The Preparation and Molecular Structure of a Diphosphonium Salt with a Linear P — O — P System

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The diphosphonium salt, hexatris(dimethylamino)-μ-oxodiphosphonium trifluoromethanesulfonate, $[(Me_2N)_3P-O-P(NMe_2)_3]^{2+}(CF_3SO_3^-)_2$, has been prepared by addition of hexamethylphosphortriamide to trifluoromethanesulfonic anhydride in CH_2Cl_2 at room temperature.

Its molecular structure has been determined by X-ray crystallographic methods. The unit cell dimensions are $a=8.242(2)$ Å, $b=16.071(3)$ Å, $c=11.204(1)$ Å, $\beta=91.72(1)°$ and $Z=2$. The salt crystallizes in the monoclinic system, space group $P2_1/c$. Full matrix, least squares refinement of 1622 diffractometer reflections gave a final, conventional R-value of 0.050.

The centrosymmetric cations have a linear P—O—P sequence with a P—O bond length of 1.573(1) Å. The dimethylamino nitrogen atoms are all sp^2-hybridized and the average P—N bond length is 1.592(4) Å. In the anions, the central C—S bond length is 1.783(4) Å. Both anions and cations have staggered conformations.

The present structure determination was undertaken to identify a new compound formed in the reaction between hexamethylphosphortriamide and methanesulfonic anhydride.[1] Since the compound from elemental analysis and molecular weight determination presumably might contain a P—O—P linked diphosphonium ion, it would also be of great interest to look at the structural environments of the oxygen and phosphorus atoms. Structural investigations of polyphosphates with P—O—P links show that linear P—O—P sequences are seldom found; and they are only claimed to exist in pyrophosphate salts.[2] In the diphosphonium salt in the present investigation, the three bulky dimethylamino groups on one phosphorus atom may interact sterically with the three dimethylamino

groups of the other phosphorus atom if the P—O—P angle differs much from 180°.

Tris(dialkylamino)phosphines and their derivatives may contain sp^2 and/or sp^3-hybridized nitrogen atoms.[3-6] Several models describing the direction of the nitrogen atom lone pairs relative to the phosphorus lone pair (or a fourth bond to phosphorus) have been proposed in connection with interpretation of ESCA spectra.[7,8] We hope that accurate structural data on this aminophosphine derivative will contribute to the somewhat limited information available on structure and bonding in such compounds.

EXPERIMENTAL

Preparation of the diphosphonium salt, $\{[(Me_2N)_3P]_2O\}(CF_3SO_3)_2$. Hexamethylphosphortriamide, $(Me_2N)_3P=O$, (4.57 g, 0.0255 mol) was dissolved in dichloromethane (40 ml). To this solution, trifluoromethanesulfonic anhydride, $(CF_3SO_2)_2O$, (3.12 g, 0.0110 mol) dissolved in dichloromethane (20 ml) was added dropwise with stirring within 5 min. After *ca.* 10 min two liquid layers formed. The solution was then stirred and crystals formed from the lower layer after 1—2 h. After an additional hour of stirring, the crystals were filtered, washed with dichloromethane, dried *in vacuo* and weighed. To improve yield and speed in crystallization, a few crystals of the product were added to the reaction mixture as soon as the two liquid layers formed. This caused crystallization to start immediately. Transparent colourless crystals were obtained upon recrystallization from a 1:1 isopropanol—ethanol mixture. M.p. 230 °C (decomp.), yield 66.5 %. ($C_{14}H_{36}F_6N_6O_7P_2S_2$ requires C 26.25; H 5.67; N 13.12; P 9.67; S 10.01; M 640.5. Found: C 26.84; H 5.59; N 13.38; P 9.38;

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S 9.63; M 643). The molecular weight was determined by titration with aqueous sodium hydroxide.

