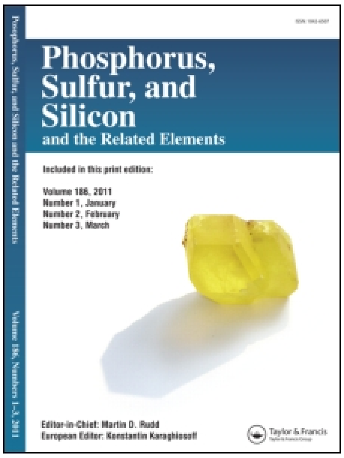

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μ-OXO-BIS[TRIS(PYRROLIDINO-N)PHOSPHONIUM] TRIFLUOROMETHANESULFONATE, A SALT WITH A DIPHOSPHONIUM ION WITH A NON-LINEAR P-O-P SEQUENCE

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μ-OXO-BIS[TRIS(PYRROLIDINO-N)PHOSPHONIUM] TRIFLUOROMETHANESULFONATE, A SALT WITH A DIPHOSPHONIUM ION WITH A NON-LINEAR P—O—P SEQUENCE

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Dedicated to Professor John Verkade on the occasion of his 60th birthday

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The title compound contains the diphosphonium ion, $[(C_4H_8N)_3P—O—P(NC_4H_8)_3]^{2+}$. The structure of the compound is disordered at room temperature. By slow cooling, it goes through a phase transition near −100°C and as a result becomes ordered. Unlike the similar cations $[(Me_2N)_3P—O—P(NMe_2)_3]^{2+}$, and $[(OC_4H_8N)_3P—O—P(NC_4H_8O)_3]^{2+}$, it has a non-linear P—O—P sequence both in the disordered and ordered phase with P—O—P angles between 155.5(3) and 159.2(3)°. The X-ray crystallographic study of the title compound, both at 273 and 103 K, shows that the P—O and P—N bond lengths are very similar to those of the linear cations. The P—O and P—N bond lengths in the title compound ranges from 1.578(4) to 1.602(4) Å and from 1.585(5) to 1.605(5) Å, respectively.

Key words: Diphosphonium ion, X-ray structure, phase transition, P—N bonds, P—O—P bond.

INTRODUCTION

We have shown earlier that trifluoromethanesulfonic anhydride reacts with phosphoryl compounds in CH_2Cl_2 to give diphosphonium salts.[1,2] The proposed reaction mechanism for the reactions involving hexamethylphosphortriamide, $(Me_2N)_3P{=}O$, is shown in Figure 1.

Both the intermediate monophosphonium salt formed in step 1 by nucleophilic attack of HMPA on the anhydride as well as the diphosphonium salt formed in step 2 are believed to be very reactive, as they are salts with triflate anions of low nucleophilicity. They should be expected to be susceptible to nucleophilic attack as demonstrated by the attack of HMPA in step 2 upon the intermediate from step 1. Several phosphoryl compounds[1-5] as well as carbonyl compounds[6,7] were found to react in a similar manner. Diphosphonium salts from phosphoryl compounds, $R_3P{=}O$, made in our labs include those with R = Me_2N, (2),[1,2] pyrrolidinyl, (1), piperidinyl, morpholyl, (3),[3] phenyl and R_3 = $Ph_2(Me_2N)$.[4]

A salt based on R = Me_2N was first made by Bates et al., reacting *p*-toluene

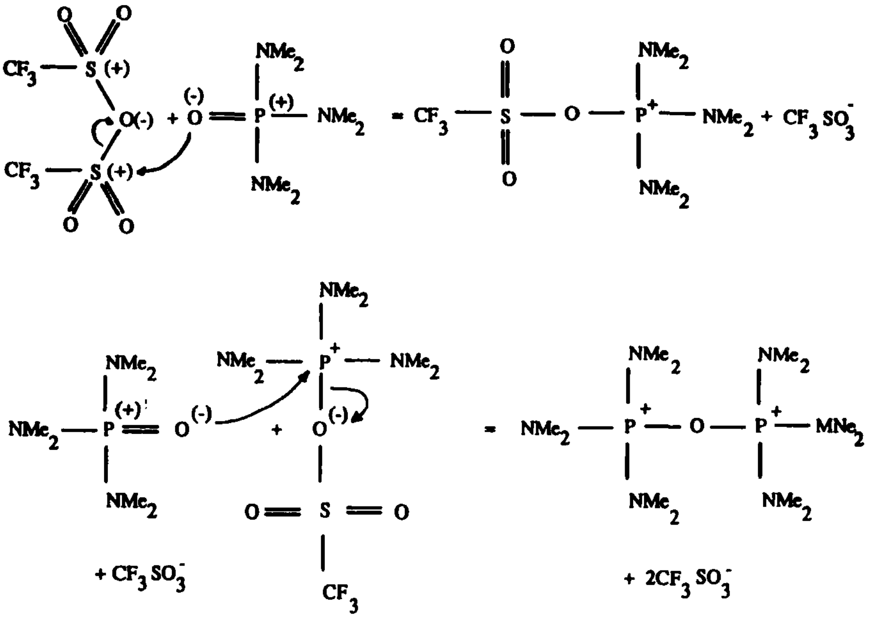


FIGURE 1 The reaction between trifluoromethanesulfonic anhydride and $(Me_2N)_3P{=}O$.

sulfonic anhydride with $(Me_2N)_3P{=}O$.[5] Bates group isolated the mono salt containing the cation of step 1. They even used the cation of **1** from its salt with BF_4^- (Bates reagent) to prepare peptides by reaction with carboxylic acids and amines.[5] With carbonyl compounds, the end products were dication ether salts such as $[(Me_2N)_2C^+{-}O{-}C^+(NMe)_2](F_3CSO_3^-)_2$.[6,7] These salts have nonlinear C—O—C sequences with average angles between 116.0–125.3°.[6]

Structural studies showed that the diphosphonium ions were stabilized by charge delocalization. It also showed that the central P—O—P sequences were linear in the cations $[(Me_2N)_3\,P{-}O{-}P(NMe_2)_3]^{2+}$ of **2** and $[(OC_4H_8N)_3\,P{-}O{-}P(NC_4H_8O)_3]^{2+}$ of **3**.[2,3] With bulky R-groups, we felt that the linearity might be partly due to steric factors (repulsion between R groups on different phosphorus atoms). We therefore decided to have a look at a structure with a relatively small R (pyrrolidinyl).

The chosen diphosphonium salt, μ-oxo-bis[tri(pyrrolidino-N)phosphonium trifluoromethanesulfonate, **1**, represented a crystallographic challenge. At room temperature it has a disordered structure. By slow cooling, a phase transformation occurs near −100°C, and the structure becomes ordered.

EXPERIMENTAL

Synthesis

The triflate salt of **1** was prepared according to the procedure used to make the corresponding salts of **2** and **3**.[1,3]

Elemental analysis for $C_{26}H_{48}F_6N_6O_7P_2S_2$, calc.% C 39.21, H 6.07, N 10.55, P 7.78, S 8.05, found % C 39.50, H 6.37, N 10.56, P 7.81, S 8.21. ^{1}H NMR(CD_3CN), δ 2.00, 3.30; ^{13}C NMR(CD_3CN), δ 48.68, 26.92; $^2J_{C-N-P}$, $^3J_{C-C-NP}$ = 1.8, 4.8 Hz; ν_{P-O-P} (as.) 1265 cm^{-1}.

