The Crystal Structure of Hexakis(morpholino-*N*)-μ-oxo-diphosphonium(V) Trifluoromethanesulfonate

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The crystal structure of the title compound, $\{[O(CH_2)_4N]_3P\text{–}O\text{–}P[N(CH_2)_4O]_3\}^{2+}(CF_3SO_3^-)_2$ (**1**), has been determined at 92 K by X-ray crystallographic methods. Unit cell parameters are: $a = 9.442(1)$, $b = 9.534(1)$, $c = 10.770(1)$ Å, $\alpha = 92.60(2)$, $\beta = 106.67(2)$, $\gamma = 86.19(1)°$ and $Z = 1$). The colourless crystals are monoclinic, space group $P\bar{1}$. Full-matrix least-squares refinement based on 3346 observed diffractometer data gave a final conventional R of 0.043. The diphosphonium ions are centrosymmetric and thus have an exactly linear P–O–P bridge with a P–O bond length of 1.588(1) Å. Linearity of such bridges is discussed and it is suggested that the linearity is due to electronic rather than steric effects. The nitrogen atoms are essentially sp^2 hybridized and the average P–N bond length is 1.604 Å. The overall symmetry of the dication is approximately S_6. Delocalization of charge over the central N_3 P–O–PN_3 group stabilizes the dication and leads to double-bond character in bonds between these atoms.

Dedicated to Professor Olav Foss on his 70th birthday

When phosphine oxides react with trifluoromethanesulfonic anhydride, diphosphonium salts are formed.[1–3] Certain carbonyl compounds, such as tetraalkylureas, also react in a similar fashion.[4,5] The crystal structure of the salt hexakis(dimethylamino)-μ-oxo-diphosphonium(V) trifluoromethanesulfonate, $[(Me_2N)_3P\text{–}O\text{–}P(NMe_2)_3]^{2+}(CF_3SO_3^-)_2$ (**2**), has been solved earlier in this laboratory.[3] The structural results showed that the cation was centrosymmetric and thus required to have a linear P–O–P group. Such linearity seems to be very rare, and it may be due to either steric or electronic effects or both.[3]

It was felt that the finding of a linear P–O–P bridge in a single structure might be fortuitous. We therefore decided to undertake another structural investigation on a similar compound. This time a low-temperature study was chosen, both because it is more accurate than one at room temperature and also because it reduces the possibility of false linearity through disorder.[3,6]

Experimental

Synthesis of the diphosphonium salt. The salt was prepared according to Ref. 2. However, in the present case the reaction was carried out under nitrogen with cooling in ice. The white product was recrystallized from CH_3CN. White crystals (yield 10.1 %) and an oily residue resulted. The residue was not further examined.

X-ray data. Data were collected on an Enraf-Nonius CAD-4 diffractometer, using graphite-monochromated Mo*K*α radiation and a small crystal with maximum dimensions less than 0.3 mm. Cell parameters were determined from a least-squares fit to the settings of 25 general reflections. The crystals of $\{[O(CH_2)_4N]_3P\text{–}O\text{–}P[N(CH_2)_4O]_3\}^{2+}(CF_3SO_3^-)_2$ (**1**) are triclinic, space group $P1$ or $P\bar{1}$, with $a = 9.442(1)$, $b = 9.534(1)$, $c = 10.770(1)$ Å, $\alpha = 92.60(2)$, $\beta = 106.67(2)$, $\gamma = 86.19(2)°$, $d_x = 1.557$ g cm^{-3}, $Z = 1$, $\mu(MoK\alpha) = 3.17$ cm^{-1}.

