N1	0.1231 (2)	0.8721 (3)	−0.0260 (15)	0.055 (2)
C1	0.2117 (2)	0.8213 (3)	0.4356 (14)	0.0341 (13)
C2	0.1671 (2)	0.8031 (3)	0.3615 (13)	0.0325 (14)
C3	0.1441 (2)	0.7443 (3)	0.4937 (14)	0.0348 (14)
C4	0.2135 (2)	0.7227 (3)	0.7593 (14)	0.0318 (13)
C5	0.2344 (2)	0.7785 (3)	0.6379 (14)	0.0342 (13)
C6	0.1424 (2)	0.8410 (3)	0.1507 (16)	0.043 (2)
C7	0.2921 (2)	0.8986 (4)	0.427 (2)	0.064 (2)
C8	0.2329 (2)	0.6732 (3)	0.9693 (14)	0.0301 (13)
C9	0.2798 (2)	0.6743 (3)	1.0243 (15)	0.045 (2)
C10	0.2973 (2)	0.6272 (3)	1.2202 (16)	0.048 (2)
C11	0.2709 (2)	0.5792 (3)	1.3627 (16)	0.044 (2)
C12	0.2242 (2)	0.5794 (3)	1.3116 (16)	0.0356 (14)
C13	0.2053 (2)	0.6245 (3)	1.1130 (13)	0.0318 (13)
C14	0.1509 (2)	0.5288 (3)	1.4193 (18)	0.049 (2)
S1′	0.48504 (5)	0.09602 (8)	0.2945 (5)	0.0479 (4)
O1′	0.64227 (13)	0.2002 (2)	0.3789 (12)	0.0560 (14)
O2′	0.58904 (13)	0.2474 (2)	0.6514 (10)	0.0392 (10)
O3′	0.61100 (15)	0.4330 (2)	1.3378 (13)	0.0596 (14)
N1′	0.5901 (2)	0.0686 (3)	−0.0737 (14)	0.0516 (15)
C1′	0.5239 (2)	0.1575 (3)	0.4300 (14)	0.0326 (13)
C2′	0.5675 (2)	0.1547 (3)	0.3286 (14)	0.0328 (13)
C3′	0.6026 (2)	0.1997 (3)	0.4428 (15)	0.0401 (15)
C4′	0.5450 (2)	0.2531 (3)	0.7416 (14)	0.0354 (14)
C5′	0.5125 (2)	0.2088 (3)	0.6410 (14)	0.0336 (13)
C6′	0.5801 (2)	0.1068 (3)	0.1088 (16)	0.0370 (14)
C7′	0.4341 (2)	0.1153 (3)	0.4831 (17)	0.050 (2)
C8′	0.5391 (2)	0.3104 (3)	0.9556 (14)	0.0344 (14)
C9′	0.4958 (2)	0.3295 (3)	1.0501 (14)	0.040 (2)
C10′	0.4910 (2)	0.3845 (3)	1.2446 (17)	0.048 (2)
C11′	0.5288 (2)	0.4212 (3)	1.3459 (17)	0.049 (2)
C12′	0.5711 (2)	0.4016 (3)	1.2553 (16)	0.042 (2)
C13′	0.5763 (2)	0.3462 (3)	1.0565 (14)	0.0375 (15)
C14′	0.6082 (2)	0.4942 (3)	1.5246 (19)	0.062 (2)

Table 2. *Selected geometric parameters (Å, °)*

S1—C1	1.731 (6)	S1′—C1′	1.738 (6)
S1—C7	1.788 (7)	S1′—C7′	1.774 (6)
O1—C3	1.203 (7)	O1′—C3′	1.201 (7)
O2—C4	1.375 (6)	O2′—C4′	1.364 (6)
O2—C3	1.385 (7)	O2′—C3′	1.382 (8)
O3—C12	1.379 (7)	O3′—C12′	1.364 (7)
O3—C14	1.433 (7)	O3′—C14′	1.442 (8)
N1—C6	1.158 (8)	N1′—C6′	1.152 (8)
C4—C8	1.465 (8)	C4′—C8′	1.478 (8)
C1—S1—C7	103.6 (3)	C1′—S1′—C7′	103.7 (3)
C4—O2—C3	122.5 (4)	C4′—O2′—C3′	122.9 (5)
C12—O3—C14	117.3 (5)	C12′—O3′—C14′	117.6 (5)
C2—C1—S1	118.4 (5)	C2′—C1′—S1′	117.5 (5)
C1—C2—C6	122.2 (5)	C1′—C2′—C6′	121.5 (5)
N1—C6—C2	178.3 (7)	N1′—C6′—C2′	178.8 (7)
C7—S1—C1—C2	−179.9 (5)	C7′—S1′—C1′—C2′	178.5 (5)
C5—C1—C2—C6	−177.0 (6)	C5′—C1′—C2′—C6′	−177.0 (5)
O2—C4—C8—C9	170.1 (6)	O2′—C4′—C8′—C9′	173.1 (5)
C14—O3—C12—C11	180.0 (6)	C14′—O3′—C12′—C11′	−3.3 (11)

The temperature of the crystal was controlled using an Oxford Cryosystem Cryostream Cooler (Cosier & Glazer, 1986). Refinement was on F^2 for all reflections except for 12 with very negative F^2 or flagged for potential systematic errors. H atoms were added at calculated positions and refined using a riding model. Anisotropic displacement parameters were used for all non-H atoms; H atoms were given isotropic displacement parameters equal to 1.2 (or 1.5 for methyl H atoms) times the equivalent isotropic displacement parameter of the atom to which they were attached.

