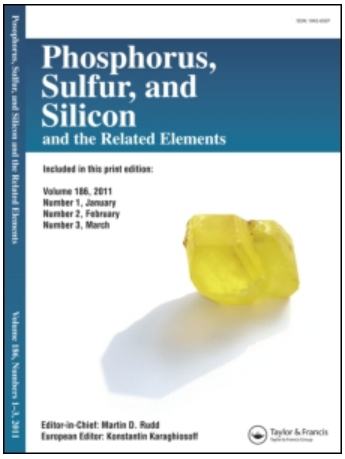

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CRYSTAL AND MOLECULAR STRUCTURE OF 4-*TERT*-BUTYLPHOSPHORINANE 1-SULFIDE DERIVATIVES

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CRYSTAL AND MOLECULAR STRUCTURE OF 4-*TERT*-BUTYLPHOSPHORINANE 1-SULFIDE DERIVATIVES

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Dedicated to Professor Reinhard Schmutzler on the occasion of his 60th birthday.

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Three derivatives of the parent 4-*tert*-butylphosphorinane sulfide were prepared and investigated by single crystal X-ray diffraction: *trans*-4-*tert*-butyl-1-phenoxyphosphorinane sulfide (**2a**) and the *cis* and *trans* isomers of 4-*tert*-butyl-1-phenylphosphorinane sulfide (**3b** and **3a**, respectively). Crystallographic data for **2a**: space group $P2_1/n$ (No. 14) with a = 6.1670(6) Å, b = 10.999(1) Å, c = 23.275(2) Å, β = 94.978(7)°, V = 1572.7(5) Å^3, and D_{calc} = 1.193 g cm^{-3} for Z = 4, R = 0.040; for **3a**: space group C2/c (No. 15) with a = 25.826(3) Å, b = 6.427(1) Å, c = 20.050(3) Å, β = 111.57(1)°, V = 3094(1) Å^3, and D_{calc} = 1.143 g cm^{-3} for Z = 8, R = 0.043; for **3b**: space group $P2_1/c$ (No. 14) with a = 6.2914(7) Å, b = 11.632(1) Å, c = 21.088(1) Å, β = 96.892(7)°, V = 1532.1(4) Å^3, and D_{calc} = 1.155 g cm^{-3} for Z = 4, R = 0.048. In every structure the phosphorinane ring adopts a chair conformation with the *tert*-butyl group in an equatorial position. The relative spatial arrangement of the latter and the phenoxy or phenyl groups define the *cis*/*trans* designation. The structure of these molecules is discussed in comparison with their P=O analogues (*trans* isomers) and similar phosphorinane sulfides. Semiempirical calculations using the PM3 method give structures with correct overall geometry, although some predictable discrepancies are observed.

Key words: Phosphorinane sulfide, crystal structure, PM3, semiempirical calculations.

INTRODUCTION

The molecular structure of six-membered, phosphorus containing heterocycles has been widely investigated; however, the majority of these investigations focus on systems containing other heteroatoms in the ring, mainly oxygen, sulfur and nitrogen.[1] The parent phosphorinane system has received far less attention. During our research on examining nucleophilic substitution at the phosphorus center, we prepared a series of phosphorinane 1-sulfides with a 4-*tert*-butyl group which presumably anchors the ring as a single conformation in solution. Since the stereochemical assignment around the phosphorus atom was required to determine the stereochemical pathway of the displacements, X-ray studies were initiated. In this

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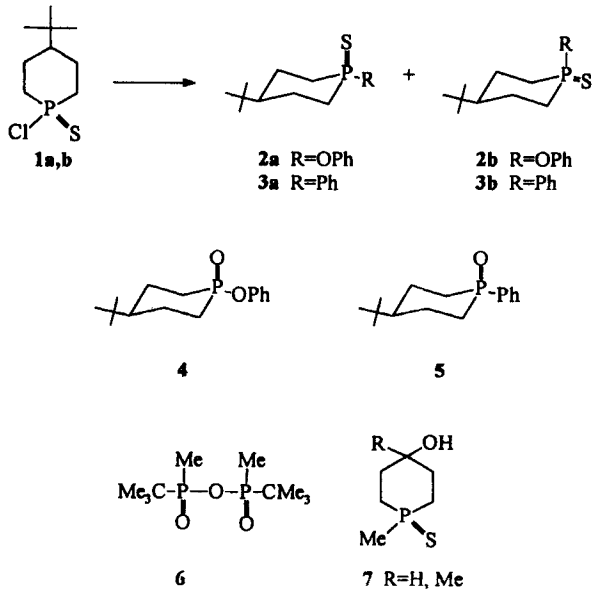
paper we wish to report a structural study of *trans*-4-*tert*-butyl-1-phenoxyphosphorinane 1-sulfide (**2a**) and *trans*- and *cis*-4-*tert*-butyl-1-phenylphosphorinane 1-sulfides (**3a** and **3b**) based on the X-ray data, semiempirical calculations, and ^{13}C NMR spectroscopy. The ^{1}H NMR spectra of these compounds are complex and not helpful for structural elucidation. The previously reported X-ray crystal structures of *trans*-4-*tert*-butyl-1-phenoxyphosphorinane 1-oxide[2] (**4**) and *trans*-4-*tert*-butyl-1-phenylphosphorinane 1-oxide[3] (**5**) were used for comparison. We were interested in the effect a change from P=O to P=S would have on the structure of the phosphorinane ring and the ^{13}C NMR spectrum. The suitability of semiempirical calculations for the prediction of the molecular structure of heterocyclic compounds containing a tetracoordinated, pentavalent phosphorus atom also was of interest.

