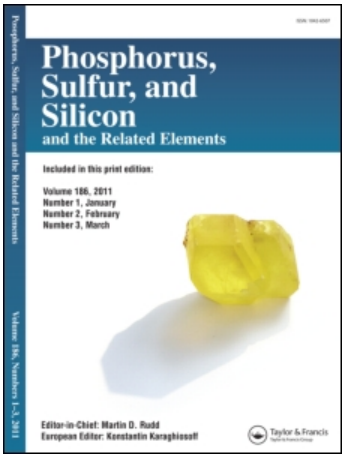

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CRYSTAL AND MOLECULAR STRUCTURE OF 4-*tert*-BUTYLPHOSPHORINANE 1-SULFIDE DERIVATIVES. PART II. *Cis/trans*-4-*tert*-BUTYL-1-CHLOROPHOSPHORINANE 1-SULFIDE

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CRYSTAL AND MOLECULAR STRUCTURE OF 4-*tert*-BUTYLPHOSPHORINANE 1-SULFIDE DERIVATIVES. PART II.† *Cis/trans*-4-*tert*-BUTYL-1-CHLOROPHOSPHORINANE 1-SULFIDE

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Cis- and *trans*-4-*tert*-butyl-1-chlorophosphorinane 1-sulfides were prepared and investigated by single crystal X-ray diffraction. *Cis*-4-*tert*-butyl-1-chlorophosphorinane 1-sulfide (**2a**): space group Pbam (No. 55) with a = 21.152(7) Å, b = 11.428(1) Å, c = 9.884(3) Å, V = 2389(2) Å^3, and D_{calc} = 1.250 g cm^{-3} for Z = 8 (two independent molecules per asymmetric unit), R = 0.057; for *trans* isomer (**2b**): space group Pbca (No. 61) with a = 11.750(1) Å, b = 10.550(2) Å, c = 20.032(3) Å, V = 2483.3(9) Å^3, and D_{calc} = 1.202 g cm^{-3} for Z = 8, R = 0.058. In both structures 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 chlorine atom defines the *cis/trans* designation. The equilibration of the title compounds under acidic conditions was studied by ^{31}P NMR spectroscopy and discussed in the context of the results of semiempirical calculations.

Key words: Phosphorinane sulfide, thiophosphinic chloride, crystal structure, molecular calculations, PM3, X-ray diffraction.

INTRODUCTION

The molecular structure of six-membered phosphorus containing heterocycles has been widely investigated; however, most 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 both *cis*- and *trans*-4-*tert*-butyl-1-chlorophosphorinane 1-sulfides (**2a** and **2b**, respectively). The 4-*tert*-butyl group was expected to anchor the ring as a single conformation in solution. Therefore, it was also possible to consider these compounds as convenient probes of the axial vs. equatorial preference of the P=S bond. X-ray studies were initially done to ascertain the stereochemical assignment around

