4289 reflections
343 parameters
$w = 1/[\sigma^2(F_o^2) + (0.0356P)^2 + 0.0168P]$
where $P = (F_o^2 + 2F_c^2)/3$

Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)*

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

	x	y	z	$U_{\rm eq}$
N	−0.6564 (4)	−0.2164 (4)	−0.5840 (3)	0.0965 (12)
O	−0.2757 (2)	0.0336 (2)	0.0596 (2)	0.0551 (6)
C1	−0.3493 (3)	−0.1034 (3)	−0.1701 (3)	0.0404 (7)
C2	−0.2333 (3)	−0.1031 (3)	−0.2363 (3)	0.0418 (8)
C3	−0.1621 (3)	0.0259 (3)	−0.1871 (3)	0.0404 (7)
C4	−0.2278 (3)	0.1201 (3)	−0.0874 (3)	0.0411 (8)
C5	−0.3577 (3)	0.1129 (3)	−0.1594 (3)	0.0510 (9)
C6	−0.4442 (3)	−0.0313 (3)	−0.2059 (3)	0.0468 (8)
C7	−0.2812 (3)	0.0220 (3)	−0.0422 (3)	0.0431 (8)
C8	−0.5167 (3)	−0.0992 (3)	−0.3384 (3)	0.0501 (8)
C9	−0.6493 (4)	−0.1385 (4)	−0.3654 (4)	0.0792 (12)
C10	−0.7126 (4)	−0.1936 (5)	−0.4867 (5)	0.112 (2)
C11	−0.5295 (5)	−0.1783 (4)	−0.5568 (4)	0.0852 (13)
C12	−0.4558 (4)	−0.1201 (4)	−0.4386 (3)	0.0707 (11)
C13	−0.4055 (3)	−0.2268 (3)	−0.1606 (3)	0.0458 (8)
C14	−0.5369 (3)	−0.2780 (3)	−0.1747 (3)	0.0574 (9)
C15	−0.5824 (4)	−0.3914 (4)	−0.1638 (3)	0.0724 (12)
C16	−0.4971 (5)	−0.4543 (4)	−0.1379 (4)	0.0806 (13)
C17	−0.3667 (5)	−0.4031 (4)	−0.1208 (4)	0.0854 (13)
C18	−0.3218 (4)	−0.2903 (4)	−0.1321 (3)	0.0667 (10)
C19	−0.2134 (3)	−0.2269 (3)	−0.3407 (3)	0.0421 (8)
C20	−0.3161 (4)	−0.3369 (3)	−0.4150 (3)	0.0648 (10)
C21	−0.3005 (4)	−0.4525 (4)	−0.5138 (3)	0.0798 (12)
C22	−0.1794 (4)	−0.4611 (4)	−0.5408 (3)	0.0730 (11)
C23	−0.0757 (4)	−0.3544 (4)	−0.4685 (3)	0.0611 (10)
C24	−0.0914 (3)	−0.2386 (3)	−0.3692 (3)	0.0507 (9)
C25	−0.0476 (3)	0.0787 (3)	−0.2262 (3)	0.0421 (8)
C26	0.0761 (4)	0.1030 (4)	−0.1667 (3)	0.0651 (10)
C27	0.1831 (4)	0.1502 (4)	−0.2035 (4)	0.0834 (13)
C28	0.1680 (4)	0.1738 (4)	−0.3015 (4)	0.0803 (13)
C29	0.0466 (5)	0.1517 (4)	−0.3609 (4)	0.0767 (12)
C30	−0.0617 (4)	0.1043 (3)	−0.3241 (3)	0.0614 (10)
C31	−0.1472 (3)	0.2577 (3)	0.0081 (3)	0.0453 (8)
C32	−0.0549 (3)	0.2734 (3)	0.1014 (3)	0.0563 (9)
C33	0.0202 (4)	0.3996 (4)	0.1914 (3)	0.0661 (10)
C34	0.0026 (4)	0.5124 (4)	0.1888 (3)	0.0662 (11)
C35	−0.0883 (4)	0.4992 (3)	0.0962 (4)	0.0643 (10)
C36	−0.1624 (3)	0.3727 (3)	0.0059 (3)	0.0562 (9)

