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New Phosphorus Sulfide Cyanides and Amides: Assigning Phosphorus NMR Spectra of Polycyclic Compounds using Low-Level *Ab Initio* Calculations of Shieldings

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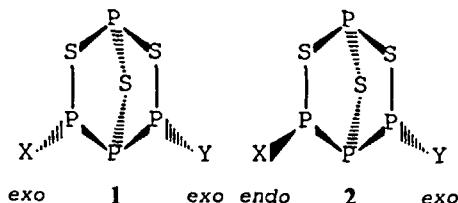
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Oxidation of P_4S_3 with ICN gives *exo,exo*- and *endo,exo*- β - $P_4S_3I_2$, $-\beta$ - $P_4S_3(CN)_2$, and $-\beta$ - $P_4S_3I(CN)$ as initial products. *Ab initio* GIAO calculations of NMR shieldings at the RHF/3-21G* level are sufficient to assign the spectrum of *endo,exo*- β - $P_4S_3(CN)_2$ and to confirm the identity of the observed *endo,exo*- β - $P_4S_3I(CN)$, which has iodine rather than cyanide in the hindered *endo* position. Reaction of enantiomerically pure (S)-1-phenyltetrahydroisoquinoline with *exo,exo*- β - $P_4S_3I_2$ gives an *exo,exo*-diamide in which the C_3 symmetry of the β - P_4S_3 cage is lost. The two amido groups, planar at nitrogen, are each capable of two orientations, giving four P-N bond rotamers at 183 K. The ^{31}P NMR spectra of three of these have been fitted, and assigned to particular rotamers by *ab initio* shielding calculations.

Keywords: phosphorus; sulfide; cage; NMR; *ab initio*; GIAO

INTRODUCTION

The first reported β - P_4S_3 molecule was *exo,exo*- β - $P_4S_3I_2$ (1, X = Y = I), in which both the iodide substituents are oriented *exo* to the



nido cage skeleton.^[1] Ring opening of P_4S_3 **3** by MeSSMe under photolysis gave a low concentration of *endo,exo*- β - $P_4S_3(SMe)_2$ (**2**, $X = Y = SMe$), as well as giving the *exo,exo* isomer **1** as the major product.^[2] Inversion of phosphorus, so as to interconvert isomers **1** and **2**, is sufficiently slow at room temperature that non-equilibrium concentrations can be measured readily over long ^{31}P NMR accumulations. Replacement of iodide in β - $P_4S_3I_2$ by hydride gave *endo,exo*- β - $P_4S_3H_2$ (**2**, $X = Y = H$) as the major product,^[3] possibly because the low steric requirement of H makes it preferable for a hydrogen atom to be in the more crowded *endo* position, rather than two lone pairs of electrons being opposed to each other in *endo* positions.

Until recently, we have relied on empirical relationships between molecular structures and phosphorus NMR chemical shifts or coupling constants to identify phosphorus chalcogenide compounds containing exocyclic substituents,^[4] but occasionally this method is unable to give a unique assignment. In such cases, even low level *ab initio* calculations of NMR shieldings can help. We established that the molecular geometry of α - $P_4Se_3(CN)_2$ or P_2Se_3 was well predicted by *ab initio* calculation at the RHF/3-21G* level.^[5] For the closed cage molecules P_3E_2X ($E = S$ or Se , $X = Cl$ or Br), we obtained geometries at the RHF/Ahlrichs pVDZ level, for which GIAO calculations of NMR isotropic shieldings at the RHF/Ahlrichs pTZV level then allowed the correct assignment of positional isomers to their spectra.^[6] We present here an example of a reaction in which GIAO calculations have allowed us to identify *endo,exo*- β - P_4S_3 cyanides (**2**, $X = CN$ or I , $Y = CN$), and a second example in which they allow assignment of low temperature phosphorus NMR spectra to particular P—N bond rotamers.

