

Tetrakis(diethylamino)phosphonium
bromide hemihydrateYunqi Liu,^a Michelle O. Fletcher^a and Frank R. Fronczek^{b*}^aAlbemarle Technical Center, Albemarle Corporation, PO Box 14799, Baton Rouge, LA 70898, USA, and ^bDepartment of Chemistry, Louisiana State University, Baton Rouge, LA 70803-1804, USA

Correspondence e-mail: fronz@chxray1.chem.lsu.edu

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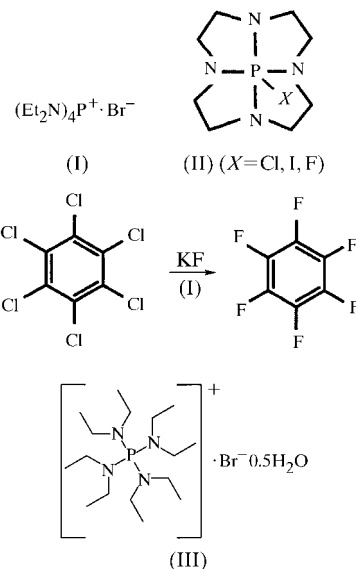
The structure of the title compound, $C_{16}H_{40}N_4P^+ \cdot Br^- \cdot 0.5H_2O$ or $[P\{N(C_2H_5)_2\}_4]Br \cdot 0.5H_2O$, at 130 K has $Z' = 4$ and is ionic, with Br not bonded to P. The P atoms are tetrahedral, with P–N distances in the range 1.628 (2)–1.6400 (19) Å. The N atoms are approximately planar. The water molecules form cyclic hydrogen-bonded $[(H_2O)_2Br_2]^{2-}$ units about inversion centers, with $O \cdots Br$ distances in the range 3.425 (2)–3.611 (3) Å.

Comment

Because of their superior thermal stability and availability, tetrakis(dialkylamino)phosphonium halides have emerged as highly efficient phase-transfer catalysts for halogen-exchange (halix) reactions where a high reaction temperature is often required (Bildinov *et al.*, 1998). They are especially suitable for reactions in which the substitution site does not have an activating group at the *ortho* or *para* positions. In one such example (Bildinov *et al.*, 1998), hexachlorobenzene is reacted with KF at high temperature in the presence of tetrakis(diethylamino)phosphonium bromide, (I), to give hexafluorobenzene (see Scheme). Synthetic and structural studies of alkylaminophosphonium halides are sparse in the literature (Schwesinger *et al.*, 1994), while cyclen phosphonium halides, (II), are more common (Richman, 1977). Based on spectroscopic studies, it was claimed that the P–X interaction is ionic when the anion is chloride or iodide, but covalent when X is fluorine. Later studies demonstrated that the P–F interaction becomes ionic when the ring size of the macrocycle increases, and the reactivity of the fluoride in these cyclen phosphonium salts has been tested by using them as nucleophiles in nucleophilic substitution reactions (Richman & Flay, 1981).

In our efforts to study tetrakis(diethylamino)phosphonium bromide-catalyzed halix reactions, we obtained a high-purity sample of the title compound, (III), *via* recrystallization from tetrahydrofuran (Berris & Cheng, 1999). Unlike the commercial sample, which is always tinted with color,

tetrakis(diethylamino)phosphonium bromide at high purity is a colorless crystalline solid.



The asymmetric unit of (III) contains four $[P\{N(C_2H_5)_2\}_4]^+$ cations, four Br^- ions and two water molecules. The Br^- is not coordinated to P, with a minimum $P \cdots Br$ distance of 5.1990 (7) Å. The cations (Fig. 1) contain tetrahedral P, with P–N distances in the range 1.628 (2)–1.6400 (19) Å. The N atoms have approximately planar coordination, lying out of the planes defined by the three atoms bonded to them by

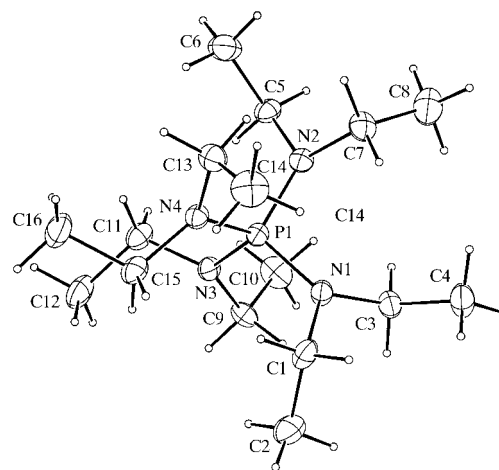


Figure 1

One of the four independent cations in (III), with displacement ellipsoids drawn at the 50% probability level. H atoms are shown as small spheres of arbitrary radii.