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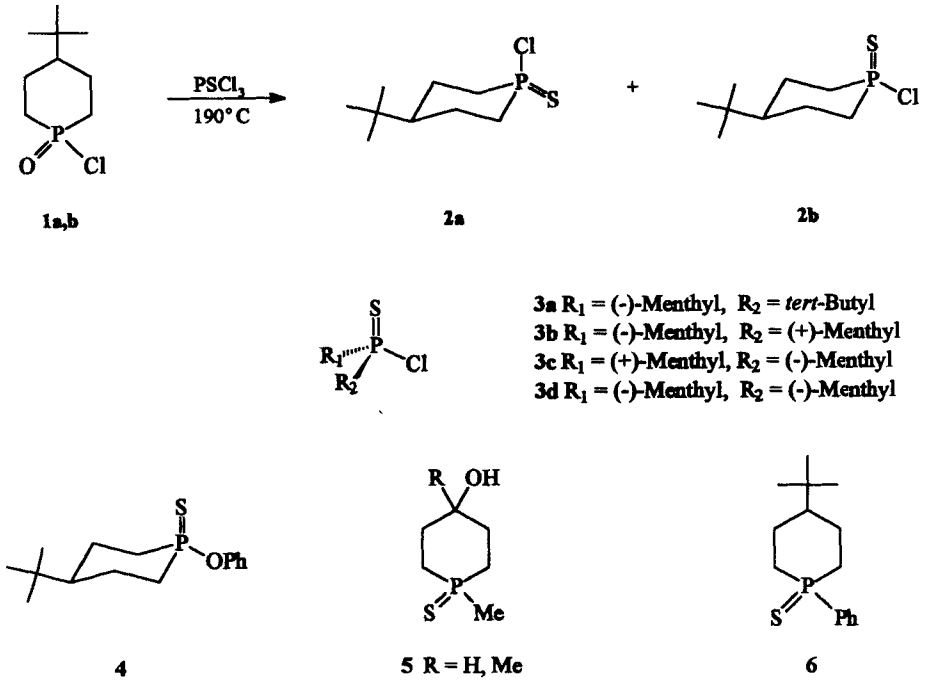
the phosphorus atom. In this paper we wish to report the structural study of both **2a** and **2b** based on X-ray data, molecular calculations, and NMR spectroscopy. According to the authors' knowledge, data presented here are the first X-ray structures of cyclic thiophosphinic chlorides. These data were compared to the known structures of phosphorinane sulfides[2,3] and a few X-ray structures of thiophosphinic chlorides that have been reported previously.[4] We were interested in the effect that a change from an axial to equatorial orientation of the P=S bond would have on the structural environment of the phosphorus atom. Semiempirical calculations at the PM3 level were used to clarify the latter task.

RESULTS AND DISCUSSION

Reaction of 4-*tert*-butyl-1-chlorophosphorinane 1-oxide (**1a,b**)[5] (mixture of isomers) with $PSCl_3$ at 190°C (Scheme I) gave a mixture of *cis/trans*-4-*tert*-butyl-1-chlorophosphorinane 1-sulfide (**2a/2b**). The latter was separated by column chromatography on silica gel, using CCl_4 as an eluent; $R_f \approx 0.15$ for **2a** and 0.21 for **2b**. The crystals used for X-ray studies were obtained by slow evaporation of the solvent from a hexane solution of **2a** and **2b**.

Tables I and II list the crystal data and the final positional parameters for nonhydrogen atoms, respectively. Tables III through V contain, respectively, the selected bond lengths, bond angles, and torsional angles for all compounds studied.



SCHEME I

TABLE I
Crystal data

	2a	2b
Molecular formula	$C_9H_{18}ClPS$	$C_9H_{18}ClPS$
Color	colorless	colorless
Formula weight	224.73	224.73
Space group	Pbam (No. 55)	Pbca (No. 61)
Temperature	293. K	293. K
a, Å	21.152(7)	11.750(1)
b, Å	11.428(1)	10.550(2)
c, Å	9.884(3)	20.032(2)
V, Å^3	2389(2)	2483.3(9)
Z	8	8
D_{calc}, g cm^{-3}	1.250	1.202
Linear absorption coef., μ, cm^{-1}	5.73	5.51
Diffractometer	Enraf-Nonius CAD4	Enraf-Nonius CAD4
Radiation (wavelength)	Mo Kα (0.71073 Å)	Mo Kα (0.71073 Å)
Monochromator	graphite	graphite
Crystal dimensions, mm	0.69 x 0.50 x 0.25	0.65 x 0.40 x 0.24
Scan method	ω - 2θ	ω - 2θ
Scan width, deg	0.62 + 0.69tan(θ)	0.41 + 0.90tan(θ)
Data collected	3197	2796
Unique data	3197	2796
2θ range, deg	5.22 - 55.64	5.16 - 52.10
Range of h, k, l	0 to 27, 0 to 14, -12 to 0	0 to 14, -13 to 0 0 to 24
Data with I > 3.0 σ(I)	1524	914
Corrections applied	Lorentzian, polarization	Lorentzian, polarization
Absorption correction	none	empirical[a]
Transmission factors: min, max	-	0.33, 1.00
Computer programs	Enraf-Nonius MolEN	Enraf-Nonius MolEN
Structure solution	SHELX-86	SHELX-86
Hydrogen atoms	not refined	not refined
Number of variables in final cycle	127	109
Largest shift/esd in final cycle	0.03	0.00
R(Fo)[b]	0.057	0.058
R_w(Fo)[c]	0.067	0.068
F(000)	960.0	960.0
Goodness of fit	1.887	1.735

[a] see ref. 13.

