

Bis[3-(trimethylsilyl)propyl] ethylene-
bisphosphonate, H₂DTMSP[EBP]Craig C. McLauchlan,^{a*} Amanda J. Ziegler,^b Cyndi R.
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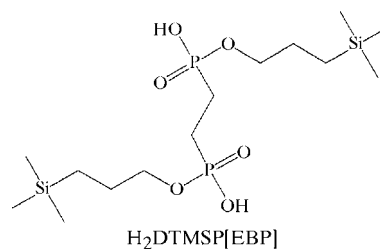
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The title compound (H₂DTMSP[EBP]), C₁₄H₃₆O₆P₂Si₂, was crystallized by the slow evaporation of a solution in a 20:1 mixture of pentane and acetone. The H₂DTMSP[EBP] molecule lies about an inversion center. In the solid state, the molecule exists in an *anti* configuration, with the molecular backbone C—C bond located on an inversion center. The compound exists in the solid state as hydrogen-bonded infinite sheets in the *ab* plane, unlike the methylene analogue, which exists as hydrogen-bonded infinite chains, demonstrating an ‘even–odd’ effect of the length of the backbone alkyl chain.

Comment

The title compound, H₂DTMSP[EBP], is the second member of a homologous series of symmetrically substituted alkylenebisphosphonic acids characterized by the P—(CH₂)_{*n*}—P molecular backbone (*n* = 1–6). This series of silyl-substituted partial esters was initially prepared and investigated as potential heavy metal ion extractants using supercritical

carbon dioxide, SC-CO₂, as the diluent (Griffith-Dzielawa *et al.*, 2000; McAlister *et al.*, 2001, 2002, 2004; Herlinger *et al.*, 2003). The trimethylsilylpropyl group, TMSP, was shown to be effective in solubilizing bisphosphonic acids in SC-CO₂, with the solubility of the TMSP partial esters showing a hydrocarbon-like even–odd effect that depends upon the number of —CH₂— groups in the alkylene chain. Earlier studies revealed the remarkable effect that the separation between the P atoms in the alkylene chain has on the aggregation, complexation and solvent-extraction properties of symmetrically substituted alkylenebisphosphonic acids (Herlinger *et al.*, 2003; Chiarizia & Herlinger, 2004).



The acid dissociation constants for the first three members (*n* = 1–3) of this series were determined in a 70:30 *w/w* methanol–water solvent by potentiometric titration and ³¹P NMR spectroscopy (Zalupski, Jensen *et al.*, 2006; Zalupski, Chiarizia *et al.*, 2006). The acid dissociation constants, *K*₁ and *K*₂, for these silyl-substituted bisphosphonic acids were found to follow a distance-dependent order of acid strength, due to the diminished inductive effect of the phosphonic acid groups upon each other as the chain length increases. The first member of the series, *P,P'*-bis[3-(trimethylsilyl)-1-propyl]-methylenebisphosphonic acid, H₂DTMSP[MBP], was found to be a stronger acid than H₂DTMSP[EBP], but the difference in acidity was not as great as expected (Zalupski, Jensen *et al.*, 2006; Zalupski, Chiarizia *et al.*, 2006). Our current interest in this series of TMSP-containing bisphosphonic acids derives from the effect that the separation between the P atoms should have on their structural chemistry. The compounds could potentially find use in the assembly of extended supra-molecular hydrogen-bonded networks, as activators in enzy-