Data collection: Siemens *P3R3* system. Cell refinement: Siemens *P3R3* system. Data reduction: *SHELXTL-Plus* (Sheldrick, 1990). Program(s) used to solve structure: *SHELXTL-Plus*. Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *SHELXTL-Plus*. Software used to prepare material for publication: *SHELXL93*.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, complete geometry and torsion angles have been deposited with the IUCr (Reference: BM1028). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Disodium D-3-Phosphoglycerate (a Reinvestigation at 80 K) and Bis(cyclohexylammonium) D-3-Phosphoglycerate Dihydrate at 85 K

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Abstract

The structure of the D-3-phosphoglycerate dianion in the disodium salt $2Na^+.C_3H_5O_7P^{2-}$ [$Na_2H(3\text{-}PGA)$, (I)] and the hydrated bis(cyclohexylammonium) salt $2C_6H_{14}N^+.C_3H_5O_7P^{2-}.2H_2O$ [$(CHA)_2H(3\text{-}PGA).2H_2O$, (II), where $H(3\text{-}PGA) = {}^-HO_3POCH_2CH(OH)COO^-$, $CHA = C_6H_{11}NH_3^+$] has been determined by X-ray analyses at 80 and 85 K, respectively. A room-temperature

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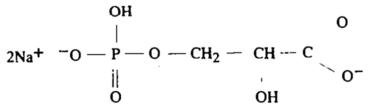
study of (I) was previously described by Fewster & Fenn [*Acta Cryst.* (1982), **B38**, 282–284]. The dianions in (I) and (II) differ in the orientations of the carboxylate and phosphate groups with respect to the carbon backbone. The P—O ester bond lengths are 1.606 (2) and 1.608 (2) Å in (I) and (II), respectively. The crystal structure of (I) is governed by Na···O interactions. The two crystallographically independent Na$^+$ cations are seven- and six-coordinate, respectively, with Na···O distances in the range 2.275 (2)–2.822 (2) Å. The crystal structure of (II) is stabilized by hydrogen bonds which utilize all N and O atoms.

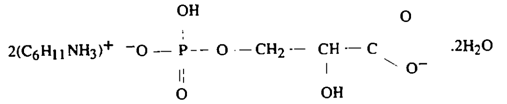
Comment

As part of our program aiming to explain how chemical environment and pH may influence the geometry of phosphoglycerates (Lis & Jerzykiewicz, 1993; Jerzykiewicz & Lis, 1994), we have recently determined crystal structures containing D-3-phosphoglycerate monoanions (Lis & Jerzykiewicz, 1995). We now present two crystal structures which contain the D-3-phosphoglycerate dianion, namely those of Na_2H(3-PGA), (I), and $(CHA)_2H$(3-PGA)$.2H_2O$, (II). Although the crystal structure of (I) was reported earlier (Fewster & Fenn, 1982), the results were not sufficiently accurate for the comparisons we wished to make [$R = 0.063$ for 1146 reflections and σ(C—C) = 0.008 Å], so we decided to reinvestigate this structure at low temperature.



$$2Na^+\ {}^-O-\overset{OH}{\underset{O}{P}}-O-CH_2-\underset{OH}{CH}-C\genfrac{}{}{0pt}{}{O}{O^-}$$

(I)



$$2(C_6H_{11}NH_3)^+\ {}^-O-\overset{OH}{\underset{O}{P}}-O-CH_2-\underset{OH}{CH}-C\genfrac{}{}{0pt}{}{O}{O^-}\ .2H_2O$$

(II)

Crystals of (I) are composed of D-3-phosphoglycerate dianions (Fig. 1) and Na$^+$ cations. Parameter e.s.d.'s are smaller than those of the previous determination (Fewster & Fenn, 1982) by about a factor of four. The new refinement reveals a slight elongation of almost all bonds by *ca* 3σ. These differences in bond lengths (of *ca* 0.02–0.03 Å) may reflect the smaller librational errors in the low-temperature analysis. Some interesting features of the crystal packing in (I) not discussed by Fewster & Fenn (1982) are worthy of mention. The crystal structure is dominated by Na···O interactions (Fig. 2). The Na$^+$ ions, which are seven- [Na(1)] or six-coordinate [Na(2)], are aggregated in layers. The D-3-phosphoglycerate anions surrounding them form bilayers which extend in the (010) planes. Each dianion in the structure is coordinated by seven Na$^+$ cations. The double layers composed of the anions and Na$^+$ cations are then interconnected through hydrogen bonds (Table 3). Moreover, the O(2) hydroxyl group takes part as donor in a bifurcated hydrogen bond, which incorporates an intramolecular hydrogen bridge [O(2)—H(20)···O(1)].

