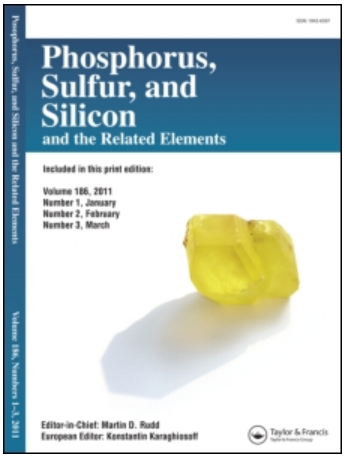

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

The Structures of the Bulky Basic Phosphine Sulfides Tris(2,6-Dimethoxyphenyl)Phosphine Sulfide (DMPP=S) and Tris(2,4,6-Trimethoxyphenyl)Phosphine Sulfide (TMPP=S)

Daniel C. Finnen[a]; A. Alan Pinkerton[a]
[a] Department of Chemistry, University of Toledo, Toledo, OH, USA

To cite this Article Finnen, Daniel C. and Pinkerton, A. Alan(1994) 'The Structures of the Bulky Basic Phosphine Sulfides Tris(2,6-Dimethoxyphenyl)Phosphine Sulfide (DMPP=S) and Tris(2,4,6-Trimethoxyphenyl)Phosphine Sulfide (TMPP=S)', Phosphorus, Sulfur, and Silicon and the Related Elements, 90: 1, 11 — 19
To link to this Article: DOI: 10.1080/10426509408016381
URL: http://dx.doi.org/10.1080/10426509408016381

Phosphorus, Sulfur, and Silicon, 1994, Vol. 90, pp. 11–19
Reprints available directly from the publisher
Photocopying permitted by license only

THE STRUCTURES OF THE BULKY BASIC PHOSPHINE SULFIDES TRIS(2,6-DIMETHOXYPHENYL)PHOSPHINE SULFIDE (DMPP=S) AND TRIS(2,4,6-TRIMETHOXYPHENYL)PHOSPHINE SULFIDE (TMPP=S)

DANIEL C. FINNEN and A. ALAN PINKERTON
Department of Chemistry, University of Toledo, Toledo, OH 43606, USA

(Received April 25, 1994; in final form June 7, 1994)

The structures of the title compounds (DMPP=S = $[2,6\text{-}(OCH_3)_2C_6H_3]_3P(=S)$, TMPP=S = $[2,4,6\text{-}(OCH_3)_3C_6H_2]_3P(=S)$) have been determined from X-ray diffractometer data. DMPP=S: orthorhombic, Pbca; a = 15.377(2), b = 17.756(2), c = 17.921(1) Å; V = 4893(1) Å^3; Z = 8; $D_{calc.}$ = 1.34 g cm^{-1}; T = 294 ± 1 K; R = 0.044 for 2456 unique observed reflections of 5306 total data. TMPP=S: monoclinic, $P2_1/c$; a = 9.067(1), b = 28.001(3), c = 11.299(1) Å, β = 109.16(1)°; V = 2710(1) Å^3; Z = 4; $D_{calc.}$ = 1.38 g cm^{-3}; T = 193 ± 1 K; R = 0.042 for 2886 unique observed reflections of 5507 total data. Both molecules have a distorted propeller geometry, one of the aryl groups being close to coplanar with the P=S bond. In both cases the P=S bond is long (DMPP=S, 1.969(1) Å; TMPP=S, 1.962(1) Å).

Key words: Phosphine sulfide, X-ray structure, basicity.