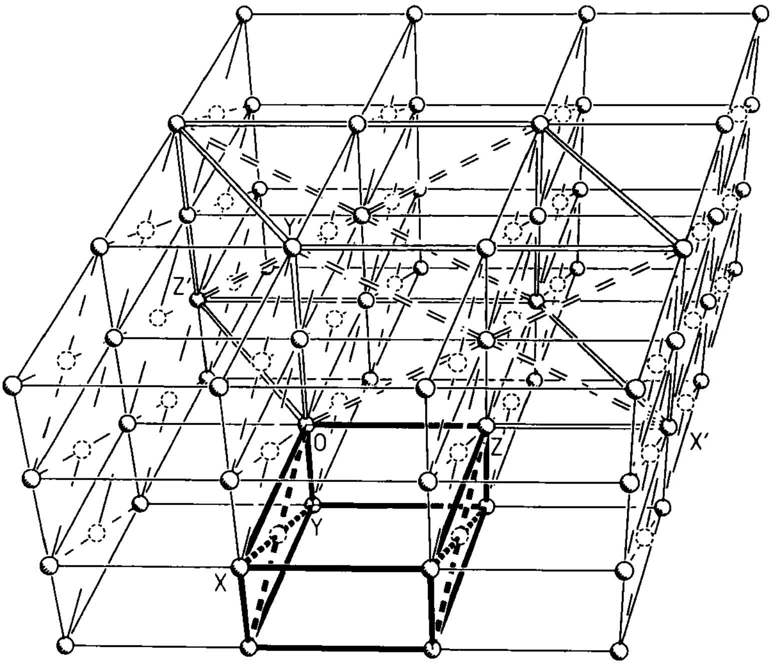


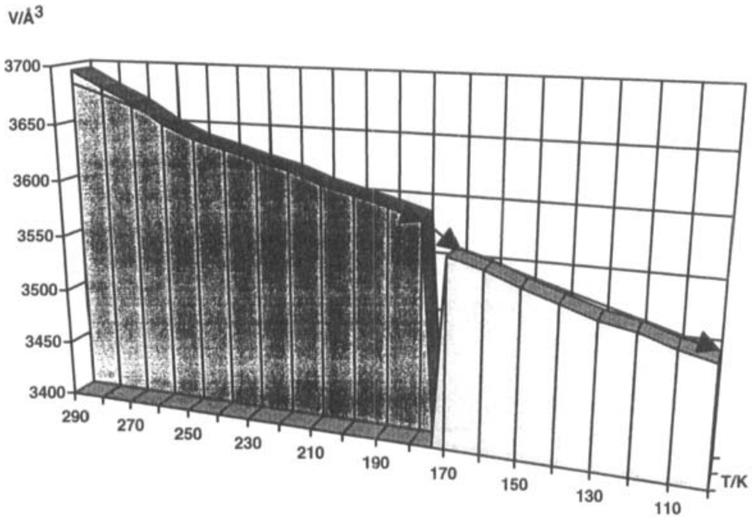
FIGURE 2 Cell transformation upon phase transition. The unit cell of the α phase is drawn as solid lines while the unit cell of the β phase is marked with double lines. The crystal lattice remains essentially unchanged and is marked with thin lines.

Crystal Structure Determinations

Cell dimensions of $[(C_4H_8N)_3POP(NC_4H_8)_3](CF_3SO_3)_2$ were determined at room temperature based on 19 carefully centered reflections with $5.6° < \theta < 9.8°$. The space group from systematic absences is either Cc or C2/c. The structure showed the same type of disorder when studied in both space groups and there was no evidence of twinning. It was therefore decided to choose the space group C2/c as it is statistically more reasonable.

After a large series of ΔF maps alternating with "soft" least squares refinements (using damping factors and restrictions on molecular geometry), the unique P atom position in the symmetry independent half of the cation was found. Subsequently two sets of positions, both equally probable, were found for the pyrrolidinyl groups and the oxygen atoms. The anion had a more complex disorder with three orientations. The main component has an occupancy factor of 2/3. The minor components have occupancy factors 2/9 and 1/9. For the last refinement cycles, the only restrictions were for interatomic distances in the anion (equivalent bonds and 1,3-nonbonded distances of the same kind were required to have equal lengths).

For low temperature work, a special procedure was used. To prevent cracking, the crystal had to be cooled slowly (24°/h). Twelve standard reflections were monitored every 25 min. Below 190 K, the breadth of the reflection profiles started to increase. At nearly 170 K, the crystal lost transparency and the intensities of the check reflections changed dramatically (6 of them became very weak), but their positions (orientation matrix, cell dimensions) changed insignificantly and the profiles remained as single, despite a certain additional breadth. Five additional check reflections used below this temperature belonged to the same matrix. However, below ca. 160 K some new strange reflections were located. Taking these new reflections into account, we found a new unit cell four times as large as the old one. Thus, a phase transition "single crystal-single crystal" has occurred. The transformation corresponds to: $h' = 2l$, $k' = -2k$, $l' = (h + l)$. The original monoclinic C-centered cell of the room temperature α-phase has transformed itself into a new, four times larger monoclinic C-centered cell of the low-temperature β phase (Figure 2). However, the space group remains the same. The phase transition is accompanied by a noticeable shock in relative volume (Figure 3) which is probably a reason for the loss in crystal quality observed.



α-modification						β-modification			
T/K	**V/ Å^3**	**T/K**	**V/ Å^3**	**T/K**	**V/ Å^3**	**T/K**	**(V/4)/ Å^3**	**T/K**	**(V/4)/ Å^3**
290	3694(1)	**250**	3639(2)	**210**	3607(2)	**170**	3564(56)	**130**	3525(9)
280	3680(4)	**240**	3632(2)	**200**	3600(2)	**160**	3556(10)	**120**	3519(9)
270	3668(4)	**230**	3624(2)	**190**	3593(3)	**150**	3545(11)	**110**	3509(9)
260	3651(2)	**220**	3617(2)	**180**	3585(2)	**140**	3535(12)	**100**	3502(1)

FIGURE 3 Graphical presentation of variation in cell volume with temperature. The cell volume of 1*β* is normalized by multiplying by 0.25. The discontinuity of the thermal expansion coefficient in the region of phase transition is displayed by broken arrows.

The cooling was finished at 103 K and data were collected at this temperature. The orientation matrix was based on 23 carefully centered reflections with $3.5° < \theta < 8.3°$. The low-temperature *β* phase turned out to be well ordered and its structure has been solved and refined using standard procedures. The main unit cell and data collection parameters are represented in Table I. All intensities were corrected for Lorentz and polarization effects.

The SHELXS-86[8] and SHELXL-93[9] programs were used for structural determination and refinement. Complete X-ray data are deposited with the Cambridge Crystallographic Data Centre, UK.

RESULTS

The Room Temperature Structure (α-Modification)

In this modification, the salt $[(C_4H_8N)_3POP(NC_4H_8)_3](CF_3SO_3)_2$, **1**, is severely disordered around a center of symmetry. The dication can be resolved into two symmetrically independent parts, A and B, related by a center of symmetry to the parts A′ and B′. The four positions of the bridging oxygen correspond to four combinations of the A, A′ and B, B′ positions of the surrounding parts (see Figures 4 and 5). We observe a superposition of four nonlinear dications. The P atom positions coincide well for all four (occupancy = 1), the pyrrolidine groups only pairwise coincide for the four dications (occupancy = 0.5), while the oxygens do not coincide at all (occupancy = 0.25).