PRESENT WORK

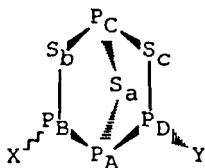
Cyanides

TABLE 1 Product distribution from $P_4S_3 + ICN$ after 2.5 hours

<i>exo,exo</i> - β - P_4S_3XY 1			<i>endo,exo</i> - β - P_4S_3XY 2		
X	Y	%	X	Y	%
I	I	53	I	I	7
I	CN	16	I	CN	18
CN	CN	3	CN	CN	3

P_4S_3 was oxidised by stirring a solution in CS_2 with suspended ICN for 2.5 hours at 17 °C, when there was a 3% conversion to products β - P_4S_3XY , as shown in Table 1. Cyanide has a low steric requirement, like hydride, and the *endo,exo* iodide cyanide 2 ($X = I$, $Y = CN$) was the cyanide-containing product in highest initial concentration.

In the spectrum of the reaction mixture, *endo,exo* compounds 2 could be distinguished from unsymmetrically substituted *exo,exo* compounds 1 by the size of coupling $^2J(P_BP_D)$. This is large in *exo,exo* compounds (e.g. 1, $X = I$, $Y = CN$: $^2J(P_BP_D) = 170.4$ Hz), corresponding to near parallel orientation of lone pairs on P_B and P_D , whereas it is small for the *endo,exo* compounds (e.g. 2, $X = I$, $Y = CN$: 11.2 Hz)



where these lone pair orbitals point away from each other. We could thus diagnose that there were three *exo,exo*- β - and three *endo,exo*- β -products, of which the NMR spectra of the diiodides were both known.^[2,7] Phosphorus carrying cyanide could be recognised by its low chemical shift, even in the *endo,exo*- β -dicyanide (2, $X = Y = CN$) where $\delta(P_B) = 11.1$ and $\delta(P_D) = 17.8$ ppm. We therefore had one isomer of *endo,exo*- β - $P_4S_3I(CN)$, with $\delta(P-I) = 131.1$ and $\delta(P-CN) = 18.7$ ppm.

We first assigned the chemical shifts $\delta(P_B)$ and $\delta(P_D)$ in the *endo,exo*- β -dicyanide. For previously known *endo,exo*- β -compounds (2, $X = Y = NHR$, F, Cl, Br, or SR) three inequalities distinguished P_B , carrying the *endo* substituent, from P_D , carrying the *exo*. These were:

$$\begin{aligned} ^2J(P_BP_C) &< ^2J(P_CP_D) \\ |^1J(P_AP_B)| &< |^1J(P_AP_D)| \\ \delta(P_B) &> \delta(P_D) \end{aligned}$$

However, all three conditions could not be met simultaneously in either the *endo,exo*- β -dicyanide or the dihydride,^[1] for which the second and third inequalities were reversed relative to the first. We hypothesised that the order of the 2J couplings would lead to the correct assignment of the spectra of the dicyanide and the dihydride, and that the order of the chemical shifts was abnormal in these compounds. Geometry and GIAO calculations were carried out at the RHF/3-21G* level for both molecules. The results, shown in Table 2, demonstrate that $\delta(P_B) < \delta(P_D)$, as hypothesised. The experimental chemical shifts shown for the dihydride are literature values,^[1] but with the assignments of $\delta(P_B)$ and $\delta(P_D)$ interchanged.

TABLE 2 ^{31}P NMR chemical shifts (ppm) for
endo,exo- β - P_4S_3 dicyanide and dihydride 2

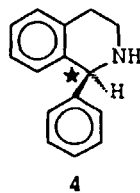
	<i>endo,exo</i> - β - $\text{P}_4\text{S}_3(\text{CN})_2$			<i>endo,exo</i> - β - $\text{P}_4\text{S}_3\text{H}_2$	
	Obs.	Calc.		Obs.	Calc.
$\delta(\text{P}_\text{C})$	191.3	184.3	$\delta(\text{P}_\text{C})$	155.0	150.6
$\delta(\text{P}_\text{A})$	111.0	98.0	$\delta(\text{P}_\text{A})$	68.9	48.0
$\delta(\text{P}_\text{B})$	11.1	22.3	$\delta(\text{P}_\text{B})$	-30.3	-4.8
$\delta(\text{P}_\text{D})$	17.8	26.6	$\delta(\text{P}_\text{D})$	16.7	16.5

