Crystal Structure of Bis(trimethylphosphine)iminium Bromide Monohydrate, $[Me_3P{=}N{=}PMe_3]Br{\cdot}H_2O$[†]

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The crystal structure of the title compound has been determined by *X*-ray analysis. The crystals are triclinic, space group $P\bar{1}$, with $a = 9.685(1)$, $b = 11.449(4)$, $c = 18.173(2)$ Å, $\alpha = 90.55(2)$, $\beta = 91.50(1)$, and $\gamma = 108.93(2)°$, and $Z = 6$. The structure refined to $R = 0.059$ using 4 103 independent reflections. There are three crystallographically independent $[Me_3P{=}N{=}PMe_3]^+$ cations, with mean PNP angles of 137.0° and mean P=N distances of 1.582 Å. The anions and water of crystallisation are present in hydrogen-bonded $Br_6(H_2O)_6{}^{6-}$ units.

There is considerable evidence from structural studies of compounds of the type $R_3SiOSiR_3$, and other isoelectronic systems, that the angle at the central atom is very easily varied. In the gas phase, this manifests itself as a large amplitude, low-frequency vibration, while in the solid phase the same molecule or ion may have widely differing angles, depending on its environment, or the angle may depend markedly on the substituents. Thus $Me_3SiOSiMe_3$ has SiOSi angles of 148.8 and 148° in the solid [1] and gas [2] phases respectively, whereas solid $Ph_3SiOSiPh_3$ has a linear SiOSi skeleton.[3] Crystalline Ph_3PCPPh_3 has two molecules in the asymmetric unit of the monoclinic form,[4a] with PCP angles of 130 and 143°, but 131.7° in the orthorhombic form, [4b] while the apparent angle in Me_3PCPMe_3 in the gas phase is 148°, and it may be that in the average structure the PCP unit is linear.[5a] In $MePh_2PCPPh_2Me$ the PCP angle is even as small as 121.8°, and a cyclic carbodiphosphorane has its PCP moiety fixed at an angle of 116.7°.[5b]

The structure of $[Ph_3PNPPh_3]^+$ has been determined many times, as it is widely used as a large cation in organometallic chemistry, and the PNP angle varies widely, normally between 134 and 142°,[6,7] but, in at least one instance, it is 180°.[8] Clearly, the skeletons of these molecules are very flexible, and we have therefore studied the structure of the ion $[Me_3P\text{-}NPMe_3]^+$, with bromide counter ions.[9a]

Experimental

A sample of $[Me_3PNPMe_3]Br$ was prepared by treatment of $Me_3P{=}NP({=}CH_2)Me_2$ with hydrogen bromide,[9b] and recrystallised from methanol. Crystals which had been stored for several years were then recrystallised from ethanol.

Crystal Data.—$C_6H_{18}BrNP_2{\cdot}H_2O$, $M = 264$, clear, colourless, triclinic crystals, $a = 9.685(1)$, $b = 11.449(4)$, $c = 18.173(2)$ Å, $\alpha = 90.55(2)$, $\beta = 91.50(1)$, $\gamma = 108.93(2)°$, $U = 1\,905$ Å^3, $Z = 6$, $D_c = 1.38$ g cm^{-3}, space group $P\bar{1}$ (no. 2), Cu-K_α radiation, $\lambda = 1.5418$ Å, $\mu = 68.9$ cm^{-1}.

Structure Determination.—A single crystal of dimensions $0.2 \times 0.2 \times 0.25$ mm was sealed into a glass capillary under a stream of nitrogen. Unit-cell dimensions and intensity data were measured on a Nonius CAD4 diffractometer. A precession photograph of the 0*kl* zone did not show *mm* symmetry, and confirmed that the unit cell was indeed triclinic. Of the 5 120 unique reflections measured to $\theta_{max.} = 55°$, 4 103 had $I > 3\sigma(I)$. No absorption correction was applied.

E-Value statistics indicated a centric distribution of atoms which implied space group $P\bar{1}$, a choice verified by the subsequent refinement. Application of the direct methods package EEES (SHELX) [10] required a number of trials before a solution was obtained for the positions of the three crystallo-

Table 1. Fractional co-ordinates of non-hydrogen atoms with standard deviations in parentheses