TABLE I

Crystal data and experimental details for the α- and β-modifications of **1**

Crystal modification	1 α	1 β
Compound	$\{[(CH_2)_4N]_3POP[N(CH_2)_4]_3\}^{2+}\cdot 2[F_3CSO_3]^-$	
Empirical formula	$C_{26}H_{48}F_6N_6O_7P_2S_2$	
Formula wt.	796.76	
Diffractometer	Enraf-Nonius CAD4	
Radiation	graphite monochromated Mo*K*α	
Wavelength/Å	0.71069	
Temperature/K	293(2)	103(2)
Crystal system	Monoclinic	
a/Å	18.862(4)	33.839(7)
b/Å	11.459(2)	23.184(5)
c/Å	17.723(4)	22.355(4)
β/°	105.36(3)	127.00(3)
V/Å^3	3693.8(13)	14006.5(49)
Space group	C2/c	
Z	4	16
D_{calc}/g·cm^{-3}	1.433	1.511
F(000)/e	1672	6688
μ(Mo*K*α)/cm^{-1}	3.10	3.28
Crystal size/mm	0.3x0.4x0.6	0.2x0.3x0.5
Scan mode	ω/2θ	
θ_{max}/°	26	22
No of check reflections	3	
Time interval between check reflections measurement/min	120	
Check reflections decay/%	16.6	8.1
No of reflections collected	7048	8733
No of independent reflections	3623	8558
R_{int}	0.036	0.047
No of reflections observed [I>2σ(I)]	2094	4443
Absorp./extinc. corrections	none/none	
Refinement method	full-matrix on all F^2	
Weighting scheme: $w=1/[\sigma^2(F_o^2)+(aP)^2+bP]$; $P=(F_o^2+2F_c^2)/3$	a=0.156, b=4.59	a=0.095, b=49.30
Hydrogens treatment	Geometrically positioned, riding model with fixed U_{iso}	
Hydrogens U_{iso}/Å^2	0.08	0.03
Data/restraints/parameters	3600/57/263	8547/0/623
$wR2=\{\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{0.5}$ (on all)	0.132	0.138
$R1=\Sigma\|\|F_o\|-\|F_c\|\|/\Sigma\|F_o\|$ (on obs. only)	0.079	0.053
$S=\{\Sigma[w(F_o^2-F_c^2)^2]/(N-n)\}^{0.5}$ (on all)	1.045	1.021
Max. in final difference map/e·Å^{-3}	0.37	0.52

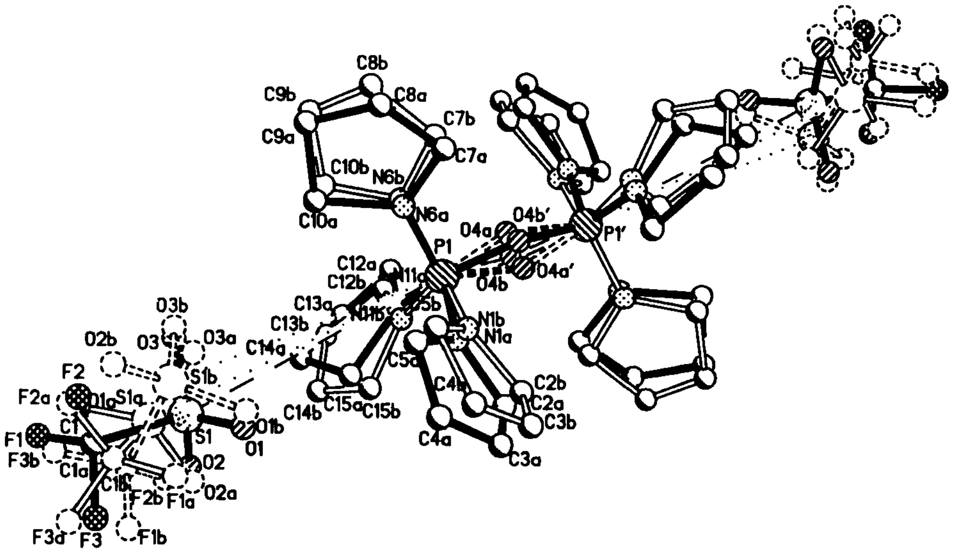


FIGURE 4 Structure of **1** in the disordered *α* phase with H atoms removed for the sake of clarity. Bonds between atoms in the A and centrosymmetrically related A′ parts of the cation are drawn as solid lines. Bonds in the corresponding B and B′ parts are drawn as open lines. For oxygens bridging A—B′ and A′—B′ parts, the bonds are dashed. For the anions, the bonds of the main component are represented by solid lines, those of the intermediate by open lines and those of the minor component by dashed lines.

The disorder in the anions is also complex. Each anion can be resolved into three components with occupancies 0.67, 0.22 and 0.11, respectively. This is also shown in Figure 4. In Figure 5, the cation is resolved into its four possible component structures.

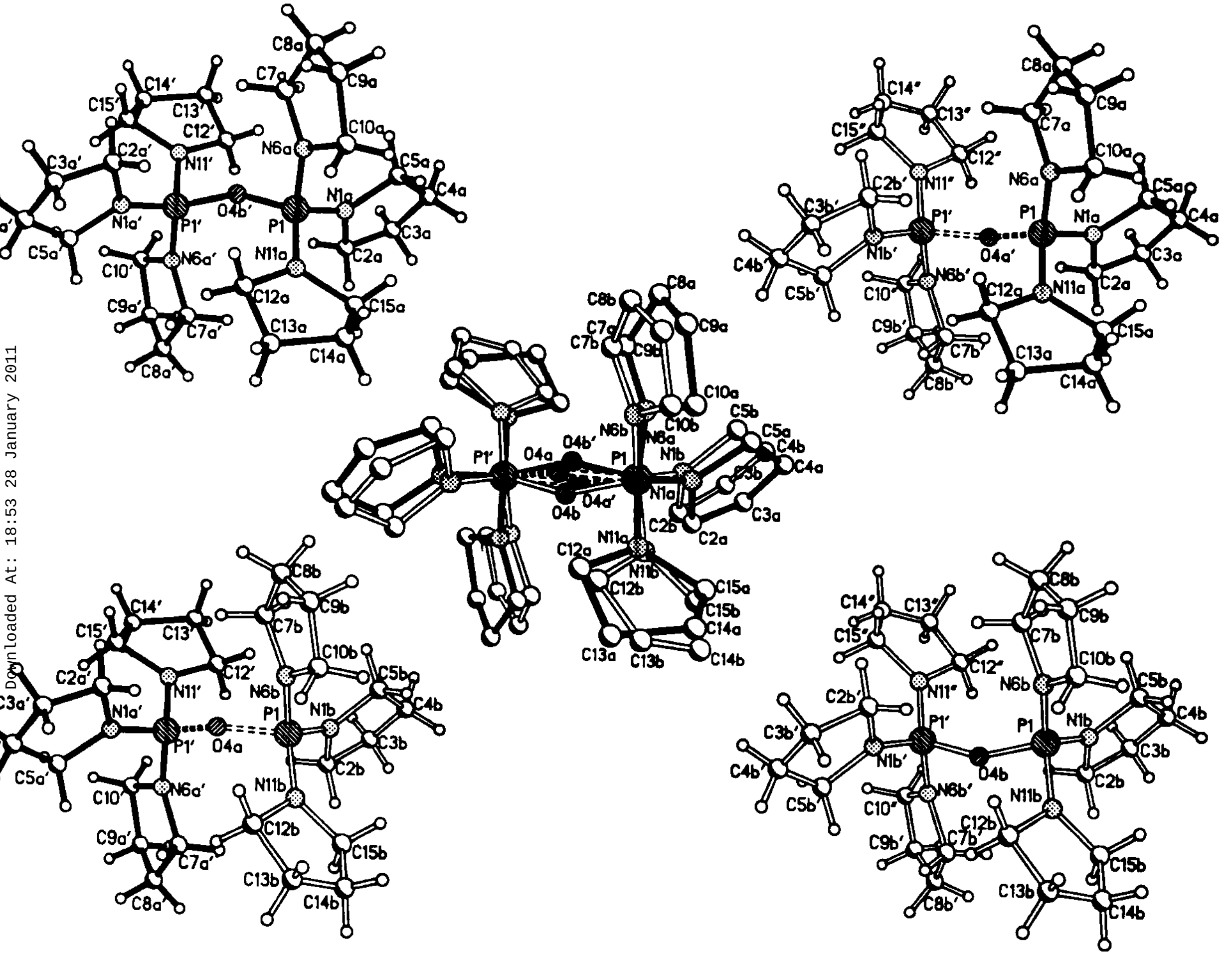
Finally, it may be seen that the P—O—P sequence is clearly nonlinear in the *α*-phase.

The Low Temperature Structure (β-Modification)

As a result of the phase change, there are now two and four crystallographically independent cations and anions, respectively, in the asymmetric unit of the unit cell. They are all shown in Figure 6. Comparison with the ions of the *α* phase shown in the same orientation on top of the figure, shows that the cations of the *β* phase (which are quite similar) are most like the component of the *α* phase drawn with solid lines. They also have kept their nonlinear P—O—P sequences. It is further seen that two of the anions of the *β* phase (left) occupy positions corresponding to the major component of the *α* phase, while the other two correspond to the minor component of the *α* phase. In both phases, anions and cations are staggered.