INTRODUCTION

The utility of tertiary phosphines in d-transition metal chemistry has been known for many years.[1] The modification of their basicities over almost ten orders of magnitude may be achieved by suitable substitution.[2–4] Similar, but more subtle effects are noted on the weaker basicities of phosphine chalcogenides. It is known that adding methoxy substituents to the aryl groups in triphenylphosphine, Ph_3P, changes the character from a weak base (pKa = 2.73) to a much stronger one, (tris(2,6-dimethoxyphenyl)phosphine, DMPP, pKa = 10.7, tris(2,4,6-trimethoxyphenyl)phosphine, TMPP, pKa = 11.2).[5–7] It has recently been shown that, although triphenylphosphine sulfide is a rather poor base, both DMPP=S and TMPP=S may easily be protonated to give the thiophosphonium salts.[8] They also react with alkyl halides to form the corresponding alkylthiophosphonium derivatives.[8,9] From the point of view of coordination chemistry, although Me_2SnCl_2 does not react with Ph_3P=S, reaction with DMPP=S or TMPP=S yields stable compounds analogous to those obtained with the more basic phosphine oxides.[9,10]

In order to better understand any correlation between molecular structure and basicity of phosphine sulfides, we have determined the structures of DMPP=S and TMPP=S and report our results herein.

RESULTS AND DISCUSSION

Both DMPP=S and TMPP=S (Figures 1 and 2) have the overall features anticipated for triarylphosphine sulfides. The geometry at phosphorus (Tables III and V) is formally tetrahedral with some folding back of the carbon atoms to make the average S—P—C angles greater than ideal, and the average C—P—C angles smaller, however, see below. The aryl groups have the familiar propeller arrangement of triphenylphosphine derivatives. Distortion from the ideal geometry has been previously analyzed for many triphenylphosphine derivatives and discussed in terms of the torsion angles about the P—C bonds.[11] In DMPP=S, one aryl group is almost coplanar with the P=S vector, whereas the two other rings are rotated in the expected manner. A similar situation exists in TMPP=S although to a lesser extent. Measuring this as a torsion angle about the P—C bonds with respect to the P=S vector (0° indicating coplanar) we observe averaged values of 73.0, 52.3 and 6.4° for DMPP=S and 63.7, 55.5 and 16.4° for TMPP=S respectively. These values approach the extreme of the previously reported distortions from C_3 symmetry,[12] but are quite similar to the values for the parent triphenylphosphine sulfide. This asymmetry is also reflected in the valence angles at phosphorus. The S—P—C angles vary by 12° and correlate strongly with the torsion angles, a small torsion

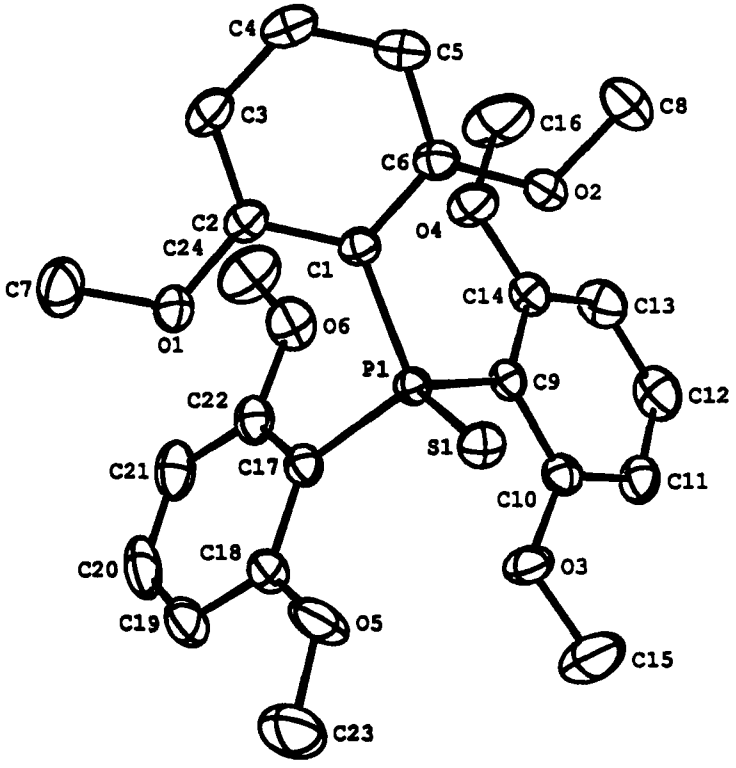

FIGURE 1 A perspective view of the DMPP=S molecule (30% probability ellipsoids) showing the atom numbering. Hydrogen atoms have been omitted for clarity.