RESULTS AND DISCUSSION

The synthesis of the phosphorinane sulfide derivatives is outlined in Scheme I. Reaction of 4-*tert*-butyl-1-chlorophosphorinane 1-sulfide (**1a,b**)[4] (mixture of isomers) with sodium phenoxide in acetonitrile at room temperature (Scheme I) gave a mixture of *cis*/*trans*-4-*tert*-butyl-1-phenoxyphosphorinane 1-sulfide (**2b/2a**). This mixture was separated by column chromatography on silica gel, using a 2:1 (v/v) $CCl_4/CHCl_3$ mixture as an eluent; R_f = 0.35 for **2a** and 0.17 for **2b**. The crystals of **2a** used for X-ray studies were obtained from pentane/CH_2Cl_2 mixture. Crystals of **2b** were unsuitable for X-ray analysis. Reaction of **1a,b** with phenyllithium in THF at −78°C gave a mixture of *cis*/*trans*-4-*tert*-butyl-1-phenylphosphorinane 1-sulfide (**3a,b**). Likewise, the isomers were separated by column chromatography on silica gel under the same conditions; R_f = 0.40 for **3a** and 0.13 for **3b**. Crystals



SCHEME I

TABLE I
Crystal data

	2a	3a	3b
Molecular formula	$C_{15}H_{23}OPS$	$C_{15}H_{23}PS$	$C_{15}H_{23}PS$
Color	colorless	colorless	colorless
Formula weight	282.39	266.39	266.39
Space group	$P2_1/n$ (No. 14)	C2/c (No.15)	$P2_1/c$ (No.14)
Temperature	293. K	293. K	293. K
a, Å	6.1670(6)	25.826(3)	6.2914(7)
b, Å	10.999(1)	6.427(1)	11.632(1)
c, Å	23.275(2)	20.050(3)	21.088(1)
β, deg	94.978(7)	111.57(1)	96.892(7)
V, Å^3	1572.7(5)	3094(1)	1532.1(4)
Z	4	8	4
D_{calc}, g cm^{-3}	1.193	1.143	1.155
Linear absorption coef., μ, cm^{-1}	2.85	26.31	2.85
Diffractometer	Enraf-Nonius CAD4	Enraf-Nonius CAD4	Enraf-Nonius CAD4
Radiation (wavelength)	Mo Kα (0.71073 Å)	Cu Kα (1.54184 Å)	Mo Kα (0.71073 Å)
Monochromator	graphite	graphite	graphite
Crystal dimensions, mm	0.65 x 0.58 x 0.52	0.30 x 0.22 x 0.13	0.63 x 0.57 x 0.50
Scan method	ω - 2θ	ω - 2θ	ω - 2θ
Scan width, deg	0.75 + 0.48tan(θ)	0.89 + 0.24tan(θ)	0.43 + 0.51tan(θ)
Data collected	4264	3516	4154
Unique data	3916	3436	3821

TABLE I (*Continued*)

	2a	3a	3b
2θ range, deg	5.42 - 55.64	5.62 - 148.66	5.40 - 55.64
Range of h, k, l	0 to 8,	-32 to 0,	0 to 8,
	0 to 14,	-8 to 0,	-15 to 0
	-30 to 30	-23 to 25	-27 to 27
Data with I > 3.0 σ(I)	2654	2414	1756
Corrections applied	Lorentzian, polarization	Lorentzian, polarization	Lorentzian, polarization
Absorption correction	none	empirical[a]	none
Computer programs	Enraf-Nonius MolEN	Enraf-Nonius MolEN	Enraf-Nonius MolEN
Structure solution	SHELX-86	SHELX-86	SHELX-86
Hydrogen atoms	not refined	not refined	not refined
Number of variables in final cycle	163	154	154
Largest shift/esd in final cycle	0.00	0.00	0.00
R(Fo)[b]	0.040	0.043	0.048
R_w(Fo)[c]	0.055	0.057	0.054
F(000)	608.0	1152.0	576.0
Goodness of fit	1.608	1.600	1.432

[a] see ref. 15.

[b] $R = \Sigma |Fo-Fc| / \Sigma Fo$.

[c] $R_w = (\Sigma w (Fo-Fc)^2 / \Sigma w Fo^2)^{1/2}$

TABLE II

Fractional atomic coordinates and equivalent isotropic thermal parameters of non-hydrogen atoms with e.s.d.'s in parentheses

Atom	*x/a*	*y/b*	*z/c*	B(Å^2)
2a:				
S	0.3890(1)	0.72892(6)	0.41092(3)	4.70(1)
P	0.20214(8)	0.85529(5)	0.43601(2)	3.166(9)
O10	0.1643(3)	0.8515(1)	0.50408(6)	4.02(3)
C2	-0.0623(3)	0.8625(2)	0.3980(1)	4.09(4)
C3	-0.0511(3)	0.9159(2)	0.3375(1)	4.08(4)
C4	0.0399(3)	1.0459(2)	0.33778(9)	3.58(4)
C5	0.2738(3)	1.0474(2)	0.36553(9)	3.97(4)
C6	0.2976(3)	1.0081(2)	0.42873(9)	3.84(4)
C11	0.1293(4)	0.7408(2)	0.53242(8)	3.65(4)
C12	-0.0718(4)	0.6874(2)	0.5271(1)	4.28(5)
C13	-0.1039(4)	0.5818(2)	0.5578(1)	5.33(6)
C14	0.0617(5)	0.5327(2)	0.5926(1)	6.01(7)
C15	0.2622(5)	0.5866(3)	0.5974(1)	6.46(7)
C16	0.2988(4)	0.6928(2)	0.5668(1)	5.03(5)
C41	0.0138(4)	1.1067(2)	0.2772(1)	4.17(4)
C42	0.1043(6)	1.2369(2)	0.2806(1)	6.63(8)
C43	0.1341(5)	1.0365(2)	0.2332(1)	5.77(6)
C44	-0.2263(5)	1.1139(3)	0.2556(1)	7.34(8)
3a:				
S	0.25476(3)	0.3578(1)	0.89187(4)	4.17(1)
P	0.23991(2)	0.0584(1)	0.88220(3)	2.75(1)
C(2)	0.25046(9)	-0.0519(4)	0.8055(1)	3.03(4)
C(3)	0.31170(8)	-0.0396(4)	0.8153(1)	3.13(5)
C(4)	0.34938(9)	-0.1676(4)	0.8793(1)	2.91(4)
C(5)	0.34698(9)	-0.0827(4)	0.9497(1)	3.46(5)
C(6)	0.28892(9)	-0.0916(4)	0.9535(1)	3.10(5)
C(11)	0.16998(9)	-0.0100(4)	0.8755(1)	3.33(5)
C(12)	0.1479(1)	-0.2044(5)	0.8517(2)	4.52(6)
C(13)	0.0932(1)	-0.2492(6)	0.8435(2)	5.67(8)
C(14)	0.0613(1)	-0.1038(6)	0.8601(2)	6.13(9)
C(15)	0.0834(1)	0.0850(6)	0.8848(2)	7.11(9)
C(16)	0.1380(1)	0.1346(5)	0.8932(2)	5.24(7)

