

## Bis(tetraethylammonium) hydrogen-sulfate dihydrogenphosphate at 292 and 150 K

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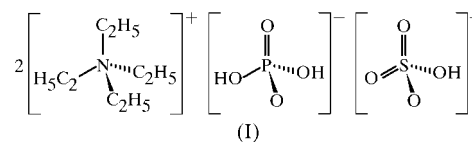
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The title compound,  $2\text{C}_8\text{H}_{20}\text{N}^+\cdot\text{HSO}_4^-\cdot\text{H}_2\text{PO}_4^-$ , was crystallized in a desiccator over  $\text{P}_4\text{O}_{10}$  from a water solution of stoichiometric amounts of tetraethylammonium hydroxide and sulfuric and phosphoric acids. The compound is deliquescent. The structure contains two symmetry-independent cations in nearly the same conformation, as well as two symmetry-independent anions, the central atoms of which are equally occupied by P and S. The anions are interconnected by short  $\text{O}\cdots\text{O}$  hydrogen bonds into one-dimensional chains. The distances and angles between some of the methyl or methylene groups and anionic O atoms indicate the presence of  $\text{C}\cdots\text{H}\cdots\text{O}$  hydrogen bonds. The structure was determined from data at 292 (2) and 150 (2) K. These room- and low-temperature structures are virtually the same, with the exception of the localization of the H atoms that participate in the symmetry-restricted  $\text{O}\cdots\text{O}$  hydrogen bonds. A differential scanning calorimetry experiment indicated no phase transition below the temperature at which the compound started to decompose (353 K), down to 93 K.

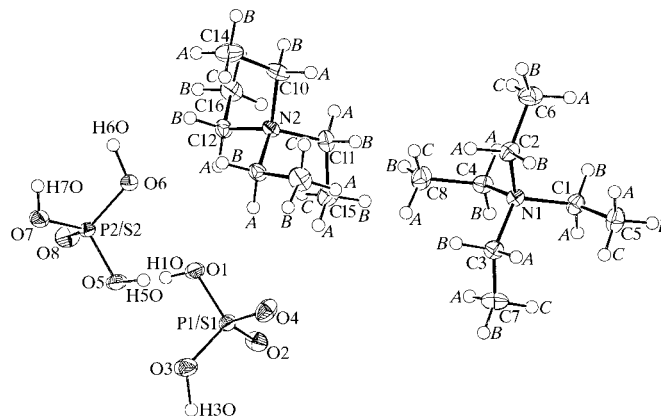
### Comment

To date, no structure of either tetraethylammonium dihydrogenphosphate or hydrogensulfate, or of tetraethylammonium with mixed dihydrogenphosphate–hydrogensulfate anions, has been studied [Cambridge Structural Database (CSD), April 2002 release; Allen, 2002]. Furthermore, until now, no structure of an organic compound with mixed dihydrogenphosphate–hydrogensulfate anions has been included in the CSD. Other reasons for the synthesis of the title compound, (I), were, firstly, to compare the architecture of the interbonded anions in compounds that contain large (*e.g.* tetraethylammonium, tetramethylammonium or  $\text{Cs}^+$ ) and small (*e.g.*  $\text{K}^+$ ) cations. Secondly, we wished to characterize plausible phase transitions in (I). For example, in

tetramethylammonium hydrogensulfate,  $[\text{N}(\text{CH}_3)_4]\text{HSO}_4$  (Speziali & Chapuis, 1991), three phase transitions were detected. In some cases, phase transitions at elevated temperatures can lead to superprotonic phases in related compounds. The above-mentioned  $[\text{N}(\text{CH}_3)_4]\text{HSO}_4$  compound can be given as such an example; this compound is reported to be a superprotonic conductor above 450 K (Blinc *et al.*, 1984). On the other hand,  $\text{CsHSO}_4\cdot\text{CsH}_2\text{PO}_4$  (Chisholm & Haile, 1999) can be given as an example of a superprotonic conductor with mixed dihydrogenphosphate–hydrogensulfate anions. The onset of the transition to the superprotonic phase in the latter compound takes place at 334 K (Chisholm & Haile, 1999). The ability for proton conduction depends, *inter alia*, on the structure of the anionic moiety as well as on the cation size. For example, while the above-mentioned  $\text{CsHSO}_4\cdot\text{CsH}_2\text{PO}_4$  is a superprotonic conductor, the closely related compound  $\text{KHSO}_4\cdot\text{KH}_2\text{PO}_4$  is not. The latter compound was found to be either strictly isostructural (Averbuch-Pouchot & Durif, 1980; Fábry *et al.*, 2002) with  $\text{CsHSO}_4\cdot\text{CsH}_2\text{PO}_4$  or to exist as a superstructure (Stiewe & Kemnitz, 2000).