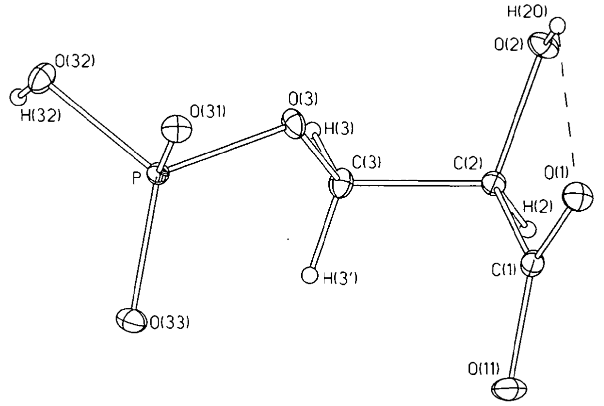


Fig. 1. The structure and numbering scheme of the 3-D-phosphoglycerate dianion in (I). The dashed line shows the intramolecular hydrogen bonding. Displacement ellipsoids are plotted at the 50% probability level.

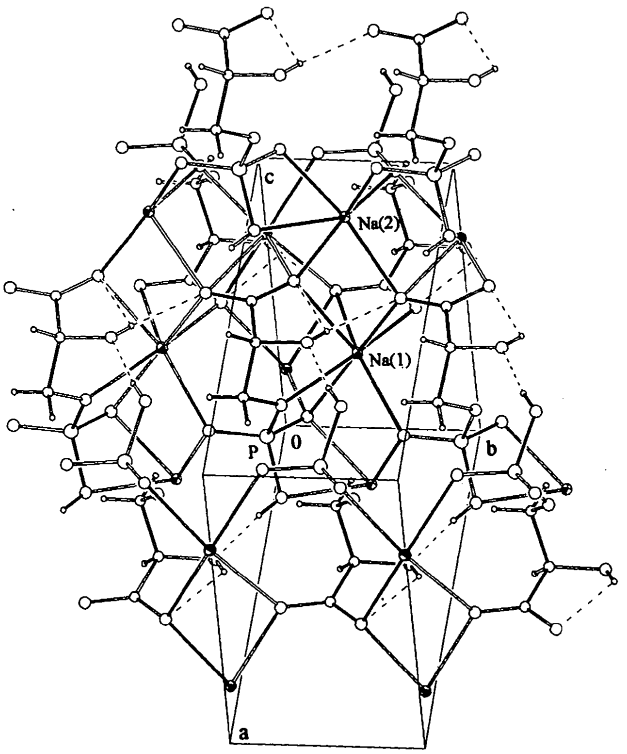


Fig. 2. The packing arrangement in the crystal of (I).

Crystals of (II) contain D-3-phosphoglycerate dianions (Fig. 3), two crystallographically independent cyclohexylammonium cations and water of hydration. The orientation of the carboxylate group relative to the carbon backbone in (II), described by the O(11)—C(1)—C(2)—C(3) torsion angle of 41.0 (3)°, differs from that found in (I) and in monoionized phosphoglycerates (Lis & Jerzykiewicz, 1995), where these torsion angles are *ca* 25° larger. The orientation of the carboxylate group in (II) is associated with a widening of the C(1)—C(2)—C(3) angle (Table 5) compared with values in other phosphoglycerate ions (Lis & Jerzykiewicz, 1995). Other structural features which may depend on the chemical environment are the conformations around the C(2)—C(3) bond. In (II), these conformations are synclinal and antiperiplanar, as indicated by O(3)—C(3)—C(2)—O(2) and O(3)—C(3)—C(2)—C(1) torsion angles of 61.2 (2) and −170.0 (2)°. It should be noted that in all D-3-phosphoglycerates the ester O(3) atom is synclinal to the hydroxyl O(2) atom, whereas it may be synclinal or antiperiplanar to C(1) (Jerzykiewicz & Lis, 1994; Lis & Jerzykiewicz, 1995). The P—O(3)—C(3)—C(2) torsion angle, which describes the orientation of the phosphate group with respect to the carbon backbone, is 172.3 (2)° in (II). Values in other phosphoglycerates vary slightly, but are always within *ca* 20° of that found in (II). The terminal O atom O(31) is in an antiperiplanar position with respect to C(3), whereas O(32) and O(33) are synclinal. This orientation of the phosphate group is also found in other phosphate esters (Starynowicz, Lis & Weichsel, 1986; Starynowicz, 1986; Jerzykiewicz & Lis, 1994). A slightly different situation is observed in (I): O(31) is antiperiplanar-anticlinal, O(32) is anticlinal-synclinal and O(33) is synclinal-synperiplanar (Table 2). The P—O bond lengths and values of O—P—O angles in (I) (Table 2) and in (II) (Table 5) are comparable. The geometry of the cyclohexylammonium cations is similar to that found in other salts of this cation (Jones, 1987; Weichsel & Lis, 1990). The cyclohexyl rings adopt the chair conformation and all C—C bond distances are equal to within 6σ. There is an extensive hydrogen-bond network in the crystal structure of (II) in which all cyclohexylammonium cations, hydroxyl groups and terminal phosphate O atoms are utilized (Table 6). N(1) links only phosphate groups of symmetry-equivalent dianions, whereas N(2) links carboxylate groups of three different dianions. The water O(4) atom (as acceptor) is attached to the phosphate group by the shortest O—H···O hydrogen bond in the structure [2.622 (2) Å] and acts as donor in hydrogen bonds to a phosphate group and to water O(5) atom. O(5) (as acceptor) is linked to hydroxyl O(2) and water O(4) atoms and bridges phosphate and carboxylate groups of symmetry-equivalent dianions. The water molecules lie in hydrophilic channels which extend along **b** and are surrounded by phosphoglycerate dianions with C(2)—C(3) nearly parallel to **a**. These hydrophilic regions are separated from each other by hydrophobic regions which contain the cyclohexyl rings.