TABLE II (*Continued*)

Atom	*x/a*	*y/b*	*z/c*	B(Å²)
C(41)	0.4096(1)	-0.1914(5)	0.8803(1)	4.01(6)
C(42)	0.4079(1)	-0.3013(7)	0.8118(2)	6.79(9)
C(43)	0.4438(1)	-0.3288(6)	0.9428(2)	6.38(9)
C(44)	0.4384(1)	0.0173(7)	0.8867(2)	6.7(1)
3b:				
S	0.0171(2)	0.47561(9)	0.13953(6)	6.64(3)
P	0.1506(1)	0.35105(7)	0.09601(4)	4.14(2)
C(2)	-0.0411(5)	0.2597(3)	0.0497(2)	4.19(7)
C(3)	0.0566(5)	0.1790(3)	0.0039(1)	4.00(7)
C(4)	0.1812(5)	0.2414(3)	-0.0437(1)	4.02(6)
C(5)	0.3752(5)	0.3020(3)	-0.0073(2)	5.05(8)
C(6)	0.3131(5)	0.3984(3)	0.0361(2)	5.38(8)
C(11)	0.3191(5)	0.2585(3)	0.1492(1)	4.25(7)
C(12)	0.2406(6)	0.1575(3)	0.1728(2)	5.41(8
C(13)	0.3696(8)	0.0898(4)	0.2153(2)	7.5(1)
C(14)	0.5767(7)	0.1228(4)	0.2343(2)	8.3(1)
C(15)	0.6570(6)	0.2218(5)	0.2117(2)	7.7(1)
C(16)	0.5307(5)	0.2912(4)	0.1696(2)	5.84(9)
C(41)	0.2349(6)	0.1645(3)	-0.0996(2)	4.86(8)
C(42)	0.3678(7)	0.0593(4)	-0.0760(2)	7.2(1)
C(43)	0.0282(8)	0.1247(4)	-0.1381(2)	8.1(1)
C(44)	0.3573(8)	0.2319(4)	-0.1447(2)	8.4(1)

Anisotropically refined atoms are given in the form of the isotropic equivalent temperature factor defined as:

$(4/3) * [a^2*\beta(1,1) + b^2*\beta(2,2) + c^2*\beta(3,3) + ab(\cos\gamma)*\beta(1,2) + ac(\cos\gamma)*\beta(1,3) + bc(\cos\alpha)*\beta(2,3)]$

of **3a** suitable for X-ray studies were obtained from hexanes; in the case of **3b** a mixture of pentane and methylene chloride was used instead.

Tables I and II list the crystal data and the final atomic fractional coordinates for non-hydrogen atoms, respectively.† Tables III through V contain, respectively, the selected bond lengths, bond angles, and torsional angles for all compounds studied. Corresponding structural data for compounds **4** and **5** taken from References 2 and 3 are included in these tables, together with the results of the calculations. Figures 1A–C are ORTEP diagrams showing the 50% probability ellipsoids for all non-hydrogen atoms. These diagrams also demonstrate the atom

†Full experimental details, as well as tables of thermal parameters are deposited as supplementary material with CCDC.

TABLE III

Selected bond lengths (experimental and calculated, [Å]) with e.s.d.'s in parentheses. Omitted values are either nonexistent or irrelevant.

Atoms		2a		4		3a		3b		5	
		Exptl.	Calc.	Exptl.[a]	Calc.	Exptl.	Calc.	Exptl.	Calc.	Exptl.[b]	Calc.
S	P	1.9282(8)	1.936	1.466(2)[c]	1.463[c]	1.9579(9)	1.947	1.957(1)	1.946	1.483(2)[c]	1.480[c]
P	O10	1.622(2)	1.744	1.618(2)	1.740	-	-	-	-	-	-
P	C2	1.788(3)	1.851	1.781(3)	1.822	1.803(2)	1.857	1.804(3)	1.864	1.791(2)	1.846
P	C6	1.794(2)	1.845	1.772(3)	1.831	1.801(2)	1.860	1.803(4)	1.859	1.795(2)	1.846
O10	C11	1.410(2)	1.364	1.380(3)	1.359	-	-	-	-	-	-
P	C11	-	-	-	-	1.815(2)	1.826	1.805(3)	1.824	1.805(2)	1.831
C2	C3	1.534(3)	1.509	1.540(4)	1.511	1.523(3)	1.508	1.528(4)	1.510	1.532(3)	1.510
C3	C4	1.537(3)	1.535	1.537(3)	1.535	1.535(3)	1.534	1.529(4)	1.533	1.539(3)	1.535
C4	C5	1.528(3)	1.534	1.540(4)	1.536	1.535(3)	1.534	1.533(5)	1.534	1.539(3)	1.535
C4	C41	1.557(3)	1.555	1.553(3)	1.555	1.557(3)	1.555	1.549(5)	1.553	1.559(3)	1.553
C5	C6	1.528(3)	1.510	1.536(4)	1.510	1.530(3)	1.508	1.529(5)	1.509	1.535(3)	1.510

a) Taken from reference 2.

b) Taken from reference 3.

c) P=O bond length.