DISCUSSION

We have shown that **1** undergoes a phase transition upon cooling. The main effect of the transition is to order an originally disordered structure. At the level of precision



e disorder of the cation of **1** in the *α* phase resolved into its four possible components. The disordered cation is placed in the centr
clockwise fashion by A—A′, A—B′, B—B′ and B—A′.

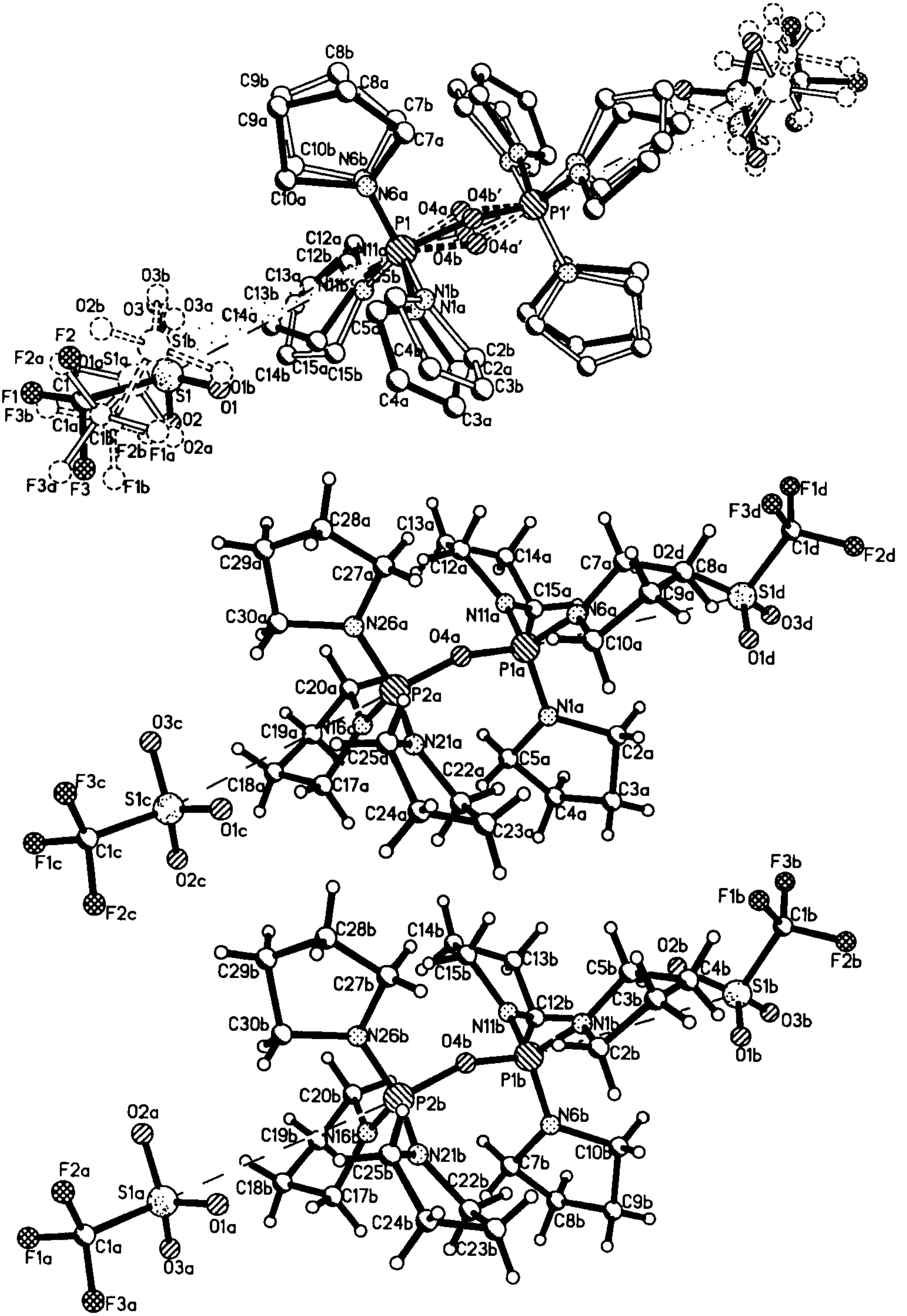


FIGURE 6 Structure of the two crystallographically independent versions of 1 in the β phase with the structure of the α phase added on top for comparison. The salts of both phases are viewed in similar orientations.

TABLE II

Atomic coordinates (×10^4) and equivalent isotropic displacement parameters (Å^2 × 10^3) for 1α. Starred atoms were refined anisotropically (U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor)

Atoms	x	y	z	$U_{iso/eq}$
Disordered anion				
	Major component (g=0.67)			
S1	1320(1)	-2520(2)	6287(1)	88(1)*
O1	829(4)	-1554(4)	6224(4)	162(4)*
O2	1882(3)	-2592(6)	7007(3)	128(3)*
O3	1553(4)	-2766(7)	5600(3)	158(4)*
C1	741(4)	-3753(7)	6345(3)	136(3)
F1	1129(5)	-4698(4)	6415(5)	232(6)*
F2	205(4)	-3798(8)	5715(6)	241(7)*
F3	483(5)	-3629(9)	6949(6)	241(7)*
	Medium component (g=0.22)			
S1a	1532(4)	-3136(7)	6414(4)	99(2)
O1a	1812(8)	-4287(9)	6379(10)	131(5)
O2a	1827(8)	-2530(16)	7134(8)	131(5)
O3a	1448(9)	-2451(16)	5723(9)	131(5)
C1a	592(7)	-3403(14)	6430(10)	136(3)
F1a	274(7)	-2415(18)	6477(16)	210(8)
F2a	254(7)	-3937(24)	5792(15)	210(8)
F3a	590(11)	-4045(25)	7030(16)	210(8)
	Minor component (g=0.11)			
S1b	899(8)	-2654(12)	5821(8)	99(2)
O1b	752(18)	-1501(14)	6046(18)	131(5)
O2b	266(13)	-3321(24)	5439(14)	131(5)
O3b	1510(14)	-2754(32)	5490(16)	131(5)
C1b	1224(15)	-3389(25)	6749(12)	136(3)
F1b	757(24)	-3224(45)	7159(15)	210(8)
F2b	1858(19)	-2966(51)	7115(19)	210(8)
F3b	1284(34)	-4493(24)	6626(24)	210(8)
Symmetrically independent half of dication (for P g=1)				
P1	2137(1)	1334(1)	5166(1)	59(1)*
	Bridging oxygen disordered (g=0.25)			
O4a	2589(14)	2362(11)	4843(13)	54(4)
O4b	2659(8)	2435(12)	5142(12)	44(3)
	Substituents disordered, position A (g=0.5)			
N1a	1496(7)	1605(11)	5601(7)	62(4)
C2a	1578(8)	2345(12)	6290(8)	77(4)
C3a	859(8)	2299(14)	6403(9)	107(4)
C4a	432(7)	1392(13)	5985(8)	93(3)
C5a	779(7)	1019(12)	5402(7)	74(3)
N6a	1757(6)	752(9)	4354(6)	63(3)
C7a	1329(7)	1400(11)	3669(7)	79(3)
C8a	956(7)	457(9)	3161(6)	85(3)
C9a	1305(9)	-712(13)	3413(8)	95(4)
C10a	1688(7)	-623(10)	4279(7)	76(3)
N11a	2788(8)	576(13)	5693(8)	68(5)
C12a	3506(9)	386(14)	5503(9)	90(5)
C13a	3866(8)	-473(14)	6112(9)	100(4)
C14a	3225(8)	-1092(12)	6368(9)	101(4)
C15a	2643(8)	-186(13)	6348(8)	87(4)

TABLE II (*Continued*)