distances in the range 0.076 (2)–0.175 (2) Å. All four cations have approximate $\bar{4}$ symmetry. The ethyl groups are arranged such that, on each diethylamino group, both P–N–C–C torsion angles have the same sign. Furthermore, one of the two P–N–C–C torsion angles in each NEt_2 group typically has a magnitude around 90° [range 81.4 (2)–115.5 (2)°], while the other is larger, typically around 130° [range 128.2 (2)–134.58 (19)°].

Two of the four independent bromides, Br1 and Br2, form cyclic hydrogen-bonded $[(\text{H}_2\text{O})_2\text{Br}_2]^{2-}$ units of rhombic shape about inversion centers, with $\text{O}\cdots\text{Br}$ distances in the range 3.425 (2)–3.611 (3) Å (Fig. 2 and Table 2). The other two, Br3 and Br4, do not interact with water and have no contacts to non-H atoms less than 3.798 (3) Å for Br3 and 3.658 (3) Å for Br4.

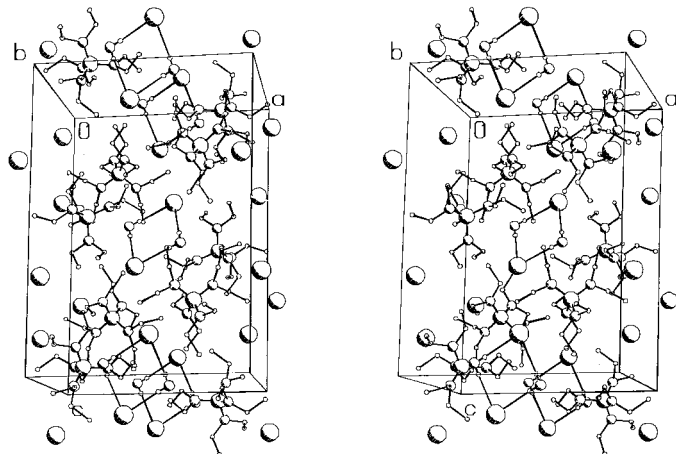


Figure 2
A stereoview of the unit cell of (III).

Unlike many structures which have low symmetry and high Z' values at low temperature but convert to a higher symmetry polymorph with $Z' = 1$ at higher temperature (Brock & Patrick, 1999; Billodeaux *et al.*, 1999), compound (III) has the same structure at temperatures up to at least 240 K. At that temperature, it is still $P\bar{1}$, with cell dimensions $a = 14.3267$ (3), $b = 15.0716$ (3) and $c = 20.8221$ (5) Å, $\alpha = 91.9325$ (13), $\beta = 91.7411$ (13) and $\gamma = 90.1032$ (13)°, and $V = 4491.6$ (2) Å³. Refinement of the reported model *versus* 240 K intensity data yielded $R = 0.037$.

A search of the Cambridge Structural Database (Allen *et al.*, 1983) yielded no examples of crystal structures containing tetrakis(dialkylamino)phosphonium ions. However, the structures of two closely related compounds are known, namely dimeric 2,2,4,4-tetrakis(diethylamino)-1,3-diethyl-1,3,2,4-diazadiphosphetidin-2,4-diium dibromide (refcode JELLAN; Marchenko *et al.*, 1988) and 2,2-bis(diethylamino)-1,3-dipropyl-4,5-dimethyl-1,3,2-diazaphospholenium trifluoromethanesulfonate (refcode KOSBOJ; Mazieres *et al.*, 1991), the latter compound having two of its N atoms bridged by $\text{C}=\text{C}$. The P–N distances to the terminal $\text{N}(\text{Et}_2)_2$ groups in KOSBOJ agree well with those in (III), while those of JELLAN may be slightly shorter, averaging 1.600 Å. In KOSBOJ, as in (III), both P–N–C–C torsion angles on each $\text{N}(\text{Et}_2)_2$ group have the same sign, with one of much larger magnitude than the other. In JELLAN, however, this pattern is not present.

