

## Carbon-13 and Phosphorus-31 Nuclear Magnetic Resonance Spectra of Some Symmetrical Long Chain Ditertiary Phosphines and the Carbon-13 Nuclear Magnetic Resonance Spectra of the Arsenic Analogues

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The proton noise decoupled pulsed Fourier transform  $^{13}\text{C}$  n.m.r. spectra of the long chain ditertiary phosphines and arsines of the general formula  $\text{Ph}_2\text{E}[\text{CH}_2]_n\text{EPh}_2$  ( $\text{E} = \text{P}$  and  $\text{As}$ ,  $n = 6-12$  and  $16$ ) have been examined. The range of significant carbon-phosphorus coupling in the phosphines studied is limited to a maximum of three bonds. The method for assigning each of the individual  $^{13}\text{C}$  resonances is discussed and the assignments are contrasted with those obtained for the corresponding linear alkanes. Systematic trends in the chemical shift parameter are observed and are explained in terms of the effect of the presence of phosphorus or arsenic atoms at both ends of the alkane chain. The  $^{31}\text{P}$  n.m.r. spectra of the phosphines have also been recorded. The correlation between the  $^{31}\text{P}$  chemical shift and the effective steric bulk of the polymethylene backbone has been examined for those ligands and compared to values reported for similar ditertiary phosphines with fewer methylene units present between the phosphorus atoms.

THE carbon-13 n.m.r. spectra of the linear alkanes up to n-decane and all the branched paraffins through the hexanes have been reported<sup>1-3</sup> and systematic trends in the chemical shift were observed. However, the trend observed for linear alkanes was not a simple one and can best be considered by dividing the linear alkanes into two distinct classes: (a) up to and including n-hexane and (b) those homologues with  $n > 6$ . The schematic spectrum of n-hexane is shown in Figure 1 and is typical of the first class of compounds.

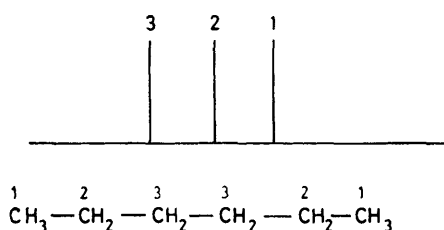


FIGURE 1 Schematic spectrum of n-hexane

The methyl carbon resonance C-1 appears at highest field while the methylene carbon resonances C-2 and C-3 appear at successively lower field. This regular trend in  $^{13}\text{C}$  chemical shift from high to low field as the number of methylene units increases does not continue when considering the homologues with  $n > 6$ . The schematic spectrum of n-decane is shown in Figure 2 and is again typical.

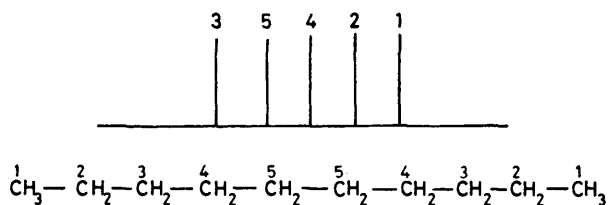


FIGURE 2 Schematic spectrum of n-decane

No satisfactory explanation of the phenomena has been presented although it has been suggested<sup>3</sup> that the possibility of pseudo-six-member ring formation with four carbon atoms in a chain and two attached hydrogens might provide an explanation of the anomalous position of the C-3 resonance either by mixing of higher paramagnetic orbitals or alteration in the degree of bond delocalization at the carbon atom.

The carbon-13 n.m.r. spectra of an extensive series of tertiary phosphines<sup>4</sup> and some polyphosphines with ethane bridges between trivalent phosphorus atoms<sup>5</sup> have been reported but until now no work has been published on diphosphines with large methylene chain bridges between trivalent phosphorus or arsenic nuclei. Not only are these compounds of interest as potential ligands<sup>6-11</sup> but a systematic examination of the  $^{13}\text{C}$  n.m.r. spectra would determine (a) whether pseudo-six-member ring formation is favoured by these alkane analogues and (b) allow the assignment of individual  $^{13}\text{C}$  resonances by the use of carbon-phosphorus coupling constants and by comparison with the spectrum of the corresponding diarsines.