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

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

TABLE II

Fractional atomic coordinates and equivalent isotropic thermal parameters of non-hydrogen atoms with e.s.d.'s in parentheses. See Figures 1 or 2 for the numbering scheme

Atom	*x/a*	*y/b*	*z/c*	B(Å²)
2a:				
Cl(1)	0.19900(9)	0.9093(2)	0.	5.49(5)
Cl(2)	0.02119(9)	0.8515(2)	1/2	7.38(6)
S(1)	0.32596(8)	1.0791(2)	0.	4.56(4)
S(2)	0.14382(9)	1.0304(2)	1/2	4.64(4)
P(1)	0.23456(8)	1.0763(1)	0.	3.15(3)
P(2)	0.11672(8)	0.8692(2)	1/2	3.49(3)
C(12)	0.1960(2)	1.1414(4)	0.1429(4)	3.62(9)
C(13)	0.1244(2)	1.1532(4)	0.1267(4)	3.55(9)
C(14)	0.1046(3)	1.2213(5)	0.	3.0(1)
C(22)	0.1399(2)	0.7818(4)	0.3580(4)	4.3(1)
C(23)	0.1243(2)	0.6512(4)	0.3732(4)	3.8(1)
C(24)	0.1524(3)	0.5963(5)	1/2	3.0(1)
C(141)	0.0346(3)	1.2623(5)	0.	3.4(1)
C(142)	-0.0118(3)	1.1581(7)	0.	6.1(2)
C(143)	0.0212(2)	1.3375(4)	0.1248(5)	5.1(1)
C(241)	0.1481(3)	0.4586(5)	1/2	3.0(1)
C(242)	0.0794(3)	0.4172(6)	1/2	4.7(2)
C(243)	0.1811(2)	0.4095(4)	0.3756(5)	4.7(1)
2b:				
Cl	0.6614(2)	0.1517(3)	0.1816(1)	10.16(8)
S	0.8222(2)	0.1876(2)	0.3155(1)	5.63(5)
P	0.6691(2)	0.1838(2)	0.2816(1)	4.50(4)
C(2)	0.5863(6)	0.3255(7)	0.2933(4)	4.9(2)
C(3)	0.5539(6)	0.3382(6)	0.3666(4)	4.3(2)
C(4)	0.4792(5)	0.2282(6)	0.3917(3)	3.2(1)
C(5)	0.5438(6)	0.1029(6)	0.3868(3)	3.9(2)
C(6)	0.5775(6)	0.0672(7)	0.3162(4)	5.0(2)
C(41)	0.4270(5)	0.2539(7)	0.4616(3)	4.0(1)
C(42)	0.3480(6)	0.1441(8)	0.4807(4)	5.5(2)
C(43)	0.5188(6)	0.2651(9)	0.5160(4)	6.6(2)
C(44)	0.3520(7)	0.3738(8)	0.4609(5)	7.3(2)

Anisotropically refined atoms are given in the form of the isotropic equivalent temperature factor defined as: (4/3) * [a^2*β(1,1) + b^2*β(2,2) + c^2*β(3,3) + ab(cosγ)*β(1,2) + ac(cosβ)*β(1,3) + bc(cosα)*β(2,3)]

TABLE III

Selected bond lengths (experimental and calculated, [Å]) with e.s.d.'s in parentheses. The atom numbering scheme is presented in Figure 4

Atoms	2a			2b	
	Experimental		PM3	Experimental	PM3
	#1	#2			
P S	1.934(2)	1.929(3)	1.917	1.923(3)	1.914
P Cl	2.052(3)	2.031(3)	2.090	2.035(3)	2.093
P C2	1.792(4)	1.792(5)	1.838	1.799(8)	1.837
P C6		a	1.838	1.775(8)	1.837
C2 C3	1.529(6)	1.536(6)	1.511	1.52(1)	1.511
C3 C4	1.532(5)	1.522(5)	1.534	1.540(9)	1.534
C4 C5		a	1.534	1.527(9)	1.534
C4 C41	1.553(9)	1.576(8)	1.553	1.553(9)	1.553
C5 C6		a	1.511	1.517(9)	1.511

a) Both molecules have crystallographical mirror plane.