Atoms	x	y	z	$U_{iso/eq}$
	Substituents disordered, position B (g=0.5)			
N1b	1493(7)	1762(11)	5496(7)	65(4)
C2b	1566(8)	2614(13)	6147(9)	84(4)
C3b	790(7)	2750(13)	6193(8)	98(4)
C4b	367(10)	1902(17)	5841(10)	128(6)
C5b	741(8)	1322(13)	5250(9)	92(4)
N6b	1913(6)	692(9)	4326(6)	58(3)
C7b	1528(7)	1243(11)	3590(7)	78(3)
C8b	1355(10)	277(14)	3055(9)	129(5)
C9b	1577(10)	-699(15)	3365(9)	110(5)
C10b	1888(7)	-519(10)	4177(7)	76(3)
N11b	2740(8)	636(13)	5795(8)	65(5)
C12b	3456(9)	274(15)	5702(9)	91(5)
C13b	3686(12)	-720(17)	6272(10)	126(6)
C14b	3245(8)	-801(13)	6722(9)	106(4)
C15b	2715(8)	125(13)	6508(8)	81(4)

obtained, there are hardly any significant differences in corresponding bond lengths between the α and β phases, except that C—F bond lengths appear to be shorter in the α phase, Table V. However, there seem to be several different bond angles as exemplified by the O—P—O and P—O—P angles. Due to the disorder the bond length and angles found for **1**α are much less accurate than those for **1**β. The discussion is therefore mainly based on the structural results from **1**β.

Bonding

From Table VI, it is seen that the P—O and P—N bond lengths are very similar in **1**, **2** and **3**, the only structures of such diphosphonium salts known. Thus the P—O—P angle does not seem to influence the bonding in the central part of the diphosphonium ion as long as it is larger than 150°. Another point may be made here. The cations of **2** and **3** are centrosymmetric, with a center of symmetry at the oxygen position. But there is a possibility that there is a deviation from linearity, albeit small.[2] In that case we should observe a contraction of the P—O bond in such a P—O—P sequence whose apparent linearity is due to a statistical distribution of two nonlinear P—O—P sequences. The absence of such a contraction relative to **3** support the contention about the linearity of the P—O—P sequences of **1** and **2**.

Using Paulings covalent radii and correcting for polarity, gives P—O = 1.64 Å and P—N = 1.72 Å. These values are ca. 0.05 and 0.12 Å larger than those found in the present and preceding work (Table V). However, a survey of P—N single bonds in X_2—P(=X)—NX_2 compounds with sp^2 hybridized, planar N, gives an average value of 1.652(24) Å[10] (A subset for P(=O)—$(NX_2)_3$ has an average P—N bond length of 1.663(26) Å[10]). The same survey gives for X—O—P(=O)—$(C,N)_2$ a P—O single bond length of 1.590(16) Å. Numerous P—O single bond lengths are also determined in connection with structural work on pyrophosphates. A small summary is found in a recent paper by Kortz and Pope.[11] The P—O bridging bond is also here centered around 1.59 Å. For comparison, a treatment of structure and bonding in tertiary phosphine chalcogenides finds a normal range of 1.475–1.490 Å for the P=O bond length in phosphine oxides.[12]

TABLE III

Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters (Å^2 $\times$ 10^3) for **1**β. Starred atoms were refined anisotropically (U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor)

Atoms	x	y	z	$U_{iso/eq}$
Anion A				
S1a	-1370(1)	7496(1)	1062(1)	23(1)*
O1a	-1187(2)	6990(2)	1531(3)	38(1)*
O2a	-1838(2)	7698(2)	836(3)	38(1)*
O3a	-1305(2)	7494(2)	484(3)	41(1)*
C1a	-953(3)	8057(3)	1681(4)	39(2)
F1a	-1058(2)	8567(2)	1327(3)	52(1)*
F2a	-987(2)	8151(2)	2236(3)	75(2)*
F3a	-489(2)	7940(2)	1975(3)	79(2)*
Anion B				
S1b	-1240(1)	12602(1)	1687(1)	23(1)*
O1b	-1755(2)	12575(2)	1096(3)	31(1)*
O2b	-987(2)	12053(2)	1893(3)	32(1)*
O3b	-1102(2)	12973(2)	2299(3)	37(1)*
C1b	-998(2)	12961(3)	1246(4)	27(2)
F1b	-1100(1)	12671(2)	658(2)	32(1)*
F2b	-1192(2)	13494(2)	1006(2)	38(1)*
F3b	-510(1)	13030(2)	1716(2)	42(1)*
Anion C				
S1c	-3806(1)	10061(1)	1145(1)	23(1)*
O1c	-3628(2)	10550(2)	1643(3)	38(1)*
O2c	-3710(2)	10081(2)	603(2)	30(1)*
O3c	-4288(2)	9868(2)	877(3)	34(1)*
C1c	-3414(2)	9475(3)	1756(4)	29(2)
F1c	-3518(2)	8985(2)	1373(3)	46(1)*
F2c	-2938(2)	9585(2)	2088(3)	58(1)*
F3c	-3468(2)	9371(2)	2287(2)	55(1)*
Anion D				
S1d	-1215(1)	10131(1)	-1595(1)	25(1)*
O1d	-697(2)	10132(2)	-996(3)	38(1)*
O2d	-1452(2)	9579(2)	-1754(3)	39(1)*
O3d	-1365(2)	10470(2)	-2236(3)	42(1)*
C1d	-1470(2)	10527(3)	-1195(4)	24(2)
F1d	-1958(1)	10568(2)	-1668(2)	49(1)*
F2d	-1295(2)	11067(2)	-1008(2)	38(1)*
F3d	-1360(2)	10277(2)	-577(2)	37(1)*
Dication A				
P1a	360(1)	8075(1)	-347(1)	17(1)*
P2a	212(1)	6931(1)	420(1)	17(1)*
O4a	-115(2)	7499(2)	118(2)	22(1)*
N1a	-58(2)	8302(2)	-640(3)	20(1)
C2a	51(2)	8928(3)	-652(4)	25(2)
C3a	337(2)	8906(3)	-978(4)	26(2)
C4a	119(2)	8396(3)	-1509(4)	24(2)
C5a	32(2)	7950(3)	-1103(4)	23(2)
N6a	-324(2)	8506(2)	235(3)	18(1)
C7a	-715(2)	8919(3)	68(4)	27(2)
C8a	-415(3)	9396(3)	642(4)	33(2)
C9a	0(2)	9068(3)	1329(4)	28(2)
C10a	141(2)	8614(3)	997(4)	25(2)
N11a	-912(2)	7899(2)	-1027(3)	19(1)
C12a	-1227(2)	7481(3)	-986(3)	20(1)
C13a	-1620(2)	7341(3)	-1810(4)	23(2)
C14a	-1705(2)	7912(3)	-2199(4)	26(2)

TABLE III (*Continued*)