TABLE IV

Selected bond angles [deg] with e.s.d.'s in parentheses. Omitted values are either nonexistent or irrelevant.

Atoms			2a		4		3a		3b		5	
			Exptl.	Calc.	Exptl.[a]	Calc.	Exptl.	Calc.	Exptl.	Calc.	Exptl.[b]	Calc.
S	P	C6	113.92(8)	118.7	115.7(1)[c]	119.1[c]	113.11(9)	117.3	114.4(1)	114.3	114.8[c]	115.4[c]
S	P	C2	115.17(9)	117.9	114.8(1)[c]	118.2[c]	112.65(9)	116.8	113.1(1)	114.7	115.0[c]	115.6[c]
S	P	C11	-	-	-	-	113.50(9)	115.5	113.8(1)	115.6	112.2	114.0
S	P	O10	114.71(2)	118.4	113.3(1)[c]	112.2[c]	-	-	-	-	-	-
C2	P	C6	101.8(1)	101.3	102.8(1)	102.7	100.6(1)	99.9	101.5(2)	102.1	99.8	102.2
O10	P	C6	101.10(9)	96.0	102.2(1)	102.7	-	-	-	-	-	-
O10	P	C2	106.4(1)	100.5	106.6(1)	99.0	-	-	-	-	-	-
C11	P	C6	-	-	-	-	108.6(1)	103.2	106.1(2)	105.2	107.6	104.0
C11	P	C2	-	-	-	-	107.5(1)	101.7	106.8(2)	103.4	106.3	104.0
P	O10	C11	121.3(1)	123.3	122.4(2)	123.4	-	-	-	-	-	-
P	C2	C3	111.1(1)	112.1	110.3(2)	110.1	110.2(2)	112.8	114.2(2)	114.5	111.3	112.1
C2	C3	C4	113.4(2)	113.5	112.7(2)	112.9	112.9(2)	113.4	113.6(3)	113.0	112.7	112.5
C3	C4	C5	110.0(2)	109.9	109.8(2)	110.1	110.6(2)	110.0	109.3(3)	109.3	109.8	109.5
C3	C4	C41	112.7(2)	110.7	113.2(2)	111.7	112.7(2)	110.7	113.7(3)	112.2	113.4	112.2
C5	C4	C41	113.5(2)	111.6	113.2(2)	110.7	113.7(2)	111.6	114.4(3)	112.2	113.7	112.2
C4	C5	C6	114.4(2)	112.9	114.0(2)	113.5	113.8(2)	112.9	113.1(3)	112.4	112.5	112.5
P	C6	C5	110.5(1)	110.2	109.7(2)	112.2	110.9(2)	111.2	113.8(2)	113.9	110.3	112.1
O10	C11	C16	117.9(2)	119.1	117.9(3)	119.4	-	-	-	-	-	-
O10	C11	C12	120.2(2)	120.1	121.8(3)	120.2	-	-	-	-	-	-
P	C11	C12	-	-	-	-	121.2(2)	120.9	121.3(3)	119.5	118.6	118.7
P	C11	C16	-	-	-	-	119.6(2)	119.6	119.6(3)	121.2	122.9	122.4

a) Taken from reference 2.

b) Taken from reference 3. E.s.d.'s not reported.

c) Corresponding bond angle in the P=O analogue.

numbering schemes. Figure 2 presents stereo views of the crystal packing diagrams. Figure 3 illustrates the ring conformation showing values of endocyclic torsional angles for all molecules studied. Figure 4 shows the statistically significant (*i.e.* $> 2\sigma$) differences of bond lengths and angles between **2a** and **4**, **3a** and **5**, and **3a** and **3b**.

In every case examined the heterocyclic ring assumes a chair conformation, with flattening at the phosphorus end relative to cyclohexane. As expected, the *tert*-butyl group remains in an equatorial position.

Endocyclic P—C bond lengths (average value 1.791(3) Å for **2a** and 1.803(3) for both **3a** and **3b**) compare well with those found for other cyclic and acyclic thiophosphinic acid derivatives (1.792 Å, an average based on literature data). When steric repulsion is present these bonds are elongated (1.848(1) Å and 1.827(1) Å for the P—CMe_3 distances in **6**).[5] Likewise, the values are similar to the average length reported by Quin for a series of 4-hydroxyphosphorinane 1-sulfides **7** (1.813(17)

TABLE V

Selected torsional angles [deg] with e.s.d.'s in parentheses. Omitted values are either nonexistent or irrelevant.

Atoms				Torsional angle		
				2a	3a	3b
S	P	C6	C5	74.06(17)	-67.30(17)	-167.16(21)
S	P	C2	C3	-74.12(16)	65.95(18)	167.13(19)
S	P	O10	C11	-41.84(17)	-	-
S	P	C11	C12	-	164.60(19)	94.28(28)
O10	P	C6	C5	-161.26(14)	-	-
C11	P	C6	C5	-	165.75(16)	66.55(28)
O10	P	C2	C3	157.59(14)	-	-
C11	P	C2	C3	-	-168.31(17)	-66.90(25)
C2	P	O10	C11	86.72(17)	-	-
C2	P	C11	C12	-	39.36(24)	-31.32(31)
C6	P	O10	C11	-167.32(16)	-	-
C6	P	C11	C12	-	-68.68(23)	-139.05(28)

Å).[6] The P—S distances (1.9282(8) Å in **2a** and 1.9575(10) Å in **3**) are somewhat shorter than the mean value 1.964(4) in **7**, although still in good agreement. This shortening can be attributed to the difference in the nature of ligands around phosphorus (P—OPh in **2a** and P—Ph in **3** versus P—Me in **7**). The P—S distance in **6** (mean value of 1.933(2) Å) is close to those found in this investigation. The C—P—C angle value (Table IV) is in the range 101.3–104.0 Å reported by Quin and corresponds favorably to literature values. The hydrocarbon portion of the rings has typical bond lengths and angles.