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

N—C11	1.311 (5)	C6—C8	1.509 (4)
N—C10	1.321 (6)	C6—C5	1.555 (4)
O—C7	1.197 (3)	C5—C4	1.557 (4)
C7—C4	1.525 (4)	C4—C31	1.500 (4)
C7—C1	1.556 (4)	C4—C3	1.537 (4)
C1—C13	1.505 (4)	C3—C2	1.355 (4)
C1—C2	1.537 (4)	C3—C25	1.480 (4)
C1—C6	1.585 (4)	C2—C19	1.480 (4)
C13—C1—C2	118.6 (3)	C31—C4—C7	117.7 (2)
C13—C1—C7	113.4 (2)	C31—C4—C3	118.0 (3)
C2—C1—C7	96.5 (2)	C7—C4—C3	96.6 (2)
C13—C1—C6	119.2 (3)	C31—C4—C5	117.1 (3)
C2—C1—C6	108.9 (2)	C7—C4—C5	98.3 (2)
C7—C1—C6	95.4 (2)	C3—C4—C5	105.6 (2)
C3—C2—C19	128.4 (3)	C6—C5—C4	105.5 (2)
C3—C2—C1	108.7 (3)	C8—C6—C5	114.0 (3)
C19—C2—C1	122.9 (3)	C8—C6—C1	118.7 (2)
C2—C3—C25	128.9 (3)	C5—C6—C1	103.4 (2)
C2—C3—C4	108.9 (3)	O—C7—C1	128.6 (3)
C25—C3—C4	121.9 (3)	C4—C7—C1	99.1 (2)
O—C7—C4	132.3 (3)		

The structure was solved by direct methods and refined by anisotropic full-matrix least squares for all non-H atoms. H-atom positions were fixed during the refinement and assigned isotropic displacement parameters 1.2 × $B_{\rm eq}$ of the corresponding C atom.

Data collection: *XSCANS* (Siemens, 1994). Cell refinement: *XSCANS*. Data reduction: *SHELXTL* (Sheldrick, 1994). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *SHELXTL*. Software used to prepare material for publication: *SHELXTL*.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: BK1217). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Tetraphenylphosphonium Perchlorate

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Abstract

Crystals of the title compound, $C_{24}H_{20}P^+.ClO_4^-$, are composed of Ph_4P^+ cations and ClO_4^- anions separated by normal van der Waals distances. The P and Cl atoms occupy special positions of $\overline{4}$ (S_4) symmetry. In the cation, the P—C distance is 1.833 (4) Å and the C—P—C angles are 110.25 (13) and 107.9 (2)°. The perchlorate anion is disordered.

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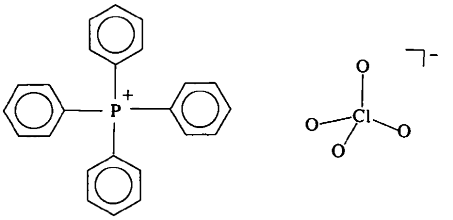
Comment

In this paper, we report the crystal and molecular structure of $Ph_4P^+.ClO_4^-$, (I). The X-ray powder data, unit-cell dimensions and IR data for this salt and similar derivatives have been presented previously (Baran, 1971).



(I)

A view of the title compound together with the atomic numbering scheme is shown in Fig. 1. The crystal structure is comprised of isolated tetrahedral ions. The anions lie on the body center of the tetragonal cell and the cations lie on the rectangular faces *A* and *B*. Both P and Cl atoms are located on crystallographic $\bar{4}$ axes. The observed P—C distance of 1.833 (4) Å is slightly longer than the mean P—C distance of 1.79 (2) Å obtained from data for the more than 860 Ph_4P^+ salts contained in the April 1996 release of the Cambridge Structural Database (Allen *et al.*, 1991). The two independent C—P—C angles are 110.25 (13) and 107.9 (3)°. Several other Ph_4P^+ salts, including $Ph_4P^+.Br^-$ (Alcock, Pennington & Willey, 1985), $Ph_4P^+.I^-$ (Schweizer, Baldacchini & Rheingold, 1989), $Ph_4P^+.PF_6^-$ (Banbery & Hamor, 1988), *etc.*, have cations of similar geometry. The ClO_4^- anion in (I) is found to be disordered. Three disorder models (with occupancies of 0.4, 0.3 and 0.3) were resolved. The Cl—O distances are 1.398 (12), 1.404 (15) and 1.344 (11) Å. A mean Cl—O distance of 1.39 (5) Å was found in the CSD search from over 1460 hits.