$^{31}\text{P}$  N.m.r. studies have been made on the ligands  $\text{Ph}_2\text{P}[\text{CH}_2]_n\text{PPh}_2$  ( $n = 1-6$ )<sup>12</sup> and some unsymmetrical bisphosphorus ligands<sup>13</sup> and correlations were drawn between the magnitude of the  $^{31}\text{P}$  chemical shift parameter and the length of the methylene backbone. In this study the values obtained for the diphosphines examined are compared with the previously reported values and the steric requirement of the long polymethylene chains are compared with their shorter chain analogues.

### RESULTS AND DISCUSSION

The  $^{13}\text{C}$  n.m.r. spectra of the compounds  $\text{Ph}_2\text{E}[\text{CH}_2]_n\text{EPh}_2$  ( $\text{E} = \text{P}$  and  $\text{As}$ ,  $n = 6-12$  and  $16$ ) are shown in Tables 1-4. The spectra can most conveniently be divided into two distinct regions: (a) the aromatic

TABLE 1  
 $^{13}\text{C}$  N.m.r. data for the aromatic region of the ligands  $\text{Ph}_2\text{P}[\text{CH}_2]_n\text{PPh}_2$   
 Chemical shifts <sup>a</sup> and coupling constants <sup>b</sup>

Ligand	<i>ipso</i>	<i>ortho</i>	<i>meta</i>	<i>para</i>
$n = 6$ DPH	<i>c</i>	+132.7 (19.3 Hz)	+128.6	+128.3
$n = 7$ DPHP	+138.85 (13.3 Hz)	+132.58 (18.5 Hz)	+128.40	+128.11
$n = 8$ DPO	<i>c</i>	+132.7 (18.3 Hz)	+128.5	+128.2
$n = 9$ DPN	+138.4 (10.2 Hz)	+132.6 (18.2 Hz)	+128.5	+128.2
$n = 10$ DPD	<i>c</i>	+132.7 (18.9 Hz)	+128.6 (4.0 Hz)	+128.3
$n = 11$ DPU	+138.5 (11.2 Hz)	+132.7 (18.1 Hz)	+128.5	+128.2
$n = 12$ DPDOD	<i>c</i>	+132.8 (17.1 Hz)	+128.9	+128.6
$n = 16$ DPHD	<i>c</i>	+132.8 (17.7 Hz)	+128.8 (4.8 Hz)	+128.3

<sup>a</sup> Chemical shifts measured in p.p.m. relative to  $\text{Me}_4\text{Si}$  internal standard. <sup>b</sup> Coupling constants in parentheses. <sup>c</sup> Peak intensity too low to be measured.

TABLE 2  
 $^{13}\text{C}$  N.m.r. data for the aliphatic region of the ligands  $\text{Ph}_2\text{P}[\text{CH}_2]_n\text{PPh}_2$   
 Chemical shifts <sup>a</sup> and coupling constants <sup>b</sup>

Ligand	C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8
$n = 6$ DPH	+30.7 (11.8 Hz)	+25.5 (14.5 Hz)	+27.9 (11.0 Hz)					
$n = 7$ DPHP	+30.86 (12.7 Hz)	+22.77 (15.7 Hz)	+27.91 (11.2 Hz)	+28.73				
$n = 8$ DPO	+31.1 (12.7 Hz)	+26.0 (15.8 Hz)	+28.1 (11.3 Hz)	+29.0				
$n = 9$ DPN	+31.1 (12.8 Hz)	+25.9 (15.4 Hz)	+28.2 (9.5 Hz)	+29.1	+29.2			
$n = 10$ DPD	+31.1 (12.8 Hz)	+25.7 (14.5 Hz)	+27.6 (6.8 Hz)	+29.1	+29.2			
$n = 11$ DPU	+31.1 (12.7 Hz)	+25.9 (15.6 Hz)	+28.3 (9.9 Hz)	+29.2	+29.2	+29.4		
$n = 12$ DPDOD	+31.0 (13.3 Hz)	+25.4 (12.2 Hz)	+26.9 <sup>c</sup>	+29.2	+29.4	+29.4		
$n = 16$ DPHD	+31.0 (12.9 Hz)	+25.8 (14.6 Hz)	+27.6 (6.5 Hz)	+29.3	+29.6	+29.6	+29.6	+29.6

<sup>a</sup> Chemical shifts measured in p.p.m. relative to  $\text{Me}_4\text{Si}$  internal standard. <sup>b</sup> Coupling constants in parentheses. <sup>c</sup> No coupling observed.