The experimentally determined molecular structures of **2a** and **3a** are very similar to those of their oxygen analogues **4** and **5**. The minor differences in the molecular geometry at the phosphorus site are presented in Figure 4. The flattening of the ring is most pronounced in **3b**; the average torsional angle around endocyclic P—C bonds is about 9° smaller than the corresponding value found for **3a**. This flattening is probably due to the axial arrangement of the phenyl group at phosphorus. The molecular structure of *cis*-4-*tert*-butyl-1-methoxyphosphorinane 1-oxide[7] with an axial methoxy group displays an even flatter ring (corresponding averaged torsional angle equals 41.3(7)° *vs.* 44.49(27)° in **3b**). The magnitudes of endocyclic torsional angles of **2a** and **3a** (Figure 3) are consistently smaller than those of **4** and **5**, respectively. The more important differences are found at the phosphorus atom, indicating a less puckered ring. As shown in Figures 3 and 4, the exchange of oxygen versus sulfur has little or no significant impact on the surrounding tor-

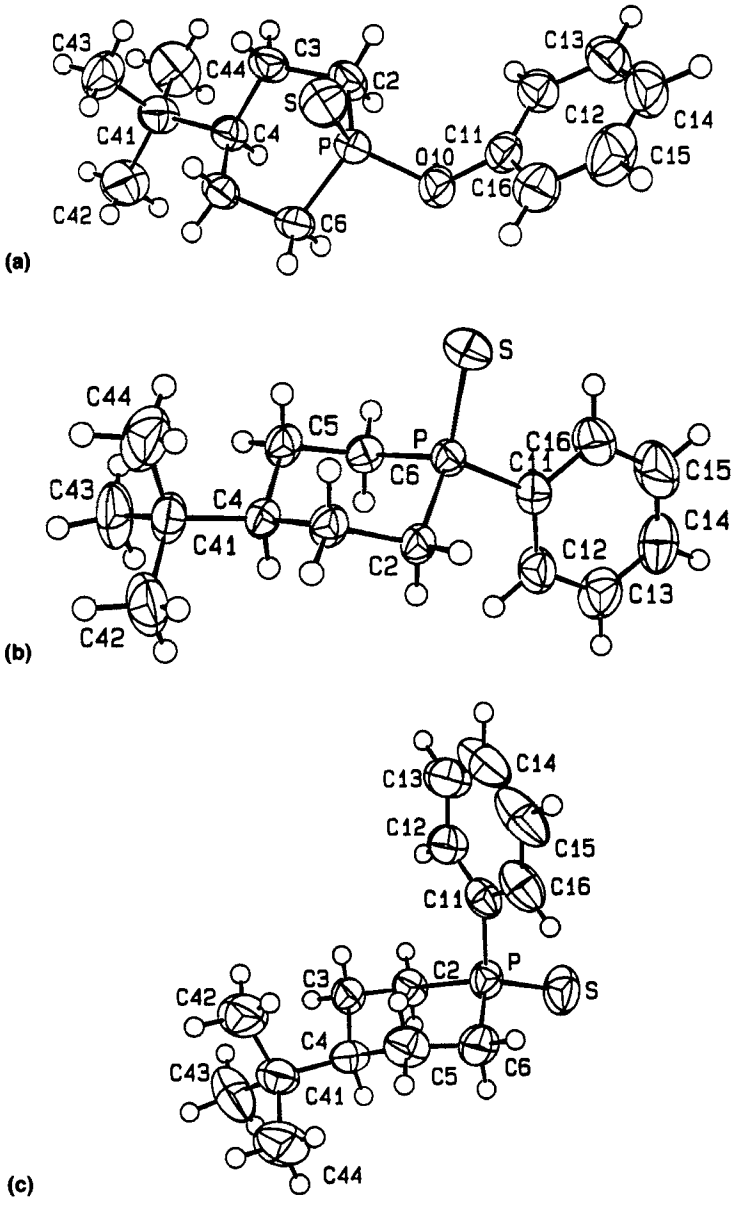


FIGURE 1 An ORTEP view of the molecule with atom labeling: a) **2a**; b) **3a**; c) **3b**.

sional angles, bond angles or bond lengths. No important difference in the geometric parameters of the phosphorus site is noted on changing from an axial to an equatorial orientation of sulfur—only the ring puckering seems to be significantly influenced.

Semiempirical calculations for all molecules were performed using the PM3 method with standard parameters. Crystallographic structures were used as starting points in the optimization process. Optimization was continued until the heat of formation