TABLE IV

Selected bond angles [deg] with e.s.d.'s in parentheses. The atom numbering scheme is presented in Figure 4

Atoms	2a			2b	
	Experimental		PM3	Experimental	PM3
	#1	#2			
S P Cl	112.4(1)	113.0(1)	115.0	113.1(1)	115.0
S P C2	116.6(2)	116.8(2)	118.6	116.3(3)	119.7
S P C6		a	118.6	116.4(3)	119.7
Cl P C2	102.7(2)	102.5(2)	99.3	104.0(3)	97.8
Cl P C6		a	99.3	104.0(3)	97.8
C2 P C6	104.0(4)	103.2(4)	102.8	101.3(3)	102.6
P C2 C3	113.9(3)	114.0(3)	112.7	109.5(5)	111.3
C2 C3 C4	113.6(4)	113.4(4)	112.6	113.0(6)	112.6
C3 C4 C5	109.6(4)	110.8(4)	109.2	110.3(5)	109.5
C3 C4 C41	114.4(3)	112.9(3)	112.1	112.8(6)	112.1
C5 C4 C41		a	112.1	113.9(6)	112.1
C4 C5 C6		a	112.6	113.9(6)	112.6
P C6 C5		a	112.7	110.5(5)	111.3

a) Both molecules have crystallographical mirror plane.

TABLE V

Selected torsional angles [deg] with e.s.d.'s in parentheses. See Figure 4 for the atom numbering scheme

Atoms	2a			2b	
	Experimental		PM3	Experimental	PM3
	#1	#2			
S P C2 C3	171.10(25)	172.42(27)	175.4	-72.33(49)	-89.1
S P C6 C5		a	-175.4	72.99(51)	89.1
Cl P C2 C3	-65.51(31)	-63.48(34)	-59.4	162.59(41)	146.1
Cl P C6 C5		a	59.4	-161.88(43)	-146.1
C6 P C2 C3	41.18(36)	42.80(39)	42.4	54.86(53)	46.3
P C2 C3 C4	-55.80(44)	-55.84(47)	-58.1	-62.16(62)	-59.9
C2 C3 C4 C5	65.09(50)	63.83(52)	69.2	62.54(70)	68.7
C3 C4 C5 C6		a	-69.2	-61.65(72)	-68.7
C4 C5 C6 P		a	58.1	61.04(65)	59.9
C5 C6 P C2		a	-42.4	-54.17(54)	-46.3

a) Both molecules have crystallographical mirror plane.

The results of the corresponding calculations are included in these tables. Figures 1 and 2 are ORTEP diagrams showing the 50% probability ellipsoids for all non-hydrogen atoms in compounds **2a** and **2b**, respectively. These diagrams present the atom numbering scheme used in Tables I and II. Figure 3 presents stereo views of the crystal packing diagrams. Figure 4 demonstrates the atom numbering scheme used in Tables III–V.

Two independent molecules of the *cis* isomer **2a** were found in the asymmetric unit of the crystallographic cell (Figure 1a,b). Both these molecules feature crystallographically imposed planes of symmetry and assume a chair conformation. As expected, the *tert*-butyl group remains in an equatorial position. As seen from Tables III–V, the corresponding geometrical parameters of both molecules are very similar.

Within experimental error, molecules of the *trans* isomer **2b** also adopt a chair conformation with an equatorial *tert*-butyl group, even though there is no crystallographic mirror plane passing through the molecules (see Figure 3). In both isomers the phosphorus center is flatter than the hydrocarbon end of the ring. When compared to cyclohexane, the relative flattening of the phosphorus site is noticeable in only the *cis* isomer.

