Nature of Bonding in Aminophosphonium Salts: Molecular Structure of *N,N*-Dimethylaminotriphenylphosphonium Tribromide

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The crystal structure of *N,N*-dimethylaminotriphenylphosphonium tribromide (3) was studied by *X*-ray diffraction analysis. Crystals are monoclinic, space group $P2_1/c$, $a = 9.921(2)$, $b = 15.426(5)$, $c = 14.048(1)$ Å, $\beta = 90.54(1)°$ and $Z = 4$. The P–N bond length is rather short, 1.63 Å, and the arrangement of bonds around nitrogen is planar. These results, compared with previous reports on analogous compounds support the idea of a strong π character of the $\overset{+}{\mathrm{P}}$–N bond.

The chemistry of phosphorus–nitrogen compounds, a large subject, is an area where correlations between chemical reactivity and molecular structure are well developed.[1] However, very few structural results are available for aminophosphonium salts, but the results do suggest the absence of $p\pi$–$d\pi$ bonding between the nitrogen lone pair and the phosphorus *d*-orbitals.[2,3] This is surprising in view of the often assumed $p\pi$–$d\pi$ bonding in aminophosphines[4] for which, in the absence of steric factors, a short P–N bond and a planar arrangement of bonds around nitrogen are generally observed;† moreover, the positive charge on the phosphorus atom of the salt should contract *d* orbitals, thus enhancing the overlap with the nitrogen lone pair,[7] as already invoked to explain the effect of electronegative ligands attached to phosphorus.[1,6] Finally, aminophosphoniums are isoelectronic with ylides ($>\overset{+}{\mathrm{P}}-\overset{-}{\mathrm{C}}<$) in which a high degree of double bond character is likely.[8] Nevertheless, the hydrazinophosphonium [$(\mathrm{Ph_3P{\cdot}NH{\cdot}NMe_2})^+\mathrm{Br}^-$] displays a markedly non-planar geometry for the nitrogen linked to phosphorus (sum of the bond angles around nitrogen, $\Sigma_N = 348°$) along with a rather short $\overset{+}{\mathrm{P}}$–N bond length[2] (1.64 Å compared with 1.77 Å for the length of a P–N single bond[1]); however, the observed conformation results from localization of a hydrogen atom engaged in hydrogen bonding with bromide, and further, the specificity of the hydrazino moiety must be taken into account. The geometry of nitrogen is also non-planar in phosphinamides,[9] where the phosphorus atom bears a partial positive charge; however, in this case, competition between nitrogen and oxygen lone pairs for the phosphorus *d* orbitals might lower the π character of the P–N bond. On the other hand, CNDO/2 calculations for $\mathrm{Me_3\overset{+}{P}{\cdot}NH_2}$ predict a pyramidal nitrogen geometry slightly favoured over the planar form,[3] although results of this kind must be viewed with caution. We therefore undertook the structural determination of a simple aminophosphonium salt, in order to clarify the nature of bonding between the nitrogen and the positively charged phosphorus atom, and thus to allow, in the future, an improved anticipation of chemical reactivity for such compounds. The chosen *N,N*-dimethylaminotriphenylphosphonium (1) has been prepared according to Fukui and Sudo.[10]

Experimental

Crystals from the bromide (1) and the iodide (2) are not of sufficient quality to allow a serious crystallographic study. The use of the tribromide ion, in which we have an interest, owing to its brominating properties,[11] led us to small suitable single crystals of compound (3) by a slow diffusion of ether into dichloromethane solution of this tribromide.

Crystal Data.—$\mathrm{(C_6H_5)_3PN(CH_3)_2Br_3}$, $M = 546.1$, monoclinic, $a = 9.921(2)$, $b = 15.426(5)$, $c = 14.048(1)$ Å, $U = 2149.82$ Å^3, $D_m = 1.66$ g cm^{-3}, $Z = 4$, $D_c = 1.69$ g cm^{-3}, F(000) 1 072, space group $P2_1/c$, μ (Mo-K_α) = 55.7 cm^{-1}. A crystal of dimensions 0.16 × 0.2 × 0.2 mm, respectively, between the faces {110}, {1$\bar{1}$0}, and {001} was used to collect three dimensional intensity data on an Enraf-Nonius four-circle diffractometer. Space-group and unit-cell parameters were determined from preliminary Weissenberg photographs, and then refined by the least-squares procedure of the diffractometer from 22 reflections. The $\theta - 2\theta$ scanning technique with variable scan speed and graphite-monochromated Mo-K_α radiation was used. No change in intensity for standard reflections was observed throughout the data collection. The data were corrected for Lorentz, polarization, and absorption effects. In the range $2 < \theta < 25°$, 1 146 reflections with $I \geqslant 3\sigma(I)$ were considered to be observed and were used for calculations. Anomalous dispersion corrections were applied to the scattering factors.