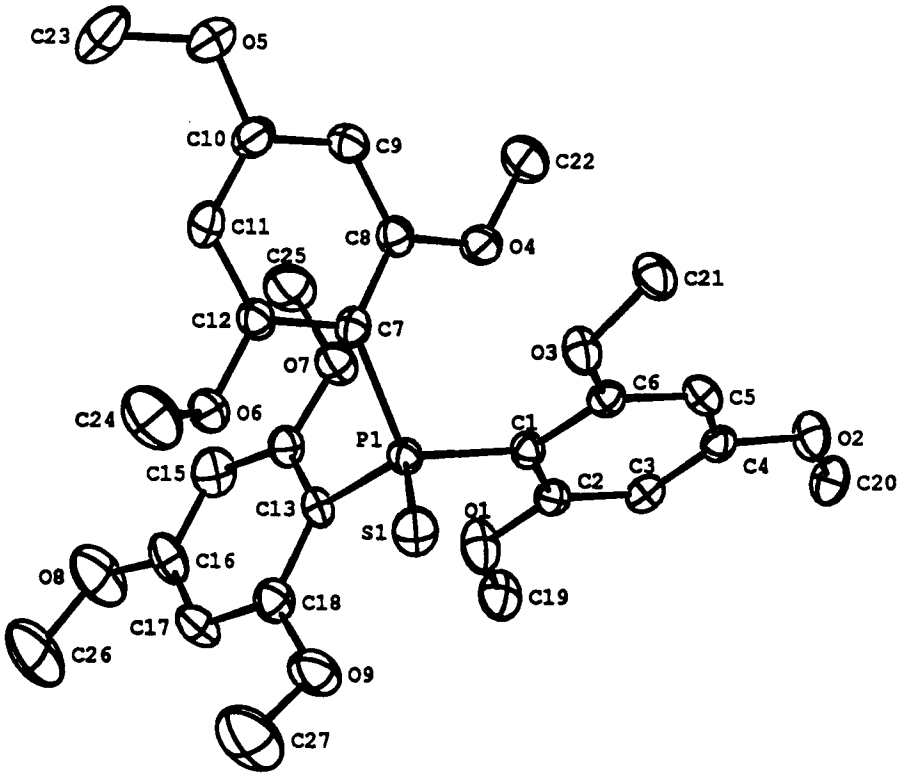

FIGURE 2 A perspective view of the TMPP═S molecule (50% probability ellipsoids) showing the atom numbering. Hydrogen atoms have been omitted for clarity.

angle producing a large S—P—C angle due to the stronger steric interaction between the aryl group and the sulfur atom. Additional steric effects are seen to modify the geometry of the *ipso* carbon atoms, the P—C—C angle *syn* to the P═S bond being smaller (117(2)° ave.) than the angle *anti* to the P═S bond (126(2)° ave.).

As observed for the parent phosphines (DMPP and TMPP), there is a marked tendency for the methoxy substituents to conjugate with the benzene rings thus keeping the methyl groups largely in the plane of the aromatic group.[13,14] The strength of the interaction is such that steric strain due to the proximity of the methyl groups to the aromatic hydrogen atoms is released by deforming the C—C—O bond angles (122.4° ave., *syn*; 115.9° ave., *anti*) rather than rotating about the C—O bond. However, interring contacts are strong enough to also deform some of the methoxy groups in this manner also. This is most noticeable in TMPP═S where one of the methoxy groups is rotated by 45°.

