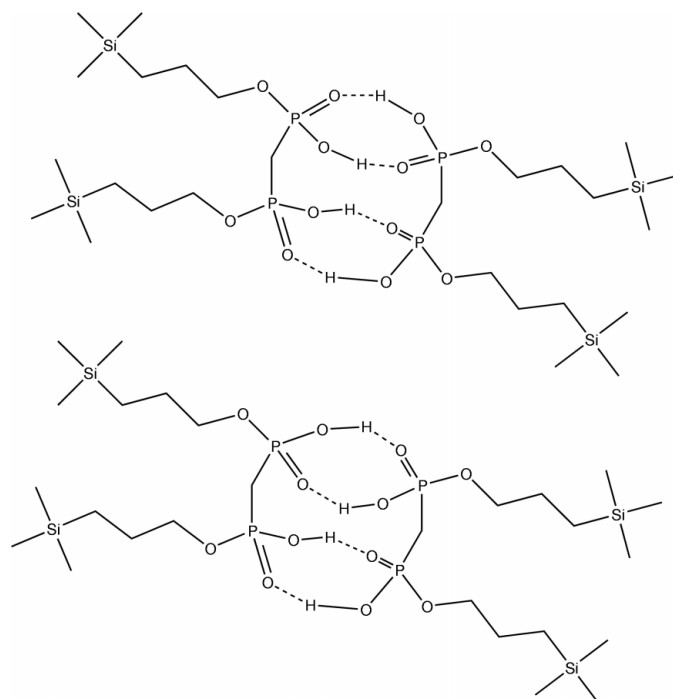


Figure 4
The proposed dimeric structures of H₂DTMSP[MBP] in toluene.

Table 1
Selected geometric parameters (Å, °).

O1–P1	1.475 (2)	O4–P2	1.481 (2)
O2–P1	1.539 (2)	O5–P2	1.543 (2)
O3–P1	1.572 (2)	O6–P2	1.559 (2)
O1–P1–O2	115.79 (12)	O4–P2–O5	113.86 (12)
O1–P1–O3	113.16 (12)	O4–P2–O6	116.29 (12)
O2–P1–O3	100.31 (11)	O5–P2–O6	104.70 (11)
O1–P1–C13	111.17 (13)	O4–P2–C13	111.41 (12)
O2–P1–C13	109.79 (12)	O5–P2–C13	108.38 (13)
O3–P1–C13	105.72 (12)	O6–P2–C13	101.16 (13)

Table 2
Hydrogen-bonding geometry (Å, °).

<i>D</i> –H... <i>A</i>	<i>D</i> –H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> –H... <i>A</i>
O2–H2...O4 ⁱ	0.82	1.78	2.518 (3)	148
O5–H5...O1 ⁱⁱ	0.82	1.83	2.493 (3)	137

Symmetry codes: (i) $-x, 1-y, -z$; (ii) $1-x, 1-y, -z$.

H atoms were positioned geometrically (C–H = 0.96–0.97 Å; O–H = 0.82 Å) and refined using a riding model, with fixed individual displacement parameters [$U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ for methylene H, $1.5U_{\text{eq}}(\text{C})$ for methyl H or $1.5U_{\text{eq}}(\text{O})$].

Data collection: *CrysAlisCCD* (Oxford Diffraction, 2004); cell refinement: *CrysAlisRED* (Oxford Diffraction, 2004); data reduction: *CrysAlisRED*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97*

(Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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