Structure Solution.—Analysis of the tridimensional Patterson map led to localization of the three bromine atoms. After refinement of positional parameters, all other non-hydrogen atoms were found by subsequent Fourier synthesis. Isotropic full-matrix least-squares refinements gave an *R*-value of 0.16. Phenyl rings were treated as rigid groups and anisotropic temperature factors were affected to phosphorus, nitrogen, and bromine atoms thus lowering *R* to 0.063. Sixteen hydrogen atoms out of 21 were located from a difference electron-density map, but all of them were introduced at calculated positions; methyls were treated as rigid groups, other hydrogen atoms being part of the aromatic rigid groups (C–H distance assumed to be 0.97 Å). The isotropic temperature factor assigned to each hydrogen was the isotropic *B*-value for the carbon to which it was bonded plus 1.0 Å^2 and was not refined. Two more cycles of refinement reduced *R* to 0.054. For the final stages of refinement, geometrical constraints on the phenyl rings were released, except for the hydrogen atoms, and all non-hydrogen atoms were refined anisotropically, yielding a final *R*-value of 0.046 for 1 146 reflections and 232 variables.

Computations were performed on the IBM 3033 of the Centre National Universitaire Sud de Calcul at Montpellier, using a local program for data reduction,[12] a program by Coppens and Hamilton for absorption corrections,[13] the

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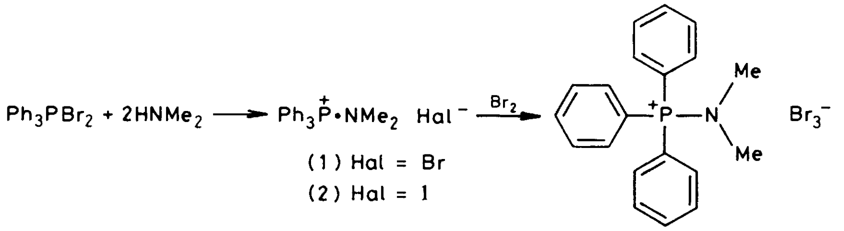
† As an alternative explanation, an overlap of the nitrogen lone pair with an antibonding *sp*-hybrid orbital of the phosphorus (n-σ^*) has also been suggested.[5,6]



(3)

Table 1. Fractional atomic co-ordinates, with estimated standard deviations in parentheses

Atom	*x*/*a*	*y*/*b*	*z*/*c*
Br(1)	0.722 7(2)	0.284 2(2)	−0.020 0(2)
Br(2)	0.690 1(2)	0.171 2(1)	0.102 2(2)
Br(3)	0.653 7(2)	0.064 5(2)	0.242 5(2)
P	0.206 3(3)	0.230 7(2)	0.255 0(3)
N	0.352 2(10)	0.279 2(8)	0.254 7(9)
C(1)	0.195 7(14)	0.166 0(9)	0.149 4(9)
C(2)	0.082 7(13)	0.165 6(10)	0.091 1(10)
C(3)	0.078 3(15)	0.110 7(10)	0.013 9(11)
C(4)	0.183 1(18)	0.055 8(10)	−0.006 4(11)
C(5)	0.294 1(17)	0.057 5(10)	0.050 0(11)
C(6)	0.304 7(14)	0.110 8(10)	0.128 1(10)
C(7)	0.205 1(13)	0.160 8(9)	0.357 5(10)
C(8)	0.310 3(7)	0.104 3(11)	0.371 3(11)
C(9)	0.306 0(18)	0.045 6(11)	0.444 7(14)
C(10)	0.199 3(22)	0.043 1(12)	0.506 0(12)
C(11)	0.096 9(18)	0.100 7(12)	0.494 3(11)
C(12)	0.097 6(14)	0.160 7(10)	0.420 6(10)
C(13)	0.066 7(12)	0.304 4(9)	0.257 9(8)
C(14)	0.093 5(15)	0.392 7(9)	0.255 3(10)
C(15)	−0.008 1(18)	0.450 8(11)	0.255 7(11)
C(16)	−0.139 4(19)	0.422 2(14)	0.257 3(12)
C(17)	−0.169 0(15)	0.334 6(13)	0.259 8(12)
C(18)	−0.066 2(13)	0.277 3(10)	0.260 5(9)
C(19)	0.403 4(16)	0.319 2(10)	0.165 8(11)
C(20)	0.418 0(16)	0.309 5(12)	0.342 2(11)
Calculated hydrogen positions			
H(2)	0.007	0.203	0.104
H(3)	−0.001	0.111	−0.027
H(4)	0.177	0.016	−0.060
H(5)	0.369	0.019	0.035
H(6)	0.385	0.111	0.168
H(8)	0.387	0.106	0.329
H(9)	0.380	0.005	0.453
H(10)	0.197	0.001	0.557
H(11)	0.022	0.100	0.538
H(12)	0.024	0.202	0.413
H(14)	0.186	0.413	0.253
H(15)	0.011	0.512	0.255
H(16)	−0.212	0.464	0.257
H(17)	−0.262	0.315	0.261
H(18)	−0.086	0.216	0.263
H(191)	0.358	0.300	0.108
H(192)	0.495	0.297	0.167
H(193)	0.406	0.382	0.168
H(201)	0.392	0.286	0.403
H(202)	0.416	0.372	0.345
H(203)	0.508	0.290	0.327