We may consider that there is some competition between the p electrons on sulfur and the π electrons of the aryl groups for the same orbitals on phosphorus. A consequence of the oxygen p electrons interacting with the aromatic π system is that this will increase the aryl π interaction with phosphorus at the expense of the P═S bond. This will increase the $Ar_3P^+—S^-$ contribution to the bonding

TABLE I

Crystallographic data, structure solution and refinement

Compound	DMPP=S	TMPP=S
Formula	$C_{24}H_{29}O_7PS$	$C_{27}H_{33}O_9PS$
F.W.	492.53	564.60
F(000)	2080	1192
Shape	plate	plate
Color	colorless	pale yellow
Crystal size mm	0.42 x 0.18 x 0.09	0.35 x 0.10 x 0.05
Radiation	---------- Mo Kα (λ = 0.71073 Å) ---------	
Temperature K	294 ± 1	193 ± 1
Space group	Pbca	$P2_1/c$
a Å	15.377 (2)	9.067 (1)
b Å	17.756 (2)	28.001 (3)
c Å	17.921(1)	11.299(1)
β		109.16 (1)
V $Å^3$	4893(1)	2710(1)
Z	8	4
ρ g/cm^3	1.34	1.38
μ cm^{-1}	2.3	2.2
Scan type:	---------- ω - θ ----------	
Scan rate	---------- 1 - 7 °/min (in omega) --------	
ω scan width °	---------- 0.8 + 0.34 tan ω ----------	
θ scan width °	0.833 ω width	0.500 ω width
Maximum 2θ °	---------- 52.0 ----------	
Reflections	5306 total, 5306 unique	5507 total, 5158 unique
Anisotropic decay	0.956 to 1.053	0.977 to 1.081
Empirical absorption	0.985 to 1.00	0.892 to 1.000[20]
Solution	---------- Direct methods[21] ----------	
Hydrogen atoms	---------- Refined as riding atoms -------	
Refinement	---------- Full-matrix least-squares ------	
Minimization function	---------- $\Sigma w(\|Fo\|-\|Fc\|)^2$ ----------	
Least-squares weights	---------- $4Fo^2/\sigma^2(Fo^2)$ ----------	
Anomalous dispersion	---------- All non-hydrogen atoms ----------	
Reflections included	2456 with $Fo^2>3.0\sigma(Fo^2)$	2887 with $Fo^2>3.0\sigma(Fo^2)$
Parameters refined	298	343
R	0.044	0.041
Rw	0.050	0.048
GoF	1.36	1.54
Largest shift	0.01σ	0.01σ
ΔFmax $e/Å^3$	0.26 (5)	0.23 (6)
ΔFmin $e/Å^3$	-0.11 (5)	-0.10 (6)
Computer hardware	---------- MicroVAX3100 ----------	
Computer software	---------- MolEN (Enraf-Nonius)[22] ----------	