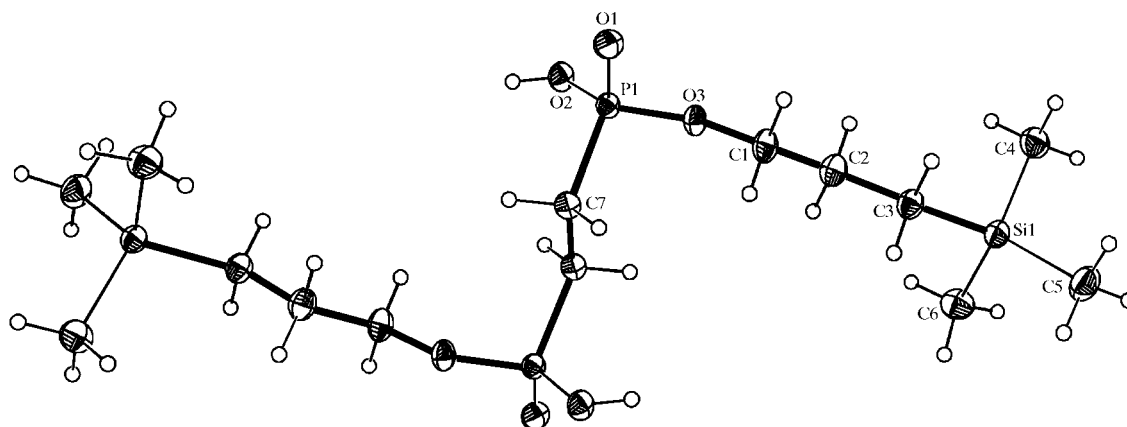


Figure 1

A plot of one molecule of H₂DTMSP[EBP], with the asymmetric unit labelled. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

matic reactions, or as models for enzyme inhibition and mechanism studies.

The title compound crystallizes with four molecules per unit cell and only one half molecule per asymmetric unit. In the solid state, the molecule exists in an *anti* configuration (Fig. 1), with the molecular backbone C–C bond located on an inversion center. The molecule exhibits herring-bone packing when viewed along the *a* axis. Each molecule of H₂DTMSP[EBP] is hydrogen bonded to four other molecules

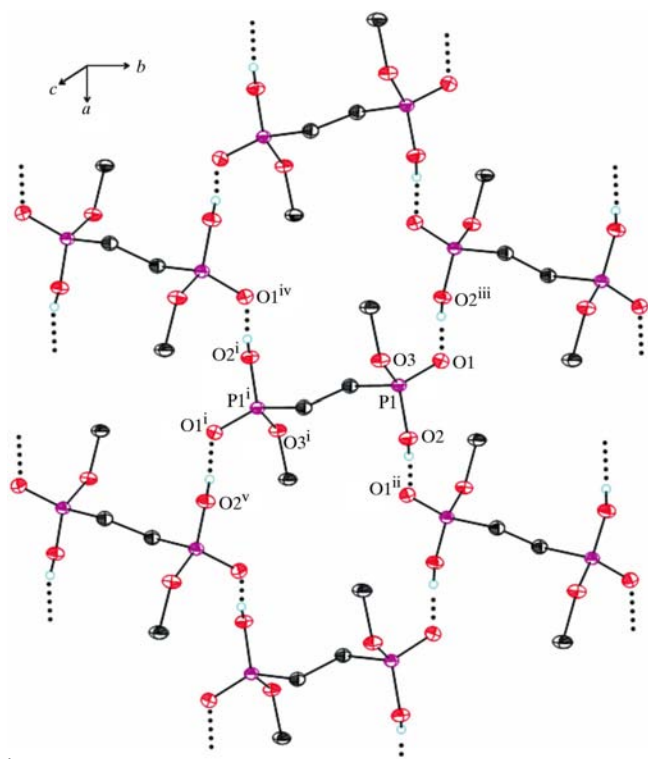


Figure 2

A view of the extended structure of H₂DTMSP[EBP] along the *c* axis. Each molecule is bound by four hydrogen bonds to four adjacent H₂DTMSP[EBP] molecules to form an infinite sheet in the *ab* plane. The bulk of the 3-(trimethylsilyl)propyl group has been omitted for clarity. Hydrogen bonds are shown as dashed lines. [Symmetry codes: (i) $2 - x, 1 - y, -z$; (ii) $\frac{1}{2} + x, \frac{3}{2} - y, -z$; (iii) $-\frac{1}{2} + x, \frac{3}{2} - y, -z$; (iv) $\frac{3}{2} - x, -\frac{1}{2} + y, z$; (v) $\frac{3}{2} - x, -\frac{1}{2} + y, z$.]