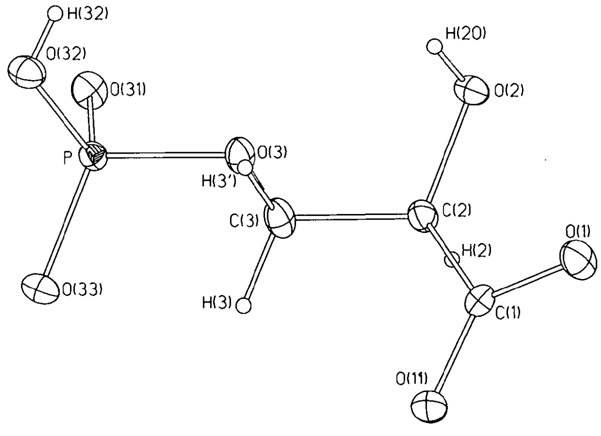


Fig. 3. The structure and numbering scheme of the 3-D-phosphoglycerate dianion in (II). Displacement ellipsoids are plotted at the 50% probability level.

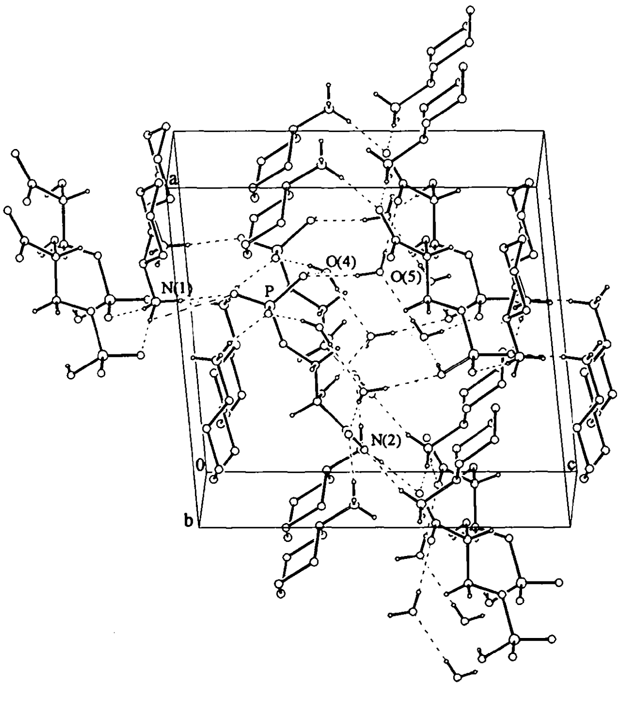


Fig. 4. The packing arrangement in the crystal of (II).

Experimental

Crystals of (I) were obtained by slow diffusion of ethanol into aqueous solutions of the commercially available compound (Sigma). Those of (II) were grown by slow concentration of aqueous solutions containing a 2:1 molar ratio of cyclohexylamine and D-3-phosphoglyceric acid (Lis & Jerzykiewicz, 1995).

Compound (I)

Crystal data

$2Na^+.C_3H_5O_7P^{2-}$
$M_r = 230.02$
Monoclinic
$P2_1$
$a = 9.812\,(9)$ Å
$b = 5.038\,(3)$ Å
$c = 7.778\,(7)$ Å
$\beta = 111.95\,(9)°$
$V = 356.6\,(6)$ Å^3
$Z = 2$
$D_x = 2.142\,(4)$ Mg m^{-3}
$D_m = 2.14$ Mg m^{-3} (at room temperature)
D_m measured by flotation in $C_2H_4Br_2/C_2H_2Br_4$

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 25 reflections
$\theta = 9$–12°
$\mu = 0.509$ mm^{-1}
$T = 80\,(2)$ K
Plate
$0.3 \times 0.2 \times 0.1$ mm
Colourless

Data collection

Kuma KM-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: none
2845 measured reflections
2579 independent reflections
2469 observed reflections [$I > 2\sigma(I)$]
$R_{\rm int} = 0.0099$