TABLE II

Positional parameters for DMPP═S

Atom	x	y	z	B(Å^2)
S1	0.03812(6)	0.18522(5)	0.20169(5)	3.27(2)
P1	-0.01441(5)	0.25924(5)	0.13344(5)	2.37(2)
O1	-0.0412(2)	0.4088(1)	0.2145(1)	3.91(6)
O2	0.1600(2)	0.2694(1)	0.0749(1)	3.90(6)
O3	-0.1042(2)	0.1277(1)	0.0938(1)	4.18(6)
O4	0.0397(2)	0.3274(1)	-0.0244(1)	4.36(6)
O5	-0.1486(2)	0.2008(2)	0.2483(2)	6.03(7)
O6	-0.1055(2)	0.3741(2)	0.0561(1)	4.63(6)
O7	0.1393(2)	0.0807(2)	0.0700(2)	7.62(9)
C1	0.0562(2)	0.3421(2)	0.1378(2)	2.65(7)
C2	0.0363(2)	0.4078(2)	0.1777(2)	2.93(7)
C3	0.0940(3)	0.4670(2)	0.1815(2)	3.79(8)
C4	0.1743(3)	0.4605(2)	0.1478(2)	4.34(9)
C5	0.1979(3)	0.3961(2)	0.1110(2)	4.21(9)
C6	0.1398(2)	0.3367(2)	0.1072(2)	3.17(7)
C7	-0.0772(3)	0.4777(2)	0.2388(2)	5.4(1)
C8	0.2347(3)	0.2654(3)	0.0281(3)	7.3(1)
C9	-0.0239(2)	0.2236(2)	0.0372(2)	2.65(7)
C10	-0.0650(2)	0.1533(2)	0.0302(2)	3.08(8)
C11	-0.0696(2)	0.1149(2)	-0.0365(2)	3.95(9)
C12	-0.0383(3)	0.1492(2)	-0.0993(2)	4.9(1)
C13	-0.0029(3)	0.2204(2)	-0.0966(2)	4.5(1)
C14	0.0054(2)	0.2569(2)	-0.0294(2)	3.21(7)
C15	-0.1280(4)	0.0524(2)	0.0998(3)	7.1(1)
C16	0.0728(4)	0.3602(3)	-0.0913(2)	8.5(2)
C17	-0.1265(2)	0.2885(2)	0.1519(2)	2.91(7)
C18	-0.1816(2)	0.2571(2)	0.2064(2)	3.77(8)
C19	-0.2661(2)	0.2833(2)	0.2157(2)	4.9(1)
C20	-0.2953(3)	0.3414(2)	0.1729(3)	5.5(1)
C21	-0.2445(3)	0.3730(2)	0.1182(2)	4.73(9)
C22	-0.1614(2)	0.3467(2)	0.1079(2)	3.59(8)
C23	-0.1994(4)	0.1645(3)	0.2998(3)	9.7(2)
C24	-0.1321(3)	0.4328(2)	0.0086(3)	6.7(1)

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

TABLE III
Selected bond distances, bond angles and torsion angles for DMPP=S

S1	P1	1.969(1)	P1	C9	1.843(3)		
P1	C1	1.829(3)	P1	C17	1.830(3)		
S1	P1	C1	105.4(1)	C1	P1	C9	111.3(1)
S1	P1	C9	112.6(1)	C1	P1	C17	108.8(1)
S1	P1	C17	117.6(1)	C9	P1	C17	101.1(1)
P1	C1	C2	124.2(2)	P1	C1	C6	118.3(2)
P1	C9	C10	115.1(2)	P1	C9	C14	128.6(3)
P1	C17	C18	125.4(3)	P1	C17	C22	117.9(3)
O1	C2	C1	116.6(3)	O1	C2	C3	122.1(3)
O2	C6	C1	115.8(3)	O2	C6	C5	122.7(3)
O3	C10	C9	114.9(3)	O3	C10	C11	122.4(3)
O4	C14	C9	117.0(3)	O4	C14	C13	121.9(3)
O5	C18	C17	116.9(3)	O5	C18	C19	122.2(3)
O6	C22	C17	113.9(3)	O6	C22	C21	124.0(3)
S1	P1	C1	C2	-103.0(3)	S1	P1	C1	C6	69.0(3)
S1	P1	C9	C10	51.9(3)	S1	P1	C9	C14	-127.2(3)
S1	P1	C17	C18	-6.8(4)	S1	P1	C17	C22	173.9(2)
C7	O1	C2	C1	-162.9(3)	C7	O1	C2	C3	19.4(5)
C8	O2	C6	C1	165.7(3)	C8	O2	C6	C5	-15.2(5)
C15	O3	C10	C9	-164.1(4)	C15	O3	C10	C11	19.2(5)
C16	O4	C14	C9	177.5(4)	C16	O4	C14	C13	-4.5(5)
C23	O5	C18	C17	-176.6(4)	C23	O5	C18	C19	3.1(6)
C24	O6	C22	C17	-179.7(3)	C24	O6	C22	C21	-0.5(5)

compared to that in triphenylphosphine sulfide. Thus, the basicity of sulfur will increase with a concomitant weakening (lengthening) of the P=S bond. Indeed, the P=S bond length in DMPP=S is even longer than that in tricyclohexylphosphine sulfide,[15] the longest P=S bond previously reported for all phosphine sulfides with only carbon bound substituents. Indeed, only 2.2% of all reported P=S bonds that are not bonded to metals are longer than those reported here.[16]