Atoms	x	y	z	$U_{iso/eq}$
Dication A				
C15a	-1189(2)	8184(3)	-1772(3)	21(1)
N16a	155(2)	6627(2)	-265(3)	19(1)
C17a	550(2)	6278(3)	-201(4)	25(2)
C18a	261(2)	5805(3)	-783(4)	29(2)
C19a	-220(2)	6111(3)	-1411(4)	27(2)
C20a	-340(2)	6472(3)	-975(3)	23(2)
N21a	772(2)	7112(2)	1053(3)	19(1)
C22a	1061(2)	7515(3)	938(4)	26(2)
C23a	1465(3)	7717(3)	1732(4)	34(2)
C24a	1568(3)	7184(3)	2191(4)	39(2)
C25a	1066(2)	6910(3)	1845(4)	27(2)
N26a	-22(2)	6578(2)	752(3)	21(1)
C27a	-206(2)	6841(3)	1150(4)	27(2)
C28a	-260(3)	6335(4)	1504(5)	52(2)
C29a	-358(3)	5821(3)	1004(4)	38(2)
C30a	-20(2)	5930(3)	790(4)	25(2)
Dication B				
P1b	-2198(1)	10611(1)	361(1)	16(1)*
P2b	-2767(1)	9471(1)	-404(1)	17(1)*
O4b	-2438(2)	10046(2)	-122(2)	21(1)*
N1b	-2228(2)	11057(2)	-212(3)	17(1)
C2b	-2682(2)	11162(3)	-981(4)	24(2)
C3b	-2525(2)	11615(3)	-1291(4)	24(2)
C4b	-2118(2)	11944(3)	-593(4)	28(2)
C5b	-1832(2)	11479(3)	-9(3)	21(1)
N6b	-2504(2)	10825(2)	648(3)	20(1)
C7b	-2581(2)	10469(3)	1132(4)	25(2)
C8b	-2627(2)	10918(3)	1579(4)	25(2)
C9b	-2884(3)	11420(3)	1030(4)	30(2)
C10b	-2631(2)	11444(3)	654(4)	21(1)
N11b	-1649(2)	10433(2)	1040(3)	18(1)
C12b	-1365(2)	10709(3)	1802(4)	24(2)
C13b	-845(2)	10501(3)	2173(4)	27(2)
C14b	-903(2)	9924(3)	1795(4)	28(2)
C15b	-1322(2)	10049(3)	980(3)	22(2)
N16b	-2702(2)	9176(2)	296(3)	18(1)
C17b	-3098(2)	8870(3)	271(4)	23(2)
C18b	-2813(2)	8390(3)	840(4)	31(2)
C19b	-2319(3)	8674(3)	1441(4)	32(2)
C20b	-2202(2)	9014(3)	987(3)	21(1)
N21b	-3331(2)	9646(2)	-1033(3)	20(1)
C22b	-3606(2)	10089(3)	-930(4)	26(2)
C23b	-3998(2)	10291(3)	-1730(4)	29(2)
C24b	-4120(3)	9740(3)	-2182(4)	31(2)
C25b	-3631(2)	9433(3)	-1817(4)	28(2)
N26b	-2533(2)	9117(2)	-727(3)	18(1)
C27b	-2354(3)	9379(3)	-1131(4)	28(2)
C28b	-2314(3)	8875(3)	-1524(4)	28(2)
C29b	-2221(2)	8354(3)	-1026(4)	26(2)
C30b	-2564(2)	8477(3)	-814(4)	21(1)

On basis of the above, we can conclude that the P—N bonds in the diphosphonium cations are partial double bonds, while the P—O bonds correspond to essentially single bonds. It may be relevant here to mention that Kortz and Pope find a connection between P—O—P angle and P—O bond lengths in pyrophosphates. The larger the angle, the shorter the bond.[11] This may be due to a slight involvement of double bonding.[3,11] The bond angles on all N atoms and the double bond character

TABLE IV

Bond lengths (Å) and angles (deg) for dications of **1**

α-modification		β-modification			
P1-O4a	1.643(11)	P1a-O4a	1.585(4)	P1b-O4b	1.578(4)
P1-O4a'	1.582(11)	P2a-O4a	1.585(4)	P2b-O4b	1.602(4)
P1-O4b	1.608(10)				
P1-O4b'	1.596(10)				
P1-N1a	1.627(12)	P1a-N1a	1.598(5)	P1b-N1b	1.600(5)
P1-N6a	1.574(10)	P1a-N6a	1.587(5)	P1b-N6b	1.590(5)
P1-N11a	1.59(2)	P1a-N11a	1.597(5)	P1b-N11b	1.592(5)
P1-N1b	1.561(13)	P2a-N16a	1.590(5)	P2b-N16b	1.597(5)
P1-N6b	1.613(10)	P2a-N21a	1.595(5)	P2b-N21b	1.599(5)
P1-N11b	1.58(2)	P2a-N26a	1.595(5)	P2b-N26b	1.585(5)
N1a-C2a	1.46(2)	N1a-C2a	1.501(8)	N1b-C2b	1.481(8)
N1a-C5a	1.47(2)	N1a-C5a	1.488(8)	N1b-C5b	1.492(8)
C2a-C3a	1.42(2)	C2a-C3a	1.522(9)	C2b-C3b	1.517(9)
C3a-C4a	1.40(2)	C3a-C4a	1.515(9)	C3b-C4b	1.525(9)
C4a-C5a	1.43(2)	C4a-C5a	1.516(9)	C4b-C5b	1.511(9)
N6a-C7a	1.47(2)	N6a-C7a	1.488(8)	N6b-C7b	1.501(8)
N6a-C10a	1.58(2)	N6a-C10a	1.488(8)	N6b-C10b	1.502(8)
C7a-C8a	1.46(2)	C7a-C8a	1.528(10)	C7b-C8b	1.515(9)
C8a-C9a	1.51(2)	C8a-C9a	1.521(10)	C8b-C9b	1.527(9)
C9a-C10a	1.52(2)	C9a-C10a	1.520(9)	C9b-C10b	1.519(9)
N11a-C12a	1.50(2)	N11a-C12a	1.483(8)	N11b-C12b	1.505(8)
N11a-C15a	1.53(2)	N11a-C15a	1.488(8)	N11b-C15b	1.486(8)
C12a-C13a	1.49(2)	C12a-C13a	1.523(9)	C12b-C13b	1.503(9)
C13a-C14a	1.57(2)	C13a-C14a	1.513(9)	C13b-C14b	1.529(9)
C14a-C15a	1.50(2)	C14a-C15a	1.534(9)	C14b-C15b	1.518(9)
N1b-C2b	1.49(2)	N16a-C17a	1.492(8)	N16b-C17b	1.487(8)
N1b-C5b	1.46(2)	N16a-C20a	1.502(8)	N16b-C20b	1.497(8)
C2b-C3b	1.50(2)	C17a-C18a	1.523(9)	C17b-C18b	1.520(9)
C3b-C4b	1.31(2)	C18a-C19a	1.539(9)	C18b-C19b	1.527(9)
C4b-C5b	1.56(2)	C19a-C20a	1.513(9)	C19b-C20b	1.513(9)
N6b-C7b	1.46(2)	N21a-C22a	1.483(8)	N21b-C22b	1.491(8)
N6b-C10b	1.41(2)	N21a-C25a	1.490(8)	N21b-C25b	1.486(8)
C7b-C8b	1.44(2)	C22a-C23a	1.522(9)	C22b-C23b	1.523(9)
C8b-C9b	1.27(2)	C23a-C24a	1.506(10)	C23b-C24b	1.525(10)
C9b-C10b	1.42(2)	C24a-C25a	1.519(10)	C24b-C25b	1.511(10)
N11b-C12b	1.46(2)	N26a-C27a	1.491(8)	N26b-C27b	1.487(8)
N11b-C15b	1.40(2)	N26a-C30a	1.505(8)	N26b-C30b	1.493(8)
C12b-C13b	1.51(2)	C27a-C28a	1.487(10)	C27b-C28b	1.515(9)
C13b-C14b	1.30(2)	C28a-C29a	1.526(11)	C28b-C29b	1.541(9)
C14b-C15b	1.44(2)	C29a-C30a	1.505(9)	C29b-C30b	1.522(9)
O4a-P1-N1b	115.6(8)	O4a-P1a-N1a	109.6(3)	O4b-P1b-N1b	103.3(2)
O4a-P1-N6b	92.3(8)	O4a-P1a-N6a	103.9(3)	O4b-P1b-N6b	110.1(3)
O4a-P1-N11b	105.4(11)	O4a-P1a-N11a	105.0(3)	O4b-P1b-N11b	105.2(3)
O4b-P1-N1b	107.8(10)	O4a-P2a-N16a	107.9(3)	O4b-P2b-N16b	108.5(3)
O4b-P1-N6b	110.3(9)	O4a-P2a-N21a	108.1(3)	O4b-P2b-N21b	108.2(3)
O4b-P1-N11b	94.8(7)	O4a-P2a-N26a	102.2(3)	O4b-P2b-N26b	101.0(2)
O4a'-P1-N1a	96.3(8)				
O4a'-P1-N6a	117.5(9)				
O4a'-P1-N11a	108.5(12)				
O4b'-P1-N1a	105.7(10)				
O4b'-P1-N6a	98.9(8)				
O4b'-P1-N11a	117.7(7)				
N1a-P1-N6a	107.4(6)	N1a-P1a-N6a	112.1(3)	N1b-P1b-N6b	112.3(3)
N1a-P1-N11a	112.4(7)	N1a-P1a-N11a	111.4(3)	N1b-P1b-N11b	113.9(3)
N6a-P1-N11a	113.5(7)	N6a-P1a-N11a	114.2(3)	N6b-P1b-N11b	111.5(3)
N1b-P1-N6b	116.8(6)	N16a-P2a-N21a	111.2(3)	N16b-P2b-N21b	111.0(3)
N1b-P1-N11b	112.3(7)	N16a-P2a-N26a	114.5(3)	N16b-P2b-N26b	114.4(3)

