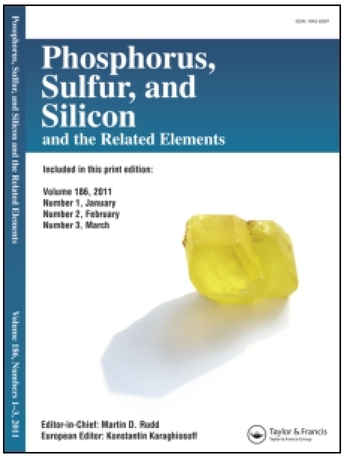

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A LINEAR CORRELATION BETWEEN THE P-31 NMR SHIFTS OF CYCLIC PHOSPHINES AND THE 0-17 SHIFTS OF THE CORRESPONDING PHOSPHINE OXIDES

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A LINEAR CORRELATION BETWEEN THE P-31 NMR SHIFTS OF CYCLIC PHOSPHINES AND THE O-17 SHIFTS OF THE CORRESPONDING PHOSPHINE OXIDES

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The O-17 NMR shifts for phosphine oxides based on six different heterocyclic ring systems, representing 16 data points, were plotted against the P-31 shifts of the corresponding phosphines. A linear correlation with R = 0.96 resulted. Each heterocyclic system occupied its own region of the correlation line, with no overlap. There was no correlation between the O-17 NMR shifts and the P-31 shifts of the phosphine oxides.

Key words: Phosphorus NMR, oxygen NMR, phosphine oxides, phosphines, aminophosphines.

We recently reported[1] that ^{17}O NMR shifts for cyclic phosphine oxides were very sensitive to structural changes, and a range of about 77 ppm was observed for the compounds examined. The most striking observation was the far downfield ^{17}O shifts (δ100–116) recorded for some phosphine oxides having the 7-phosphanorbornene framework with a *syn* P-substituent. In later work,[2] the range was extended in the upfield direction to δ18, found for an oxide with the 3-membered ring of a phosphirane. With a range of about 100 ppm, one must regard the ^{17}O shift as having the potential for structural diagnostic value. We then realized that exactly the same structural types give rise to the two extremes of shifts of ^{31}P NMR for tertiary *phosphines,* with the *syn*-substituted 7-phosphanorbornene phosphines giving the most downfield shifts for phosphines known, and phosphiranes the most upfield. The range of shifts is a remarkable 350 ppm. This observation has led us to plot the ^{17}O NMR shifts of a number of tertiary phosphine oxides against the ^{31}P shifts of the corresponding tertiary phosphines, and as shown in Figure 1, there is a good correlation. A great variety of structural types (shown in Table I) are included in this plot of 16 data points, lending strength to the suggestion that there is a definite relation between what appear to be two very different properties. Had the ^{17}O correlation been found with the ^{31}P shifts of the phosphine oxides, the discovery would have been less surprising. However, there is definitely no relation between these parameters. Thus, as an illustration one could compare the values for the *syn* and *anti* isomers of the 7-phosphanorbornene system; compounds **11** and **14** have nearly the same ^{31}P NMR shifts (δ81.1 and 83.3, respectively) but differ by 55.6 ppm in their ^{17}O NMR shifts.

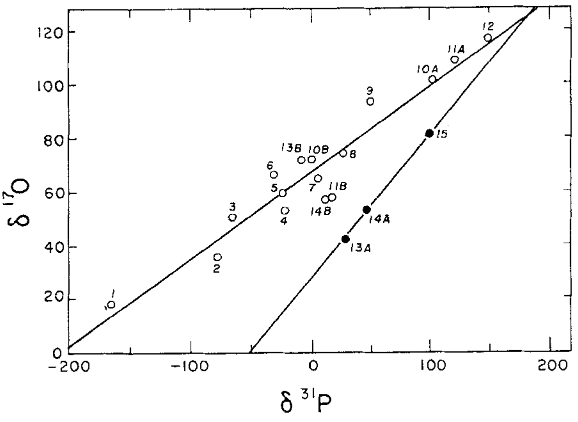


FIGURE 1 A plot of ^{17}O NMR shifts of phosphine oxides *vs.* ^{31}P shifts of phosphines using data from Table I. The lower line includes only data for *anti*-7-phosphanorbornene derivatives. The correlation coefficient is 0.96.