We note that the oxidation of the phosphorus produces the expected down field shift of the ^{31}P resonances (DMPP=S, $\Delta\delta$ = 79.76 ppm; TMPP=S, $\Delta\delta$ = 81.46 ppm with respect to the parent phosphines).

TABLE IV
Positional parameters for TMPP=S

Atom	x	y	z	B(Å^2)
S1	0.9206(1)	0.12725(3)	0.94205(8)	2.52(2)
P1	0.75386(9)	0.11010(3)	0.78693(7)	1.69(2)
O1	0.4238(2)	0.08574(8)	0.7870(2)	3.02(5)
O2	0.5271(2)	-0.08107(8)	0.8878(2)	2.58(5)
O3	0.9161(2)	0.02075(7)	0.8374(2)	2.17(5)
O4	0.7324(3)	0.03012(8)	0.5867(2)	2.60(5)
O5	1.0001(3)	0.11168(9)	0.3541(2)	3.74(6)
O6	0.9009(3)	0.18734(8)	0.7027(2)	2.69(5)
O7	0.5112(2)	0.11127(8)	0.5383(2)	2.44(5)
O8	0.2918(3)	0.26288(9)	0.5493(3)	4.65(7)
O9	0.6440(3)	0.19149(9)	0.9232(2)	3.52(6)
C1	0.6698(3)	0.0534(1)	0.8085(3)	1.66(7)
C2	0.5172(3)	0.0465(1)	0.8103(3)	1.73(6)
C3	0.4647(3)	0.0020(1)	0.8354(3)	1.91(7)
C4	0.5650(3)	-0.0362(1)	0.8610(3)	1.82(7)
C5	0.7183(3)	-0.0311(1)	0.8628(3)	2.00(7)
C6	0.7680(3)	0.0132(1)	0.8370(3)	1.68(6)
C7	0.8291(3)	0.1069(1)	0.6546(3)	1.81(6)
C8	0.8154(3)	0.0686(1)	0.5719(3)	1.96(7)
C9	0.8790(4)	0.0709(1)	0.4759(3)	2.33(7)
C10	0.9487(4)	0.1125(1)	0.4561(3)	2.50(7)
C11	0.9611(4)	0.1514(1)	0.5321(3)	2.45(7)
C12	0.9003(4)	0.1482(1)	0.6300(3)	2.06(7)
C13	0.5971(3)	0.1539(1)	0.7278(3)	1.87(7)
C14	0.5020(3)	0.1521(1)	0.6008(3)	2.04(7)
C15	0.4042(4)	0.1887(1)	0.5450(3)	2.86(8)
C16	0.3934(4)	0.2284(1)	0.6140(3)	2.84(8)
C17	0.4754(4)	0.2305(1)	0.7403(3)	2.71(8)
C18	0.5738(4)	0.1926(1)	0.7963(3)	2.42(8)
C19	0.2689(3)	0.0824(1)	0.7909(3)	3.01(8)
C20	0.3709(3)	-0.0894(1)	0.8866(3)	2.69(8)
C21	1.0112(3)	-0.0195(1)	0.8395(3)	2.58(8)
C22	0.7147(4)	-0.0096(1)	0.5058(3)	3.31(9)
C23	1.0011(4)	0.1555(1)	0.2929(3)	3.88(9)
C24	1.0414(4)	0.2142(1)	0.7472(4)	4.2(1)
C25	0.4703(4)	0.1138(1)	0.4058(3)	3.70(9)
C26	0.3005(5)	0.3083(1)	0.6057(4)	5.6(1)
C27	0.7117(6)	0.2334(2)	0.9845(4)	5.7(1)