X-Ray data. Intensity data and data for measurement of unit cell parameters were obtained on an Enraf-Nonius CAD-4 diffractometer. The crystal used for data collection had approximate dimensions of $0.25 \times 0.12 \times 0.11$ mm^3. Unit cell parameters were determined by least-squares refinement of the setting angles of 24 high-angle reflections and found to be $a = 8.242(2)$ Å, $b = 16.071(3)$ Å, $c = 11.204(1)$ Å and $\beta = 91.72(1)°$. From systematic absences on Weissenberg films; $0k0$, $k = 2n+1$ and $h0l$, $l = 2n+1$, the space group is $P2_1/c$ (No. 14). D_m(flotation) $= 1.44$ g/cm^3; $D_x = 1.434$ g/cm^3 with two formula units per cell.

Reflection intensities were collected using the $\theta - 2\theta$ scan technique, a graphite monochromator and Mo$K\alpha$ radiation. The scan width was set to $\pm 1.00°$ and the scan rate varied from 1.33 to 3.35° min^{-1}, with the actual rate determined from a preset intensity value and a preliminary prescan for each reflection. Two control reflections measured after every 100 reflections gave no indication of crystal deterioration. Background counts were taken for 1/4 of the calculated scan time on each side of every reflection. The net intensity of a reflection, I, is defined as $I = [P - 2(B1 + B2)]k$, where P is the peak scan count, $B1$ and $B2$ are the left and right back-ground counts and k is a factor related to the scan rate. The intensity data were given standard deviations according to the expression $\sigma(I) = [(P + 4(B1 + B2))k]^{1/2}$. Out of 2602 unique reflections with $2\theta < 50°$, 1622 had intensities greater than $2\sigma(I)$ and were treated as observed. Because of the very small linear absorption coefficient ($\mu = 3.69$ cm^{-1}), no absorption correction was applied. A few reflections seemed to be affected by secondary extinction, and a correction was made for this effect. The scattering factors were corrected for anomalous dispersion.[9]

In the least-squares full-matrix refinement, the quantity minimized was $\Sigma w(F_o - F_c)^2$ where $w = 4F_o^2/\sigma(F_o^2)^2$ and $\sigma(F_o^2) = [\sigma(I)^2 + (pI)^2]^{1/2}$ with $p = 0.02$. The factors R and R_w were defined as follows: $R = \Sigma \|F_o| - |F_c\|/\Sigma|F_o|$, $R_w = [\Sigma w(\|F_o| - |F_c\|)^2/\Sigma w|F_o|^2]^{1/2}$.

STRUCTURE DETERMINATION

The structure of the diphosphonium salt was solved by means of direct methods (MULTAN). With only two formula units per cell, the asymmetric unit was, as expected, found to consist of half a cation plus an anion, *i.e.* half a formula unit. It is related to the other half through a centre of symmetry in (0, 0, 0). All *non*-hydrogen atomic positions were found after two cycles of Fourier syntheses. The refinement then proceeded by least-squares full matrix methods. The positions of the hydrogen atoms were found partly from a difference map and partly from stereochemical considerations. The structure was further refined with

Table 1. Atomic coordinates for the asymmetric unit (= half a cation plus one anion) of the diphosphonium salt, in fractions of cell edges. Standard deviations in parentheses.