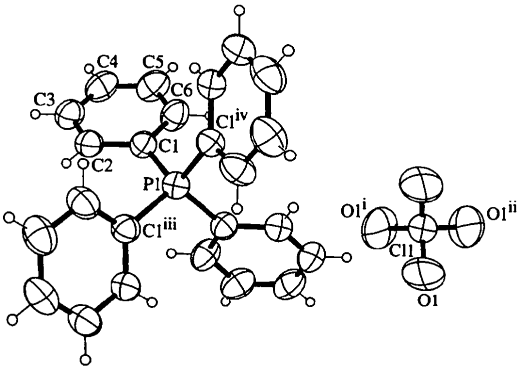


Fig. 1. Perspective view of $Ph_4P^+.ClO_4^-$ showing the atom-numbering scheme. Displacement ellipsoids are shown at the 50% probability level and H atoms are drawn as small circles of arbitrary radii. The O atoms are disordered and only one disorder model is shown in ClO_4^-. Symmetry codes are as in Table 2.

A wide variety of salts of Ph_4P^+ and isosteric cations crystallize in the tetragonal space group $I\bar{4}$ with $Z = 2$. These include: $[M(py)_4](ClO_4)$, where py is pyridine and M = Li (Harvey, Kildea, Skelton & White, 1992) or Ag and Cu (Nilsson & Oskarsson, 1981, 1982); $[Cu(N\text{-methylimidazole})_4](ClO_4)$ (Clegg, Acott & Garner, 1984); $[Ph_4E^+](ClO_4)$, where E = Bi (Bordner & Freedman, 1973), Sb (Ferguson, Glidewell, Lloyd & Metcalfe, 1988) or As (Walford, Blattner, Feldman & Bain, 1970; Couldwell, 1979); $Ph_4As^+.X^-$, where X = WOF_5 (Massa, Hermann & Dehnicke, 1982), PF_6, AsF_6, SbF_6 and BF_4 (Walford *et al.*, 1970), HCS_2 (Gattow, Drager & Engler, 1971), MnO_4 (Baran, 1971), IO_4 (Klobasa, Burkert & Muller, 1992), SiF_5 (Corfield & Ibers, 1968), $FeCl_4$ (Cotton & Murillo, 1975) or NCS (Lazarini & Golic, 1972); $Ph_4P^+.E^-$, where E = PBr_2S_2 (Muller & Mohammed, 1984), Br (Alcock, Pennington & Willey, 1985), I (Schweizer, Baldacchini & Rheingold, 1989), TeH (Huffman & Haushalter, 1989), MnO_4 (Baran, 1971), VF_2O_2 (Fairhurst, Hughes, Leigh, Sanders & Weisner, 1994), PF_6 (Banbery & Hamor, 1988), $[CrO_3(OH)]$ and $[CrO_3(OH_2)]$ (Mukherjee, Mukhopadhaya, Mukherjee & Ray, 1994), or (ReS_4) (Diemann & Muller, 1976). In these salts, the central atoms of the cations and anions occupy the crystallographic $\bar{4}$ axes. In some cases, the anions were disordered but were very close to the $\bar{4}$ axis. These isomorphous salts are isostructural in the sense of matching of positions occupied by the central atoms of the counterions (rather than of all atomic positions). This observation can be interpreted in terms of the effective radii of the cations and anions and the corresponding packing of the ions (Mingos & Rohl, 1991*a*,*b*). In each salt, $r(\text{eff})_{\text{anion}} < r(\text{eff})_{\text{cation}}$ and the range of $r(\text{eff})_{\text{anion}}/r(\text{eff})_{\text{cation}}$ in the cited salts is limited, leading to packing of a constant lattice type. Alternatively, the general pattern can be discussed in terms of specific cation–cation interactions (Dance & Scudder, 1995, 1996). Evidently, these occur with a constant motif over the limited range of anion sizes encountered.

