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INFLUENCES OF CONFIGURATION AT PHOSPHORUS ON THE ^{13}C NMR SPECTRA AND SOLID-STATE CONFORMATION OF 4-PHOSPHORINANOL SULFIDES[1]

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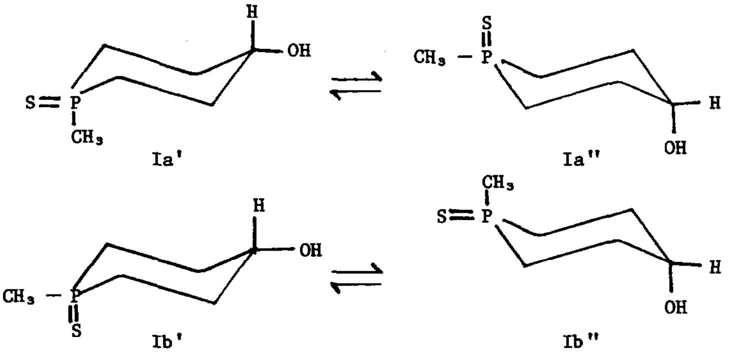
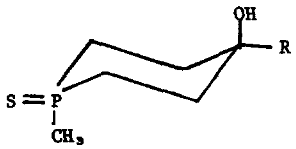
The conformational equilibrium for the phosphorinane ring with trivalent phosphorus has been studied previously[2,3], but no consideration has been given to the steric consequences of placing an oxygen or sulfur atom on phosphorus. We have initiated such a study with sulfides of the 4-phosphorinanol system, since much is known about the conformational properties of the corresponding phosphines. For these latter compounds, ^{13}C nmr spectroscopy has been particularly convincing in discriminating cis, trans structure[4], as it has in other cyclic systems. However, the ^{13}C nmr spectra for isomeric phosphorinanol sulfides[5] Ia and Ib proved to be remarkably similar (Table I) and lacked features useful for structure assignment. One cause of this could be the occurrence of equilibration between the conformers of each isomer without the strong bias in one direction that is usually found in six-membered rings. This is already known to be true in the corresponding phosphines[2,3] and would tend to equalize the steric compression effects that are so useful in causing unique chemical shift differences to appear for each isomer[7].



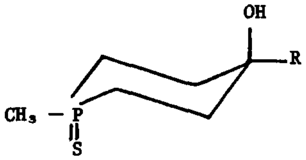
Since the sulfides were solids, single-crystal X-ray analysis was performed. The unique observation was made that one of them (Ib) had crystallized in both conformations (Ib' and Ib"), with ratio 2:1. Such co-occurrence of two conformers in the same crystal is without precedent in conformational studies of simple, saturated six-membered ring compounds, and it is clearly compatible with the proposal that in solution also the two conformers have substantial concentrations. Sulfide Ia crystallized in only one conformation (Ia'), but this does not necessarily mean that the other conformer is of insignificant concentration in solution since preferential crystallization of Ia' could have occurred.

Crystal data: Ia, $\underline{a}$ = 9.97(2), $\underline{b}$ = 7.82(2), $\underline{c}$ = 22.22(3)Å, β = 91.9(1)°, Monoclinic, space group $\underline{P2_1/c}$ ($\underline{C^5_{2h}}$), $\underline{Z}$ = 8; Ib, $\underline{a}$ = 10.55(2), $\underline{b}$ = 12.44(2), $\underline{c}$ = 11.46(2)Å, β = 120.4(1)°, Monoclinic, space group $\underline{P2_1}$($\underline{C^2_2}$), $\underline{Z}$ = 6. Intensity data were recorded photographically and estimated visually. The structure of Ia was solved by the heavy-atom method and that of Ib was solved by direct phase-determining methods with the aid of MULTAN[8]. Refinement of the atomic parameters (anisotropic C,O,P,S; fixed H contributions) by full-matrix least-squares calculations converged at $\underline{R}$ = 0.097 (2692 reflections) for Ia and $\underline{R}$ = 0.082 (2001 reflections) for Ib.

Although tertiary alcohols in this series are conformationally biased[2,4], those that were examined also gave ^{13}C nmr that failed to allow definitive structure assignment[9]. The spectra for three isomer pairs[5] (Table I) did show substantial differences, especially for the P-CH_3 signal, but that isomer with the more upfield P-CH_3 signal also had the more downfield $C_{3,5}$ signal. Usually, the steric compression in the axial isomer would cause all involved carbons to be upfield of the positions for the equatorial conformer[2]. An exception has recently been noted among cyclohexanes with polar groups[10]; axial OH has a greater shielding effect at $C_{3,5}$ than does axial CH_3, and it was suspected that in the phosphorinane sulfides axial sulfur may be exerting a similar strong effect at $C_{3,5}$. X-Ray analysis therefore was again used to establish the structure for an isomer pair (IIa and IIb).