Atom	x	y	z
Cation			
P	$-0.01761(11)$	$0.06639(6)$	$-0.10275(8)$
O1	0	0	0
N1	$-0.2061(3)$	$0.0757(2)$	$-0.1335(3)$
N2	$0.0634(3)$	$0.1494(2)$	$-0.0506(3)$
N3	$0.0755(4)$	$0.0296(2)$	$-0.2138(3)$
C1	$-0.3238(5)$	$0.0887(3)$	$-0.0397(4)$
C2	$-0.2747(5)$	$0.0842(3)$	$-0.2556(4)$
C3	$0.2211(5)$	$0.1509(3)$	$0.0137(5)$
C4	$0.0022(6)$	$0.2318(3)$	$-0.0807(6)$
C5	$0.0336(7)$	$-0.0526(3)$	$-0.2615(5)$
C6	$0.2034(7)$	$0.0733(4)$	$-0.2761(5)$
H1	$-0.343(5)$	$0.143(2)$	$-0.030(3)$
H2	$-0.276(5)$	$0.091(3)$	$0.037(4)$
H3	$-0.393(6)$	$0.053(3)$	$-0.043(4)$
H4	$-0.315(5)$	$0.138(3)$	$-0.262(4)$
H5	$-0.368(8)$	$0.043(4)$	$-0.270(5)$
H6	$-0.204(5)$	$0.089(3)$	$-0.307(4)$
H7	$0.191(6)$	$0.182(3)$	$0.094(4)$
H8	$0.259(6)$	$0.097(3)$	$0.044(4)$
H9	$0.306(8)$	$0.160(4)$	$-0.052(5)$
H10	$-0.084(5)$	$0.233(3)$	$-0.130(4)$
H11	$-0.061(6)$	$0.246(3)$	$0.013(5)$
H12	$0.039(6)$	$0.263(3)$	$-0.055(5)$
H13	$-0.054(6)$	$-0.081(3)$	$-0.217(5)$
H14	$0.115(6)$	$-0.088(3)$	$-0.261(4)$
H15	$0.013(5)$	$-0.046(3)$	$-0.332(4)$
H16	$0.224(5)$	$-0.136(2)$	$-0.241(3)$
H17	$0.283(8)$	$0.044(4)$	$-0.279(6)$
H18	$0.142(6)$	$0.078(3)$	$-0.350(5)$
Anion			
S	$0.50849(13)$	$0.17197(7)$	$0.28322(9)$
O2	$0.4855(4)$	$0.0986(2)$	$0.2161(3)$
O3	$0.3847(4)$	$0.2320(2)$	$0.2759(3)$
O4	$0.6678(4)$	$0.2056(2)$	$0.2711(3)$
C7	$0.5120(7)$	$0.1384(3)$	$0.4350(4)$
F1	$0.6210(5)$	$0.0816(2)$	$0.4574(3)$
F2	$0.3711(5)$	$0.1045(3)$	$0.4606(3)$
F3	$0.5325(5)$	$0.1985(2)$	$0.5115(2)$

anisotropic temperature factors for all atoms except hydrogen and with the weights mentioned above. The final conventional R-factor was 0.050, R_w was 0.045. A final difference map showed no peaks above 0.4 e/Å^3.

Final atomic coordinates and temperature parameters are listed in Tables 1 and 2. Tables of observed

and calculated structure factors are available from the author S. H. upon request.

RESULTS

Interatomic distances and angles are given in Tables 3, 4 and 6 while other structural data are

Table 2. Thermal parameters with standard deviations. The anisotropic temperature factors are given by the expression $\exp-2\pi^2(U_{11}a^{*2}h^2+\ldots+2U_{12}a^*b^*hk+\ldots)$.

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{12}
P	0.0291(4)	0.0406(5)	0.0419(5)	0.0017(5)	0.0003(4)	0.0106(5)
S	0.0588(6)	0.0526(6)	0.0481(5)	0.0034(5)	−0.0079(5)	−0.0044(6)
O1	0.063(2)	0.068(2)	0.076(2)	0.002(2)	−0.004(2)	0.041(2)
N1	0.032(1)	0.054(2)	0.051(2)	0.002(2)	−0.002(1)	0.007(2)
N2	0.040(2)	0.048(2)	0.064(2)	−0.002(1)	−0.014(2)	0.008(2)
N3	0.055(2)	0.061(2)	0.064(2)	−0.002(2)	0.022(2)	−0.001(2)
C1	0.047(2)	0.090(3)	0.100(3)	0.018(2)	0.020(2)	0.011(3)
C2	0.065(3)	0.074(3)	0.077(3)	0.004(2)	−0.032(2)	0.003(3)
C3	0.063(3)	0.090(3)	0.105(3)	−0.021(3)	−0.037(2)	0.022(3)
C4	0.084(3)	0.051(3)	0.203(6)	0.005(3)	−0.054(4)	−0.008(4)
C5	0.114(4)	0.076(3)	0.087(3)	0.013(3)	0.022(3)	−0.024(3)
C6	0.106(3)	0.120(5)	0.113(4)	−0.025(3)	0.059(3)	−0.007(4)
C7	0.129(4)	0.064(3)	0.056(3)	0.019(3)	0.021(3)	0.001(2)
F1	0.228(3)	0.118(2)	0.074(2)	0.094(2)	−0.010(2)	0.018(2)
F2	0.196(3)	0.189(3)	0.131(2)	−0.011(3)	0.093(2)	0.047(2)
F3	0.262(4)	0.119(2)	0.055(2)	0.062(2)	−0.031(2)	−0.029(2)
O2	0.101(2)	0.076(2)	0.067(2)	−0.003(2)	−0.005(2)	−0.023(2)
O3	0.122(2)	0.118(3)	0.075(2)	0.070(2)	−0.004(2)	−0.005(2)
O4	0.084(2)	0.114(3)	0.122(3)	−0.041(2)	−0.005(2)	0.015(2)