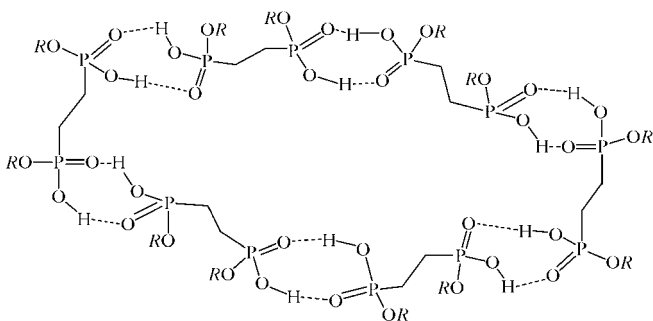


Figure 3

The proposed hexameric structure of H₂DTMSP[EBP] in toluene (*R* = TMSP = trimethylsilylpropyl). Data suggest a more spherical nature for the hexamer in solution, with the lipophilic TMSP groups extending away from a hydrophilic center created by the phosphonic acid groups pointing inward, but a flattened projection is shown for clarity.

through P=O...H–OP interactions to create infinite sheets in the *ab* plane. Each of these four hydrogen bonds is symmetry equivalent and the donor–acceptor distance is 2.4986 (16) Å. (Fig. 2)

In contrast, the crystal structure of the first member of this series, H₂DTMSP[MBP], reveals a quite different pattern of hydrogen bonding (McLauchlan *et al.*, 2004). In the solid state, the molecules of H₂DTMSP[MBP] are stitched together by hydrogen bonds to form an infinite chain along the *a* axis, with each molecule of H₂DTMSP[MBP] bound by two hydrogen bonds to two neighbouring molecules, with average donor–acceptor distances of 2.506 (3) Å. The P=O, P–OH and P–OR distances and angles are comparable for H₂DTMSP[EBP] and H₂DTMSP[MBP].

In aromatic solvents such as toluene, the silyl-substituted alkylenebisphosphonic acids H₂DTMSP[ABP] (*n* = 1–6) are strongly aggregated, exhibiting an even–odd effect as the number of –CH₂– bridging groups varies. Results from vapour-phase osmometry suggest that the odd members of the series are strongly hydrogen-bonded dimers, whereas the even members of the series are more highly aggregated, existing primarily as strongly hydrogen-bonded hexamers (Fig. 3). This effect is most likely due to the ‘zigzag’ (herring-bone-like) pattern adopted by the alkylene chain separating the P atoms. For the odd members of the series, the pattern directs the phosphonic acid P=O and POH groups to the same side of the alkylene chain, whereas for the even members of the series the phosphonic acid groups are on opposite sides of the chain. Thus, these two different orientations control the geometry of the hydrogen-bonded aggregates that can be formed (Chiarizia & Herlinger, 2004). In hydrogen-bonding solvents such as methanol, however, vapour-phase osmometry suggests that both the odd and even members of the series exist primarily as monomers. The even–odd effect appears to be reflected in the solid-state structures of the first two members of the series, though, with H₂DTMSP[MBP] forming infinite chains and H₂DTMSP[EBP] creating infinite sheets. Efforts to see if the same patterns emerge with the heavier members of the series are underway.

Experimental

The title compound, which was prepared by a previously described DCC-coupling procedure, was initially isolated as a colorless viscous oil in 96% yield (Griffith-Dzielawa *et al.*, 2000). X-ray diffraction quality crystals were obtained by very slow evaporation of a 20:1 (*v/v*) pentane–acetone solution at 253 K. The purity of the compound was established by potentiometric titration, ³¹P NMR spectroscopy and melting point. The equivalent weight was determined by titrating a weighed amount of the compound in a 2:1 (*v/v*) propan-2-ol–toluene solution with 0.1 M NaOH using an Orion EA 940 pH meter. The ³¹P NMR spectrum was obtained on a VXR 400 MHz spectrometer using CDCl₃ as the solvent. The melting point was measured using an Arthur H. Thomas, Hoover, capillary melting-point apparatus with a calibrated thermometer [m.p. 364 (1) K; literature value 363–365 K]. Equivalent weight, calculated: 209 g mol^{−1}; found: 212 g mol^{−1}. ³¹P NMR (CDCl₃, versus external 85% H₃PO₄): δ 31.44 (s) (literature value: 31.43).