$\theta_{\rm max} = 32.5°$
$h = 0 \rightarrow 14$
$k = 0 \rightarrow 7$
$l = -11 \rightarrow 11$
3 standard reflections monitored every 100 reflections intensity decay: 2%

Refinement

Refinement on F^2
$R(F) = 0.0205$
$wR(F^2) = 0.0550$
$S = 1.067$
2579 reflections
137 parameters
All H-atom parameters refined except $U_{\rm iso}$[H(3′)]
$w = 1/[\sigma^2(F_o^2) + (0.0352P)^2 + 0.034P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = 0.168$
$\Delta\rho_{\rm max} = 0.46$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.30$ e Å^{-3}

Extinction correction: *SHELXL*93 (Sheldrick, 1993)
Extinction coefficient: 0.055 (6)
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)
Absolute configuration: Flack (1983)
Flack parameter = −0.06 (5)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2) for* (I)

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
P	0.23188 (3)	0.0	0.23384 (3)	0.00462 (6)
O(31)	0.09285 (8)	0.15394 (16)	0.14608 (11)	0.00709 (13)
O(32)	0.33753 (9)	0.09115 (17)	0.13203 (11)	0.00804 (14)
O(33)	0.22584 (9)	−0.29559 (17)	0.24356 (11)	0.00815 (14)
O(3)	0.30362 (9)	0.12282 (16)	0.43878 (10)	0.00734 (14)
O(2)	0.40863 (9)	0.33463 (17)	0.80176 (11)	0.00779 (13)
O(1)	0.12878 (9)	0.17482 (18)	0.69738 (11)	0.00806 (14)
O(11)	0.18725 (10)	−0.25690 (18)	0.71290 (12)	0.00978 (15)
C(1)	0.21894 (10)	−0.0127 (3)	0.72435 (12)	0.00628 (15)
C(2)	0.37969 (11)	0.0584 (2)	0.76220 (14)	0.00588 (16)
C(3)	0.41006 (10)	−0.0181 (2)	0.59119 (13)	0.00664 (15)
Na(1)	0.09992 (5)	0.45149 (11)	0.39888 (6)	0.00901 (9)
Na(2)	0.13596 (5)	0.47274 (11)	0.95046 (6)	0.00778 (9)

Table 2. *Selected geometric parameters (Å, °) for* (I)

P—O(31)	1.493 (2)	Na(1)—O(3)	2.524 (2)
P—O(32)	1.589 (2)	Na(1)—O(1$^{\rm i}$)	2.368 (2)
P—O(33)	1.493 (2)	Na(1)—O(33$^{\rm ii}$)	2.393 (2)
P—O(3)	1.606 (2)	Na(1)—O(11$^{\rm ii}$)	2.701 (2)
C(3)—O(3)	1.440 (2)	Na(1)—O(11$^{\rm i}$)	2.822 (3)
C(2)—O(2)	1.430 (2)	Na(2)—O(1)	2.455 (2)
C(1)—O(1)	1.257 (2)	Na(2)—O(31$^{\rm i}$)	2.275 (2)
C(1)—O(11)	1.264 (2)	Na(2)—O(31$^{\rm iii}$)	2.357 (2)
C(1)—C(2)	1.535 (2)	Na(2)—O(33$^{\rm iv}$)	2.415 (2)
C(2)—C(3)	1.518 (2)	Na(2)—O(11$^{\rm ii}$)	2.494 (2)
Na(1)—O(31)	2.453 (2)	Na(2)—O(32$^{\rm iii}$)	2.741 (2)
Na(1)—O(1)	2.631 (2)		
O(33)—P—O(31)	119.6 (1)	O(1)—C(1)—O(11)	125.5 (1)
O(33)—P—O(32)	111.0 (1)	O(1)—C(1)—C(2)	117.7 (2)
O(31)—P—O(32)	106.1 (1)	O(11)—C(1)—C(2)	116.7 (1)
O(33)—P—O(3)	110.2 (1)	O(2)—C(2)—C(3)	110.3 (1)
O(31)—P—O(3)	103.9 (1)	O(2)—C(2)—C(1)	112.0 (1)
O(32)—P—O(3)	104.9 (1)	C(3)—C(2)—C(1)	107.3 (2)
C(3)—O(3)—P	122.7 (1)	O(3)—C(3)—C(2)	106.1 (2)

C(3)—O(3)—P—O(31)	158.4 (1)
C(3)—O(3)—P—O(32)	−90.4 (1)
C(3)—O(3)—P—O(33)	29.2 (1)
P—O(3)—C(3)—C(2)	−144.9 (1)
O(2)—C(2)—C(3)—O(3)	−65.5 (2)
O(1)—C(1)—C(2)—O(2)	13.1 (2)
O(11)—C(1)—C(2)—O(2)	−170.7 (1)
O(1)—C(1)—C(2)—C(3)	−108.1 (1)
O(11)—C(1)—C(2)—C(3)	68.1 (2)
C(1)—C(2)—C(3)—O(3)	56.8 (2)

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

Table 3. *Hydrogen-bonding geometry (Å, °) for* (I)