	B		B		B		B		B
H1	7.4(1.1)	H5	13.8(1.9)	H9	14.5(2.0)	H13	10.5(1.5)	H17	15.8(2.3)
H2	8.8(1.3)	H6	7.9(1.2)	H10	9.1(1.3)	H14	9.2(1.3)	H18	10.9(1.5)
H3	10.1(1.4)	H7	11.0(1.5)	H11	12.1(1.7)	H15	8.7(1.2)		
H4	7.9(1.2)	H8	10.0(1.4)	H12	11.9(1.6)	H16	6.8(1.1)		

Table 3. Bond lengths (Å) with standard deviations.

Cation		Anion	
P—O1	1.573(1)	S—C7	1.783(4)
P—N1	1.588(2)	S—O2	1.408(2)
P—N2	1.595(2)	S—O3	1.405(2)
P—N3	1.594(2)	S—O4	1.430(2)
N1—C1	1.466(5)	C7—F1	1.300(4)
N1—C2	1.471(4)	C7—F2	1.322(5)
N2—C3	1.468(4)	C7—F3	1.300(4)
N2—C4	1.452(5)		
N3—C5	1.464(5)		
N3—C6	1.462(5)		
C—H	0.94 (ave.)		

Table 4. Bond angles (°) with standard deviations.

Cation		Anion	
P−O1−P	180	C7−S−O2	104.7(2)
P−N1−C1	121.5(3)	C7−S−O3	104.8(2)
P−N1−C2	123.8(3)	C7−S−O4	102.5(2)
C1−N1−C2	114.1(3)	O2−S−O3	117.3(2)
P−N2−C3	123.3(3)	O2−S−O4	112.0(2)
P−N2−C4	122.6(3)	O3−S−O4	113.7(2)
C3−N2−C4	113.3(4)	S−C7−F1	112.9(3)
P−N3−C5	120.4(3)	S−C7−F2	110.0(3)
P−N3−C6	124.4(3)	S−C7−F3	113.7(3)
C5−N3−C6	115.2(4)	F1−C7−F2	106.0(4)
O1−P−N1	106.90(9)	F1−C7−F3	108.6(4)
O1−P−N2	105.73(9)	F2−C7−F3	105.1(4)
O1−P−N3	106.47(10)		
N1−P−N2	113.36(12)		
N1−P−N3	110.88(13)		
N2−P−N3	112.93(13)		
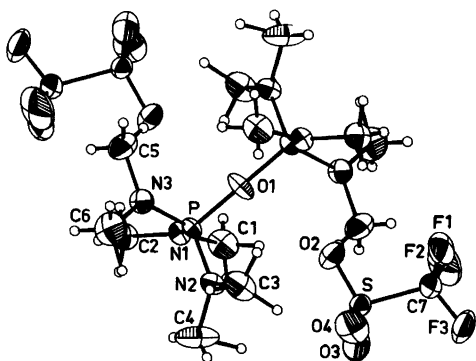
Fig. 1. The diphosphonium salt as seen along *a**. The *c*-axis is horizontal and the *b* axis is vertical (pointing down).
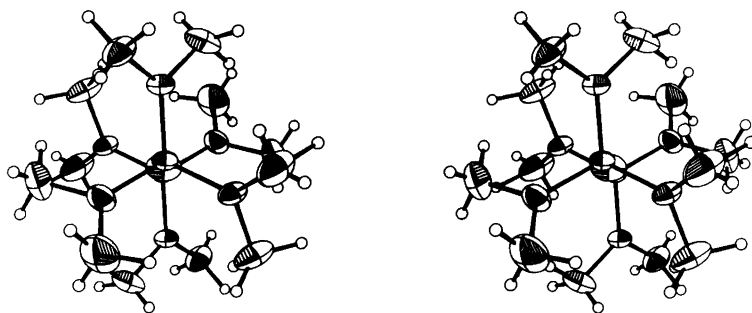
shown in Table 5. A perspective drawing of the salt (one cation and two anions) with atomic numbering is shown in Fig. 1. Fig. 2 is a stereo drawing of the cation seen in a direction nearly parallel with P−O−P. The packing of ions in the unit cell is shown in Fig. 3.