The interatomic distances and angles in the cationic moieties of (I) are normal. Both tetraethylammonium cations (Fig. 1) have a similar conformation; the unit-weight r.m.s. fit on the non-H atoms of both molecules resulted in values of 0.024 and 0.031 Å for the room- and low-temperature data, respectively (Spek, 2002). Application of the instructions SAME and DELU with their default values (*SHELXL97*; Sheldrick, 1997) for both tetraethylammonium cations in the refinement of either the room- and low-temperature data resulted in almost the same coordinates and displacement parameters, within standard uncertainty, as in the corresponding refinements where these restraints were not applied.



**Figure 1**

A view of the independent ions of (I) at 150 K. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii and have labels corresponding to the atoms to which they are attached.

The very large tetraethylammonium cations are situated in cavities formed by the zigzag anionic chains. The cations are interconnected by short  $O \cdots O$  hydrogen bonds (Tables 2 and 4, and Fig. 2). In addition to the  $O-H \cdots O$  hydrogen bonds that are discussed below, there are a number of relatively short  $C-H \cdots O$  contacts. Some of these conform to the geometrical criteria for  $C-H \cdots O$  hydrogen bonds (Desiraju & Steiner, 1999). The latter contacts are also listed in Tables 2 and 4. It is of interest that the H atoms of the methylene groups tend to be closer to the O atoms than those of the methyl groups.

As stated above, the anions are interconnected by the hydrogen bonds, thus forming one-dimensional chains. These chains are parallel to [110] (Fig. 2) and are arranged in a hexagonal packing. The non-equivalent anions differ by their hydrogen bonding. There are two symmetry-restricted hydrogen bonds that connect a pair of anions with the central P2/S2 atom. A symmetry-free  $O2 \cdots O3$  hydrogen bond links another pair of symmetry-equivalent anions with the central P1/S1 atom. Another symmetry-free hydrogen bond,  $O1 \cdots O5$ , links both pairs of symmetry-non-equivalent anions. The sites that can be occupied by H atoms from the OH groups indicate, assuming that all the sites are fully occupied by the hydroxyl H atoms, that the ratio of the hydrogensulfate and dihydrogenphosphate anions is 1:1. It should be noted that stoichiometric considerations exclude a higher content of P than of S because there would then be no room left for the excess H atom.

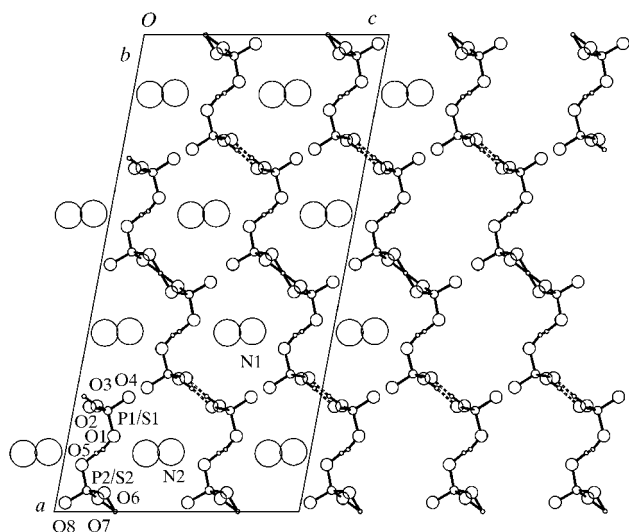
In order to determine the ratio of P to S, an electron microprobe analysis was carried out, using a Jeol JXA-733 (Jeol Ltd., Tokyo, Japan) with a Kevex Quantum energy-dispersive spectrometer [Delta Class Analyzer; Kevex