The authors had used the normal order of these shifts in making their assignment. The calculated shifts were obtained by fitting the calculated shieldings to the observed shifts separately for each compound, with the coefficient fixed at -1.¹⁶¹ A calculation on *endo,exo*- β - $\text{P}_4\text{S}_3(\text{NHMe})_2$ showed the normal order $\delta(\text{P}_\text{B}) > \delta(\text{P}_\text{D})$, confirming the assignment previously published.¹⁴¹

For the observed isomer of *endo,exo*- β - $\text{P}_4\text{S}_3\text{I}(\text{CN})$, the ambiguity to be resolved was whether the iodide or the cyanide group occupied the *endo* position X. We found $^2J(\text{P}_\text{C}-\text{PI}) = 44.9$ and $^2J(\text{P}_\text{C}-\text{P}(\text{CN})) = 23.0$ Hz, so, following the $^2J(\text{P}_\text{B}\text{P}_\text{C}) < ^2J(\text{P}_\text{C}\text{P}_\text{D})$ rule, we hypothesised that the less sterically demanding CN was in the *endo* position X, attached to P_B . Here, however, the *ab initio* results supported the opposite conclusion, as shown in Table 3. Of the two known isomers of *endo,exo*- β - $\text{P}_4\text{S}_3\text{IH}$ (2, X = I, Y = H and 2, X = H, Y = I),¹³¹ that with *endo*-iodide also has $^2J(\text{P}_\text{B}\text{P}_\text{C}) > ^2J(\text{P}_\text{C}\text{P}_\text{D})$.

Amides

We wished to investigate the steric effect of bulky substituents on the geometry and NMR parameters of P_4S_3 cages. We selected (*S*)-1-phenyltetrahydroisoquinoline (pthiqH) 4 as likely to give amide groups of readily predictable conformation and a high steric influence. Because P_B and P_D in an *exo,exo*- β - P_4S_3 cage are related by a mirror plane, they have opposite chirality. If a substituent of one chirality is attached to each, they become chemically non-equivalent.¹⁹¹ The resulting diastereotopic differences in their NMR properties then reflect mainly steric influences.



A suspension of *exo,exo*- β - $\text{P}_4\text{S}_3\text{I}_2$ reacted with a solution of pthiqH and Et_3N in toluene, in molar ratio 1:2:2 at 0 °C, to give a solution containing *exo,exo*- β - $\text{P}_4\text{S}_3(\text{pthiq})_2$ as 83% of the total phosphorus content. At 290 K, the internal ^{31}P chemical shift

TABLE 3 ^{31}P NMR chemical shifts (ppm) for isomers of *endo,exo*- β - $\text{P}_4\text{S}_3\text{I}(\text{CN})$

	Observed	Calculated for 2 (X = I, Y = CN)	Calculated for 2 (X = CN, Y = I)
$\delta(\text{P}_\text{C})$	198.4	191.1	189.5
$\delta(\text{P}_\text{A})$	110.8	110.9	101.1
$\delta(\text{P-I})$	131.1	137.0	137.1
$\delta(\text{P-CN})$	18.7	20.1	31.4

$|\Delta(\delta(\text{P}_\text{B}) - \delta(\text{P}_\text{D}))|$ was 2.63 ppm. From *ab initio* calculations, using at least the polarisation basis set 3-21G*, for this and other P_4S_3 compounds,^[9] the geometry of the amide nitrogen is planar, with the orientation of the plane, relative to the P_4S_3 cage, practically independent of the other groups attached to nitrogen. For the unsymmetric amide pthiq, each amide group had two possible rotation positions about the P-N bond, at almost exactly 180° to each other. Since there were two diastereotopically non-equivalent amide groups, the whole molecule could exist as one of four rotamers.