From the figures, it is easily seen that the compound is a diphosphonium salt with separate diphosphonium cations and trifluoromethanesulfonyl anions in the ratio 2:1. The dipositive cation is centrosymmetric with the oxygen atom in a centre of symmetry. Thus the P−O−P sequence is required by symmetry to be linear. The nitrogen atoms are all sp^2-hybridized and the three independent planar P−N−C$_2$ groups are twisted relative to each other in a propeller-like fashion similar to that found for the phenyl groups bonded

Fig. 2. The diphosphonium ion viewed in a direction nearly parallel to the P−O−P sequence (stereo).

Table 5. Some structural data of the diphosphonium cation.

Torsional angles (°)

O1 P N1 C1	− 49.4
O1 P N1 C2	40.3
O1 P N2 C3	46.1
O1 P N2 C4	34.8
O1 P N3 C5	55.1
O1 P N3 C6	54.2
N1 P N2 C3	17.1
N1 P N2 C4	28.4
N1 P N3 C5	60.8
N1 P N3 C6	61.8
N2 P N1 C1	66.7
N2 P N1 C2	− 75.8
N2 P N3 C5	9.3
N2 P N3 C6	10.3
N3 P N1 C1	14.9
N3 P N1 C2	− 24.0
N3 P N2 C3	69.9
N3 P N2 C4	81.2

Angles (°) between p_π orbitals of the N atoms and between these orbitals and the P – O bond

N1 N2	82.9
N1 N3	71.5
N2 N3	79.3
N1 P – O	48.3
N2 P – O	52.4
N3 P – O	38.7

to phosphorus in the bis(triphenylphosphine)-iminium cation with the linear P – N – P sequence.[10] The P(NMe$_2$)$_3$ groups have roughly C_3 symmetry and the cation possesses an approximate S_6-axis coincident with P – O – P.

DISCUSSION

The P – O – P group. Structural data are known for numerous polyphosphates containing P – O – P groups. A common feature for these groups are that they are *non*-linear with P – O – P angles usually between 125 and 145° and that the P – O bond length mostly varies between 1.57 and 1.67 Å. The studies of Calvo *et al.*[11−14] have shown that the P – O – P angle in pyrophosphates is dependent upon the environment. They found that the apparent linearity of the P – O – P group in the high temperature β-forms of divalent Zn, Mg, Cu and Mn pyrophosphates might well be due to a disorder effect and hence not real. However, the P – O – P angle in the low temperature α-form of the copper salt is as high as 157°.[12] Earlier investigations indicate that the pyrophosphate ion is required by symmetry to have a linear P – O – P sequence in the Zr and some isomorphous salts.[2,15] If there is no disorder in the structures of these salts, they may contain the only linear P – O – P sequences previously known.