TABLE 3  
 $^{13}\text{C}$  N.m.r. data for the aromatic region of the ligands  $\text{Ph}_2\text{As}[\text{CH}_2]_n\text{AsPh}_2$   
 Chemical shifts <sup>a</sup>

Ligand	<i>ipso</i>	<i>ortho</i>	<i>meta</i>	<i>para</i>
$n = 6$ DAH	+140.92	+132.95	+128.45	+128.11
$n = 7$ DAHP	<i>b</i>	+133.06	+128.53	+128.19
$n = 8$ DAP	+140.95	+133.05	+128.50	+128.16
$n = 9$ DAN	<i>b</i>	+132.90	+128.50	+128.06
$n = 10$ DAD	+141.21	+133.01	+128.46	+128.09
$n = 11$ DAU	<i>b</i>	+133.14	+128.62	+128.26
$n = 12$ DADOD	+141.10	+132.98	+128.45	+128.11
$n = 16$ DAHD	<i>b</i>	+133.13	+128.59	+128.24

<sup>a</sup> Chemical shifts measured in p.p.m. relative to  $\text{Me}_4\text{Si}$  internal standard. <sup>b</sup> Peak intensity too low to be measured.

TABLE 4  
 $^{13}\text{C}$  N.m.r. data for the aliphatic region of the ligands  $\text{Ph}_2\text{As}[\text{CH}_2]_n\text{AsPh}_2$  <sup>a</sup>  
 Chemical shifts

Ligand	C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8
$n = 6$ DAH	+31.14	+26.36	+27.91					
$n = 7$ DAHP	+31.42	+25.56	+28.13	+28.68				
$n = 8$ DAO	+31.63	+26.51	+28.07	+29.07				
$n = 9$ DAN	+31.40	+26.47	+28.04	+29.02	+29.08			
$n = 10$ DAD	+31.59	+26.56	+28.13	+29.17	+29.40			
$n = 11$ DAU	+31.73	+26.71	+28.27	+29.31	+29.58	+29.58		
$n = 12$ DADOD	+31.65	+26.51	+28.03	+29.03	+29.50	+29.56		
$n = 16$ DAHD	+31.79	+26.66	+28.20	+29.38	+29.78	+29.78	+29.78	+29.78

<sup>a</sup> Shifts measured in p.p.m. relative to  $\text{Me}_4\text{Si}$  internal standard.

region and (b) the aliphatic region. The most striking feature of the data is the fact that the chemical shifts of the individual  $^{13}\text{C}$  resonances are virtually unaffected by the nature of the donor atom present at both ends of the methylene chain; this fact makes assignment of both the diposphine and diarsine spectra an easier task by allowing direct comparison of the two sets of data. The range of significant carbon-phosphorus coupling is

limited to a maximum of three bonds in agreement with other reports.<sup>4,5,13</sup>

The aromatic region shows resonances for the *ortho*-, *meta*-, and *para*-carbons of the phenyl groups and in some cases the *ipso*-carbon can be observed as well.

The *ipso*-carbon does not possess a directly bound hydrogen atom and hence proton noise decoupling does not result in any nuclear Overhauser enhancement. In

the case of the diphosphines, when the *ipso*-carbon is observed it is split by coupling to phosphorus. The *ortho*-carbon resonances for the diphosphines are also coupled to phosphorus and appear as doublets in the  $^{13}\text{C}$  n.m.r. spectra. The values for  $^1J_{\text{P-C}}$  and  $^2J_{\text{P-C}}$  obtained

TABLE 5

Phosphorus-31 chemical shift data for the diphosphines

$\text{Ph}_2\text{P}[\text{CH}_2]_n\text{PPh}_2$  ( $n = 6-12$  and 16)

Ligand	Chemical shift <sup>a</sup>
$n = 6$ DPH	-15.5
	(+16.0) <sup>b</sup>
$n = 7$ DPHP	-15.6
$n = 8$ DPO	-15.6
$n = 9$ DPN	-15.65
$n = 10$ DPD	-15.7
$n = 11$ DPU	-15.5
$n = 12$ DPDOD	-15.65
$n = 16$ DPHD	-15.5

<sup>a</sup> Chemical shift measured relative to 85%  $\text{H}_3\text{PO}_4$  external standard ( $\text{CDCl}_3$  lock solvent). <sup>b</sup> From ref. 12.

from the *ipso*- and *ortho*-carbon resonances are in good agreement with literature values.<sup>4,5</sup> No coupling is observed for the *meta*- and *para*-carbons of the phenyl ring in the diphosphines except when  $n = 10$  or 16 where this coupling constants are *ca.* 4 Hz. These ligands are usually prepared from either triphenylphosphine or triphenylarsine both of whose  $^{13}\text{C}$  n.m.r. spectra show significant differences in the chemical shift parameter for all phenyl carbons when compared to these ligands, and therefore  $^{13}\text{C}$  n.m.r. is an ideal probe for the determination of ligand purity.