D—H···A	D—H	H···A	D···A	D—H···A
O(2)—H(20)···O(1)	0.80 (3)	2.21 (3)	2.680 (3)	118 (2)
O(2)—H(20)···O(11$^{\rm i}$)	0.80 (3)	2.14 (3)	2.882 (2)	153 (3)
O(32)—H(32)···O(2$^{\rm ii}$)	0.84 (3)	1.84 (3)	2.679 (2)	174 (3)

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

Compound (II)

*Crystal data**

$2C_6H_{14}N^+.C_3H_5O_7P^{2-}.2H_2O$
$M_r = 420.44$
Monoclinic
$P2_1$
$a = 12.427\,(5)$ [12.565 (8)] Å
$b = 6.556\,(3)$ [6.557 (4)] Å
$c = 13.085\,(5)$ [13.224 (9)] Å
$\beta = 94.64\,(6)$ [93.68 (9)]°
$V = 1062.6\,(8)$ [1087.3 (13)] Å^3
$Z = 2$
$D_x = 1.314\,(2)$ [1.284 (2)] Mg m^{-3}
$D_m =$ [1.290] Mg m^{-3}
D_m measured by flotation in $CHCl_3/C_6H_5Cl$

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 49 reflections
$\theta = 10$–14°
$\mu = 0.176$ mm^{-1}
$T = 85\,(2)$ [297 (2)] K
Plate
$0.5 \times 0.15 \times 0.15$ mm
Colourless

Data collection

Kuma KM-4 diffractometer
$\omega/2\theta$ scans

$\theta_{\rm max} = 30°$
$h = 0 \rightarrow 17$

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* Values in square brackets refer to 297 K.

Absorption correction: none
3381 measured reflections
3328 independent reflections
2746 observed reflections [$I > 2\sigma(I)$]
$R_{\text{int}} = 0.0220$

$k = 0 \rightarrow 9$
$l = -18 \rightarrow 18$
3 standard reflections monitored every 100 reflections
intensity decay: 3%

Refinement

Refinement on F^2
$R(F) = 0.0295$
$wR(F^2) = 0.0699$
$S = 1.094$
3328 reflections
391 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.048P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\text{max}} = 0.126$

$\Delta\rho_{\text{max}} = 0.42$ e Å^{-3}
$\Delta\rho_{\text{min}} = -0.22$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)
Absolute configuration: Flack (1983)
Flack parameter = −0.12 (8)

Table 4. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2) for* (II)

$U_{\text{eq}} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	U_{eq}
P	0.53138 (3)	0.25	0.22303 (3)	0.00773 (9)
O(3)	0.41008 (10)	0.1920 (3)	0.24639 (10)	0.0104 (3)
O(31)	0.54891 (12)	0.1384 (3)	0.12539 (10)	0.0115 (3)
O(32)	0.60392 (11)	0.1602 (3)	0.31760 (11)	0.0117 (3)
O(33)	0.54615 (11)	0.4771 (3)	0.22420 (10)	0.0121 (3)
O(2)	0.23177 (11)	0.0081 (3)	0.33010 (11)	0.0114 (3)
O(1)	0.10608 (11)	0.2417 (3)	0.43965 (10)	0.0138 (2)
O(11)	0.19783 (11)	0.5267 (3)	0.41106 (11)	0.0142 (3)
C(3)	0.36314 (14)	0.2839 (4)	0.33159 (14)	0.0116 (4)
C(2)	0.24505 (14)	0.2218 (3)	0.32411 (13)	0.0093 (4)
C(1)	0.17888 (14)	0.3393 (3)	0.39974 (13)	0.0090 (4)
O(4)	0.55534 (13)	−0.2137 (3)	0.36839 (12)	0.0172 (3)
O(5)	0.63618 (11)	0.2777 (3)	0.52943 (11)	0.0147 (3)
N(1)	0.54553 (12)	0.2571 (3)	−0.08237 (11)	0.0112 (3)
C(11)	0.66171 (14)	0.2753 (4)	−0.10562 (13)	0.0108 (4)
C(12)	0.71470 (16)	0.4517 (4)	−0.04432 (15)	0.0128 (4)
C(13)	0.83290 (17)	0.4713 (4)	−0.06674 (16)	0.0154 (4)
C(14)	0.89429 (14)	0.2732 (4)	−0.04330 (14)	0.0148 (4)
C(15)	0.83961 (16)	0.0934 (4)	−0.10142 (16)	0.0159 (4)
C(16)	0.72018 (16)	0.0747 (4)	−0.07986 (15)	0.0122 (4)
N(2)	0.03981 (13)	−0.1681 (3)	0.41819 (12)	0.0103 (3)
C(21)	−0.02610 (15)	−0.1916 (3)	0.31727 (14)	0.0106 (4)
C(22)	−0.10302 (16)	−0.0113 (4)	0.30000 (15)	0.0138 (4)
C(23)	−0.17033 (17)	−0.0368 (4)	0.19819 (16)	0.0143 (4)
C(24)	−0.23176 (14)	−0.2376 (4)	0.19412 (14)	0.0157 (4)
C(25)	−0.15598 (19)	−0.4192 (4)	0.21391 (17)	0.0174 (4)
C(26)	−0.08634 (17)	−0.3937 (4)	0.31581 (16)	0.0149 (4)