Intensity data were recorded using the ω scan technique with a constant scan rate of 4° min^{-1} and a scan width of 1.50° including background. Crystal orientation was checked every 100 min and 3 standard reflections were remeasured every 2 h. Of the 4470 reflections with $2\theta < 56°$, 3346 had $I > 2\theta(I)$ and were regarded as observed. The intensities of the standard reflections showed

Table 1. Positional parameters and their estimated standard deviations.[a]

Atom	*x*	*y*	*z*	*B*/Å^2
O	0.500	0.500	0.500	1.03(4)
P	0.52439(6)	0.40981(6)	0.37947(5)	0.74(1)
N11	0.4739(2)	0.2549(2)	0.3918(2)	0.84(4)
C12	0.5511(3)	0.1241(2)	0.3589(2)	1.10(4)
C13	0.4412(3)	0.0299(3)	0.2701(2)	1.30(5)
O14	0.3272(2)	−0.0001(2)	0.3270(2)	1.34(3)
C15	0.2458(3)	0.1268(3)	0.3444(2)	1.31(5)
C16	0.3437(2)	0.2300(2)	0.4363(2)	1.08(4)
N21	0.4199(2)	0.4910(2)	0.2559(2)	0.89(4)
C22	0.3734(3)	0.4157(3)	0.1277(2)	1.27(5)
C23	0.2165(3)	0.4652(3)	0.0593(2)	1.60(5)
O24	0.2066(2)	0.6128(2)	0.0415(2)	1.67(4)
C25	0.2431(3)	0.6852(3)	0.1643(2)	1.37(5)
C26	0.4009(3)	0.6461(2)	0.2423(2)	1.05(4)
N31	0.6967(2)	0.3986(2)	0.3864(2)	0.95(4)
C32	0.8097(3)	0.3338(3)	0.4983(2)	1.13(4)
C33	0.9289(3)	0.2551(3)	0.4499(2)	1.23(5)
O34	0.9917(2)	0.3465(2)	0.3834(2)	1.25(3)
C35	0.8860(3)	0.4013(3)	0.2723(2)	1.27(5)
C36	0.7638(2)	0.4869(2)	0.3109(2)	1.13(4)
S	0.79248(6)	−0.16598(6)	0.20411(6)	1.08(1)
O1	0.9212(2)	−0.2615(2)	0.2226(2)	1.68(4)
O2	0.7784(2)	−0.0935(2)	0.3208(2)	1.65(4)
O3	0.6575(2)	−0.2199(2)	0.1211(2)	1.66(4)
C	0.8283(3)	−0.0265(3)	0.1092(2)	1.81(5)
F1	0.8491(2)	−0.0777(2)	−0.0025(1)	2.76(4)
F2	0.7158(2)	0.0702(2)	0.0803(2)	2.93(4)
F3	0.9491(2)	0.0394(2)	0.1728(2)	2.77(4)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter.

Table 2. Bond lengths (Å) with standard deviations.

Cation			
P–O	1.588(1)	N31–C32	1.488(2)
P–N11	1.605(2)	N31–C36	1.484(2)
P–N21	1.607(2)	C32–C33	1.513(3)
P–N31	1.604(2)	C33–O34	1.429(2)
N11–C12	1.484(2)	O34–C35	1.428(2)
N11–C16	1.477(2)	C35–C36	1.513(3)
C12–C13	1.509(3)		
C13–O14	1.432(2)		
O14–C15	1.425(2)	Anion	
C15–C16	1.521(3)	S–C	1.820(2)
N21–C22	1.490(2)	S–O1	1.441(1)
N21–C26	1.487(2)	S–O2	1.442(1)
C22–C23	1.507(3)	S–O3	1.442(1)
C23–O24	1.422(3)	C–F1	1.339(2)
O24–C25	1.425(2)	C–F2	1.334(3)
C25–C26	1.516(3)	C–F3	1.331(3)

no significant variations. No absorption or extinction corrections were applied to the intensity data. Computer programs used were supplied by Enraf-Nonius (SPD-plus 1983 and CAD 4-OS11).

Structure determination

Space group $P\bar{1}$ was chosen on the basis of E statistics. The structure was then solved using direct methods (MULTAN) and refined as described previously.[7] A weighting scheme with $w = [\sigma(F)^2 + (0.005F^2)^2]^{-1}$ was used. Non-hydrogen atoms were given anisotropic temperature factors, while hydrogen atoms were refined isotropically. Refinement converged to give the final conventional $R = 0.043$, $R_w = 0.037$ and $S = 1.447$. No peaks above 0.5 eÅ^{-3} were found in the difference electron density map. The successful refinement justified the choice of space group, which was also supported by the results of an attempted refinement in space group *P*1.