Atom	*X*	*Y*	*Z*
Br(1)	0.322 82(8)	0.692 42(6)	0.501 91(4)
Br(2)	0.219 16(9)	0.183 54(6)	0.257 55(4)
Br(3)	0.488 92(9)	0.255 76(7)	0.883 00(5)
O(1)	0.150 2(6)	0.140 2(5)	0.945 9(4)
O(2)	0.071 4(8)	0.086 1(6)	0.091 1(4)
O(3)	0.439 1(8)	0.800 4(7)	0.673 7(4)
P(1)	0.334 1(2)	0.838 31(13)	0.875 98(8)
N(1)	0.293 4(6)	0.695 2(4)	0.862 1(3)
C(11)	0.250 7(9)	0.901 4(6)	0.806 1(4)
C(12)	0.526 8(8)	0.921 2(6)	0.875 4(5)
C(13)	0.276 0(11)	0.875 7(8)	0.962 3(4)
P(2)	0.359 0(2)	0.587 50(13)	0.874 36(8)
C(21)	0.358 6(9)	0.508 6(7)	0.789 4(4)
C(22)	0.543 6(8)	0.631 1(7)	0.909 2(4)
C(23)	0.254 4(9)	0.478 9(7)	0.936 8(5)
P(3)	0.094 3(2)	0.767 60(13)	0.232 45(8)
C(31)	0.140 5(7)	0.799 6(6)	0.138 8(3)
C(32)	−0.046 8(8)	0.829 7(6)	0.249 5(4)
C(33)	0.248 9(9)	0.852 2(6)	0.287 0(5)
P(4)	0.100 5(2)	0.514 23(13)	0.250 33(8)
N(2)	0.034 7(5)	0.625 3(4)	0.249 1(3)
C(41)	0.107 8(8)	0.451 9(7)	0.160 7(4)
C(42)	−0.016 7(8)	0.393 5(6)	0.303 0(4)
C(43)	0.281 1(7)	0.552 2(7)	0.289 8(4)
P(5)	0.222 9(2)	0.306 82(12)	0.543 02(7)
N(3)	0.167 2(5)	0.163 9(4)	0.560 9(2)
C(51)	0.074 4(7)	0.364 8(6)	0.553 1(4)
C(52)	0.364 8(8)	0.396 5(6)	0.603 6(4)
C(53)	0.288 7(8)	0.340 7(6)	0.452 7(3)
P(6)	0.239 4(2)	0.057 93(12)	0.563 71(8)
C(61)	0.106 3(7)	−0.079 2(5)	0.593 7(4)
C(62)	0.393 0(8)	0.088 6(7)	0.623 7(4)
C(63)	0.295 7(9)	0.020 9(7)	0.475 5(4)

[†] *Supplementary data available* (No. SUP 23392; 29 pp.): observed and calculated structure factors, all fractional co-ordinates, thermal parameters. See Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

Table 2. Molecular parameters for $[Me_3P{=}N{=}PMe_3]Br{\cdot}H_2O$ with estimated standard deviations in parentheses