Table 5. *Selected geometric parameters (Å, °) for* (II)

P—O(31)	1.503 (2)	C(11)—C(16)	1.527 (3)
P—O(32)	1.584 (2)	C(12)—C(13)	1.526 (3)
P—O(33)	1.500 (2)	C(13)—C(14)	1.525 (3)
P—O(3)	1.608 (2)	C(14)—C(15)	1.532 (3)
O(3)—C(3)	1.432 (2)	C(15)—C(16)	1.538 (3)
O(2)—C(2)	1.414 (2)	N(2)—C(21)	1.504 (3)
O(1)—C(1)	1.255 (2)	C(21)—C(26)	1.521 (3)
O(11)—C(1)	1.258 (2)	C(21)—C(22)	1.525 (3)
C(3)—C(2)	1.519 (2)	C(22)—C(23)	1.524 (3)
C(2)—C(1)	1.543 (2)	C(23)—C(24)	1.521 (3)
N(1)—C(11)	1.504 (2)	C(24)—C(25)	1.527 (3)
C(11)—C(12)	1.526 (3)	C(25)—C(26)	1.539 (3)
O(33)—P—O(31)	117.8 (1)	N(1)—C(11)—C(16)	109.5 (2)
O(33)—P—O(32)	107.4 (1)	C(12)—C(11)—C(16)	111.1 (2)
O(31)—P—O(32)	111.7 (1)	C(11)—C(12)—C(13)	110.1 (2)
O(33)—P—O(3)	110.4 (1)	C(14)—C(13)—C(12)	111.3 (2)
O(31)—P—O(3)	104.4 (1)	C(13)—C(14)—C(15)	111.2 (2)
O(32)—P—O(3)	104.3 (1)	C(14)—C(15)—C(16)	111.5 (2)
C(3)—O(3)—P	119.7 (2)	C(11)—C(16)—C(15)	109.9 (2)
O(3)—C(3)—C(2)	106.8 (2)	N(2)—C(21)—C(26)	109.4 (2)
O(2)—C(2)—C(3)	112.3 (2)	N(2)—C(21)—C(22)	109.9 (2)
O(2)—C(2)—C(1)	112.9 (2)	C(26)—C(21)—C(22)	111.8 (2)
C(3)—C(2)—C(1)	112.8 (2)	C(23)—C(22)—C(21)	109.7 (2)
O(1)—C(1)—O(11)	125.7 (2)	C(24)—C(23)—C(22)	111.3 (2)
O(1)—C(1)—C(2)	116.9 (2)	C(23)—C(24)—C(25)	111.6 (2)
O(11)—C(1)—C(2)	117.3 (2)	C(24)—C(25)—C(26)	111.0 (2)
N(1)—C(11)—C(12)	109.5 (2)	C(21)—C(26)—C(25)	110.3 (2)
C(3)—O(3)—P—O(31)	−175.8 (2)		
C(3)—O(3)—P—O(32)	66.8 (2)		
C(3)—O(3)—P—O(33)	−48.3 (2)		
P—O(3)—C(3)—C(2)	172.3 (2)		
O(2)—C(2)—C(3)—O(3)	61.2 (2)		
O(1)—C(1)—C(2)—O(2)	−14.8 (3)		
O(11)—C(1)—C(2)—O(2)	169.6 (2)		
O(1)—C(1)—C(2)—C(3)	−143.4 (2)		
O(11)—C(1)—C(2)—C(3)	41.0 (3)		
C(1)—C(2)—C(3)—O(3)	−170.0 (2)		

Table 6. *Hydrogen-bonding geometry (Å, °) for* (II)

D—H···A	D—H	H···A	D···A	D—H···A
O(32)—H(32)···O(4)	0.68 (4)	1.95 (4)	2.622 (2)	173 (4)
O(2)—H(20)···O(5$^{\text{i}}$)	0.81 (4)	2.02 (4)	2.804 (2)	165 (4)
N(1)—H(11N)···O(33$^{\text{ii}}$)	0.86 (3)	1.94 (3)	2.787 (2)	166 (3)
N(1)—H(12N)···O(31$^{\text{iii}}$)	0.90 (4)	1.90 (4)	2.800 (3)	174 (4)
N(1)—H(13N)···O(31)	0.88 (3)	1.94 (3)	2.825 (2)	176 (3)
N(2)—H(21N)···O(1)	0.88 (3)	1.96 (4)	2.818 (3)	164 (3)
N(2)—H(22N)···O(11$^{\text{iv}}$)	0.89 (4)	1.92 (4)	2.810 (2)	176 (3)
N(2)—H(23N)···O(1$^{\text{v}}$)	0.84 (3)	1.95 (3)	2.764 (2)	161 (3)
O(4)—H(4)···O(5$^{\text{i}}$)	0.71 (4)	2.11 (4)	2.823 (3)	175 (4)
O(4)—H(41)···O(33$^{\text{iv}}$)	0.91 (4)	1.86 (4)	2.765 (2)	174 (4)
O(5)—H(5)···O(32)	0.80 (4)	2.12 (4)	2.874 (2)	157 (4)
O(5)—H(51)···O(11$^{\text{i}}$)	0.79 (4)	1.92 (3)	2.704 (2)	168 (3)

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

The collection of data at low temperature was carried out using an Oxford Cryosystem cooler for both compounds.