Experimental

The title salt was obtained in quantitative yield as one of the products of the metathesis of $Mg(ClO_4)_2$ and $(Ph_4P)[Cd(SCOPh)_3]$ (Vittal & Dean, 1996) in MeCN. The block-like colorless single crystals were grown by slow evaporation of the solution in MeCN at room temperature.

Crystal data

$C_{24}H_{20}P^+.ClO_4^-$
$M_r = 438.82$
Tetragonal
$I\bar{4}$
$a = 12.383\ (3)$ Å
$c = 7.188\ (2)$ Å

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 33 reflections
$\theta = 10.9–12.4°$
$\mu = 0.273\ \text{mm}^{-1}$

$V = 1102.2\,(5)$ Å^3
$Z = 2$
$D_x = 1.322$ Mg m^{-3}
$D_m = 1.43\,(5)$ Mg m^{-3}
D_m measured by flotation in a CCl_4/hexane mixture

$T = 293\,(2)$ K
Block
0.32 × 0.22 × 0.20 mm
Colorless

Data collection

Siemens *P*4 diffractometer
ω scans
Absorption correction: Gaussian (*SHELXTL/PC*; Sheldrick, 1994)
$T_{\min} = 0.945$, $T_{\max} = 0.954$
1246 measured reflections
1146 independent reflections
655 observed reflections $[I > 2\sigma(I)]$

$R_{\rm int} = 0.0187$
$\theta_{\max} = 30.02°$
$h = -1 \rightarrow 17$
$k = -1 \rightarrow 17$
$l = -1 \rightarrow 10$
3 standard reflections monitored every 197 reflections intensity decay: 1.58%

Refinement

Refinement on F^2
$R(F) = 0.0491$
$wR(F^2) = 0.0944$
$S = 1.087$
1146 reflections
87 parameters
All five H atoms were located and placed in calculated ideal positions for structure-factor calculations only
$w = 1/[\sigma^2(F_o^2) + (0.0343P)^2 + 0.8674P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = -0.001$

$\Delta\rho_{\max} = 0.215$ e Å^{-3}
$\Delta\rho_{\min} = -0.249$ e Å^{-3}
Extinction correction: *SHELXTL/PC*
Extinction coefficient: 0.012 (2)
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 = −0.2 (2)

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

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

	x	y	z	$U_{\rm eq}$
Cl1	0	0	0	0.0681 (7)
O1†	−0.0973 (17)	−0.023 (3)	0.091 (5)	0.191 (14)
O2‡	−0.090 (3)	0.065 (5)	0.042 (6)	0.172 (12)
O3‡	−0.033 (2)	0.035 (3)	0.167 (3)	0.184 (15)
P1	0	1/2	3/4	0.0487 (5)
C1	0.0659 (3)	0.5999 (3)	0.6000 (6)	0.0502 (9)
C2	0.0447 (3)	0.7119 (3)	0.6102 (6)	0.0572 (10)
C3	0.0961 (3)	0.7838 (3)	0.4861 (8)	0.0700 (13)
C4	0.1693 (4)	0.7448 (3)	0.3537 (7)	0.0723 (13)
C5	0.1930 (4)	0.6339 (4)	0.3432 (7)	0.0724 (13)
C6	0.1399 (3)	0.5617 (3)	0.4636 (6)	0.0646 (12)

† Site occupancy = 0.40. ‡ Site occupancy = 0.30.

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

Cl1—O3	1.344 (11)	C1—C6	1.423 (5)
Cl1—O1	1.398 (12)	C2—C3	1.412 (6)
Cl1—O2	1.404 (15)	C3—C4	1.400 (6)
P1—C1	1.833 (4)	C4—C5	1.407 (6)
C1—C2	1.414 (5)	C5—C6	1.407 (6)
O1$^{\rm i}$—Cl1—O1	124 (4)	C6—C1—P1	117.9 (3)
O1$^{\rm ii}$—Cl1—O1	102.6 (15)	C3—C2—C1	120.1 (4)
C1$^{\rm iii}$—P1—C1	107.9 (2)	C4—C3—C2	120.3 (4)
C1$^{\rm iv}$—P1—C1	110.25 (13)	C3—C4—C5	120.5 (4)
C2—C1—C6	118.8 (4)	C4—C5—C6	119.3 (5)
C2—C1—P1	123.3 (3)	C5—C6—C1	120.9 (4)