Instruments, San Carlos, California, USA (company no longer trading)]. The experiment was performed on a sample that had previously been dissolved and then dried, in order to create a thin film that was easier to handle than a hygroscopic bulk of crystals in the sample. The dry precipitate was covered with a graphite layer 30–40 nm thick. The energy of the impinging electron beam was 8 KeV, the current was 4 nA, and the scanned area was  $0.3 \times 0.2$  mm. The measurement was performed in five regions. The standards used were sphalerite ZnS (for S) and apatite (for P). The problem of the present analysis is that the light elements (H, C, N and O) are difficult to account for accurately. Therefore, the weight concentrations of P and S were calculated by the ZAF method (Philibert & Tixier, 1968), while the concentrations of the remaining elements that corresponded to the results of the structure analysis were kept fixed during the iterative calculation. The contents of P and S were found to be 1.04 (2) and 0.95 (2), respectively. If we estimate a total analytical error of  $\sim 5\%$  *rel.*, which is commonly accepted, we can conclude that the assumed ratio of 1:1 for P and S is valid, and is therefore in accordance with the highest number of H atoms that can be accommodated into the structural model. Thus, the electron microprobe analysis shows that the structure most probably contains an equal number of dihydrogenphosphate and hydrogensulfate ions.

Another observation is that the chains are composed of two different pairs of anions. This fact would rather support the idea that the dihydrogenphosphate and hydrogensulfate ions are unequally distributed between the independent anionic sites. In order to elucidate this hypothesis, several models with different substitutions of P and S were refined. However, the best indicators of refinement yielded an unrealistic model, where the central anionic atoms were composed of P only, while the worst result yielded a model with the central atoms composed of S only. Also, refinement of both models where one of the central atoms was either P or S resulted in refinement indicators comparable with those of the model with the central atom composed purely of S. The constrained refinement of occupation by P and S at both sites occupied by the central anionic atoms was unstable for both structure determinations at the two temperatures.

On the other hand, there are arguments that favour occupational disorder of the anions at both anionic sites. Firstly, the electron density of both central atoms is about the same. Moreover, the distances between the central atoms (P/S) and neighbouring O atoms correspond excellently to the P/S–O distances observed, for example, in  $KHSO_4 \cdot KH_2PO_4$  (Averbuch-Pouchot & Durif, 1980). Finally, the distribution of the H atoms is intimately dependent on the composition of the central atoms of the anionic pairs, *i.e.* whether the anions are dihydrogenphosphates or hydrogensulfates; according to the acid strengths, a dihydrogenphosphate anion should be a hydrogen-bond acceptor, while a hydrogensulfate should be a donor.

All the H atoms could be distinguished in the difference Fourier maps, although those maxima that were assigned to the hydroxyl H atoms were the least prominent, being as low



**Figure 2**

A view of the structure of (I) at 292 K, projected along the monoclinic *b* axis. The structure at 150 K is virtually the same, except for the disorder of atoms H6O and H7O, which are involved in the symmetry-restricted  $O6 \cdots O6$  and  $O7 \cdots O7$  hydrogen bonds, respectively. The tetraethylammonium cations are symbolized by large circles. The right-hand side of the picture shows the anionic chains only.

as  $\sim 0.3 \text{ e } \text{\AA}^{-3}$  (the H atoms were then fixed to the pertinent O atoms). It is noteworthy that, for the 150 K data, atoms H1O and H5O involved in the O1...O5 symmetry-unrestricted hydrogen bond were invariably found disordered, irrespective of whether the central anionic atoms were assumed to be P or S. The difference Fourier maps calculated by *JANA2000* (Petříček & Dušek, 2000) showed a build-up of saddle-like smeared electron density in the region of atoms O1 and O5, with two peaks. [*JANA2000* uses unweighted  $|F_{\text{obs}}|$ , in contrast to *SHELXL97* (Sheldrick, 1997).] This particular H-atom disorder concerning the H atoms on O1 and O5 serves as another piece of evidence that occupationally disordered dihydrogenphosphate and hydrogensulfate ions are present in both anionic sites of (I).

With regard to these facts, a model with equal distribution of P and S at each site was chosen. The H-atom positions, however, should be taken with some caution.