Comparison of the values for  $^1J_{\text{P-C}}$  and  $^2J_{\text{P-C}}$  shows that  $^2J_{\text{P-C}} > ^1J_{\text{P-C}}$ . This rather surprising observation is a general one for carbon-phosphorus coupling in phosphines<sup>4,5</sup> and is extremely useful in assigning individual resonances even though no satisfactory theoretical explanation has been put forward to explain these observations.

The aliphatic region contains only the  $^{13}\text{C}$  resonances assignable to the methylene bridge carbon nuclei. It is well known that carbon nuclei attached directly to phosphorus resonate at lowest field<sup>4,5</sup> and hence C-1 can easily be assigned and by comparison so can C-1 for the corresponding arsenic ligand (see Figure 3). The value of

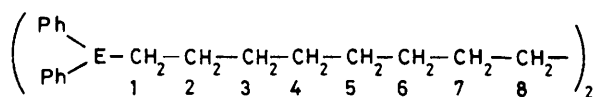


FIGURE 3 Number system used to designate individual carbon atoms in the methylene backbone of the ligands

the carbon phosphorus coupling constant ( $^1J_{\text{P-C}}$  *ca.* 10–13 Hz) is consistent with this assignment.

The second carbon present in the methylene backbone, C-2, resonates at highest field. This carbon is so identified as it possesses the largest carbon-phosphorus coupling constant of any of the observed resonances and is in the correct range for  $^2J_{\text{P-C}}$ ; again the corresponding arsenic resonance is assigned by comparison of chemical shifts with the phosphine analogue.

The third carbon present in the methylene backbone, C-3, is also coupled to phosphorus and again possesses a value of  $^3J_{\text{P-C}}$  in good agreement with literature values<sup>4,5</sup> and appears at a point between the high-field value for C-3 and the low field value for C-1. A schematic representation of the spectrum  $\text{Ph}_2\text{P}[\text{CH}_2]_6\text{PPh}_2$  is shown in Figure 4.

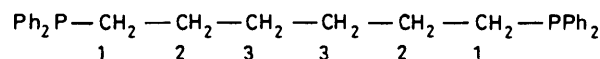
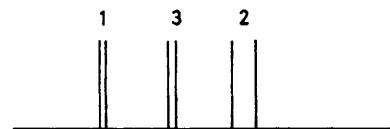


FIGURE 4 Schematic representation of the aliphatic region of the  $^{13}\text{C}$  n.m.r. spectrum of bis(diphenylphosphine)hexane

Assignment of the C-4 resonance in the case of the ligand bis(diphenylphosphino)heptane is rather more difficult. In this case the C-1, -2, and -3 resonances are all split into doublets and the C-4 resonance appears as a singlet. However, there are two equivalent carbons for each of the C-1, -2, and -3 resonances and only one for C-4.

The spectrum appears as a seven line system, with all lines of equal intensity. It is a reasonably straightforward matter to assign C-1 and -2 in this spectrum but absolute assignment of C-3 and -4 can only be made by comparison with the corresponding arsine, bis(diphenylarsino)heptane. This spectrum does not, of course, exhibit any coupling whatsoever so the C-4 resonance should be roughly half the height of the others and is shown schematically in Figure 5.

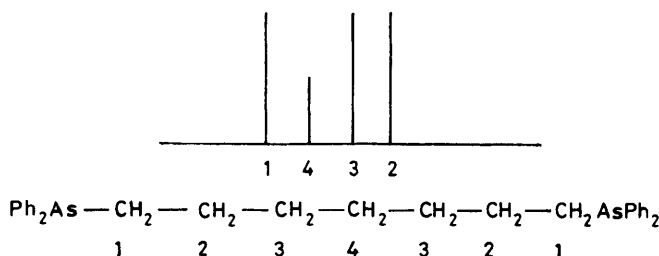


FIGURE 5 Schematic spectrum for bis(diphenylarsino)heptane

Even though the spectrum is N.O.E. enhanced and absolute integration of the peak areas cannot be used with any confidence, and relative size of the peaks allows us to distinguish between and assign peaks C-3 and -4 as does comparison of the position of the C-3 resonance in DAHP with the position of the C-3 resonance in the unequivocally assigned bis(diphenylarsino)hexane. Comparison of the arsine spectrum with the corresponding phosphine allows us to assign the C-3 and -4 resonances in bis(diphenylphosphino)heptane.