TABLE IV (*Continued*)

α-modification		β-modification			
N11b-P1-N6b	112.5(6)	N21a-P2a-N26a	112.3(3)	N21b-P2b-N26b	113.0(3)
P1-O4a-P1'	151.8(10)	P1a-O4a-P2a	159.2(3)	P1b-O4b-P2b	155.5(3)
P1-O4b-P1'	155.2(8)				
P1-N1a-C2a	125.5(10)	P1a-N1a-C2a	123.5(4)	P1b-N1b-C2b	123.9(4)
P1-N1a-C5a	123.5(9)	P1a-N1a-C5a	123.6(4)	P1b-N1b-C5b	124.5(4)
C2a-N1a-C5a	110.7(11)	C2a-N1a-C5a	111.2(5)	C2b-N1b-C5b	111.0(5)
N1a-C2a-C3a	101.7(12)	N1a-C2a-C3a	102.2(5)	N1b-C2b-C3b	104.0(5)
C2a-C3a-C4a	112.8(12)	C2a-C3a-C4a	104.6(5)	C2b-C3b-C4b	103.2(5)
C3a-C4a-C5a	107.3(12)	C3a-C4a-C5a	104.0(5)	C3b-C4b-C5b	104.0(5)
N1a-C5a-C4a	105.0(10)	N1a-C5a-C4a	103.8(5)	N1b-C5b-C4b	102.4(5)
P1-N6a-C7a	123.9(9)	P1a-N6a-C7a	125.6(4)	P1b-N6b-C7b	123.8(4)
P1-N6a-C10a	120.3(8)	P1a-N6a-C10a	123.5(4)	P1b-N6b-C10b	124.1(4)
C7a-N6a-C10a	114.7(9)	C7a-N6a-C10a	110.3(5)	C7b-N6b-C10b	110.2(5)
N6a-C7a-C8a	101.8(10)	N6a-C7a-C8a	102.3(5)	N6b-C7b-C8b	103.3(5)
C7a-C8a-C9a	111.9(10)	C7a-C8a-C9a	103.3(6)	C7b-C8b-C9b	103.1(5)
C8a-C9a-C10a	107.1(11)	C8a-C9a-C10a	102.9(6)	C8b-C9b-C10b	103.6(5)
N6a-C10a-C9a	99.1(10)	N6a-C10a-C9a	104.5(5)	N6b-C10b-C9b	103.2(5)
P1-N11a-C12a	123.5(11)	P1a-N11a-C12a	125.5(4)	P1b-N11b-C12b	123.5(4)
P1-N11a-C15a	119.4(11)	P1a-N11a-C15a	122.7(4)	P1b-N11b-C15b	125.1(4)
C12a-N11a-C15a	116.2(13)	C12a-N11a-C15a	111.6(5)	C12b-N11b-C15b	110.7(5)
N11a-C12a-C13a	101.5(13)	N11a-C12a-C13a	101.6(5)	N11b-C12b-C13b	103.0(5)
C12a-C13a-C14a	105.8(12)	C12a-C13a-C14a	103.5(5)	C12b-C13b-C14b	104.9(5)
C13a-C14a-C15a	107.1(11)	C13a-C14a-C15a	104.5(5)	C13b-C14b-C15b	102.3(5)
N11a-C15a-C14a	97.8(11)	N11a-C15a-C14a	103.1(5)	N11b-C15b-C14b	102.4(5)
P1-N1b-C2b	125.1(10)	P2a-N16a-C17a	124.4(4)	P2b-N16b-C17b	125.2(4)
P1-N1b-C5b	124.8(10)	P2a-N16a-C20a	122.4(4)	P2b-N16b-C20b	121.5(4)
C2b-N1b-C5b	110.0(12)	C17a-N16a-C20a	109.7(5)	C17b-N16b-C20b	110.6(5)
N1b-C2b-C3b	102.7(12)	N16a-C17a-C18a	103.3(5)	N16b-C17b-C18b	102.3(5)
C2b-C3b-C4b	112.2(14)	C17a-C18a-C19a	103.3(5)	C17b-C18b-C19b	103.2(6)
C3b-C4b-C5b	108.1(14)	C18a-C19a-C20a	102.4(5)	C18b-C19b-C20b	102.9(5)
N1b-C5b-C4b	103.2(12)	N16a-C20a-C19a	104.5(5)	N16b-C20b-C19b	103.5(5)
P1-N6b-C8b	125.0(8)	P2a-N21a-C22a	124.6(4)	P2b-N21b-C22b	124.4(4)
P1-N6b-C10b	127.6(8)	P2a-N21a-C25a	123.9(4)	P2b-N21b-C25b	123.9(4)
C7b-N6b-C10b	105.9(9)	C22a-N21a-C25a	111.4(5)	C22b-N21b-C25b	111.4(5)
N6b-C7b-C8b	103.2(11)	N21a-C22a-C23a	102.4(5)	N21b-C22b-C23b	102.4(5)
C7b-C8b-C9b	113.7(14)	C22a-C23a-C24a	102.7(6)	C22b-C23b-C24b	102.5(5)
C8b-C9b-C10b	108(2)	C23a-C24a-C25a	105.4(6)	C23b-C24b-C25b	105.3(5)
N6b-C10b-C9b	108.6(11)	N21a-C25a-C24a	102.5(5)	N21b-C25b-C24b	103.2(5)
P1-N11b-C12b	125.2(11)	P2a-N26a-C27a	124.8(4)	P2b-N26b-C27b	124.4(4)
P1-N11b-C15b	131.0(11)	P2a-N26a-C30a	123.4(4)	P2b-N26b-C30b	123.9(4)
C12b-N11b-C15b	103.5(12)	C27a-N26a-C30a	111.3(5)	C27b-N26b-C30b	110.5(5)
N11b-C12b-C13b	104.4(13)	N26a-C27a-C28a	103.0(6)	N26b-C27b-C28b	104.3(5)
C12b-C13b-C14b	110(2)	C27a-C28a-C29a	105.6(6)	C27b-C28b-C29b	103.7(5)
C13b-C14b-C15b	107.4(13)	C28a-C29a-C30a	103.3(6)	C28b-C29b-C30b	102.5(5)
N11b-C15b-C14b	111.0(12)	N26a-C30a-C29a	101.9(5)	N26b-C30b-C29b	102.6(5)

Symmetry transformations used to generate equivalent atoms A': -x+1/2,-y+1/2,-z+1

of the P—N bonds correspond to sp^2 hybridization of the N atoms. This is a result of the delocalization of the cationic charge over the PN_3 (or event the N_3POPN_3) groups.[2] We have further observed that these diphosphonium salts are more or less hygroscopic and that the salts with the least charge delocalization (the ones with Ph groups replacing NR_2 groups on phosphorus) are most hygroscopic, as expected.