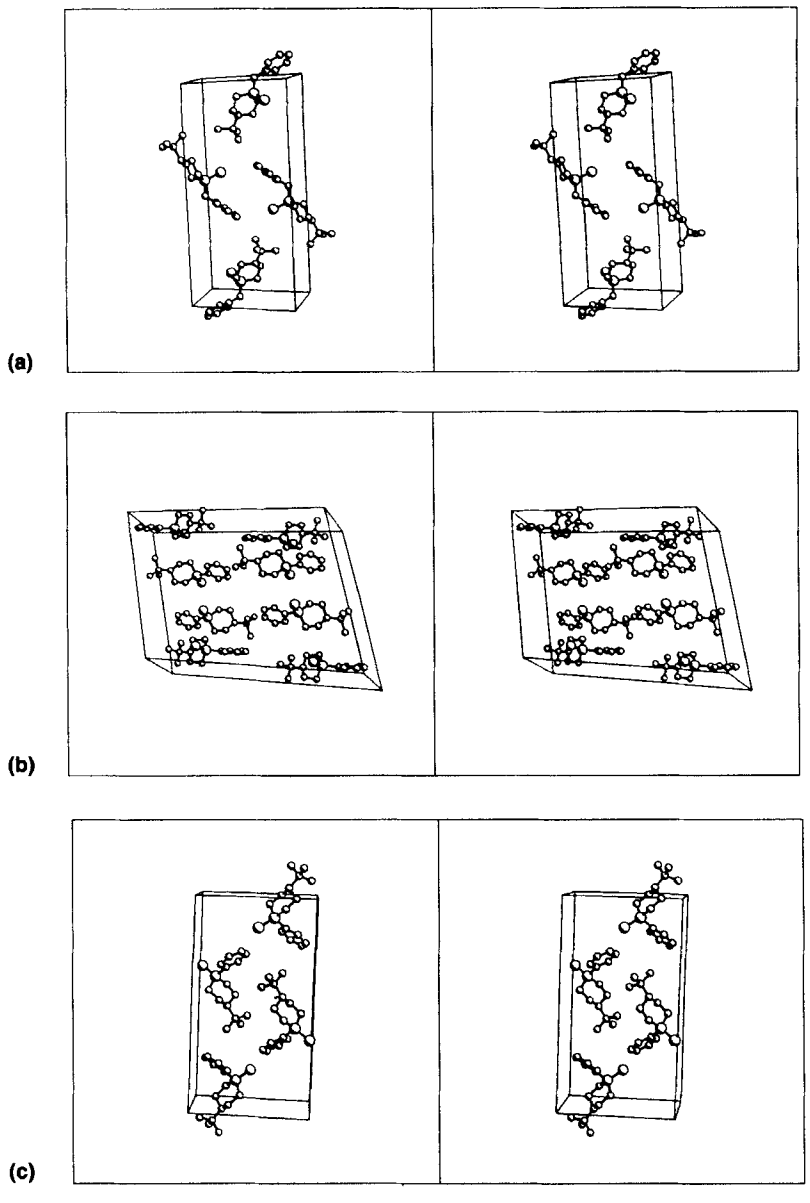


FIGURE 2 Stereoscopic illustration of the crystal packing. Hydrogen atoms are omitted for clarity. The *c* axis of the unit cell is oriented vertically; horizontal axes are : *b* for **2a** and **3b** and *a* for **3a**. a) **2a**; b) **3a**; c) **3b**.

gradient was lower than 0.02 kcal mol^{-1} $Å^{-1}$. The calculations reproduced qualitatively the trends in structural parameters found experimentally; however, the magnitude of these changes or the absolute values of the calculated parameters did not always duplicate the experimental results. Calculated single bond lengths, both P—C and P—O, are much bigger than those from X-ray data; the lengths of P=O and P=S bonds are in good agreement with the measured values. Surprisingly, the

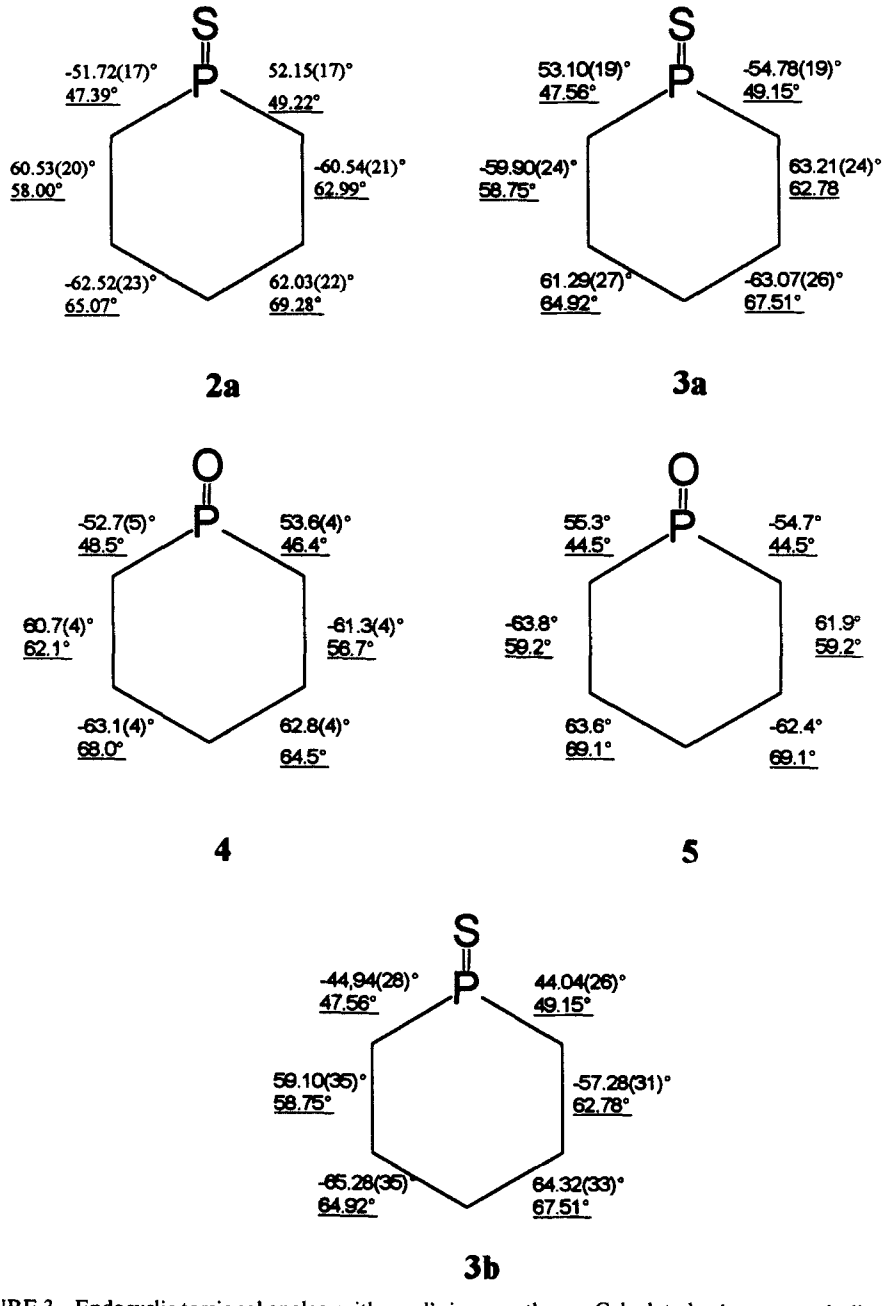


FIGURE 3 Endocyclic torsional angles, with e.s.d's in parentheses. Calculated values are underlined.

