

## N.M.R. Spectra of $\alpha$ -Tetraphosphorus Trisulphide Isothiocyanates: Extreme Broadening of Phosphorus-31 Absorptions by Nitrogen-14 and Large Phosphorus–Nitrogen Coupling Constants

Bruce W. Tattershall

*Department of Chemistry, The University, Newcastle upon Tyne NE1 7RU, U.K.*

The collapse of the  $P_B$  parts of the  $^{31}\text{P}$  n.m.r. spectra of  $\alpha\text{-P}_4\text{S}_3(^{14}\text{NCS})_2$  (**1a**),  $\alpha\text{-P}_4\text{S}_3(^{14}\text{NCS})\text{I}$  (**2a**), and  $\alpha\text{-P}_4\text{S}_3(^{14}\text{NCS})\text{Cl}$  (**3a**) at room temperature is due to  $^{14}\text{N}$  relaxation effects rather than to chemical exchange, as shown by analysis of the spectra of the corresponding  $^{15}\text{N}$  isotopomers (**1b**), (**2b**), and (**3b**), which show very large  $^1J_{\text{PN}}$  coupling constants.

The  $^{31}\text{P}$  n.m.r. spectra of  $\alpha\text{-P}_4\text{S}_3(^{14}\text{NCS})_2$  (**1a**) at 200 K corresponded to the expected AA'BB' spin system, but at 300 K the high frequency,  $P_B$  half of the spectrum collapsed into broad peaks.<sup>1</sup> It has now been found that  $\alpha\text{-P}_4\text{S}_3(^{14}\text{NPh}_2)_2$  (**4**) showed a normal, quite sharp  $^{31}\text{P}$  n.m.r. spectrum. Since it was not possible to distinguish, using the available evidence,<sup>1</sup> between  $^{14}\text{N}$  broadening of the  $^{31}\text{P}$  spectrum, and chemical exchange, as causes for the anomalous spectrum of the di-isothiocyanate (**1a**), the isothiocyanate halides (**2a**) and (**3a**) have now been made [by reaction of  $\alpha\text{-P}_4\text{S}_3\text{I}_2$  with  $\alpha\text{-P}_4\text{S}_3(^{14}\text{NCS})_2$  (**1a**) ( $\text{CS}_2$  solvent, 46 °C, 86 h) and of  $\alpha\text{-P}_4\text{S}_3\text{Cl}_2$  with  $\text{Me}_3\text{SiNCS}$  ( $\text{CS}_2$  solvent, 20 °C, 22 h) respectively] in solution along with the di-isothiocyanate (**1a**) and the corresponding dihalide. For each compound (**2a**) and (**3a**),  $^{31}\text{P}$

n.m.r. peaks primarily due to the phosphorus nucleus carrying the NCS group,  $P_B$  (Figure 1), were broadened so as to be invisible at 300 K, but had sharpened sufficiently by 200 K for a crude computer fit as a static ABCD spin system, without  $^{14}\text{N}$  coupling, to be carried out. The isothiocyanate halides (**2a**) and (**3a**) thus behaved similarly to the di-isothiocyanate (**1a**).

To remove the possibility of  $^{14}\text{N}$  broadening, the isothiocyanates have now been made as the completely  $^{15}\text{N}$ -substituted isotopomers (**1b**), (**2b**), and (**3b**). [ $\text{Na}^{15}\text{NCS}$  was converted to  $\text{Ag}^{15}\text{NCS}$  and hence to a solution of pure  $\alpha\text{-P}_4\text{S}_3(^{15}\text{NCS})_2$  (**1b**);  $\alpha\text{-P}_4\text{S}_3(^{15}\text{NCS})\text{I}$  (**2b**) was produced in an equilibrium mixture as for the  $^{14}\text{N}$  isotopomer (**2a**) above; this was further converted to an equilibrium mixture containing

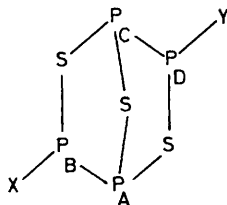


Figure 1

- (1a) X = Y =  $^{14}\text{NCS}$ ;  
 (1b) X = Y =  $^{15}\text{NCS}$ ;  
 (2a) X =  $^{14}\text{NCS}$ , Y = I;  
 (2b) X =  $^{15}\text{NCS}$ , Y = I;  
 (3a) X =  $^{14}\text{NCS}$ , Y = Cl;  
 (3b) X =  $^{15}\text{NCS}$ , Y =  $^{35}\text{Cl}$ ;  
 (4) X = Y =  $^{14}\text{NPh}_2$ ;  
 (7) X =  $^{13}\text{C}^{14}\text{N}$ , Y =  $^{12}\text{C}^{14}\text{N}$