The 202.5 MHz ^{31}P NMR spectrum of *unsym-exo,exo*- β - $\text{P}_4\text{S}_3(\text{pthiq})_2$ at 183 K showed the expected four multiplets in the P_C region. Except for the rotamer in lowest concentration, enough of the rest of the spectrum could be found for computer fits to be made, and all coupling constants and chemical shifts obtained, as shown in Tables 4 and 5. The most stable rotamer showed the biggest internal differences in $^2J(\text{P-S-P})$ couplings, 1J couplings, and P_B and P_D chemical shifts. RHF/GIAO calculations were made on RHF/3-21G* geometries, using a locally dense Ahlrichs pTZV basis for N, P and S, with 3-21G* for C and H. Calculated shieldings were fitted to observed shifts separately for P_C over the four rotamers, for P_A over three, and for P_B and P_D together over three, to give the calculated shifts included in Table 5. Rotamers are represented according to which group of the pthiq substituent points (backwards as drawn) towards S, of the cage: e.g. $\text{CH}_2(\text{O})\text{CHPh}$ means that CH_2 points

TABLE 4 ^{31}P - ^{31}P coupling constants at 183 K for *unsym-exo,exo*- β - $\text{P}_4\text{S}_3(\text{pthiq})_2$

Rotamer	1	2	3
$^2J(\text{P}_\text{B}\text{P}_\text{C})$	39.8	44.3	52.5
$^2J(\text{P}_\text{C}\text{P}_\text{D})$	56.2	50.5	51.1
$^1J(\text{P}_\text{A}\text{P}_\text{B})$	-337.9	-330.1	-331.2
$^1J(\text{P}_\text{A}\text{P}_\text{D})$	-311.3	-326.5	-327.5
Integral	52.9	26.9	12.2

TABLE 5 ^{31}P NMR chemical shifts (ppm) at 183 K for
unsym-exo,exo-β-P₄S₃(pthiq)₂

Rotamer	1		2		3		4	
	CH ₂ ()CHPh Obs.	CH ₂ ()CHPh Calc.	CH ₂ ()CH ₂ Obs.	CH ₂ ()CH ₂ Calc.	CHPh()CH ₂ Obs.	CHPh()CH ₂ Calc.	CHPh()CHPh Obs.	CHPh()CHPh Calc.
δ(P _C)	153.0	155.2	157.0	157.9	161.8	159.8	158.4	157.4
δ(P _A)	53.9	53.4	49.6	50.7	54.8	54.3		56.7
δ(P _B)	120.4	117.9	121.6	120.0	117.8	116.7		114.4
δ(P _D)	110.5	111.6	119.1	122.8	122.4	122.7		111.7
Integral	52.9		26.9		12.2		6.5	

backwards on the P_B (left) side of the cage, and CHPh on the P_D side. The large observed internal shift $\Delta(\delta(\text{P}_B) - \delta(\text{P}_D))$ in rotamer 1 (9.91 ppm) was well represented. The values of $\delta(\text{P}_B)$ and $\delta(\text{P}_D)$ found (and calculated) for rotamer 2 were close together, and here the relative assignment, reverse to that supported by the GIAO calculation, was taken to conform better to coupling constant calculations (by McConnell's method),^[6] which were also done.

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References

- [1] G.J. Penney and G.M. Sheldrick, *J. Chem. Soc. (A)*, 1100 (1971).
- [2] B.W. Tattershall, *J. Chem. Soc., Dalton Trans.*, 1707 (1985).
- [3] R. Blachnik and K. Hackmann, *Z. Naturforsch.*, **50b**, 884 (1995).
- [4] R. Blachnik, K. Hackmann and B.W. Tattershall, *Polyhedron*, **15**, 1415 (1996).
- [5] B.W. Tattershall, E.L. Sandham and W. Clegg, *J. Chem. Soc., Dalton Trans.*, 81 (1997).
- [6] B.W. Tattershall, R. Blachnik and A. Hepp, *J. Chem. Soc., Dalton Trans.*, 2551 (2000).
- [7] R. Blachnik and K. Hackmann, *Z. Anorg. Allg. Chem.* **621**, 1015 (1995).
- [8] B.W. Tattershall, *Phosphorus Sulfur Silicon*, **124**, 193 (1997).
- [9] B.W. Tattershall and E.L. Sandham, *Z. Anorg. Allg. Chem.* **622**, 1635 (1996).