Table 2. Bond lengths, with estimated standard deviations in parentheses

Bond	Length (Å)	Bond	Length (Å)
Br(1)–Br(2)	2.470(4)	C(6)–C(1)	1.411(17)
Br(2)–Br(3)	2.596(4)	C(7)–C(8)	1.372(18)
P–N	1.629(11)	C(8)–C(9)	1.373(19)
P–C(1)	1.791(13)	C(9)–C(10)	1.371(21)
P–C(7)	1.799(14)	C(10)–C(11)	1.359(21)
P–C(13)	1.793(12)	C(11)–C(12)	1.388(19)
N–C(19)	1.487(16)	C(12)–C(7)	1.392(17)
N–C(20)	1.464(16)	C(13)–C(14)	1.388(17)
C(1)–C(2)	1.382(17)	C(14)–C(15)	1.349(18)
C(2)–C(3)	1.377(18)	C(15)–C(16)	1.375(21)
C(3)–C(4)	1.373(19)	C(16)–C(17)	1.384(22)
C(4)–C(5)	1.351(19)	C(17)–C(18)	1.349(18)
C(5)–C(6)	1.374(18)	C(18)–C(13)	1.384(16)

Table 3. Bond angles, with estimated standard deviations in parentheses

Bond	Angle (°)	Bond	Angle (°)
Br(1)–Br(2)–Br(3)	174.4(0.1)	C(6)–C(1)–C(2)	119.4(1.3)
C(1)–P–N	107.4(0.6)	P–C(7)–C(8)	118.8(1.2)
C(7)–P–N	106.9(0.6)	P–C(7)–C(12)	121.4(1.2)
C(13)–P–N	113.3(0.6)	C(7)–C(8)–C(9)	119.7(1.5)
C(1)–P–C(7)	109.1(0.6)	C(8)–C(9)–C(10)	121.3(1.6)
C(1)–P–C(13)	109.4(0.6)	C(9)–C(10)–C(11)	119.1(1.7)
C(7)–P–C(13)	110.5(0.6)	C(10)–C(11)–C(12)	121.1(1.6)
P–N–C(19)	120.2(1.0)	C(11)–C(12)–C(7)	119.0(1.4)
P–N–C(20)	122.2(1.0)	C(12)–C(7)–C(8)	119.7(1.4)
C(19)–N–C(20)	114.9(1.2)	P–C(13)–C(14)	118.3(1.0)
P–C(1)–C(2)	122.3(1.1)	P–C(13)–C(18)	123.1(1.1)
P–C(1)–C(6)	118.2(1.1)	C(13)–C(14)–C(15)	120.5(1.4)
C(1)–C(2)–C(3)	119.3(1.3)	C(14)–C(15)–C(16)	119.7(1.6)
C(2)–C(3)–C(4)	121.7(1.4)	C(15)–C(16)–C(17)	121.0(1.6)
C(3)–C(4)–C(5)	118.7(1.5)	C(16)–C(17)–C(18)	118.7(1.6)
C(4)–C(5)–C(6)	122.4(1.5)	C(17)–C(18)–C(13)	121.5(1.5)
C(5)–C(6)–C(1)	118.5(1.3)	C(18)–C(13)–C(14)	118.7(1.2)

SHELX system[14] for Patterson, Fourier and least-squares refinements, and ORTEP[15] for drawing.