The P—Cl bond lengths were found in the range 2.053(3)–2.031(3) Å. These limits correspond to the values found in the independent molecules of **2a**. The value 2.035(3) Å found for the *trans* isomer **2b** is not significantly different from the range above. The bonds are therefore slightly shorter than the one reported for **3a** (2.071(1) Å).[4a] The P—Cl distance is 2.033(3) Å in **3b** and 1.985(3) Å in

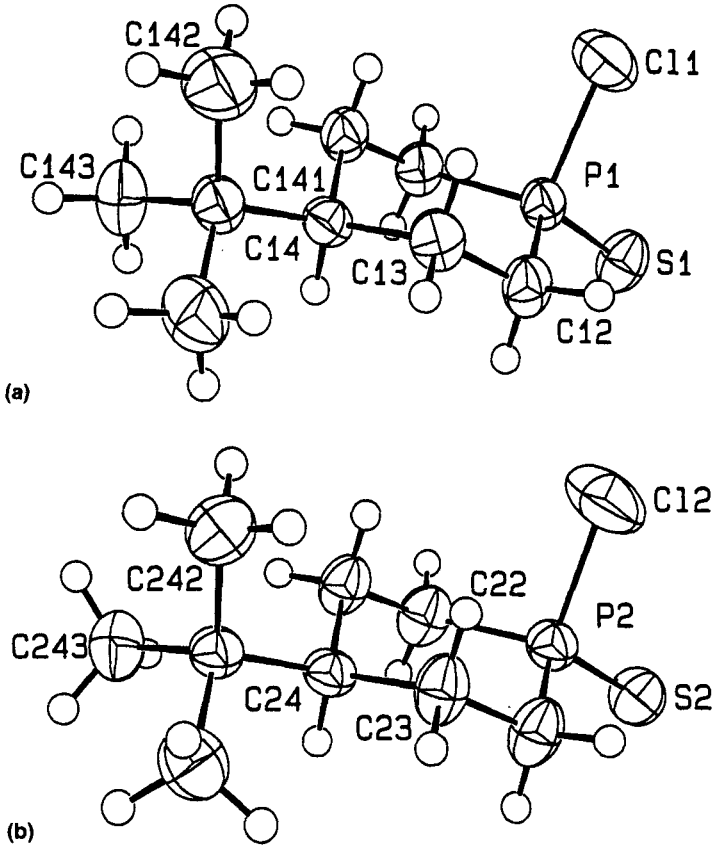


FIGURE 1 An ORTEP view of **2a**—two independent molecules. (a) molecule #1; (b) molecule #2.

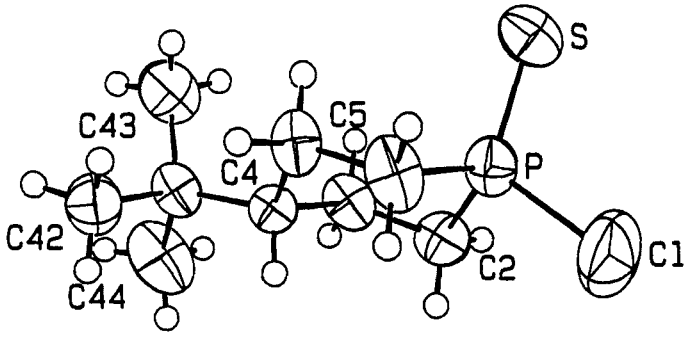


FIGURE 2 An ORTEP view of **2b**.