Molecule 1		Molecule 2		Molecule 3	
(*a*) Bond lengths (Å)					
N(1)-P(1)	1.572(5)	N(2)-P(3)	1.577(5)	N(3)-P(5)	1.588(5)
N(1)-P(2)	1.575(6)	N(2)-P(4)	1.597(6)	N(3)-P(6)	1.586(6)
P(1)-C(11)	1.769(8)	P(3)-C(31)	1.783(6)	P(5)-C(51)	1.782(8)
P(1)-C(12)	1.799(7)	P(3)-C(32)	1.765(9)	P(5)-C(52)	1.772(7)
P(1)-C(13)	1.775(8)	P(3)-C(33)	1.768(8)	P(5)-C(53)	1.777(6)
P(2)-C(21)	1.781(8)	P(4)-C(41)	1.784(7)	P(6)-C(61)	1.779(6)
P(2)-C(22)	1.789(7)	P(4)-C(42)	1.783(6)	P(6)-C(62)	1.759(7)
P(2)-C(23)	1.769(8)	P(4)-C(43)	1.788(7)	P(6)-C(63)	1.797(8)
(*b*) Bond angles (°)					
P(1)-N(1)-P(2)	140.1(4)	P(3)-N(2)-P(4)	135.9(3)	P(5)-N(3)-P(6)	135.1(3)
N(1)-P(1)-C(11)	109.3(3)	N(2)-P(3)-C(31)	113.5(3)	N(3)-P(5)-C(51)	108.2(3)
N(1)-P(1)-C(12)	114.2(3)	N(2)-P(3)-C(32)	107.7(3)	N(3)-P(5)-C(52)	113.8(3)
N(1)-P(1)-C(13)	112.8(3)	N(2)-P(3)-C(33)	114.5(3)	N(3)-P(5)-C(53)	114.3(3)
N(1)-P(2)-C(21)	110.0(4)	N(2)-P(4)-C(41)	112.7(3)	N(3)-P(6)-C(61)	108.2(3)
N(1)-P(2)-C(22)	116.6(3)	N(2)-P(4)-C(42)	107.8(3)	N(3)-P(6)-C(62)	114.7(3)
N(1)-P(2)-C(23)	111.0(4)	N(2)-P(4)-C(43)	114.9(3)	N(3)-P(6)-C(63)	113.5(3)
C(11)-P(1)-C(12)	106.9(4)	C(31)-P(3)-C(32)	106.1(3)	C(51)-P(5)-C(52)	106.2(3)
C(11)-P(1)-C(13)	108.1(4)	C(31)-P(3)-C(33)	106.8(3)	C(51)-P(5)-C(53)	107.9(4)
C(12)-P(1)-C(13)	105.2(4)	C(32)-P(3)-C(33)	107.8(4)	C(52)-P(5)-C(53)	106.0(3)
C(21)-P(2)-C(22)	105.0(4)	C(41)-P(4)-C(42)	107.4(3)	C(61)-P(6)-C(62)	107.5(3)
C(21)-P(2)-C(23)	108.0(4)	C(41)-P(4)-C(43)	105.9(4)	C(61)-P(6)-C(63)	106.2(3)
C(22)-P(2)-C(23)	105.8(4)	C(42)-P(4)-C(43)	107.7(3)	C(62)-P(6)-C(63)	106.3(4)
(*c*) Dihedral angles (°)					
C(11)-P(1)-N(1)-P(2)	149.0	C(31)-P(3)-N(2)-P(4)	66.9	C(51)-P(5)-N(3)-P(6)	−179.1
C(12)-P(1)-N(1)-P(2)	29.4	C(32)-P(3)-N(2)-P(4)	−176.0	C(52)-P(5)-N(3)-P(6)	−61.2
C(13)-P(1)-N(1)-P(2)	−90.7	C(33)-P(3)-N(2)-P(4)	−56.1	C(53)-P(5)-N(3)-P(6)	60.7
C(21)-P(2)-N(1)-P(1)	−125.4	C(41)-P(4)-N(2)-P(3)	−80.6	C(61)-P(6)-N(3)-P(5)	176.8
C(22)-P(2)-N(1)-P(1)	−6.0	C(42)-P(4)-N(2)-P(3)	161.1	C(62)-P(6)-N(3)-P(5)	56.8
C(23)-P(2)-N(1)-P(1)	115.2	C(43)-P(4)-N(2)-P(3)	41.0	C(63)-P(6)-N(3)-P(5)	−65.6

graphically independent Br^- ions. A difference-Fourier synthesis phased on the Br^- ions provided positions for all non-hydrogen atoms in the structure. Subsequent difference-Fourier maps revealed a further three peaks each about 3 Å from the Br^- ions, and these were assigned as the oxygen atoms of water of crystallisation. The 54 methyl hydrogen atoms were refined as rigid groups (SHELX), for the final cycles of refinement. All non-hydrogen atoms were allowed to refine anisotropically. The 54 methyl hydrogen atoms were constrained to have the same temperature factor. The weighting scheme $w = 1/[\sigma^2(F) + 0.000\,45\,F^2]$ gave an even distribution of variance in $|F|$ analysed in ranges of both $|F|$ and sin θ. In the final cycle of refinement no positional shifts were greater than 0.2 times their estimated standard deviations. The final *R* factor was 0.059 ($R' = 0.083$).

Positional parameters of non-hydrogen atoms are given in Table 1, and bond lengths and angles are listed in Table 2.

Results and Discussion

In the crystalline phase of $[Me_3PNPMe_3]Br{\cdot}H_2O$ there are three crystallographically independent sets of cations, anions, and molecules of water of crystallisation. The three cations have broadly similar structures, but differ in the conformations adopted, while the bromide anions and water molecules are in positions such that there are isolated $Br_6(H_2O)_6{}^{6-}$ hydrogen-bonded units. Two views of the packing are given in Figure 1.

There is little variation in the P–C distances and CPC angles in the cations, mean values being 1.779 Å and 106.7° respectively. The former value is small, and may be compared with distances of 1.814 Å in Me_3PCPMe_3[5] and 1.841 Å in trimethylphosphine.[11] However, the mean non-bonded C···C distance (2.856 Å) is slightly greater than in Me_3PCPMe_3, and is therefore associated with a much wider CPC angle (mean 106.7°, compared with 101.4°).