Proton NMR of **1** (CD_3CN solution, signals in ppm relative to TMS) shows two signals (both multiplets) centered at 2.00 and 3.30 ppm. The first (H on beta C) represents a downfield shift of 0.23 ppm, the second (H on alpha C) a downfield

TABLE V

Bond lengths (Å) and angles (deg) for anions of **1**

α-modification		β-modification			
S1-O1	1.429(4)	S1a-O1a	1.443(5)	S1c-O1c	1.442(5)
S1-O2	1.429(4)	S1a-O2a	1.421(5)	S1c-O2c	1.432(4)
S1-O3	1.428(4)	S1a-O3a	1.434(5)	S1c-O3c	1.429(5)
S1-C1	1.805(10)	S1a-C1a	1.803(8)	S1c-C1c	1.814(7)
C1-F1	1.294(5)	C1a-F1a	1.346(9)	C1c-F1c	1.335(8)
C1-F2	1.294(5)	C1a-F2a	1.331(9)	C1c-F2c	1.331(8)
C1-F3	1.295(5)	C1a-F3a	1.314(9)	C1c-F3c	1.329(8)
		S1b-O1b	1.421(5)	S1d-O1d	1.428(5)
		S1b-O2b	1.445(5)	S1d-O2d	1.437(5)
		S1b-O3b	1.436(5)	S1d-O3d	1.434(5)
		S1b-C1b	1.817(7)	S1d-C1d	1.818(6)
		C1b-F1b	1.325(7)	C1d-F1d	1.326(8)
		C1b-F2b	1.351(8)	C1d-F2d	1.340(8).
		C1b-F3b	1.331(8)	C1d-F3d	1.328(7)
O1-S1-O2	115.2(2)	O1a-S1a-O2a	115.1(3)	O1c-S1c-O2c	115.1(3)
O1-S1-O3	115.2(2)	O1a-S1a-O3a	114.9(3)	O1c-S1c-O3c	114.2(3)
O1-S1-C1	102.8(2)	O1a-S1a-C1a	103.5(3)	O1c-S1c-C1c	103.4(3)
O2-S1-O3	115.3(2)	O2a-S1a-O3a	115.0(3)	O2c-S1c-O3c	116.0(3)
O2-S1-C1	102.8(2)	O2a-S1a-C1a	103.1(3)	O2c-S1c-C1c	103.1(3)
O3-S1-C1	102.8(2)	O3a-S1a-C1a	102.8(3)	O3c-S1c-C1c	102.4(3)
S1-C1-F1	109.0(5)	S1a-C1a-F1a	111.9(5)	S1c-C1c-F1c	111.2(5)
S1-C1-F2	109.1(5)	S1a-C1a-F2a	111.6(5)	S1c-C1c-F2c	111.6(5)
S1-C1-F3	109.0(5)	S1a-C1a-F3a	112.5(5)	S1c-C1c-F3c	112.1(5)
F1-C1-F2	110.0(5)	F1a-C1a-F2a	105.3(6)	F1c-C1c-F2c	106.5(5)
F1-C1-F3	109.8(5)	F1a-C1a-F3a	106.8(6)	F1c-C1c-F3c	107.1(6)
F2-C1-F3	109.9(5)	F2a-C1a-F3a	108.3(7)	F2c-C1c-F3c	108.0(6)
		O1b-S1b-O2b	114.8(3)	O1d-S1d-O2d	114.8(3)
		O1b-S1b-O3b	115.2(3)	O1d-S1d-O3d	115.6(3)
		O1b-S1b-C1b	102.5(3)	O1d-S1d-C1d	102.5(3)
		O2b-S1b-O3b	115.7(3)	O2d-S1d-O3d	115.6(3)
		O2b-S1b-C1b	101.7(3)	O2d-S1d-C1d	102.3(3)
		O3b-S1b-C1b	104.3(3)	O3d-S1d-C1d	103.3(3)
		S1b-C1b-F1b	112.0(5)	S1d-C1d-F1d	112.1(4)
		S1b-C1b-F2b	111.5(4)	S1d-C1d-F2d	112.0(4)
		S1b-C1b-F3b	112.1(5)	S1d-C1d-F3d	111.9(4)
		F1b-C1b-F2b	107.1(5)	F1d-C1d-F2d	106.6(5)
		F1b-C1b-F3b	107.6(5)	F1d-C1d-F3d	107.1(5)
		F2b-C1b-F3b	106.1(5)	F2d-C1d-F3d	106.7(5)

TABLE VI

Selected bond lengths (Å) and angles (deg) in **1**, **2** and **3**. Only average bond lengths, except for P—O in **2** and **3**, are listed

COMPOUND	P-O	P-N	∠P-O-P
1 α	1.607(26)	1.591(25)	151.8(10),155.2(8)
1 β	1.588(10)	1.594(5)	155.5(3),159.2(3)
2	1.573(1)	1.592(4)	180
3	1.588(1)	1.605(2)	180

shift of 0.22 ppm relative to the parent phosphine oxide, $(C_4H_8N)_3P{=}O$.[4] The ^{13}C NMR multiplet signals at 48.68 ppm (alpha carbon) and 26.92 (beta carbon) are shifted downfield by 1.17 ppm and upfield by 0.65 ppm, respectively, relative to the phosphine oxide.[4] The downfield shifts of the alpha carbon and its hydrogens reflect the charge delocalization in the cation. This charge delocalization gives an increasing positive charge on phosphine oxide nitrogen upon salt formation. The result is a deshielding of the alpha carbons and their hydrogens.

The average N—C bond lengths are 1.47(5) and 1.492(7) Å in **1**α and **1**β, respectively. Corresponding C—C bond lengths are 1.45(9) and 1.519(10) Å. The anions have normal bond lengths and angles.[1,3] The C—S bond length is 1.805(10) Å in **1**α (only values from the main component are quoted here), while the average is 1.813(7) for **1**β. For the S—O and C—F bond lengths, average values are 1.428(1) and 1.294(1) Å for **1**α and 1.434(8) and 1.332(10) Å for **1**β, respectively.

The P—O—P Sequence

This sequence is linear in **2** and **3** and nonlinear in **1**. Since the bulkiness of the pyrrolidinyl group presumably is smaller than that of the morpholyl or NMe_2 groups, this may explain the differences. The central P^+—O—P^+ sequence is isoelectronic with the Si(IV)—O—Si(IV) sequence. Calculations on the latter and similar systems show that the barrier to linearity is small.[3,13,14] Thus, relatively small steric factors (including also molecular packing effects) may influence the P—O—P angle. In the present investigation, repulsion between pyrrolidinyl groups across the P—O—P bridge results in larger P—O—P angles for the groups interacting closest to the acute P—O—P angle, as these are on the average 4.4° larger than the rest in **1**β. Oxygen-phosphorus π overlap is optimal for a linear sequence. Since the π-bond order is small or nonexistent for the P—O bonds in all three diphosphonium salts, this factor seems less important. Linear P—O—P sequences have been claimed in some pyrophosphates. However, this apparent linearity is contested and doubtful.[11] Nevertheless, angles above 140° are often found and a literature search reveal an almost linear system in the 18-molybdopyrophosphate anion, $[(P_2O_7)Mo_{18}O_{54}]^{4-}$.[11] This large, complex anion encloses a practically linear (177.7(13)°) and eclipsed pyrophosphate anion, the bridging P—O bond lengths have an average value of 1.575(17) Å not significantly different from those observed in our studies of the P^+—O—P^+ sequences.

Both linear and nonlinear (dominating, P—N—P angle mostly 131–142°) sequences have been observed in cations, $(Ph_3PNPPh_3)^+$, and in anions. $(Ph_2(S)PNP(S)Ph_2)^-$ and is the object of a recent investigation by Haiduc and coworkers.[15] They also find a trend towards a slight shortening of the P—N bonds when going from a bent to a linear conformation in both anions and cations. This effect is ascribed either to a small π-electron delocalization in the P—N—P sequence, or alternately simply to a change in hybridization of N from sp^3 (bent) to sp (linear). Calculation of the energy barrier between bent and linear forms of $(Ph_3PNPPh_3)^+$ show that it is small,[16] so that packing effects may well affect the geometry of such ions. The $(P—N—P)^+$ sequence is isoelectronic with the $(P—O—P)^{2+}$ sequence, and the bonding and structure in these systems are therefore probably similar.

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