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Barriers to rotation around the P-N bond in 2-thiono-2-amino-1,3,2-dithiaphosphorinanes

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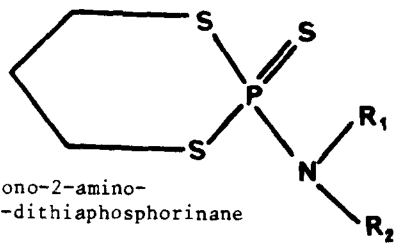
Several examples of large rotational barriers around the P-N bond have been recently reported. Most of these studies are dealing with three co-ordinate phosphorus compounds (1). Considerably less attention has been devoted to tetra (2) and penta co-ordinate (3) phosphorus derivatives. The cause of the barrier is not clear, but some possibilities include nitrogen lone-pair-phosphorus lone-pair interactions, multiple bonding due to nitrogen-phosphorus, $p_\pi - d_\pi$ overlap and dipole-dipole interaction (4). In order to provide further insight into the origin of the P-N barrier we wish to report here some preliminary results of hindered P-N rotation as observed by ^1H n m r spectroscopy on 2-thiono-2-amino-1,3,2-dithiaphosphorinanes.

Compounds 1, 2, 3 and 4 have been readily synthesized by reacting 2-chloro-1,3,2-dithiaphosphorinane (5) with the corresponding amine (6) followed by addition of sulfur (7). All the compounds under study gave satisfactory elemental analysis, and the ^1H, ^{13}C and ^{31}P n m r spectra are in agreement with the chemical formula.



2-thiono-2-amino-1,3,2-dithiaphosphorinane

	R_1	R_2
1	tBu	iPr
2	iPr	iPr
3	tBu	CH_3
4	CH_3	CH_3

The proton n m r spectral analysis of compounds 1, 2 and 3 show that these molecules exist in solution in a rigid chair conformation ($^3J(H_{4a}H_{5a}) \sim 12$Hz. An X-ray structure analysis of molecule 2 (8) has been performed and refined to an R value of 0.05. The structure shows that the ring adopts a C_s chair conformation with the P-N bond lying in the equatorial orientation. The trigonal exocyclic nitrogen and the atoms which are bounded to it lye in the symmetry plane of the ring. From the X-ray diffraction study of molecule 2, all the distances between atoms of nearest neighbor molecules are larger than the sum of the corresponding Van der Waals radii, thus we shall assume that molecule 2 exists in solution in a conformation similar to the one observed in the solid state. Since 1 and 3 have alkyl groups attached to the nitrogen atom sterically and chemically similar to those of 2 it is reasonable to consider that these molecules also exist in solution in a C_s chair conformation in which the P=S bond lies in the axial orientation and the plane of the nitrogen bonds bisects the S-P-S intracyclic angle. In molecule 4 the proton

spectrum shows the existence of an equilibrium between two forms, which must be strongly shifted toward the P=S axial conformer (80%) (6) (9).

Variable temperature n m r experiments show dramatic changes in the methyl proton and ^{31}P signals for molecules 1, 2 and 3. These spectral modifications are summarized in the Table.

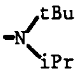
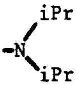
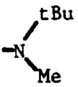
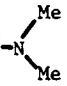
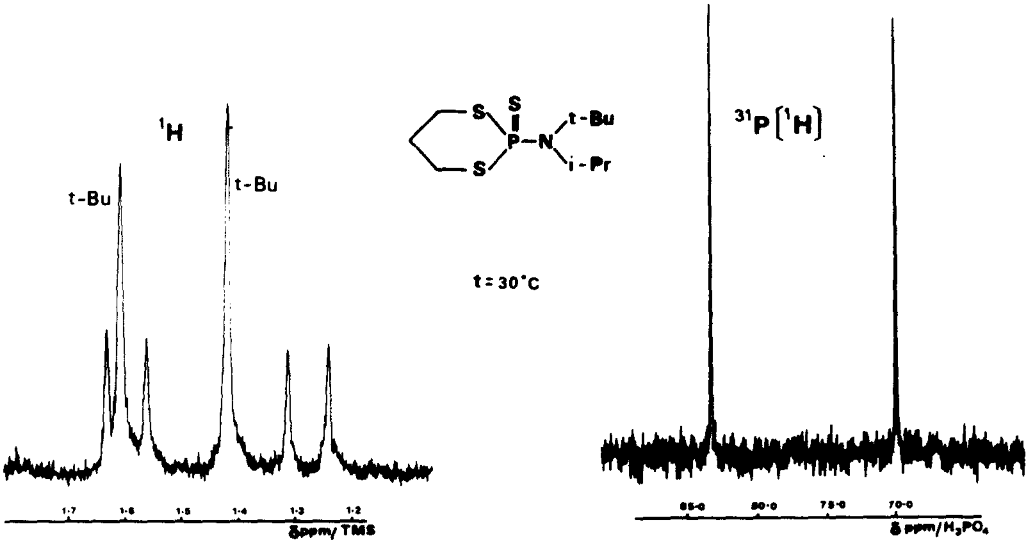
compound	solvent	temperature (°C)	$\delta(^{31}P)$* (ppm)	$\delta(CH_3)$* (ppm)	coalescence** temp. (°C)	ΔG(Kcal/mol)
 1	o-$C_6H_4Cl_2$	30 150	83.1 69.7 76.5	1.60 (tBu) 1.41 (tBu) 1.53 (tBu)	90	18.7
 2	CD_2Cl_2 CH_2=CHCl (1:1)	30 -88	75.0	1.40 (iPr) 1.59 (iPr) 1.20 (iPr)	-58	10.6
 3	CD_2Cl_2 CH_2=CHCl (1:1)	30 -110	78.2 80.7 69.8	3.06 (Me) 3.10 (Me) 2.98 (Me)	-100	9.2
 4	CD_2Cl_2 CH_2=CHCl (1:1)	-130	82.9	2.90	<-140	<7.