In spite of the generally good correlation seen over the wide shift ranges of Figure 1, it is not possible to use the plot to predict shifts for similar compounds that differ in structure at close proximity to the ^{17}O and ^{31}P nuclei. This is in part due to the fact that a structural effect may influence these nuclei in opposite ways. Thus, a carbon substituent that is *beta*- to ^{31}P (hence causing deshielding in a tertiary phosphine[3]) will be *gamma*- to ^{17}O in the oxide and cause an upfield shift.[1] Similarly, replacement of alkyl on a tertiary phosphine by phenyl causes a downfield ^{31}P shift, but generally (with exceptions) an upfield ^{17}O shift.[1] Such effects seem responsible for some of the dispersion of the data around the correlation line. The success of the correlation seems to arise from the dominance of the structure of the ring over all other factors. The data points on Figure 1 for a particular ring system are clustered in unique locations on the plot, with no overlap among ring types.

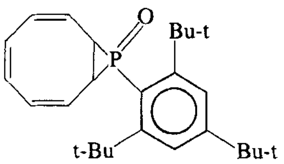
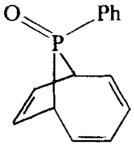
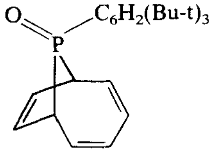
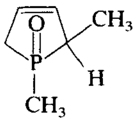
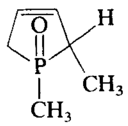
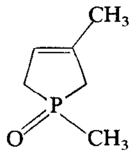
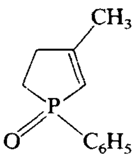
The *anti* isomers of the 7-phosphanorbornene derivatives are not well correlated by the main line of Figure 1. A plot of the NMR data for three such structures gives a separate straight line, shown also on Figure 1. This is the only ring type found so far that requires a different correlation line. However, the same trend in the ^{17}O—^{31}P relation is present.

The correlation we have observed is not restricted to the couple phosphine-phosphine oxide. Although data are only available for compounds with the phosphole dimer-framework at this time, the relation between ^{31}P shifts of aminodialkylphosphines and the ^{17}O shifts of the corresponding oxides (phosphinamides) is of the same nature (Table II). Thus, the ^{31}P shift of a *syn*-7-aminophosphine[4] shows the very strong deshielding as found in the tertiary phosphines, and the corresponding oxide has a ^{17}O shift that is similarly far downfield.

Variations in electron density are the cause of major chemical shift effects for nuclei sensitive to paramagnetic shielding. The ^{31}P—^{17}O correlation seems to suggest that the structural factors influencing the electron density on ^{31}P of a

TABLE I[a]

NMR spectral data for tertiary phosphines oxides and phosphines

Compound		Phosphine oxide			Phosphine
		$\delta\,^{17}$O	J(PO)	$\delta\,^{31}$P	$\delta\,^{31}$P
1[2]		18.0[2]	166[2]	-38[2]	-166[2]
2[6]		36.1	180	+38[6]	-79[6]
3[2]		50.5	167	+27.3[7]	-67.0[2]
4[8]		53.1[1]	167[1]	+62.4[7]	-23.7[7]
5[8]		59.2[1]	182[1]	+70.5[7]	-24.8[7]
6[8]		66.0[1]	164[1]	+64.6[7]	-32.5[7]
7[8]		64.7[b]	163[b]	+60.5[9]	+3.6[7]

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[a] Reference citations by the compound numbers indicate the compound source. O-17 NMR measurements were made as described previously.[1] NMR entries without reference numbers describe results of the present study.[1]

[b] Data first reported in Reference 1 were incorrectly listed and are revised in this Table.