The hydroxyl atoms H6O and H7O are involved in the respective symmetry-restricted hydrogen bonds. The refinement based on the room-temperature data resulted in localization of these latter H atoms just at the mid-point between the O atoms, in contrast to the refinement based on the low-temperature data. This is in accordance with the observation of Wilson (2001), who studied an adduct of urea and phosphoric acid (1:1) by neutron diffraction between 150 and 335 K. He found that the H atom in a short symmetry-free hydrogen bond ( $\sim 2.40 \text{ \AA}$  long) tends, with increasing temperature, to move towards the centre of the hydrogen bond.

Although the hydrogen bond between atoms O2 and O3 is symmetry-unrestricted, the pertinent atom HO3 is closer to the centre of this hydrogen bond at room temperature. This can be compared with the structure of  $\text{K}_4(\text{HSeO}_4)_3(\text{H}_2\text{PO}_4)$ , which was determined from neutron diffraction data by Troyanov *et al.* (2000).

The main difference in the anionic arrangement between (I) and other compounds with known mixed phosphate-sulfate anions, such as  $\text{KHSO}_4 \cdot \text{KH}_2\text{PO}_4$  (Averbuch-Pouchot & Durif, 1980),  $\text{NH}_4\text{SO}_4 \cdot \text{NH}_4\text{H}_2\text{PO}_4$  (Averbuch-Pouchot, 1981),  $\text{CsHSO}_4 \cdot \text{CsH}_2\text{PO}_4$  (Chisholm & Haile, 1999),  $\alpha\text{-Cs}_3(\text{HSO}_4)_2 \cdot (\text{H}_2\text{PO}_4)$  (Haile *et al.*, 1995) and  $\beta\text{-Cs}_3(\text{HSO}_4)_2[\text{H}_{2-x}(\text{P}_{1-x}\text{S}_x)\text{O}_4]$  ( $x \sim 0.5$ ; Haile *et al.*, 1998; Haile & Klooster, 1999), is the existence of interbonded anion chains in the latter compounds, while in (I), these chains are one-dimensional.

Differential scanning calorimetry [PerkinElmer DSC 7; *Pyris Software* (PerkinElmer Instruments, 2001);  $m = 22 \text{ mg}$ , temperature interval 93–398 K, scanning rate  $10 \text{ K min}^{-1}$ ] showed an anomaly (hump) indicating the start of decomposition at 353 K. It did not show any reproducible anomaly indicating a structural phase transition.

## Experimental

Compound (I) was crystallized in a desiccator over  $\text{P}_4\text{O}_{10}$  from a water solution of stoichiometric amounts of tetraethylammonium hydroxide and sulfuric and phosphoric acids.

## Compound (I) at 292 (2) K

### Crystal data

$2\text{C}_8\text{H}_{20}\text{N}^+ \cdot \text{HSO}_4^- \cdot \text{H}_2\text{PO}_4^-$   
 $M_r = 454.56$   
 Monoclinic,  $C2/c$   
 $a = 28.0787 (6) \text{ \AA}$   
 $b = 11.8671 (2) \text{ \AA}$   
 $c = 14.1533 (2) \text{ \AA}$   
 $\beta = 100.7390 (10)^\circ$   
 $V = 4633.46 (14) \text{ \AA}^3$   
 $Z = 8$

$D_x = 1.303 \text{ Mg m}^{-3}$   
 Mo  $K\alpha$  radiation  
 Cell parameters from 20 021 reflections  
 $\theta = 1.0\text{--}27.5^\circ$   
 $\mu = 0.25 \text{ mm}^{-1}$   
 $T = 292 (2) \text{ K}$   
 Plate, colourless  
 $0.40 \times 0.20 \times 0.05 \text{ mm}$

### Data collection

Nonius KappaCCD area-detector diffractometer  
 $\omega$  scans  
 17 929 measured reflections  
 5298 independent reflections  
 4578 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.029$   
 $\theta_{\text{max}} = 27.5^\circ$   
 $h = -36 \rightarrow 36$   
 $k = -15 \rightarrow 15$   
 $l = -18 \rightarrow 18$

### Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.042$   
 $wR(F^2) = 0.123$   
 $S = 1.10$   
 5298 reflections  
 262 parameters  
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0535P)^2 + 3.5454P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\text{max}} = 0.001$   
 $\Delta\rho_{\text{max}} = 0.32 \text{ e } \text{\AA}^{-3}$   
 $\Delta\rho_{\text{min}} = -0.34 \text{ e } \text{\AA}^{-3}$   
 Extinction correction: *SHELXL97* (Sheldrick, 1997)  
 Extinction coefficient: 0.0024 (5)

**Table 1**

Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ ) for (I) at 292 (2) K.