Results and discussion

Atomic parameters are listed in Table 1, interatomic distances and angles in Tables 2 and 3, and molecular planes and interplanar angles in Table 4. Tables of observed and calculated structure factors, anisotropic temperature factors, and hydrogen atom parameters are available from one of the authors (K.M.-M.) on request. The structure of the diphosphonium ion is shown in Fig. 1. The cation in **1** is very similar to that in **2**.[3] It has a staggered conformation of P–N bonds with respect to the P–O–P axis and has approximately S_6 symmetry. All the morpholyl groups have the chair conformation (Table 4).

Linearity of the P–O–P sequence. The diphosphonium ion in hexakis(morpholino-*N*)-μ-oxo-diphosphonium(V) trifluoromethanesulfonate (**1**) is centrosymmetric. It is therefore required to have an exactly linear P–O–P sequence like the corresponding ion in hexakis(dimethylamino)-μ-oxo-diphosphonium(V) trifluoromethanesulfonate (**2**). The final difference map and the oxygen temperature factors eliminate the possibility that oxygen is disordered in the present investigation. The P–O–P fragment is thus strictly linear in **1**. Linearity of M–O–M sequences in compounds of the type R_3M–O–MR_3 (M = C, Si, Ge, Sn and P) has been discussed by several authors.[3,8–11] From studies on the Si–O–Si group in silica polymorphs, the barrier to linearity was found to be only about $3kT$ at room temperature.[11,12] That the energy difference between systems containing linear and bent M–O–M systems is small is illustrated by the fact that the R_3M–O–MR_3 molecules with M = Si, Ge, Sn and R = $PhCH_2$ have linear M–O–M sequences,[10,13,14] while those with M = Ge, Sn and R = Ph are bent at oxygen.[15,16] The corresponding Si compound with R = Ph is linear,[17] but if one of the phenyl groups on each Si atom is replaced by a *t*-butyl group, the Si–O–Si angle is reduced to 152.4°.[11] Several other linear and non-linear Si–O–Si systems of this type are also known.[11]

Karle *et al.* have found an approximately linear

Table 3. Bond angles (°) with standard deviations.

Cation	
P–O–P	180
O–P–N11	106.50(7)
O–P–N21	103.98(6)
O–P–N31	110.04(6)
N11–P–N21	113.21(8)
N11–P–N31	108.36(8)
N21–P–N31	114.39(8)
P–N11–C12	123.7(1)
P–N11–C16	122.5(1)
C12–N11–C16	113.7(1)
P–N21–C22	119.7(1)
P–N21–C26	125.7(1)
C22–N21–C26	111.7(2)
P–N31–C31	121.3(1)
P–N31–C36	123.9(1)
C32–N31–C36	112.0(2)
N11–C12–C13	110.2(2)
C12–C13–O14	110.9(2)
C13–O14–C15	109.7(1)
O14–C15–C16	111.6(2)
C15–C16–N11	110.3(2)
N21–C22–C23	108.6(2)
C22–C23–O24	110.6(2)
C23–O24–C25	109.9(2)
O24–C25–C26	111.1(2)
C25–C26–N21	109.2(2)
N31–C32–C33	109.0(2)
C32–C33–O34	111.0(2)
C33–O34–C35	110.1(1)
O34–C35–C36	111.1(2)
C35–C36–N31	109.4(2)
Anion	
C–S–O1	104.02(2)
C–S–O2	103.6(1)
C–S–O3	102.8(1)
O1–S–O2	114.5(1)
O1–S–O3	114.8(1)
O2–S–O3	115.0(1)
S–C–F1	111.1(2)
S–C–F2	111.5(2)
S–C–F3	111.6(2)
F1–C–F2	107.7(2)
F1–C–F3	107.5(2)
F2–C–F3	107.3(2)

Table 4. Best planes and interplanar angles in cation.