TABLE I[a] *Continued*

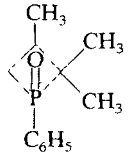
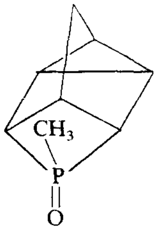
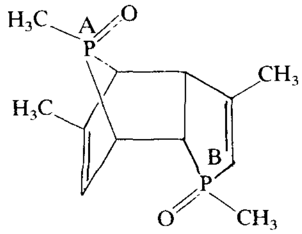
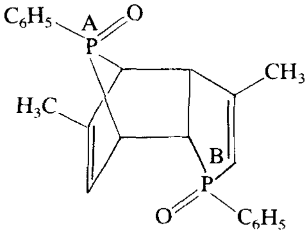
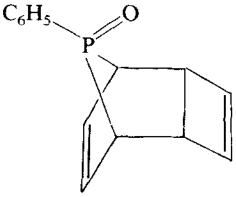
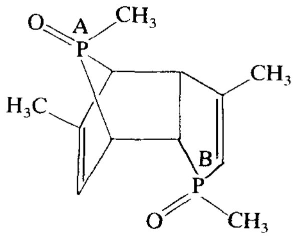
Compound	Phosphine oxide			Phosphine
	$\delta\ ^{17}O$	$J(PO)$	$\delta\ ^{31}P$	$\delta\ ^{31}P$
8[10] 	74.0[1]	175	+43.8[10]	+25.3[11]
9[10] 	93.1[1]	179[1]	+55.2[11]	+47.5[11]
10[11] 	A: 100.8[1] B: 71.8[1]	163[1] 160[1]	+86.8[11] +60.8[11]	+100.7[12] −1.9[12]
11[11] 	A: 108.3[1] B: 57.3[1]	137[1] 133[1]	+81.7[11] +55.1[11]	+119.8[12] +15.0[12]
12[6] 	116.4[1]	183[1]	+95.0[13]	+146.6[13]
13[11] 	A: 42.1[1] B: 71.5[1]	175[1] 163[1]	+87.5[11] +63.4[11]	+26.5[14] −9.6[14]

TABLE I[a] *Continued*

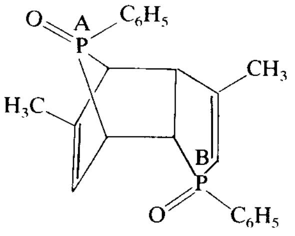
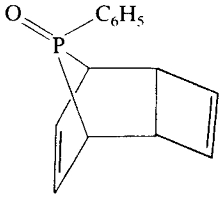
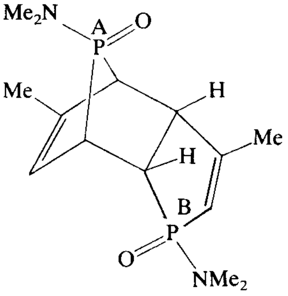
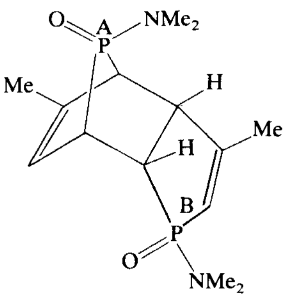
Compound	Phosphine oxide			Phosphine
	δ ^{17}O	J(PO)	δ ^{31}P	δ ^{31}P
14[7] 	A:52.7[1] B:56.5[1]	127[1] 122[1]	+83.3[7] +57.6[7]	+44.9[14] +9.9[14]
15[6] 	80.9[1]	181[1]	+98.8[14]	+98.8[14]

TABLE II

NMR spectral data[4] for phosphinamides and aminophosphines

Compound	Phosphinamide		Aminophosphine
	δ ^{17}O	δ ^{31}P	δ ^{31}P
16 	A: 102.7 B: 77.1	83.0 64.8	163.0 65.0
17 	A:48.9 B:75.5	83.1 64.5	89.9 61.2

phosphine are capable of transmitting their effect through this nucleus to a ^{17}O atom bonded to it. This simplistic view does not speak to the randomness of the ^{31}P shifts in the resulting phosphine oxides, and leaves unaddressed also the apparent insensitivity of the one-bond ^{31}P—^{17}O coupling constants to structural effects that cause major changes in chemical shifts. Most of the compounds included in this study have coupling constants of 160–180 Hz; even oxides that differ in ^{17}O shifts by as much as 100 ppm fall within this range. A recent study[5] of phosphoryl compounds other than phosphine oxides suggests that the observed constant is composed of contributions from three different coupling mechanisms, namely, Fermi contact, spin-dipole, and orbital, with the latter in dominance and compensating effects in operation. It is possible that compensating effects are involved in the family of cyclic phosphine oxides as well, thus accounting for the apparent lack of relation to structural change.

EXPERIMENTAL

Compounds. All compounds were available from previous studies; references are provided in Tables I and II.

0-17 *NMR Measurements.* Chemical shifts were determined at 40.662 MHz on a Varian XL300 spectrometer, using solutions in CD_3CN at 70°C. Shifts are downfield of water as 0 ppm. Other details are given in Reference 1. Only spectra for **2** and **3** have not been previously reported; data for **7** are corrected values for those previously reported.[1] All other data appear in Reference 1.

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