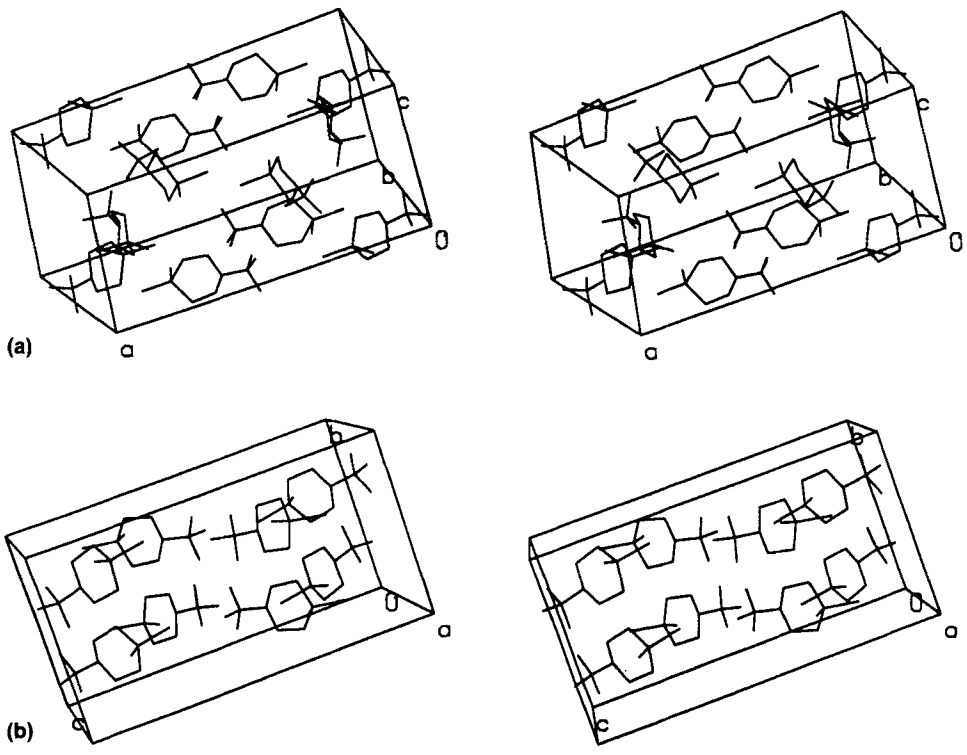
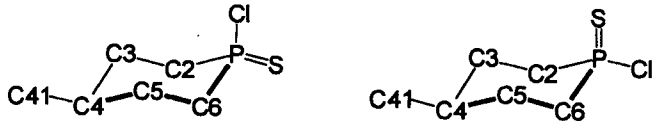


FIGURE 3 Stereoscopic illustration of the crystal packing.[9] (a) **2a**; (b) **2b**.



2a **2b**

FIGURE 4 Illustration of the atom numbering scheme used in Tables III–V.

3c[6]; both molecules were found in one unit cell.[4d] The large difference between these values may indicate that this bond distance is rather sensitive to crystal packing forces. The same conclusion is suggested by the relatively large standard deviation of an average P—Cl bond length reported in a review by Allen *et al.*[7]: 2.008(35) Å. The review is based upon data from the Cambridge Structural Database. Until additional examples of P(=S)Cl bond lengths are available,[8] the diversity of the P—Cl distance observed here may not be unusual.

Endocyclic P—C bond lengths (average value 1.792(5) Å for **2a** and 1.787(8) Å for **2b**) compare well with those found for other cyclic thiophosphinic acid derivatives (1.792 Å, an average based on literature data). The P—C bonds in **3a** and **3b** are longer (1.857(2) Å and 1.866(3) Å in **3a**, 1.858(7) Å, and 1.855(4) Å in **3b**,

1.860(6) Å and 1.846(6) Å in **3c**), due to the non-cyclic structure and an increased steric congestion around the phosphorus atom.

The P—S distances (1.932(5) Å in **2a** and 1.923(3) Å in **2b**) correlate favorably with the values found in similar compounds (1.928(1) Å in *tert*-butyl-(−)-menthylchlorophosphine sulfide (**3a**),[4a] 1.9282(8) in **4**[2]). The length of this bond seems particularly sensitive to the nature of substituents on phosphorus. According to Allen[7] the average length of the P=S bond increases with the number of carbon atoms attached to phosphorus. Therefore, the P=S bonds in **3b** (1.948(3) Å) and, especially, in **3c** (1.998(2) Å) are rather long.[6] The hydrocarbon portion of the ring has typical bond lengths in both isomers.

In both isomers, the respective bonding distances (P—C, P—Cl, and P—S) and bond angles around the phosphorus atoms are not significantly different. Both S—P—C angles (an average value of 116.7(4)° in **2a** and 116.4(3)° in **2b**) and the S—P—Cl angles (112.7(2)° in **2a** and 113.1(1)° in **2b**) are the same in each isomer. A slightly larger, but still virtually insignificant difference, is observed in C—P—C angles (an average value of 103.6(8)° in **2a** vs. 101.3(3)° in **2b**). The values reported here are close to the endocyclic C—P—C angles in other phosphorinane sulfides (101.8(1)° in **4** 101.3–104.0° in **5**). Similarly, the S—P—Cl angles compare well with that found in **3** (113.1° in **3a** and 113.3(1)° in **3b** and **3c**).