In the present case, the P – O – P sequence is linear or nearly so. The thermal movement for oxygen is relatively large at right angles to the P – O bond, but not larger than those for the other oxygen and carbon atoms in the salt. Thus the linearity is probably real. A possible deviation from linearity in case of false centrosymmetry caused by disorder is not likely to be more than a few degrees. (The root mean square displacement of O1 has a maximum of 0.337 Å). An important effect contributing to the linearity of the P – O – P sequence is the steric interaction between dimethylamino groups on different phosphorus atoms. It is
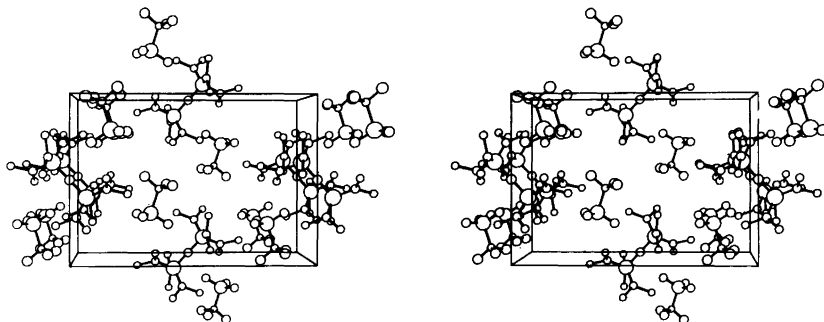

Fig. 3. A stereo view of the packing of the ions of the diphosphonium salt in the unit cell. The *b*-axis is horizontal, *c* is vertical while *a** is pointing up from the page. The origin is at the center of the lower cation to the left.

Table 6. Some short nonbonded distances in the diphosphonium salt with standard deviations (Å).

a. Intramolecular

Within the asymmetric unit

H1 – H4	2.61(6)
H3 – H5	2.56(7)
H7 – H11	2.47(6)
H7 – H12	2.43(7)
H9 – H16	2.23(6)
H14 – H17	2.55(8)
H15 – H18	2.26(6)
P – H2	2.71(4)
P – H6	2.75(4)
P – H8	2.82(4)
P – H10	2.75(4)
P – H13	2.71(4)
P – H16	2.79(3)
O1 – H2	2.74(4)
O1 – H8	2.68(4)
O1 – H13	2.79(4)
O1 – C1	3.046(4)
O1 – C2	3.843(4)
O1 – C3	3.035(4)
O1 – C4	3.833(5)
O1 – C5	3.070(6)
O1 – C6	3.752(5)
F1 – O2	2.907(3)
F1 – O4	2.920(4)
F2 – O2	2.925(3)
F2 – O3	2.917(4)
F3 – O3	2.924(3)
F3 – O4	2.949(4)

Across the centre of symmetry at O1 in the cation[a]

C1 – C3′	3.951(6)
C3 – C5′	3.868(9)
H2 – H14′	2.80(6)
H3 – H8′	2.64(6)
H7 – H13′	2.43(6)
H8 – H13′	2.63(6)

b. Interionic

O2 – C1	$(1+x, y, z)$	3.314(5)
O2 – C3	(x, y, z)	3.209(5)
O4 – C4	$(1+x, 1/2-y, 1/2+z)$	3.330(6)
O2 – H5	$(-x, -y, -z)$	2.55(5)
O3 – H16	$(x, 1/2-y, -1/2+z)$	2.50(4)
O4 – H4	$(1+x, 1/2-y, 1/2+z)$	2.54(4)
O4 – H10	$(1+x, 1/2-y, 1/2-z)$	2.50(5)
O4 – H14	$(1-x, -y, -z)$	2.60(5)
F1 – C2	$(1+x, y, 1+z)$	3.303(5)
F2 – C6	$(x, y, 1+z)$	3.333(6)

[a] A prime marks an atom related to the original one in the asymmetric unit by the centre of symmetry in (0.0.0). Interionic distances are from atoms in the asymmetric unit to atoms whose transformations are listed.

at a minimum when P – O – P is linear and even then there are intramolecular distances between such groups that are close to or smaller than van der Waals contacts (Table 6).