two equivalent C2-C3 and C5-C6 distances are systematically calculated to be 0.015 Å shorter than the other endocyclic C—C bonds. No particular shortening of these bonds was found experimentally. For both oxygen and sulfur derivatives the calculated endocyclic C—P—C bond angles are in good agreement with the experimental values. Other bond angles around phosphorus are calculated to be within

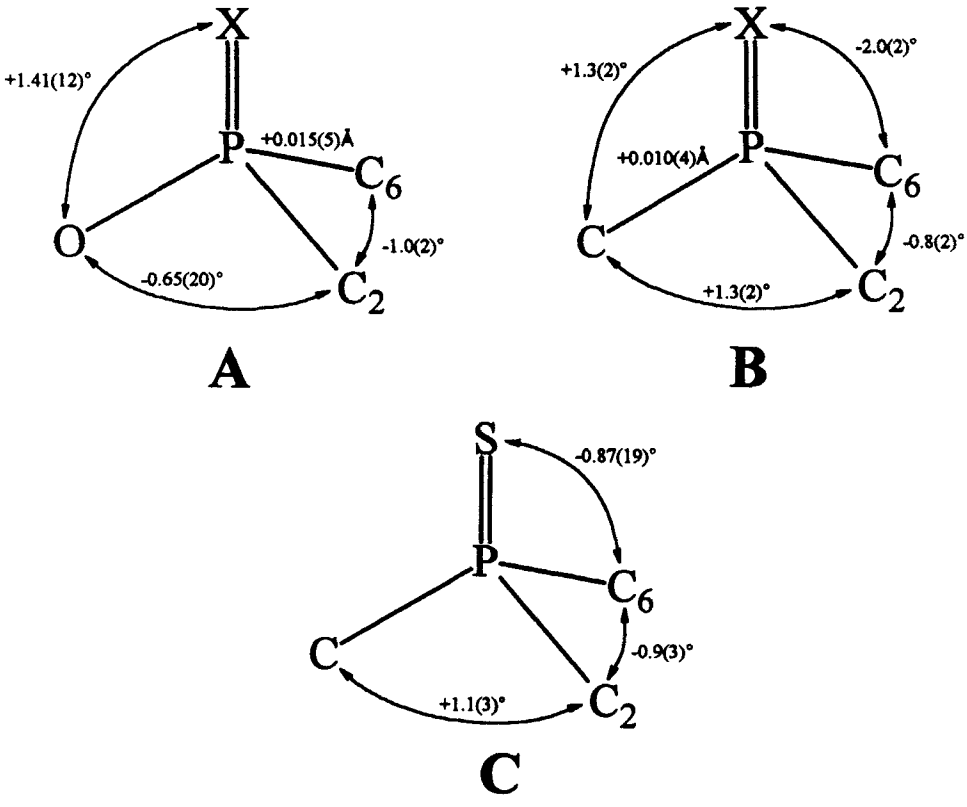


FIGURE 4 Differences in geometric parameters at the phosphorus site. Non-significant values (*i.e.* $|\Delta| < 2\sigma$) are omitted. For symmetrically equivalent P—C bond lengths, C—P—O and X=P—C angles only one difference is indicated; averaged values of bond lengths and angles were used to calculate the differences in these cases. X denotes either oxygen or sulfur. A) Δ = **2a–4**; B) Δ = **3a–5**; C) Δ = **3a–3b**.

the $\pm 5°$ range of the experimental values. As confirmed by the data in Figure 3, the heterocyclic rings are predicted to be flatter at the phosphorus end and more puckered at the other than found by X-ray diffraction.

Even though the crystal structures for **2a** and **4** are different and no significant intermolecular contacts were found in either, the orientation of the phenoxy group with respect to the rest of the molecule is the same in both compounds. A similar orientation has been found in crystals of cyclic phosphates[8] and phosphonates.[9] For both **2a** and **4** the P—O bond is almost perpendicular to the plane of the aromatic ring. This orientation is also suggested by the calculations.[10]

Good structural agreement between phosphorinane sulfides and oxides found in the solid state extends to the solution phase, as confirmed by ^{13}C NMR measurements (Table VI). The greatest differences in chemical shifts and coupling constants are observed for the C-2,6 carbon atoms. The NMR signal of these carbons is shifted about 6.9 ppm downfield in **2a** compared to **4**; simultaneously, the coupling constant is about 25% smaller. Similar changes are observed if **3a** is compared to **5**, the downfield shift of the C-2,6 carbon being somewhat smaller (3.2 ppm). Also,

TABLE VI

^{13}C NMR chemical shifts [ppm] and carbon-phosphorus coupling constants [Hz] (in parentheses)