Crystal data

$C_{14}H_{36}O_6P_2Si_2$ $Z = 4$
 $M_r = 418.55$ $D_x = 1.219 \text{ Mg m}^{-3}$
 Orthorhombic, *Pbca* Mo $K\alpha$ radiation
 $a = 7.6865 (3) \text{ \AA}$ $\mu = 0.32 \text{ mm}^{-1}$
 $b = 11.0294 (8) \text{ \AA}$ $T = 100 (2) \text{ K}$
 $c = 26.8912 (13) \text{ \AA}$ Prism, colorless
 $V = 2279.8 (2) \text{ \AA}^3$ $0.39 \times 0.24 \times 0.21 \text{ mm}$

Data collection

Oxford Xcalibur3 CCD area-detector diffractometer 10013 measured reflections
 φ and ω scans 2598 independent reflections
 Absorption correction: analytical 2091 reflections with $I > 2\sigma(I)$
 numerical absorption correction $R_{\text{int}} = 0.026$
 using a multifaceted crystal model based on expressions derived by Clark & Reid (1995) $\theta_{\text{max}} = 27.5^\circ$
 $T_{\text{min}} = 0.923$, $T_{\text{max}} = 0.948$

Refinement

Refinement on F^2 $w = 1/[\sigma^2(F_o^2) + (0.0448P)^2 + 0.9918P]$
 $R[F^2 > 2\sigma(F^2)] = 0.033$ where $P = (F_o^2 + 2F_c^2)/3$
 $wR(F^2) = 0.087$ $(\Delta/\sigma)_{\text{max}} = 0.001$
 $S = 1.05$ $\Delta\rho_{\text{max}} = 0.40 \text{ e \AA}^{-3}$
 2598 reflections $\Delta\rho_{\text{min}} = -0.28 \text{ e \AA}^{-3}$
 113 parameters
 H-atom parameters constrained

Table 1

Selected geometric parameters (\AA , $^\circ$).

O1—P1	1.4898 (12)	O3—P1	1.5687 (11)
O2—P1	1.5407 (11)		
O1—P1—O2	115.09 (7)	O1—P1—C7	110.91 (7)
O1—P1—O3	113.44 (7)	O2—P1—C7	108.49 (7)
O2—P1—O3	100.98 (6)	O3—P1—C7	107.25 (7)
C1—O3—P1—C7	−69.73 (12)	C7 ⁱ —C7—P1—O3	−50.88 (17)

Symmetry code: (i) $-x + 2, -y + 1, -z$.

Table 2

Hydrogen-bond geometry (\AA , $^\circ$).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O2—H2 \cdots O1 ⁱⁱ	0.82	1.68	2.4986 (16)	174

Symmetry code: (ii) $x + \frac{1}{2}, -y + \frac{3}{2}, -z$.

H atoms were refined using a riding model with fixed individual displacement parameters [$O-H = 0.82 \text{ \AA}$, methyl $C-H = 0.96 \text{ \AA}$ and methine $C-H = 0.97 \text{ \AA}$; $U_{\text{iso}}(\text{H}) = 1.2U_{\text{iso}}(\text{methine C}), 1.5U_{\text{iso}}(\text{methyl C})$ or $1.5U_{\text{iso}}(\text{O})$].

Data collection: *CrysAlis CCD* (Oxford, 2006); cell refinement: *CrysAlis RED* (Oxford, 2006); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXL97*; software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SQ3056). Services for accessing these data are described at the back of the journal.

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