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

Data collection: *XSCANS* (Siemens, 1994). Cell refinement: *XSCANS*. Data reduction: *XSCANS*. Program(s) used to solve structure: *SHELXTL/PC* (Sheldrick, 1994). Program(s) used to refine structure: *SHELXTL/PC*. Molecular graphics: *SHELXTL/PC*. Software used to prepare material for publication: *SHELXTL/PC*.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: SK1044). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Mannose Phenylhydrazone, an Acyclic Monosaccharide Derivative

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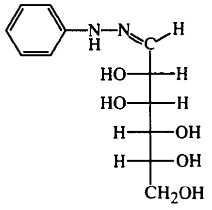
Abstract

In determining whether mannose phenylhydrazone ($C_{12}H_{18}N_2O_5$) is cyclic or acyclic, chemical and spectroscopic methods have yielded contradictory results. X-ray crystallography has now shown that this compound occurs in an acyclic form in the solid state. The conformation is closely similar to that assumed by mannose *p*-bromophenylhydrazone [Furberg & Solbakk (1969). *Acta Chem. Scand.* **23**, 3248–3256], and the hydrogen-bonding arrangements found in the two structures are identical.

Comment

Reaction of monosaccharides with phenylhydrazine and related compounds yields both cyclic and acyclic products (Staněk, Černý, Kocourek & Pacák, 1963). Crystal structure analyses of the *p*-bromophenylhydrazones of glucose (Bjamer, Dahm, Furberg & Petersen, 1963; Dukefos & Mostad, 1965) and arabinose (Furberg & Petersen, 1962) and the tosylhydrazones of glucose, galactose and arabinose (Ojala, Ojala & Gleason, 1996) have shown that these derivatives occur in ring form in the solid state, but the *p*-bromophenylhydrazones of ribose (Bjamer, Furberg & Petersen, 1964) and mannose (Furberg & Solbakk, 1969) have been found to occur in open-chain form. The structure of mannose phenylhydrazone is particularly interesting because the experimental evidence is ambiguous. The behavior of this compound in the formazan reaction (Mester & Major, 1955) suggests that in solution the molecule is acyclic, but the absence from the IR spectrum (Nujol) of an obvious C═N band suggests that the sugar assumes a ring structure and that the molecule is a phenylhydrazide and not a phenylhydrazone (Blair & Roberts, 1967). In our own investigation of the structures of monosaccharide derivatives, we have avoided relying on IR spectra for structure assignments because we have found that even such clear-cut hydrazones as cyclopentanone tosylhydrazone and cyclohexanone tosylhydrazone exhibit only very weak absorption bands in the C═N region ($\sim 1640\,\mathrm{cm}^{-1}$). We have instead relied on X-ray crystallographic evidence. As part of this study we have determined the crystal structure of mannose phenylhydrazone, (1), and have found that this compound assumes an open-chain structure in the solid state.



(1)

The molecular conformation and atom-numbering scheme are shown in Fig. 1. The conformation of mannose phenylhydrazone is closely similar to that of mannose *p*-bromophenylhydrazone. Both molecules possess a planar, fully extended zigzag chain of C atoms. In both structures, the atoms N(2), N(1), C(1) and C(2) are coplanar within experimental error, and in both cases this plane assumes an angle of 124° with the plane of the sugar C atoms. The orientation of the phenyl group is similar in the two molecules with the least-squares plane through the phenyl C atoms assuming an angle

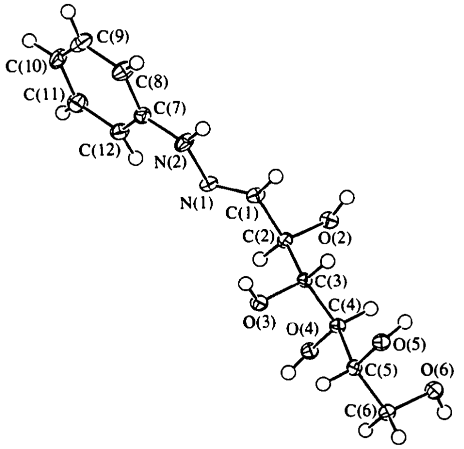


Fig. 1. *ORTEP*II (Johnson, 1976) view of (1), showing the atom numbering. For non-H atoms, 50% probability ellipsoids are shown.

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