The refinement of the structure of (I) used the parameters of Fewster & Fenn (1982) as a starting model. All H atoms in (I) were found from a difference map. As the value of U_{iso} for H(3′) became negative during refinement its value was set equal to U_{eq} for C(3) in the final cycles.

The space group and approximate unit-cell dimensions of (II) were determined from oscillation and Weissenberg photographs. Data collection at room temperature was discontinued when the intensities of the control reflections dropped to 80% of their initial values after 600 measurements. The structure was solved by direct methods (*SHELXS*86; Sheldrick, 1990) from the 85 K data; H atoms bonded to C were initially placed in calculated positions and the remainder were located in a difference map.

For both compounds, data collection: *Kuma KM*4 *Software* (Kuma Diffraction, 1989); cell refinement: *Kuma KM*4 *Software*; data reduction: *Kuma KM*4 *Software*; program(s) used to refine structures: *SHELXL*93 (Sheldrick, 1993); molecular graphics: *ORTEP*II (Johnson, 1976).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, bond distances and angles involving non-H atoms, and torsion angles have been deposited with the IUCr (Reference: MU1203). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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1,3-Bis(2-chlorophenyl)thiourea

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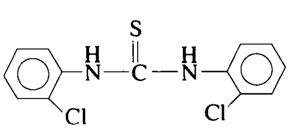
Abstract

The crystal structure determination of the title compound, $C_{13}H_{10}Cl_2N_2S$, at 173 K is reported. There are two molecules in the asymmetric unit connected by N—H···S hydrogen bonds and a short Cl···Cl contact. The molecules exist as dimers and the crystal lattice consists of two-dimensional parallel layers of these dimers connected by C—H···Cl hydrogen bonds.

Comment

Crystal structure analyses of many metal complexes of thiourea have been reported in the past, but only a few of these involve substituted thioureas and there is no structural report exclusively concerning substituted thiourea derivatives, which may be due to the difficulty in preparing crystals suitable for X-ray diffraction studies. These thiourea complexes have applications as rubber accelerators, as intermediates in dye preparation and they are also very useful agrochemical intermediates (Ramadas, Srinivasan & Janarthanan, 1993). We are interested in the molecular conformations and the N—H···S hydrogen-bond details of these molecules in the solid state. In this paper, we report the crystal structure determination of a symmetrically substituted thiourea derivative, 1,3-bis(*o*-chlorophenyl)thiourea (OCDPTU), at 173 K.



OCDPTU

A displacement ellipsoid plot of the two molecules in the asymmetric unit, together with the numbering scheme, is shown in Fig. 1. There are some notable differences in the corresponding bond angles of the two molecules, such as angle C1—N2—C8 and the angles around C1. The S1=C1 bond lengths agree well with the value observed in diphenyl thiourea (DPTU; Akilan, Sivakumar, Subramanian, Janarthanan, Ramadas & Fun, 1995) and the unweighted mean value (1.681 Å) given for C=S in thioureas (Allen, Kennard, Watson, Brammer, Orpen & Taylor, 1987). It is only in these two symmetrically substituted thiourea derivatives, OCDPTU and DPTU, that the C=S bond lengths show shorter values, whereas in other structures, C=S is observed to be more than 1.700 Å (Akilan, Sivakumar, Subramanian, Meerarani, Ramadas & Fun, 1996).

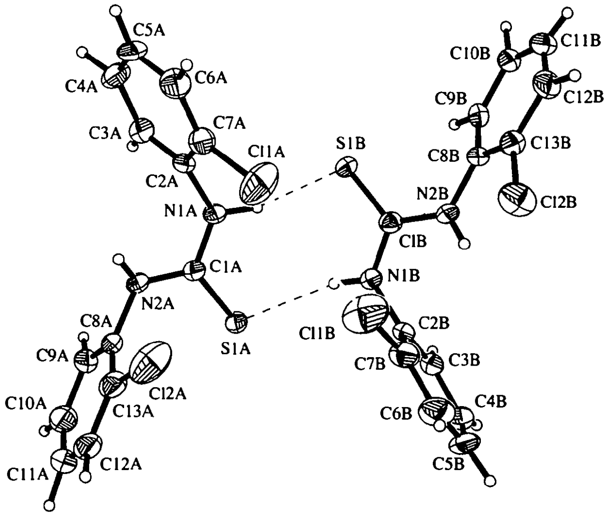


Fig. 1. Displacement ellipsoid plot of the two independent molecules in the asymmetric unit, showing the numbering scheme and ellipsoids at the 50% probability level. The N—H···S hydrogen bonds are shown as dashed lines and the Cl···Cl short contact as a dotted line.

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