Table 3. Bond distances (Å) and angles (°) in isoelectronic Me_3MQMMe_3 species

Molecule or ion	Phase	Distance	Angle	Ref.
$Me_3SiOSiMe_3$	Gas	Si–O 1.63	SiOSi 148	2
	Solid	Si–O 1.626	SiOSi 148.8	1
$Me_3PNSiMe_3$	Gas	P–N 1.542 Si–N 1.705	PNSi 144.6	*a*
Me_3PCPMe_3	Gas	P–C 1.594	PCP 147.6	5
$[Me_3PNPMe_3]^+$	Solid	P–N 1.582	PNP 137.0	*b*

[a] E. E. Astrup, A. M. Bouzga, and K. A. Ostoja-Starzewski, *J. Mol. Struct.*, 1979, **51**, 51. [b] This work.

The P=N distances are also self-consistent, averaging 1.582 Å, and the three PNP angles (140.1, 135.9, and 135.1°) are reasonably similar. These distances are very close to those reported for the cation $[Ph_3PNPPh_3]^+$ when its PNP angle is around 135—140°,[6,7] although the distance drops to 1.53 Å in $[Ph_3PNPPh_3][V(CO)_6]$, in which the PNP unit is linear.[8] In Table 3 the corresponding distances and angles for a series of isoelectronic species are listed. What is remarkable about the angles presented there is their consistency. In particular, the apparent angles for the gas-phase species (with no account taken of the, possibly considerable, shrinkage effects [12,13]) are close to the more meaningful angles for solid-phase species. It may be that observed angles in either phase depend on the minimum angle that is possible without 'too-close' contact between the two silicon or phosphorus atoms.

Comparison with the nickel complex (1) is also interesting.

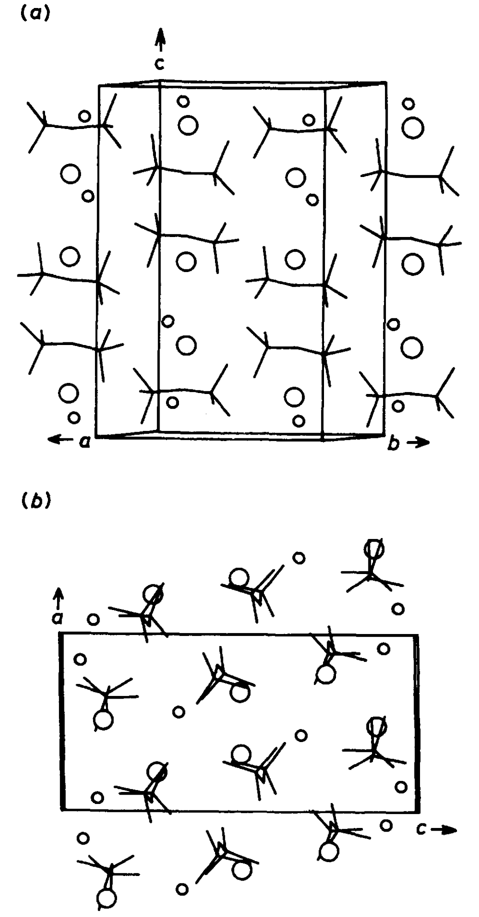
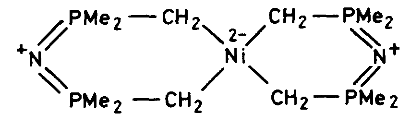
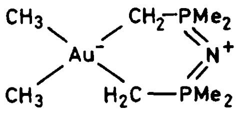


Figure 1. Unit-cell contents viewed (*a*) along *a*, and (*b*) along *b*; bromide ions are represented by large circles and the oxygen atoms of water of crystallisation by small circles



(1)



(2)

In this compound,[14] the P–N bonds are longer (1.597 Å) than in the iminium salt, and the PNP angles (124.2°) are considerably narrower. In the related gold complex, (2), the PNP angle is 130.5°.[15]