The change from an axial to an equatorial orientation of sulfur mostly influences the ring puckering, as evidenced in Table V. Generally, the phosphorus end of the ring in the *cis* isomer is flatter than in the *trans* isomer. The same trend was observed in a *cis/trans* pair of isomers **6**.[2]

Semiempirical calculations for both molecules were performed using the PM3 method. Crystallographic structures were used as starting points in the optimization processes. Optimization was continued until the heat of formation gradient was lower than 0.01 kcal mol^{-1} $Å^{-1}$. Consistent with the experimental result, the calculations show no significant differences of bond lengths in both isomers. Calculated single bond lengths, both P—C and P—Cl, are about 0.04 Å bigger than those from X-ray data; the lengths of P=S bonds are in better agreement with the measured values. As found previously[2] using PM3 calculations, the two equivalent C2—C3 and C5—C6 (cf Figure 4) distances are systematically predicted to be 0.02 Å shorter than the other endocyclic C—C bonds. No particular shortening of these bonds was found experimentally.

The calculated bond angles around the phosphorus site for both isomers do not strictly replicate the experimental values. Nevertheless, the calculations correctly predict no significant difference in bond angles between the isomers. The same is true with respect to the endocyclic torsional angles: the calculations highly underestimate the influence of the spatial disposition of the substituents on the ring puckering. However, the relative trends are predicted correctly, the *cis* isomer is computed to be flatter than the *trans* isomer at the phosphorus center. As confirmed by the data in Table V, the heterocyclic rings are generally predicted flatter than found from X-ray diffraction.

Isomerization Studies

The *cis/trans* isomerization of the title compound was investigated in chloroform and benzene solutions. Measurement of the integrated ^{31}P NMR signals due to

each isomer revealed a *cis/trans* ratio of 79:21 ($CHCl_3$); the same value was found starting from either pure isomer. The amount of HCl found in commercial $CHCl_3$ was enough to isomerize the compound in minutes; sometimes, however, the isomer ratio sufficiently far from the equilibrium could be measured for samples in $CDCl_3$. In C_6D_6, the isomerically pure samples could be stored at room temperature for several weeks without any visible isomerization. When DCl was added to the sample, slow isomerization was achieved converging to the same ratio of isomers (79:21, at 20 ± 1°C).

The ratio of isomers found in this investigation shows an enhanced preference for equatorial P=S. The P=O bond tends to display the same preference.[1h] Surprisingly, the total energy and the heat of formation computed for both isomers are not in agreement with this finding. The more stable *cis* isomer was predicted to be 0.12 kcal mol^{-1} higher in energy than the *trans* isomer. By comparison, calculations made for the P=O analogues **1a,b** anticipate the *trans* isomer (with an axially disposed oxygen atom) to be 0.23 kcal mol^{-1} more stable. More sophisticated investigations to resolve this inconsistency between experimental and calculated results are underway.

EXPERIMENTAL

All NMR spectra were recorded on a GE 300NB OMEGA spectrometer. $CDCl_3$ (7.26 ppm) or C_6D_6 (7.15 ppm) was used as the internal standard for proton NMR spectroscopy (300 MHz). Internal $CDCl_3$ (77.00 ppm) or C_6D_6 (128.00 ppm) was used as the standard for ^{13}C NMR spectra (75 MHz). Chemical shifts for ^{31}P (121 MHz) 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 fluorescent indicator, and were developed with iodine.

Crystallographic calculations were performed on a VAX computer. Semiempirical molecular structure calculations at the PM3[10] level were made using a HyperChem package[11] installed on a Gateway 2000 4DX2-66V microcomputer.