$\alpha\text{-P}_4\text{S}_3(^{15}\text{NCS})\text{Cl}$  (**3b**) by treatment with AgCl (50 °C, 5 days) to replace completely iodide but not thiocyanate. Low concentrations of  $\text{P}(^{15}\text{NCS})_3$  (**5**) and  $\text{ClP}(^{15}\text{NCS})_2$  (**6**), identified by their  $^{31}\text{P}$  chemical shifts<sup>2</sup> and expected multiplicities, appeared during slight, slow decomposition (20 °C, 15 weeks) of this solution. An attempt to convert the chloride (**3b**) further to  $\alpha\text{-P}_4\text{S}_3(^{15}\text{NCS})(\text{C}^{14}\text{N})$  by treatment with excess  $\text{Me}_3\text{SiCN}$  (20 °C, 28 h) failed to produce a useful yield because cyanide almost completely displaced thiocyanate, as well as chloride, on phosphorus. The  $^{15}\text{N}$ -isothiocyanates (**1b**), (**2b**), and (**3b**) all showed sharp  $^{31}\text{P}$  n.m.r. spectra at 300 K;  $^{15}\text{N}$  n.m.r. spectra were also measured and fitted for compounds (**1b**) and (**2b**). There was no evidence for chemical exchange on the n.m.r. timescale, and the spectra have been completely analysed assuming static AA'BB'XX' (**1b**) or ABCDX [(**2b**) and (**3b**)] spin systems. Preliminary results of variable temperature studies have shown in each case only small and systematic changes of coupling constants with temperature. Clearly the extreme broadening of  $\text{P}_B$  peaks of the  $^{14}\text{N}$  isotopomers was due to  $^{31}\text{P}$ - $^{14}\text{N}$  scalar coupling relaxation

effects. A simulation of a completely  $^{14}\text{N}$ -coupled  $^{31}\text{P}$  spectrum for the di-isothiocyanate (**1a**), using parameters calculated from those obtained for the  $^{15}\text{N}$  isotopomer (**1b**), bore little resemblance to the broadened spectrum observed at 300 K: the  $^{14}\text{N}$  relaxation rate was beyond the value at which splittings in the  $^{31}\text{P}$  spectrum caused by coupling to  $^{14}\text{N}$  had collapsed.

The mononuclear phosphorus(III) isothiocyanates showed large  $^1J(^{31}\text{P}\text{-}^{15}\text{N})$  coupling constants of 78.8 Hz for  $\text{P}(^{15}\text{NCS})_3$  (**5**) and 95 Hz for  $\text{ClP}(^{15}\text{NCS})_2$  (**6**), compared with 60.1 Hz for  $\text{P}(^{15}\text{NMe}_2)_3$  and 77.6 Hz for  $\text{ClP}(^{15}\text{NMe}_2)_2$ .<sup>3</sup> The values of  $^1J(^{31}\text{P}\text{-}^{15}\text{N})$  found for the  $\alpha\text{-P}_4\text{S}_3$  cage isothiocyanates were even larger: +103.64 Hz for  $\alpha\text{-P}_4\text{S}_3(^{15}\text{NCS})_2$  (**1b**), +104.52 Hz for  $\alpha\text{-P}_4\text{S}_3(^{15}\text{NCS})\text{I}$  (**2b**), and +103.9 Hz for  $\alpha\text{-P}_4\text{S}_3(^{15}\text{NCS})\text{Cl}$  (**3b**), the expected positive sign (*i.e.* negative  $^1K$ ) being confirmed [for (**1b**) and (**2b**)] by the correctly simulated asymmetry of the  $^{15}\text{N}$  multiplet. In phosphorus(III) compounds, large negative  $^1K_{\text{PN}}$  is associated with high s-orbital character of the phosphorus non-bonding electron pair, and hence with bond angles at phosphorus approaching 90°, and electronegative ligands. Although sulphur and phosphorus are less electronegative than, *e.g.* chlorine, the nature of the bonding in, and bond angles of, the  $\alpha\text{-P}_4\text{S}_3$  skeleton must have been peculiarly contributing to the negative  $^1K$ .  $\alpha\text{-P}_4\text{S}_3(^{12}\text{CN})(^{13}\text{CN})$  (**7**) has similarly been found to show a large (presumed negative)  $^1J_{\text{PC}}$  of -114 Hz.

Dr. M. N. S. Hill is thanked for obtaining the n.m.r. spectra, and the University of Newcastle Small Grants Research Sub-Committee for funding the purchase of  $\text{Na}^{15}\text{NCS}$ .

Received, 6th October 1988; Com. 8/03996H

## References

- 1 B. W. Tattershall, *J. Chem. Soc., Dalton Trans.*, 1987, 1515.
- 2 E. Fluck, *Z. Naturforsch., Teil B*, 1964, **19**, 869.
- 3 J. P. Gouesnard, J. Dorie, and G. J. Martin, *Can. J. Chem.*, 1980, **58**, 1295.