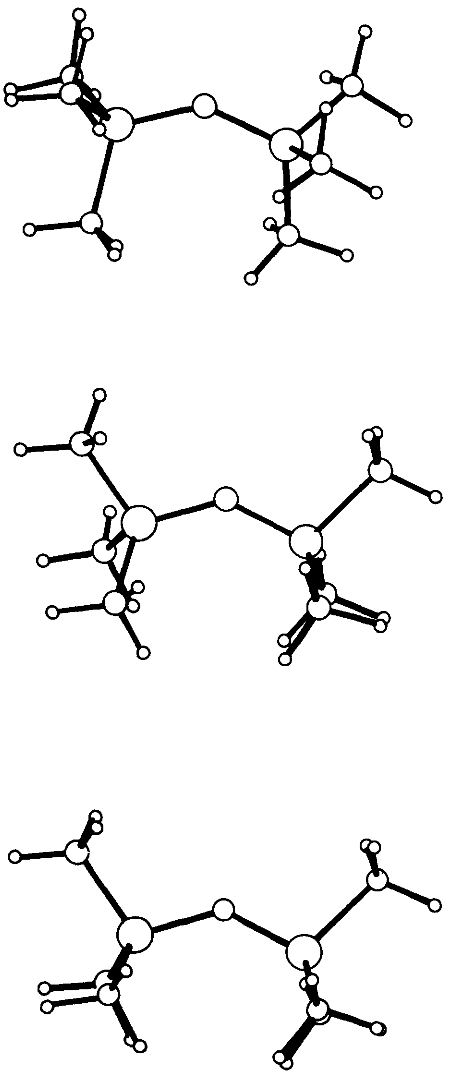


Figure 2. The three crystallographically distinct $[Me_3PNPMe_3]^+$ cations, each viewed perpendicular to its PNP plane

All 18 methyl groups, refined as idealised rigid groups, adopted staggered orientations (±12°) with respect to the C–P bonds. However, the conformations of the six PC_3 groups are rather variable, as may be seen from the drawings of the three cations (Figure 2) or from the listed CPNP dihedral angles (Table 2). Figure 3 shows that there is a marked correlation between dihedral angles and the associated NPC valence angles. As the CPC angles are not very variable this suggests that the non-bonded P ··· C interaction tends to tilt the PMe_3 unit as a whole (by an average of 3°) rather than simply enlarging one NPC angle.

The arrangement of the bromide anions and water molecules in the lattice is interesting. Although hydrogen atom positions were not determined, it is clear from the positions of oxygen atoms and bromide ions that four water molecules form a hydrogen-bonded ring about the crystallographic centre of symmetry. Each is further hydrogen-bonded to a bromide ion. The third pair of water molecules bridge from two of these central Br^- ions to another outlying pair. It should be noted that this distinctive hydrogen-bonded constellation, illustrated in Figure 4, does not form an infinite chain through the lattice. Short O ··· O and O ··· Br contacts are listed in Table 4.

There are no short intermolecular van der Waals contacts.

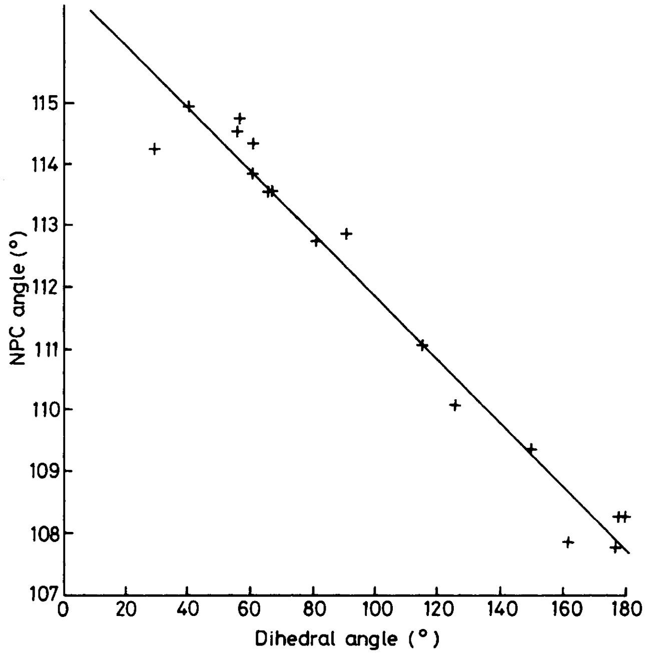


Figure 3. A plot of C_x–P_y–N–P dihedral angle *versus* N–P_y–C_x valence angle

Table 4. Non-bonded contacts (Å) between bromide ions and water molecules

Atoms	Distance
O(1) ··· O(2)	2.838(8)
O(1) ··· O(2)	2.786(9)
O(1) ··· Br(3)	3.351(6)
O(2) ··· Br(2)	2.335(6)
O(3) ··· Br(1)	3.374(6)
O(3) ··· Br(2)	3.454(8)

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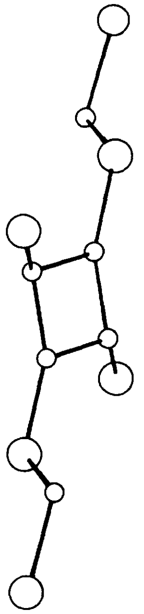

Figure 4. View of the hydrogen-bonded $Br_6(H_2O)_6^{6-}$ unit; the bromide ions are represented by large circles and the oxygen atoms by small circles

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