P1—O4	1.4559 (14)	P2—O8	1.4528 (14)
P1—O2	1.5123 (13)	P2—O5	1.5140 (12)
P1—O1	1.5145 (12)	P2—O7	1.5201 (13)
P1—O3	1.5210 (14)	P2—O6	1.5247 (12)
O4—P1—O2	112.59 (9)	O8—P2—O5	109.97 (8)
O4—P1—O1	109.16 (8)	O8—P2—O7	112.02 (9)
O2—P1—O1	107.55 (8)	O5—P2—O7	107.26 (8)
O4—P1—O3	112.57 (10)	O8—P2—O6	112.80 (9)
O2—P1—O3	107.99 (7)	O5—P2—O6	106.54 (7)
O1—P1—O3	106.69 (8)	O7—P2—O6	107.96 (7)

**Table 2**

Hydrogen-bonding geometry ( $\text{\AA}$ ,  $^\circ$ ) for (I) at 292 (2) K.

$D\text{---}H\text{---}A$	$D\text{---}H$	$H\text{---}A$	$D\text{---}A$	$D\text{---}H\text{---}A$
O3—H3O...O2 <sup>i</sup>	1.22	1.30	2.5125 (18)	178
O1—H1O...O5	1.13	1.44	2.5636 (19)	174
O5—H5O...O1	1.10	1.46	2.5636 (19)	175
O6—H6O...O6 <sup>ii</sup>	1.26	1.26	2.518 (2)	179
O7—H7O...O7 <sup>ii</sup>	1.26	1.26	2.513 (2)	173
C1—H1A...O5 <sup>iii</sup>	0.97	2.53	3.431 (2)	155
C2—H2A...O3 <sup>iv</sup>	0.97	2.55	3.358 (2)	140
C4—H4A...O4 <sup>v</sup>	0.97	2.45	3.344 (2)	154
C9—H9A...O4	0.97	2.54	3.428 (2)	152
C11—H11B...O2 <sup>v</sup>	0.97	2.53	3.467 (2)	163

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

Compound (I) at 150 (2) K

Crystal data

2C<sub>8</sub>H<sub>20</sub>N<sup>+</sup>·HSO<sub>4</sub><sup>-</sup>·H<sub>2</sub>PO<sub>4</sub><sup>-</sup>  
*M<sub>r</sub>* = 454.56  
 Monoclinic, C2/c  
*a* = 27.9460 (4) Å  
*b* = 11.7480 (2) Å  
*c* = 14.0590 (2) Å  
 β = 100.971 (9)°  
*V* = 4531.35 (18) Å<sup>3</sup>  
*Z* = 8  
*D<sub>x</sub>* = 1.333 Mg m<sup>-3</sup>  
 Mo Kα radiation  
 Cell parameters from 52 330 reflections  
 θ = 1.0–30.0°  
 μ = 0.26 mm<sup>-1</sup>  
*T* = 150 (2) K  
 Plate, colourless  
 0.40 × 0.20 × 0.05 mm

Data collection

Nonius KappaCCD area-detector diffractometer  
 ω scans  
 21 366 measured reflections  
 6641 independent reflections  
 5957 reflections with *I* > 2σ(*I*)  
*R<sub>int</sub>* = 0.032  
 θ<sub>max</sub> = 30.1°  
*h* = -38 → 39  
*k* = -16 → 16  
*l* = -19 → 19