IIa, R = CH_3
IIIa, R = t-C_4H_9
IVa, R = C_6H_5



IIb, R = CH_3
IIIb, R = t-C_4H_9
IVb, R = C_6H_5

Crystal data: IIa, $\underline{a}$ = 10.42(1), $\underline{b}$ = 13.85(1), $\underline{c}$ = 6.67(1)Å, Orthorhombic, space group $\underline{P2_12_12_1}$($\underline{D^4_2}$), $\underline{Z}$ = 4; IIb, $\underline{a}$ = 9.79(1), $\underline{b}$ = 7.75(1), $\underline{c}$ = 6.08(1)Å, β = 90.9(1)°, Monoclinic, space group $P2_1/m(C^2_{2h})$, $\underline{Z}$ = 2. Intensity data were recorded on an Enraf-Nonius CAD-3 Automated Diffractometer with Zr-filtered Mo-$\underline{K}_\alpha$ radiation (λ = 0.7107Å). The structures were solved by the heavy-atom method and the atomic parameters (anisotropic C,O,P,S; isotropic H) refined by full-matrix least-squares calculations to $\underline{R}$ = 0.038 (906 reflections) for IIa and $\underline{R}$ = 0.048 1606 reflections) for IIb.

That steric compression is indeed operative in the axial methyl compounds is revealed by the significantly higher (by 4-6 ppm) chemical shift for the methyl carbon when in this position than in the equatorial position. However, the larger γ-shielding exerted at $C_{3,5}$ by axial sulfur rather than by axial methyl clearly cannot alone be due to the relative size and steric compression effects of the two groups, for (i) the estimated van der Waals' radius[11] of sulfur (1.85Å) is smaller than methyl (2.0Å), (ii) P = S bond lengths average 1.964(4)Å which is significantly longer than average P-C lengths 1.813(17)Å, (iii) C-P-C angles are consistently found to be smaller than tetrahedral (109.5°) while C-P-S angles exceed this value. Consequently, axial P-methyl would be expected to cause more severe overcrowding of the syn-axial hydrogens, and the smaller torsion angles about the P-C bonds in that isomer are in accord with this. It is clear, therefore, that the polarity of the P=S group figures in the upfield shift of $C_{3,5}$, and points out the need for caution in interpreting the ^{13}C spectra of tetracovalent phosphorus compounds on the basis of steric size alone.

Structural data from the X-ray analyses appear in Table II.

Table I. M.p. and ^{13}C Nmr Data[a] for Phosphorinanol Sulfides

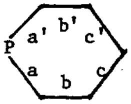
	M.p., °C	δ C-2,6	δ C-3,5	δ C-4	δ P-CH_3
Ia	89-90	165.9 (49)	164.0 (5)	127.3 (6)	173.8 (53)
Ib	79-80.5	164.8 (46)	163.5 (6)	126.7 (6)	175.0 (53)
IIa	168-170	162.3 (50)	155.5 (4)	122.7 (6)	175.4 (50)
IIb	103-105	163.6 (52)	157.4 (6)	122.2 (8)	171.2 (54)
IIIa	146-148	164.7 (51)	164.5 (6)	119.4 (5)	178.0 (52)
IIIb	-b	165.8 (49)	167.0[b]	118.4[b]	172.0 (55)
IVa	182-184	161.8 (50)	155.0 (8)	119.1 (7)	-[c]
Ivb	190-192	163.5 (50)	157.2 (6)	118.1 (6)	167.0 (65)

[a] Chemical shifts are relative to CS_2 = 0. Coupling constants (J_{PC}, Hz) are given in parentheses. Proton-decoupled spectra were obtained at 22.62 MHz with a Bruker HFX-10 system using the Fourier transform technique. Samples were run in chloroform (I and III) or methanol (II and IV), in a tube with a coaxial insert containing C_6F_6.

[b] This isomer was obtained in enriched form only. Complete analysis of the spectrum of the mixture was not possible.

[c] This doublet was not clearly discernible at the concentrations employed.

Table II. Endocyclic Bond and Dihedral Angles



Valency angles, deg	Ia'	Ib'	Ib''	IIa	IIb
a/a'	103.3	101.3	104.0	103.2	101.9
a/b	112.4	111.6	113.3	113.1	110.7
b/c	112.8	112.8	113.4	114.2	114.2
c/c'	113.2	113.3	113.8	112.0	112.0
Dihedral angles, deg					
ω_a	45	50	44	45	52
ω_b	56	59	55	56	59
ω_c	64	63	62	61	60

References

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5. The sulfides were synthesized either by adding sulfur to the isomeric mixture of the corresponding phosphines (for IIa-IIb, IIIa-IIIb, IVa-IVb) or additions to the carbonyl of 1-methyl-4-phosphorinanone 1-sulfide (Ia-Ib; also for IVa-IVb). Separation of the isomeric sulfides was accomplished by fractional crystallization or by chromatographic (thick-layer or high-pressure liquid) techniques. All products gave the correct analysis. Complete details will be reported elsewhere[6].

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