	C-2,6	C-3,5	C-4	C-41	C-42[a]	C-11	C-12,16	C-13,15	C-14
2a	34.2	24.2	48.7	32.8	27.7	150.6	121.7	129.4	124.9
	(65)	(4)	(4)	(0)	(0)	(10)	(4)	(1)	(2)
2b	34.6	24.5	47.6	32.8	27.6	150.7	121.4	129.5	124.9
	(65)	(8)	(5)	(0)	(0)	(9)	(5)	(1)	(1)
4	27.3	24.0	48.6	32.8	27.6	150.4	120.3	129.4	124.0
	(86)	(4)	(5)	(1)	(0)	(9)	(4)	(0)	(1)
3a	31.9	22.3	49.0	33.0	27.6	132.8	130.5	128.6	131.6
	(52)	(5)	(4)	(1)	(0)	(77)	(10)	(12)	(3)
3b	32.5	24.9	47.3	32.7	27.4	132.2	129.4	129.1	131.2
	(51)	(7)	(4)	(1)	(0)	(77)	(9)	(11)	(3)
5	28.7	22.5	49.1	33.0	27.5	133.3	129.8	127.3	131.4
	(66)	(6)	(3)	(1)	(0)	(95)	(9)	(11)	(0)

a) All methyl groups in the *tert*-butyl group are equivalent.

the decrease in the coupling constant is smaller in that case. A β-deshielding effect of similar magnitude is observed when thiocarbonyl compounds are compared to their oxygen analogues; the difference in chemical shifts at the α-carbons is about 10 ppm.[11] Other differences in ^{13}C chemical shifts of the ring carbons for both pairs of analogues are not bigger than 0.2 ppm, and the coupling constants are nearly the same.

EXPERIMENTAL

All NMR spectra were recorded on a GE 300NB OMEGA spectrometer. $CDCl_3$ (7.26 ppm) was used as the internal standard for proton NMR spectroscopy. Internal $CDCl_3$ (77.00 ppm) was used as the standard for ^{13}C NMR spectra. Chemical shifts for ^{31}P are reported in ppm downfield from external 85% H_3PO_4. Elemental analyses were performed by Midwest Microlab, Ltd., Indianapolis, Indiana. Melting points (Thomas-Hoover apparatus) are uncorrected. Thin layer chromatography was conducted using Eastman chromatography plates, No. 13179 silica gel, without a fluorescence indicator, and were developed with iodine. 4-*tert*-Butyl-1-chlorophosphorinane 1-sulfide was synthesized according to the literature.[4]

Crystallographic calculations were performed on a VAX computer. Semiempirical molecular structure calculations at the PM3[12] level were made using a HyperChem[13] package installed on a Gateway 2000 4DX2-66V microcomputer.

Trans/cis-4-tert-butyl-1-phenoxyphosphorinane 1-sulfide (**2a/2b**). A slurry of sodium phenoxide in acetonitrile was prepared from 940 mg (10 mmol) of phenol in 50 mL of CH_3CN and was added dropwise to a stirred solution of 2.25 g (10 mmol) of 4-*tert*-butyl-1-chlorophosphorinane 1-sulfide in 10 mL of CH_3CN. The mixture was maintained at room temperature with a cold water bath. Stirring was continued for 2 hrs. The mixture was then poured into 30 mL of water and extracted with diethyl ether. The ether phase was washed with 5% NaOH and water, dried with $MgSO_4$ and evaporated. The solid residue (2.10 g, 71%) was recrystallized from hexanes. The mixture was separated by column chromatography on silica gel using a 2:1 (v/v) $CCl_4/CHCl_3$ mixture as an eluent (R_f = 0.35 for **2a** (m.p. 124–126°) and 0.17 for **2b** (m.p. 71–73°)). Anal. Calcd for $C_{15}H_{23}OPS$: C, 63.80; H, 8.21%. Found: C, 63.77; H, 8.09%.

Trans/cis-4-tert-butyl-1-phenylphosphorinane 1-sulfide (**3a/3b**). 4-*tert*-Butyl-1-chlorophosphorinane 1-sulfide (2.28 g, 10 mmol) was dissolved in 20 mL of dry THF and the solution was cooled to −78°C in a Dry Ice-acetone bath. A solution of phenyllithium (1.8 M in cyclohexane-ether, 6.5 mL, 11.7 mmol) was added dropwise at this temperature over a period of 20 min. The mixture was maintained for 5 hrs at −78° and then it was allowed to warm-up slowly overnight, with stirring. The mixture was poured slowly into 50 mL of ice water and extracted with CH_2Cl_2; the combined organic layer was dried with anhydrous Na_2SO_4 and evaporated, giving 2.64 g (99%) of a crude mixture of isomers. The mixture was separated by column chromatography on silica gel using a 2:1 (v/v) $CCl_4/CHCl_3$ mixture as an eluent (R_f = 0.40 for **3a** (m.p. 146–150°) and 0.13 for **3b** (m.p. 165–166°)). Anal. Calcd for $C_{15}H_{23}PS$: C, 67.63; H, 8.70%. Found: C, 67.54; H, 8.90.

X-Ray Analysis

Single crystals of **3a** useful for X-ray studies were prepared by dissolving the compound in hexanes followed by slow evaporation of the solvent. Likewise, evaporation of a clear solution obtained by careful addition of CH_2Cl_2 to a dispersion of **2a** and **3b** in pentane yielded single crystals used for structure determination.

The details of crystallographic data collection and structure solving are shown in Table I.

The crystals were mounted on a glass fiber (**2a**, **3a**) or in a glass capillary (**3b**) in random orientation. The preliminary examination and diffraction data collection were performed on an Enraf-Nonius CAD4 computer controlled kappa axis diffractometer with a graphite monochromator. The data were collected at (20 ± 1)°C using the ω-2θ scan technique, with the variable scan rate. The ω scan range (in deg.) was determined as a function of θ to correct for the separation of the Kα doublet.[14] Lorentz and polarization corrections were applied to the data. For **3a**, an empirical absorption correction based on the method of Walker and Stuart[15] was applied, using relative transmission coefficients from 0.581 to 1.000 with an average value of 0.728. The structures were solved using the solution program SHELX-86.[16] The remaining atoms were located in succeeding difference Fourier syntheses. Hydrogen atoms were located and added to the structure factor calculations, but their positions were not refined.

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