No. of plane	Atoms included	Δmax[a]/Å	Dist. from plane/Å	Dihedral angles/°
1	P, C12, C16	0	N11: −0.005	1,2: 95.07
2	P. C22, C26	0	N21: −0.151	1,3: 59.49
3	P, C32, C36	0	N31: 0.146	2,3: 82.93
4	C12, C13, C15, C16	0.008	N11: 0.572, O14: −0.680	4,5:36.33
5	C22, C23, C25, C26	0.011	N21: −0.642, O24: 0.679	4,6: 93.02
6	C32, C33, C35, C36	0.003	N31: 0.633, O34: −0.673	5,6: 99.51
7	N11, P, O	0	N21: 1.352, N31: −1.339	7,8: 119.83
8	N21, P, O	0	N11: −1.335, N31: 1.264	7,9: 117.24
9	N31, P, O	0	N11: −1.368, N21: 1.308	8,9: 122.93

[a] Max. deviation of constituent atoms from plane.

relationship between Si–O bond length and Si–O–Si bond angle, and this also seems to be the case for similar Ge and Sn compounds.[11] This supports Cruickshank's studies of the π-bonding role of empty *d*-orbitals on M in linear M–O–M systems (M = P, Si etc.).[3,8] A recent structure analysis of $O[Si(CH_2CH_2CH_2)_3N]_2$ shows a relatively long Si–O bond [1.631(3) Å] in a linear Si–O–Si bridge.[18] However, this compound has a weak Si–N bond *trans* to Si–O, and that bond probably exerts a *trans* influence on Si–O.

Secondary Jahn-Teller effects have been invoked to explain the variation between linearity and non-linearity in M–O–M bridges.[9,19] If the symmetry species of the transition density $\psi_0\psi_1$ (ψ_0 and ψ_1 are the HOMO and LUMO of M–O–M) corresponds to a normal bending mode of the molecule, then a second-order Jahn-Teller distortion is possible (linear → angular M–O–M). Such distortion stabilizes the HOMO as the HOMO and the LUMO are mixed together. This is the case for OF_2 and $O(SiH_3)_2$. An increase in the electronegativity of M relative to O enhances the effect. Inclusion of π-orbitals on M in the bonding scheme will lead to interaction with the HOMO (π_u sym.) and change the HOMO–LUMO gap.[19] For outer, empty d_π orbitals on M the gap will increase, and bending in M–O–M is then less advantageous. For M = Si(IV) and isoelectronic P(V), the π overlap in M–O–M plus

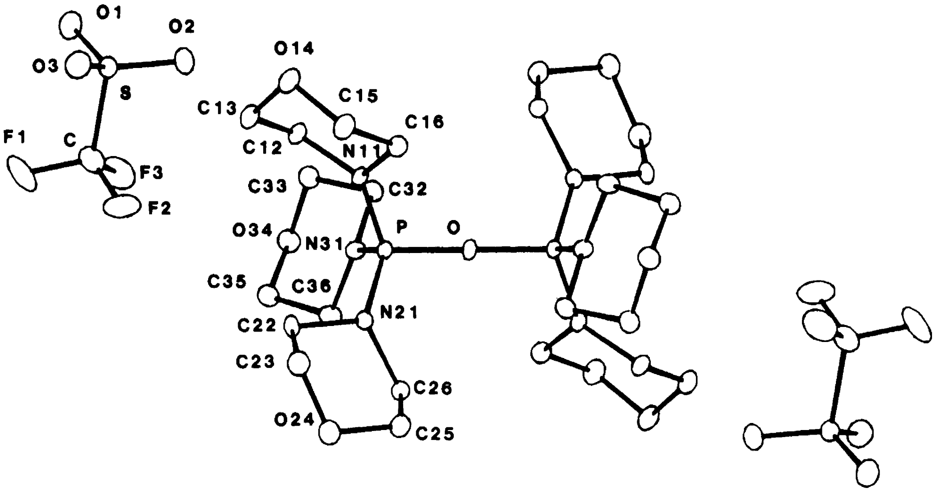

Fig. 1. The structure of the salt. The plane through atoms N31, P and O of the centrosymmetric cation is at right angles to the paper plane, with P–O horizontal.

low electronegativity of M relative to oxygen (no strongly electron-accepting substituents on M) should therefore make the M–O–M group less susceptible to bending distortion. In such cases, as, for example, in the present investigation, linear M–O–M bridges should be expected.