Cis/trans-4-tert-butyl-1-chlorophosphorinane 1-sulfide (**2a/2b**): Under a nitrogen atmosphere, a *cis/trans* mixture of 4-*tert*-butyl-1-chlorophosphorinane-1-oxide (**1a,b**) (17.7 g, 84.8 mmol) was placed in a 250 mL round bottom flask fitted with a Claisen adapter with a Vigreux column in the side-arm. The outlet of the Vigreux column was connected to a distillation condenser. The contents of the flask were then heated to 190°C (oil-bath temperature). With stirring, 19 mL (31.7 g, 187 mmol) of $PSCl_3$ was added in 1 mL portions every 5 minutes; some $POCl_3$ distilled off during this time. After the addition was complete, heating and stirring were continued for an additional 1.5 hrs; then the residual $PSCl_3$ was removed *in vacuo*. The black residue was sublimed under vacuum, yielding 14.2 g (75%) of a colorless, crystalline mixture of *cis* and *trans* 4-*tert*-butyl-1-chlorophosphorinane 1-sulfide (**2a**:**2b** ratio 76:24, from integration of ^{31}P NMR signals). Anal. Calcd for $C_9H_{18}ClPS$: C, 48.10; H, 8.07%. Found: C, 48.11; H, 7.96%. The mixture was separated by column chromatography on silica gel using CCl_4 as an eluent: **2a** (*cis* isomer). $R_f \approx 0.15$, m.p. 97–98°C, ^{31}P NMR δ 91.9 (C_6D_6), 92.6 ($CDCl_3$); ^{13}C NMR ($CDCl_3$, in mixture of isomers) δ 47.3 (d, J_{PC} = 4.9 Hz, C-4), 40.2 (d, J_{PC} = 51.3 Hz, C-2,6), 32.8 (s, $\underline{C}Me_3$), 27.5 (s, $C\underline{Me}_3$), 24.8 (d, J_{PC} = 7.3 Hz, C-3,5); ^{13}C NMR (C_6D_6, single isomer) δ 46.7 (d, J_{PC} = 4.9 Hz, C-4), 40.2 (d, J_{PC} = 51.9 Hz, C-2,6), 32.4 (d, J_{PC} = 1.2 Hz, $\underline{C}Me_3$), 27.3 (s, $C\underline{Me}_3$), 24.7 (d, J_{PC} = 7.9 Hz, C-3,5); ^1H NMR (C_6D_6) δ 0.28–0.4 (m, 1H), 0.55 (s, 9H), 1.05–1.45 (m, 4H), 1.55–1.66 (m, 2H), 2.03–2.23 (m, 2H).

2b (*trans* isomer), $R_f \approx 0.21$, m.p. 99–102°C, ^{31}P NMR δ 93.1 (C_6D_6), 93.5 ($CDCl_3$); ^{13}C NMR ($CDCl_3$, a mixture of isomers) δ 48.36 (d, J_{PC} = 3.7 Hz, C-4), 40.54 (d, J_{PC} = 52.5 Hz, C-2,6), 32.8 (s, $\underline{C}Me_3$), 27.6 (s, $C\underline{Me}_3$), 24.75 (d, J_{PC} = 12.2 Hz, C-3,5); ^{13}C NMR (C_6D_6, single isomer) δ 47.87 (d, J_{PC} = 3.8 Hz, C-4), 40.4 (d, J_{PC} = 51.9 Hz, C-2,6), 32.5 (s, $\underline{C}Me_3$), 27.4 (s, $C\underline{Me}_3$), 24.7 (d, J_{PC} = 6.1 Hz, C-3,5). ^1H NMR (C_6D_6) δ 0.35–0.48 (m, 1H), 0.59 (s, 9H), 1.20–1.35 (m, 2H), 1.40–1.75 (m, 4H), 2.04–2.20 (m, 2H).

Quantitative ^{31}P NMR Measurements

Samples were dissolved in the appropriate solvent. The spectral window was 1024 Hz, 8 K points were collected (the acquisition time 8 s). A predelay period of 10 s was applied and the spectra were recorded using an inverse gated decoupling pulse sequence.

X-Ray Analysis

Single crystals of **2a** and **2b** useful for X-ray studies were prepared by dissolving the compound in hexanes, followed by slow evaporation of the solvent. The details of crystallographic data collection and structure solving are shown in Table I.§

The crystals were mounted on a glass fiber (**2a**) or in a glass capillary (**2b**) in a random orientation. The preliminary examination and diffraction data collection were performed on an Enraf-Nonius CAD4 computer controlled kappa axis diffractometer with a graphite crystal, incident beam 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.[12] Lorentz and polarization corrections were applied to the data. For **2b**, an empirical absorption correction based on the method of Walker and Stuart[13] was applied with the minimum and maximum transmission factors equal to 0.3 and 1.00, respectively. The structures were solved using the solution program SHELX-86.[14] 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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§Full experimental details, as well as tables of thermal parameters are deposited as supplementary material with CDCC.