Cruickshank[16] showed that for phosphate and related ions, $d_\pi - p_\pi$ overlap was important in P – O bonding. For P – O – P bridges he predicted that the π-bonding would increase with increasing P – O – P angle. At one end a 120° angle corresponds to sp^2-hybridization on oxygen and therefore only one filled oxygen p orbital available for π-bonding, while at the other end, a 180° angle corresponds to sp hybridization on oxygen and two filled p-orbitals on oxygen available for π-bonding to phosphorus. A P – O single bond length corrected for polarity is 1.64 Å.[17] In the isolated phosphate ion, it is 1.545 Å (π-bond order = 1/2).[16] Thus the P – O bond length of 1.573(1) Å found in the present case implies that the two $p\pi$ orbitals on the central oxygen atom overlap with empty d-orbitals on both phosphorus atoms. A similar, linear system is the P – N – P group in the bis-(triphenylphosphine)iminium cation in the $[(Ph_3P)_2N]^+$ $[V(CO)_6]^-$ salt.[10] There, the P – N – P sequence is coincident with an S_6 axis and thus crystallographically required to be linear. Structure determinations of other salts show the bis(triphenylphosphine)iminium ion with a bent P – N – P group,[18,19] as is the case for the P – C – P group in isoelectronic $(Ph_3P)_2C$[20,21] and $[(Ph_3P)_2CH]^+$ and in $(Ph_2(Se)P)_2CH_2$.[22] For the $[(Ph_3P)_2N]^+$ ion, the existence of two types of structures is suggested to indicate a small energy difference between bent and linear forms since they both originate from a common precursor $(Ph_3P)_2NCl$.[10] The P – N bond length in going from a bent to a linear form is reduced from 1.575(2) to 1.539(2) Å.[10] This effect may be due to increased π-bonding (as for P – O – P) and probably also to a contraction in the nitrogen radius upon change in hybridization from sp^2 to sp.

The P – N bonding. The P – N bond lengths are not significantly different and their average is 1.592(4) Å. This is much shorter than 1.76 Å, the length of a single bond corrected for polarity,[17] or 1.77 Å the single bond length found in the $PO_3NH_3^-$ ion.[16] It is also significantly lower than the average value found in some tris(dialkylamino)-phosphine chalcogenides for the length of the $P – N_{sp^2}$ bond, 1.653(5) Å (uncorr.),[6] and implies strong π-bonding. The stronger π-bonding in the phosphonium ion may be due to a higher positive

charge on phosphorus effectively contracting its outer d-orbitals and making them more suitable for overlap with the filled p_π orbital on nitrogen. In accordance with this, it is found that in $[(R_2N)_3PCH_2C_6H_4NO_2]^+$ ions (R_2N = piperidine and morpholine), the average $P-N$ distance is 1.63 Å,[23] significantly lower than the values found in the corresponding neutral selenides $(R_2N)_3P=$ Se.[6] Another example of a short $R_2N-P(V)$ bond to a phosphorus atom with a high positive charge is also known.[24] However these short bonds are all significantly longer than the $P=N_{imino}$ double bond of 1.503 Å.[25]

The p-orbital available for π-bonding on nitrogen is at right angles to the plane through nitrogen and its three nearest neighbours. Interplanar angles of this type then correspond to angles between the p-orbitals above. These angles and those between these orbitals and the $P-O$ bond are shown in Table 5. The $p-p$ angles vary between 71.5 and 82.9°, making the orbitals approximately orthogonal to each other. The angles between the $P-O$ bond and the orbitals range from 38.7 to 52.4°. Approximate C_3 symmetry found for each $-O-P(NMe_2)_3$ group requires that the three dimethylamino groups are twisted in the same direction. This corresponds to the model mentioned by Hargis and Worley with the three N p_π orbitals skew to the P lone pair in a propeller-like fashion (In the present investigation, the $P-O$ bond replaces the P lone pair in a tris(dialkylamino)phosphine).[8]

The torsional angles of the dimethylamino groups around the $P-N$ bonds are similar (Table 5). Therefore the Newman projections along the $P-N$ bonds are nearly identical; the one for $P-N1$ is shown in Fig. 4.