Refinement

Refinement on *F*<sup>2</sup>  
*R*[*F*<sup>2</sup> > 2σ(*F*<sup>2</sup>)] = 0.041  
*wR*(*F*<sup>2</sup>) = 0.113  
*S* = 1.17  
 6641 reflections  
 262 parameters  
 H-atom parameters constrained  
*w* = 1/[σ<sup>2</sup>(*F<sub>o</sub>*<sup>2</sup>) + (0.0418*P*)<sup>2</sup> + 4.9683*P*]  
 where *P* = (*F<sub>o</sub>*<sup>2</sup> + 2*F<sub>c</sub>*<sup>2</sup>)/3  
 (Δ/σ)<sub>max</sub> = 0.002  
 Δρ<sub>max</sub> = 0.42 e Å<sup>-3</sup>  
 Δρ<sub>min</sub> = -0.47 e Å<sup>-3</sup>  
 Extinction correction: *SHELXL97*  
 Extinction coefficient: 0.0041 (3)

Table 3

Selected geometric parameters (Å, °) for (I) at 150 (2) K.

P1—O4	1.4636 (11)	P2—O8	1.4653 (11)
P1—O2	1.5204 (11)	P2—O5	1.5207 (10)
P1—O1	1.5235 (10)	P2—O7	1.5268 (11)
P1—O3	1.5253 (12)	P2—O6	1.5298 (10)
O4—P1—O2	112.65 (7)	O8—P2—O5	110.11 (6)
O4—P1—O1	109.26 (6)	O8—P2—O7	111.83 (7)
O2—P1—O1	107.40 (6)	O5—P2—O7	107.38 (6)
O4—P1—O3	112.41 (7)	O8—P2—O6	112.76 (7)
O2—P1—O3	108.00 (6)	O5—P2—O6	106.47 (6)
O1—P1—O3	106.85 (6)	O7—P2—O6	108.01 (6)

Table 4

Hydrogen-bonding geometry (Å, °) for (I) at 150 (2) K.

<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>
O3—H3O...O2 <sup>i</sup>	1.09	1.42	2.5132 (15)	175
O1—H1O...O5	0.80	1.80	2.5635 (15)	158
O5—H5O...O1	0.90	1.66	2.5635 (15)	175
O6—H6O...O6 <sup>ii</sup>	0.99	1.53	2.5107 (19)	177
O7—H7O...O7 <sup>ii</sup>	0.84	1.70	2.527 (2)	169
C1—H1A...O5 <sup>iii</sup>	0.97	2.50	3.4087 (17)	155
C1—H1A...O8 <sup>iii</sup>	0.97	2.57	3.3590 (18)	139
C2—H2A...O1 <sup>iv</sup>	0.97	2.56	3.4204 (19)	147
C2—H2A...O3 <sup>iv</sup>	0.97	2.49	3.3109 (18)	142
C4—H4A...O4 <sup>v</sup>	0.97	2.39	3.2774 (17)	153
C7—H7B...O8 <sup>vi</sup>	0.96	2.58	3.445 (2)	150
C8—H8B...O2 <sup>v</sup>	0.96	2.60	3.4142 (19)	142
C9—H9A...O4	0.97	2.51	3.3925 (18)	151
C11—H11B...O2 <sup>v</sup>	0.97	2.51	3.4491 (18)	164

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

Atoms P1/S1 and P2/S2 were assumed to occupy the same respective sites and to have the same respective anisotropic displacement parameters [instructions EXYZ and EADP in *SHELXL97* (Sheldrick, 1997)]. The occupancy of each S and P atom

was considered to be the same (0.5). The methylene and methyl H atoms were constrained by instructions AFIX23 and AFIX137 (*SHELXL97*), respectively. The anionic H atoms were constrained by instruction AFIX3 (*SHELXL97*). This means that all the H atoms were assumed to ride on the atoms to which they were attached. In addition, the methyl groups were assumed to rotate about the C—C bonds and to maintain tetrahedral angles. The methylene geometry was also idealized with the same C—H distances. The isotropic displacement parameters of the H atoms were assumed to be 1.2 times those of the pertinent C or O atom for methylene and anionic H atoms, respectively, and 1.5 times those of the parent C atom for methyl H atoms.

At both temperatures, data collection: *COLLECT* (Nonius, 1997–2000); cell refinement: *HKL SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *HKL DENZO* (Otwinowski & Minor, 1997) and *SCALEPACK*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPIII* (Burnett & Johnson, 1996) at 292 K and *PLATON* (Spek, 2002) at 150 K.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1608). Services for accessing these data are described at the back of the journal.

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