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

TABLE V

Selected bond distances, bond angles and torsion angles for TMPP═S

S1	P1	1.962(1)	P1	C7	1.838(4)		
P1	C1	1.812(3)	P1	C13	1.830(3)		
S1	P1	C1	109.21(9)	C1	P1	C7	110.6(1)
S1	P1	C7	110.85(9)	C1	P1	C13	109.0(1)
S1	P1	C13	116.2(1)	C7	P1	C13	100.8(1)
P1	C1	C2	125.6(2)	P1	C1	C6	118.0(2)
P1	C7	C8	127.2(3)	P1	C7	C12	116.1(2)
P1	C13	C14	119.3(2)	P1	C13	C18	124.2(2)
O1	C2	C1	116.2(3)	O1	C2	C3	121.9(3)
O2	C4	C3	124.6(3)	O2	C4	C5	114.5(3)
O3	C6	C1	115.3(3)	O3	C6	C5	122.0(3)
O4	C8	C7	117.2(3)	O4	C8	C9	121.5(3)
O5	C10	C9	114.8(3)	O5	C10	C11	124.0(3)
O6	C12	C7	117.1(3)	O6	C12	C11	120.1(3)
O7	C14	C13	115.9(3)	O7	C14	C15	122.1(3)
O8	C16	C15	115.2(3)	O8	C16	C17	124.2(3)
O9	C18	C13	117.6(3)	O9	C18	C17	120.1(3)

S1	P1	C1	C2	113.3(3)	S1	P1	C1	C6	-60.8(3)
S1	P1	C7	C8	126.4(3)	S1	P1	C7	C12	-57.3(3)
S1	P1	C13	C14	160.1(2)	S1	P1	C13	C18	-12.9(3)
C19	O1	C2	C1	-178.0(3)	C19	O1	C2	C3	1.6(4)
C20	O2	C4	C3	1.5(4)	C20	O2	C4	C5	-179.3(3)
C21	O3	C6	C1	-167.2(3)	C21	O3	C6	C5	12.8(4)
C22	O4	C8	C7	-180.0(2)	C22	O4	C8	C9	2.5(4)
C23	O5	C10	C9	150.2(3)	C23	O5	C10	C11	-28.5(5)
C24	O6	C12	C7	136.9(3)	C24	O6	C12	C11	-46.6(4)
C25	O7	C14	C13	-155.9(3)	C25	O7	C14	C15	25.4(5)
C26	O8	C16	C15	-166.3(4)	C26	O8	C16	C17	17.0(5)
C27	O9	C18	C13	139.1(4)	C27	O9	C18	C17	-44.5(5)

EXPERIMENTAL

All NMR data were collected on a Varian Gemini-200 NMR Spectrometer equipped with a 5 mm probe. Solutions for NMR measurements were prepared as dilute solutions in $CDCl_3$. ^{31}P NMR chemical

shifts were referenced to 85% H_3PO_4. All IR samples were prepared as KBr pellets and run on a Nicolet FXQ-60 Spectrometer.

Synthesis and Characterizations: DMPP═S and TMPP═S were easily prepared by the reported methods.[8] The crude products were recrystallized from ethanol (DMPP═S) or toluene (TMPP═S), the DMPP═S crystallizing as the hydrate. Elemental analyses, melting points, and ^1H and ^{13}C NMR parameters agree closely with the literature values.[8]

DMPP═S: ^{31}P NMR, δ = 13.11 ppm; IR 777 cm^{-1} (ν P═S). TMPP═S: ^{31}P NMR, δ = 11.96; IR 810 cm^{-1} (ν P═S).