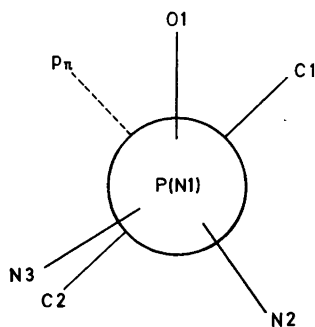*Charge delocalization in the cation.* ESCA studies

Fig. 4. The Newman projection of the $(Me_2N)_3P-$ O1-group as seen along the $P-N1$ bond.

have been interpreted in terms of $Ph_3\overset{+}{P}-\bar{N}-\overset{+}{P}Ph_3$ for the iminium ion.[26] The $\overset{+}{P}-\bar{N}-\overset{+}{P}$ system is isoelectronic with $\overset{+}{P}-O-\overset{+}{P}$ in $[(NMe_2)_2P-O-P-(NMe_2)_3]^{2+}$. The main difference between bonds to phosphorus is that whereas the phenyl carbons essentially form σ-bonds with phosphorus in the iminium ion, the nitrogen atoms form both σ-bonds and fractional π-bonds to phosphorus. Thus the resonance hybrid shown below with the positive charge delocalized over the entire ion, except for the methyl groups, will probably best describe the bonding and also explain the stability of the diphosphonium cation.
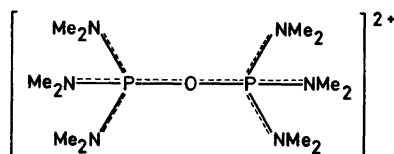
Other details of the structure. Repulsive effects between methyl groups on neighbour nitrogen atoms on the same phosphorus atom being greater than those between methyl groups on nitrogen atoms belonging to different phosphorus atoms are probably responsible for the large $N-P-N$ and small $N-P-O$ angles found in the present investigation. Their average values are 112.4(13) and 106.4(6)°, respectively, indicating a flattening of the aminophosphine group. These results may be compared to corresponding $N-P-N$ and $N-P-Se$ angles of 105.7 and 112.7° found in $(Me_2N)_3P=Se$.[6] The reason for this difference in $N-P-N$ and $N-P-$chalcogen angles in the two compounds is probably partly due to the difference in π-bond character of the bonds involved, (average $P-N$ bond lengths in $(Me_2N)_3P=Se$ are 1.66 Å[6] *vs.* 1.59 Å in the diphosphonium ion), and partly to the difference in hybridization of the nitrogen atoms in the solid state and to the difference in size between O and Se. Some sp^3 character in the selenide *vs.* only sp^2 in the diphosphonium ion makes the average dimethylamino groups bulkier in the latter; the average $C-N-C$ angles are 119.8[6] and 122.7° respectively. Also the conformation of the $(Me_2N)_3P$ group is different in the two compounds. In the diphosphonium ion, all dimethylamino groups are twisted the same way and similar to the twist found for the two dimethylamino groups containing essentially sp^2-hybridized nitrogen in $(Me_2)_3P=Se$. The third such group in the latter compound con-

tains sp^3 hybridized nitrogen and this group has a different twist.[6] The $C-N$ bond lengths are normal within the error limits.

The structure of the anion. The $S-C7$ bond length of 1.783(4) Å is comparable to a normal single bond. One of the $S-O$ bond lengths, $S-O4$, is significantly longer than the other two, being 1.430(2) Å as compared to 1.408(2) and 1.405(2) Å for $S-O2$ and $S-O3$, respectively. But then O4 makes most short contacts with the cation (Table 6). The $C-F$ bond lengths are normal with an average value of 1.307(13) Å. Bond angles at the sulfur atom conform to the VSEPR rules,[27] with $O2-S-O3$ being the largest at 117.3(2)° and $C7-S-O4$ at 102.5(2)° being the smallest.

The packing of the ions in the salt. The cations are stacked on top of each other in columns parallel to *a*. Also the anions are stacked in this manner. The result is that each cation column is surrounded by six anion columns (four closer than the other two) and each anion column is surrounded by three cation and three anion columns. Some short interionic contacts are found in Table 6.

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