What about steric effects? These have been deemed of little importance for M = Si, Ge, Sn as a cause of linearity in M–O–M systems.[10] In $[Ph_2(t\text{-}Bu)Si]_2O$, it is probably the presence of the bulky *tert*-butyl group that results in a bent Si–O–Si bridge rather than a linear one as in $(Ph_3Si)_2O$.[17] For a linear $\overset{+}{P}-O-\overset{+}{P}$ sequence, which is isoelectronic with an Si–O–Si sequence, the P···P distance is ca. 0.1 Å shorter than the Si···Si distance. Thus, steric interactions between substituents on different P atoms in the same ion are larger than those between the same substituents in the corresponding Si compound. These effects are small compared to those in $(Ph_3C)_2O$, which is angular.[20] $[(Me_2N)_2C\text{–}O\text{–}C(NMe_2)_2]^{2+}$, which is similar to **1** and **2**, is also angular.[5] Few such contacts shorter than a van der Waals contact were found in **2**. In the present investigation on **1**, in which the substituents on phosphorus are "slimmer" than in **2**, interactions between substituents on different P atoms are relatively small. Only one H···H contact of less than 2.5 Å was found (H7···H15 = 2.44 Å). This is illustrated by the widening of the N–P–N angles and the narrowing of the O–P–N angles (Table 3).

On the basis of the above discussion one may tentatively conclude that the linearity of the P–O–P bridge is due to electronic rather than steric effects.

Bonding and charge distribution in the cation. The P–O and P–N bond lengths are 1.588(1) and 1.604(2) Å (average values) in **1**. They may be compared with the corresponding bond lengths of 1.573(1) and 1.592(4) Å found in **2**.[3] These bond lengths correspond to some double-bond character in the P–O bonds, and strong double-bond character in the P–N bonds. This π-bonding then favors a linear P–O–P bridge on two counts: π-interaction in the P–O–P bridge and electron transfer from nitrogen to phosphorus render the latter less electronegative (see discussion on P–O–P bridge). The π bonding results in delocalization of charge over all the P and N atoms, and the central oxygen atoms of the cation. Thus, the stability of the cation is enhanced.

The N-atoms are essentially sp^2 hybridized, with average C–N bond lengths of 1.485 Å as compared to 1.464 Å in **2**.[3] However, both N21 and N31 are bonded in a slightly pyramidal fashion to their neighbours. By comparison it is seen that there is an increase in corresponding bond lengths on going from **2** to **1**. This is probably due mainly to the difference in the temperatures at which the data were collected: 92K for **1** and 295K for **2**. Furthermore, **2** had somewhat larger temperature factors than normal. The average C–C and C–O bond lengths are normal (1.513 and 1.427 Å, respectively).

The structure of the anion, and packing in the unit cell. The trifluoromethanesulfonate anion has a C–S bond length of 1.820(3) Å, and average S–O and C–F bond lengths of 1.442 and 1.335 Å, respectively. These are normal values.[5] However, all the C–F and all the S–O bond lengths are equal within error limits. This is not the case in **2**. The reason for this probably lies in the packing of the ions in the unit cell. The packing of anions and cations in **1** is markedly different from that in **2**. The anions in **2** are closer to the positively charged skeleton of the cations than in **1**, and are thus more susceptible to the polarizing action of the cation. The nearest anions in **1** are close to the amino ends of the cation, while those in **2** are closer to the center of the cation. There are no particularly short interionic interactions in the cell.

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