Results and Discussion

Atomic co-ordinates are listed in Table 1, bond lengths in Table 2, and bond angles in Table 3. The conformation obtained for the organic cation is shown in Figure 1. The tribromide ion is asymmetric [Br–Br = 2.470 (4) and 2.596 (4) Å] and diverges from linearity [Br–Br–Br = 174.4 (1)°].[16]

The angles at phosphorus are close to tetrahedral (from 106.9 to 113.3°). The equation of the best least-squares planes through the phenyl rings are given in Table 4 along with the deviations of the atoms. Aromatic C–C bond lengths vary from 1.35 to 1.41 Å and the average value, 1.375, is slightly shorter than the standard value of 1.394 Å,[17] as previously found for four co-ordinate phosphorus compounds.[2,6,8b]

The arrangement of bonds around nitrogen is quasi-planar: Σ_N = 357.3°, deviation of N from the plane through P, C(19), and C(20) is 0.145 Å (see Table 4). This reflects a net trend to sp^2 hybridization, arising from involvement of the nitrogen lone pair in π bonding with phosphorus. That the P–C(Ph) bonds (mean value 1.79 Å), as expected for a four

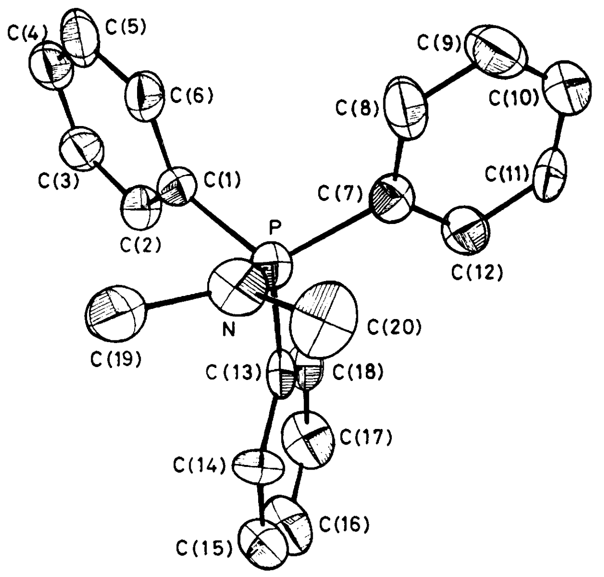


Figure 1. Molecular structure of $Ph_3P{\cdot}NMe_2^+$ with ellipsoids at the 40% probability level; the hydrogen atoms are omitted for clarity

Table 4. Equations of best least-squares planes with the deviation of atoms (10^{-4} Å)

Plane 1	$4.057x + 10.980y - 8.077z = 1.416$					
C(1)–C(6)	C(1)	−59	C(4)	−86	P	−1 053
	C(2)	22	C(5)	49		
	C(3)	50	C(6)	23		
Plane 2	$4.618x + 10.143y + 8.259z = 5.547$					
C(7)–C(12)	C(7)	−158	C(10)	−98	P	−1 479
	C(8)	109	C(11)	49		
	C(9)	20	C(12)	78		
Plane 3	$0.160x + 0.342y + 14.040z = 3.737$					
C(13)–C(18)	C(13)	−15	C(16)	−27	P	−450
	C(14)	−35	C(17)	−23		
	C(15)	56	C(18)	44		
Plane 4	$-5.306x + 12.980y + 1.153z = 2.194$					
P,C(19),C(20)	N	−1 450				

co-ordinate phosphorus,[2,6,9,18] are about 0.05 Å shorter than the same bonds in a three co-ordinate phosphorus,[19] can be ascribed to σ-bond polarization; the same effect, lowered in strength as a consequence of the greater electronegativity of nitrogen compared with carbon, may contract the $\overset{+}{\mathrm{P}}$–N bond, but cannot account, in our opinion, for the 0.14 Å shortening observed here (1.63 Å compared with 1.77 Å for a $\overset{+}{\mathrm{P}}$–N single bond). Thus, the $\overset{+}{\mathrm{P}}$–N bond length contraction obtained also favours the idea of a strong π character for this bond.

The molecular packing shows no particular feature. The closest intermolecular contact, 3.24 Å, is between H(15) in one molecule and H(18) in a molecule in symmetry position $-x, 0.5 + y, 0.5 - z$. The closest atom of the tribromide ion is H(10) in symmetry position $-x, 0.5 + y, 0.5 - z$: Br(1) ⋯ H(10) = 3.44 Å.

In conclusion, our results show that, as previously found in aminophosphines, the existence of *d*π–*p*π bonding in aminophosphonium salts is very likely, but, at present, it is difficult to know to what extent the phenomenon is reinforced by the positive charge on the phosphorus atom.

The structure factors and vibrational parameters are contained in Supplementary Publication No. SUP 23762 (7 pp.).*

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* For details of the Supplementary Publications Scheme see Instructions for Authors, *J. Chem. Soc., Perkin Trans. 2*, 1984, Issue 1.