The other carbon resonances are assigned in a similar fashion, *i.e.* by comparison of the corresponding diarsine

and diphosphine spectra and with the spectra of the preceding members in the series. The clearest comparison with n-decane<sup>3</sup> can be made by considering the spectrum of bis(diphenylarsino)decane where there is no carbon-phosphorus coupling to complicate the spectrum (see Figure 6). The ordering of the carbon resonances is

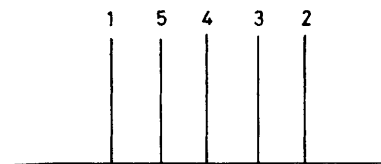


FIGURE 6 Schematic spectrum for bis(diphenylarsino)-decane

clearly different from that of n-decane and the spectrum of the diphosphine and diarsine substituted hexanes is also different from n-hexane.

The reasons for the differences between the linear alkanes and their  $\alpha,\omega$ -substituted diphosphine or diarsine analogues may be explained as follows. First, the presence of phosphorus or arsenic attached to C-1 reduces the effective shielding about the C-1 nucleus causing it to resonate at lowest field; secondly, the presence of the bulky diphenylarsino- or diphenylphosphino-groups on the  $\alpha$ - and  $\omega$ -positions in the alkane chain prevents the formation of the pseudo-six-membered rings thought responsible for the anomalous chemical shift values for the C-3 resonances in the linear alkanes thus making the C-3 resonance position unexceptional when compared with the other carbon atoms in the bis(diphenylphosphino)- or bis(diphenylarsino)-alkanes.

<sup>31</sup>P N.m.r. Spectra.—In monodentate tertiary phosphines one of the most important parameters determining <sup>31</sup>P chemical shift is the steric bulk of the substituent groups attached to the phosphorus atom.<sup>4,14,15</sup> The other important parameter affecting  $\delta(^{31}\text{P})$  in general is the electronegativity of substituents at phosphorus. However, in this study all substituents are of almost identical electronegativity to one another and to that of phosphorus<sup>15</sup> and so this factor can be ignored. Thus,  $\delta(^{31}\text{P})$  may be used as an extremely sensitive means of measuring the effective steric bulk of the substituents around the phosphorus.

In symmetrical diphosphines with shorter chelate backbones<sup>12</sup> and for diphosphines of the types  $\text{R}_2\text{P}[\text{CH}_2]_n\text{PPh}_2$  (R = Me and Et,  $n = 3$  and 4) and  $\text{EtPhP}[\text{CH}_2]_n\text{PPh}_2$  ( $n = 3, 4$ , and 6),<sup>13</sup> the length of the polymethylene chain plays a crucial role in determining the value of the phosphorus-31 chemical shift. The series  $\text{EtPhP}[\text{CH}_2]_n\text{PPh}_2$  ( $n = 3, 4$ , and 6) shows a decrease in chemical shift

with increasing chain length for both phosphorus nuclei. Thus, the longer the polymethylene chain, the greater is the steric bulk of the  $\text{RPPH}[\text{CH}_2]_n$  or  $\text{Ph}_2\text{P}[\text{CH}_2]_n$  group, presumably due to the greater flexibility of the backbone as the number of methylene units increases. This was also shown to hold true for the symmetrical series  $\text{Ph}_2\text{P}[\text{CH}_2]_n\text{PPh}_2$  ( $n = 1-6$ ).<sup>12,13</sup>

The phosphorus-31 chemical shift data for the diphosphines  $\text{Ph}_2\text{P}[\text{CH}_2]_n\text{PPh}_2$  ( $n = 6-12$  and 16) is shown in Table 5. It appears from these that the phosphorus-31 chemical shift values remain constant and do not move to lower field as the length of the methylene chain increases. Thus, a chain length of six methylene units appears to be that which exerts the largest steric influence on the phosphorus nucleus and chain lengths greater than six do not greatly affect this optimum value. This indicates that substituent groups placed a distance of at least six carbon atoms away from phosphorus do not exert any influence on the donor phosphorus atom.

#### EXPERIMENTAL

The preparation of the ligands is described elsewhere.<sup>16,17</sup> The <sup>31</sup>P and <sup>13</sup>C n.m.r. spectra were obtained on a Varian CFT-20 spectrometer. All spectra were recorded using  $\text{CDCl}_3$  as lock solvent.

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