Experimental

The single crystal of (III) used in this study was obtained by controlled solvent evaporation in tetrahydrofuran of a sample synthesized locally. The compound is quite hygroscopic, which necessitated cryogenic data collection.

Crystal data

$\text{C}_{16}\text{H}_{40}\text{N}_4\text{P}^+\cdot\text{Br}^-\cdot 0.5\text{H}_2\text{O}$
 $M_r = 408.4$
 Triclinic, $P\bar{1}$
 $a = 14.2475$ (2) Å
 $b = 14.9756$ (3) Å
 $c = 20.7125$ (5) Å
 $\alpha = 92.144$ (2)°
 $\beta = 91.799$ (2)°
 $\gamma = 90.246$ (2)°
 $V = 4414.0$ (3) Å³

$Z = 8$
 $D_x = 1.229$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 43 363 reflections
 $\theta = 1.0$ – 27.5 °
 $\mu = 1.94$ mm⁻¹
 $T = 130$ K
 Fragment, colorless
 $0.27 \times 0.25 \times 0.22$ mm

Data collection

Nonius KappaCCD diffractometer
 with Oxford Cryosystems
 Cryostream cooler
 ω scans with κ offsets
 Absorption correction: multi-scan
 (SORTAV; Blessing, 1995)
 $T_{\min} = 0.600$, $T_{\max} = 0.652$
 43 363 measured reflections

20 107 independent reflections
 11 547 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.064$
 $\theta_{\max} = 27.5$ °
 $h = -18 \rightarrow 18$
 $k = -19 \rightarrow 19$
 $l = -26 \rightarrow 26$

Refinement

Refinement on F^2
 $R(F) = 0.036$
 $wR(F^2) = 0.072$
 $S = 0.89$
 20 107 reflections
 860 parameters
 H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0282P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.005$
 $\Delta\rho_{\max} = 0.66$ e Å⁻³
 $\Delta\rho_{\min} = -0.45$ e Å⁻³
 Extinction correction: SHELXL97
 (Sheldrick, 1997)
 Extinction coefficient: 0.00103 (8)

Table 1

Selected geometric parameters (Å).

P1–N4	1.6343 (19)	P3–N10	1.6338 (18)
P1–N1	1.6355 (19)	P3–N9	1.6340 (19)
P1–N2	1.6371 (19)	P3–N11	1.6342 (19)
P1–N3	1.6395 (18)	P3–N12	1.6382 (17)
P2–N6	1.6339 (19)	P4–N15	1.628 (2)
P2–N7	1.6357 (19)	P4–N16	1.6305 (18)
P2–N8	1.637 (2)	P4–N14	1.6343 (18)
P2–N5	1.6397 (19)	P4–N13	1.6400 (18)

Table 2

Hydrogen-bonding geometry (Å, °).

$D\cdots H\cdots A$	$D\cdots H$	$H\cdots A$	$D\cdots A$	$D\cdots H\cdots A$
O1W–H2W1 \cdots Br1	0.773 (17)	2.656 (18)	3.425 (2)	174 (3)
O1W–H1W1 \cdots Br1 ⁱ	0.789 (16)	2.824 (17)	3.611 (3)	176 (3)
O2W–H1W2 \cdots Br2	0.766 (17)	2.711 (18)	3.467 (3)	169 (3)
O2W–H2W2 \cdots Br2 ⁱⁱ	0.790 (16)	2.682 (17)	3.471 (2)	177 (3)

Symmetry codes: (i) $1 - x, 2 - y, -z$; (ii) $1 - x, 1 - y, 1 - z$.

The water H atoms were located in difference maps and refined with O–H distances restrained using $DFIX0.80$ (SHELXL97; Sheldrick, 1997). Their isotropic displacement parameters were refined individually. Other H atoms were placed in calculated positions, with C–H bond distances of 0.99 Å for methylene and 0.98 Å for methyl, and thereafter were treated as riding with $U_{\text{iso}} = 1.2U_{\text{eq}}$ of the attached C atom (1.5 for methyl groups). A torsional parameter was refined for each methyl group.

Data collection: *COLLECT* (Nonius, 1999); cell refinement: *DENZO* (Otwinowski & Minor, 1997); data reduction: *DENZO*; program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPIII* (Burnett & Johnson, 1996) and *PLUTON* (Spek, 1990); software used to prepare material for publication: *maXus* (Mackay *et al.*, 1999).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: DA1144). Services for accessing these data are described at the back of the journal.

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