Crystallography: Preliminary examination and intensity measurements[17] were carried out with an Enraf-Nonius CAD4 diffractometer using a graphite monochromator. The crystallographic details and structure determination and refinement are summarized in Table I. Scattering factors for neutral atoms and the values for $\Delta f'$ and $\Delta f''$ were taken from International Tables for X-ray Crystallography.[18] Final refined atomic coordinates are reported in Tables II and IV. Selected bond lengths, bond angles and torsion angles are given in Tables III and V. Perspective views[19] of the two molecules are shown in Figures 1 and 2.*

ACKNOWLEDGEMENTS

The authors thank the College of Arts and Sciences of the University of Toledo for generous support of the X-ray facility.

REFERENCES

1. C. A. McAuliffe, "Comprehensive Coordination Chemistry," Pergamon, New York, 1987, 989 and references therein.
2. C. A. Streuli, *Anal. Chem.*, **32,** 985 (1960).
3. W. A. Henderson and C. A. Streuli, *J. Am. Chem. Soc.*, **82,** 5791 (1960).
4. R. G. Goel and T. Allman, *Can. J. Chem.*, **60,** 716 (1982).
5. M. Wada and S. Higashizaki, *J. Chem. Soc. Chem. Commun.*, 482 (1984).
6. M. Wada, S. Higashizaki and A. Tsuboi, *J. Chem. Res.*, 38 (1985).
7. M. Wada and A. Tsuboi, *J. Chem. Soc. Perkin Trans. I*, 151 (1987).
8. M. Wada, M. Kanzaki, M. Fujiwara, K. Kajihara and T. Erabi, *Bull. Chem. Soc. Jpn.*, **64,** 1782 (1991).
9. M. Wada, T. Fujii, S. Iijima, S. Hayase, T. Erabi and G. Matsubayashi, *J. Organomet. Chem.*, **445,** 65 (1993).
10. M. Wada, S. Miyake, M. Fujiwara, S. Hayashi, T. Kawaguchi and T. Erabi, *Phosphorus, Sulfur, and Silicon*, **75,** 179 (1993).
11. E. Bye, W. B. Schweizer and J. D. Dunitz, *J. Am. Chem. Soc.*, **104,** 5893 (1982).
12. P. W. Codding and K. A. Kerr, *Acta Cryst.*, **B34,** 3785 (1978).
13. P. Livant, Y. J. Sun and T. R. Webb, *Acta Cryst.*, **C47,** 1003 (1991).
14. G. Nemeth, A. A. Pinkerton, J. A. Stowe and C. A. Ogle, *Acta Cryst.*, **C48,** 2200 (1992).
15. K. A. Kerr, P. M. Boorman, B. S. Misner and J. G. H. vanRoode, *Can. J. Chem.*, **55,** 3081 (1977).
16. F. H. Allen, J. E. Davies, J. J. Galloy, O. Johnson, O. Kennard, C. F. Macrae, E. M. Mitchell, G. F. Mitchell, J. M. Smith and D. G. Watson, *J. Chem. Info. Comp. Sci.*, **31,** 187 (1991).
17. R. H. Blessing, P. Coppens and P. Becker, *J. Appl. Cryst.*, **7,** 488 (1974).
18. "International Tables for X-Ray Crystallography," Vol. IV, Birmingham: Kynoch Press (1974).
19. C. K. Johnson, ORTEP. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA (1976).
20. N. Walker and D. Stuart, *Acta Cryst.*, **A39,** 158 (1983).
21. P. Main, S. J. Fiske, S. E. Hull, L. Lessinger, G. Germain, J. P. DeClerq and M. M. Woolfson, MULTAN80. University of York, England (1980).
22. C. K. Fair, MolEN, An Interactive Intelligent System for Crystal Structure Analysis, User Manual, Enraf-Nonius, Delft, The Netherlands (1990).

*Complete crystallographic data have been deposited with the Cambridge Crystallographic Data Centre, U.K. Tables of observed and calculated structure factors are available from the authors.