Table : n m r spectral changes with temperature of the ^1H methyl and ^{31}P signals of dithiaphosphorinanes 1,2,3 and 4 . $^{*31}P$ chemical shifts are given in ppm downfield from external H_3PO_4 (85%), the ^1H chemical shift are in ppm downfield from TMS.** Coalescence temperature refers to the proton signal.

The n m r signal changes reported in the table for compounds 1,2 and 3 are consistent with a slowing down of the phosphorus nitrogen single bond rotation within the time scale of the n m r measurements, thus placing the methyl groups in distinctively different environments. The corresponding $\Delta G^{\neq}$ values were calculated from the formula $\Delta G^{\neq}_c = T_c(45.67 + 4.58 \log \frac{Tc}{\Delta\nu})$ which results from substituting kc the expression for determining the rate constant at coalescence ($k_c = \frac{\pi\Delta\nu}{\sqrt{2}}$) into the Eyring equation for compounds 1 and 2 (10).

In compound 1 (Figure) the two t-Butyl signals which exist at room temperature (δ_1=1.41ppm δ_2= 1.60 ppm) coalesce at 90°C; the $[^1H]^{31}P$ spectrum shows at room temperature two peaks at 69.7 ppm and 63.1 ppm respectively and one peak at 150°C. The ratio of conformers at room temperature as measured by the t-Butyl peakarea is approximatively 11:10. At low temperature the $[^1H]^{31}P$ n m r spectrum of compound 3 shows two distinct peaks δ = 69.8 ppm and δ = 80.7 ppm respectively in a 1:2 ratio. The t-Butyl signal remains unique which is the opposite of that observed in compound 1, where two t-Butyl peaks ($\Delta\delta$ = 0.19 ppm) are observed at room temperature. In compound 4 the methyl signal remains unchanged down to −130°C, thus the barrier to the rotation must be lower than 7 Kcal.



The figure shows the ^1H n m r signals (left) of the tBu and iPr protons and the $^{31}P\{^1H\}$ n m r peaks of the two conformers of molecule 1 at room temperature.

The $^3J(PH)$ n m r coupling which are highly dependent upon the bond orientation around the phosphorus in the three co-ordinate phosphorus compounds (1) show here only a small differente in a 180° rotation around the P-N bond.

The importance of the steric effect is apparent from the data reported in the Table which show that the torsionnal barrier increases quite markedly with increasing size of the groups attached to nitrogen. Since the conformers of compound 1 at room temperature are in a concentration ratio close to one, the steric effect is due presumably to crowding in the transition state. The large $\Delta G^{\neq}$ difference observed between compounds 1 and 2 should be better understood in terms of a transition state in which the nitrogen is pyramidal.

It must be pointed out that in the three co-ordinate phosphorus 1,3,2-dithiaphosphorinanes corresponding to 1,2,3 and 4 no hindrance to the rotation around the phosphorus nitrogen bond has been observed at room temperature. This suggest that in the transition state the nitrogen lone pair of the pyramidal nitrogen should be trans with respect to the P=S bond in the 2-thiono-1,3,2-dithiaphosphorinane.

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(10) For compound **3**, the ΔG value has been obtained by using the DNMR (G. BINSCH, J. Am. chem. soc., 91, 1304 (1969)) program, in order to take into account the fact that the conformers ratio is different from unity.