^{13}C Nuclear Magnetic Resonance of Organophosphorus Compounds: Triphenyl Phosphite and Triphenyl Phosphate

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Summary The ^{13}C n.m.r. spectra of triphenyl phosphite and triphenyl phosphate show significant differences in chemical shifts and C–P coupling constants.

NATURAL ABUNDANCE ^{13}C n.m.r. spectra of phenoxy-substituted phosphorus compounds demonstrate the power of ^{13}C resonance in structure studies. In particular, the ^{13}C spectra of triphenyl phosphite and triphenyl phosphate show significant differences in both ring carbon chemical shifts and P–C coupling constants. These differences result solely from the change in co-ordination and, therefore, bonding characteristics of the relatively remote phosphorus atom.

Utilization of complete ^{1}H decoupling by noise modulation at 100 MHz[1] permits determination of P–C coupling to all positions of the phenyl rings.[2] The spectra (Figures 1 and 2) were recorded on a Varian XL-100-15 spectrometer at 25·2 MHz. Internal field/frequency lock was obtained in deuterium lock mode from $(CD_3)_2CO$ solvent (*ca.* 50% v/v). Chemical shifts are reported in p.p.m. downfield from tetramethylsilane, using benzene as secondary internal standard (= 129·7 p.p.m.). Satisfactory single-scan spectra were recorded using 12 mm spinning tubes. Achieved resolution was *ca.* 0·5 Hz at a sweep rate of 0·5 Hz/s.

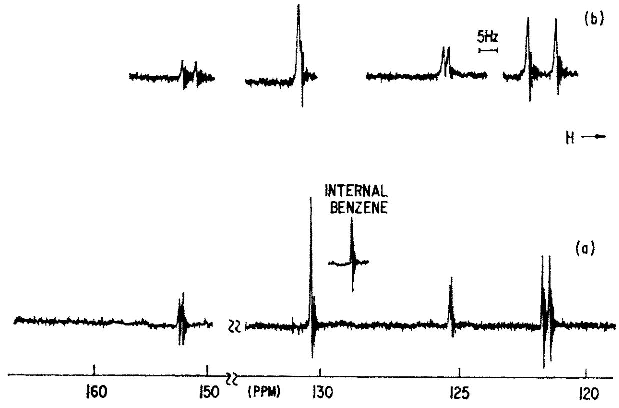

FIGURE 1. *Triphenyl phosphite.* (a) 1000 *Hz sweep width*; (b) *enlarged to* 250 *Hz sweep width.*

Assignments (see Table) for the lower intensity ring carbons were confirmed by off-resonance partial ^{1}H decoupling. Assignments of resonances to *ortho*- and *meta*-carbons were based on the larger *ortho* coupling and also on chemical-shift parameters.[3]

It is interesting to note that P–C coupling extends through the entire phenyl ring. In triphenyl phosphite, spin–spin coupling from the phosphorus to the first ring carbon (site of substitution) is smaller (3·2 Hz) than the coupling to the *ortho*-carbon (6·7 Hz). This is not unusual for phosphorus–carbon coupling.[4] In triphenyl phosphate, the phosphorus coupling to the first ring carbon is larger (7·2 Hz) than to the *ortho*-carbon (5·0 Hz). A similar switchover for quadrivalent phosphorus compounds has been noted in the P–H coupling constants of an aliphatic phosphite–phosphate pair.[5] As can be seen in the Table, all chemical shifts are affected by the change in phosphorus co-ordination. As expected, the change in *meta*-carbon chemical shift is least significant. On the other hand, the *para*-carbon resonance in triphenyl phosphate, 1·2 p.p.m. downfield of the analogous signal in triphenyl phosphite, mirrors the larger electron withdrawal in the phosphate.

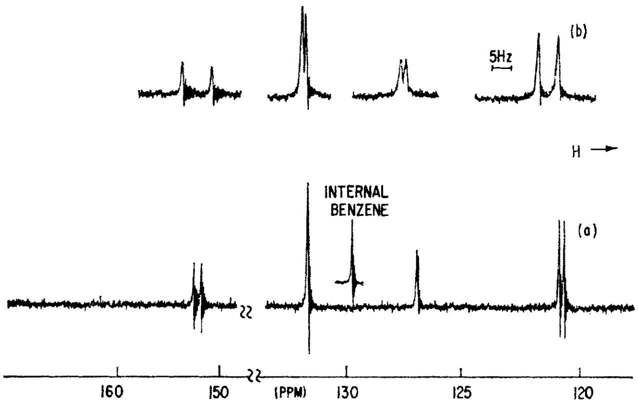

FIGURE 2. *Triphenyl phosphate.* (a) 1000*Hz sweep width*; (b) *enlarged to* 250*Hz sweep width.*

TABLE

^{13}C *Chemical shifts and* C–P *coupling constants*[a]

	C–O–P	C_{ortho}	C_{meta}	C_{para}
Triphenyl phosphite				
Chemical shift	153·2	122·1	131·3	125·9
$J_{C,P}$	3·2	6·7	< *ca.* 0·5	1·3
Triphenyl phosphate				
Chemical shift	152·2	121·4	131·4	127·1
$J_{C,P}$	7·2	5·0	0·9	1·5

[a] Chemical shifts ± 0·1 p.p.m.; coupling constants ± 0·1 Hz (sign unspecified).

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[1] (a) R. R. Ernst, *J. Chem. Phys.*, 1966, **45**, 3845; (b) Varian Associates, Palo Alto, California, U.S.A.

[2] ^{13}C–^{13}C Coupling not observable due to low isotopic abundance.

[3] J. W. Emsley, J. Feeney, and L. H. Sutcliffe, "High Resolution Nuclear Magnetic Resonance Spectroscopy," Vol. 2, Pergamon, London, 1966, p. 1004.

[4] D. E. Dorman and J. D. Roberts, *Proc. Nat. Acad. Sci. U.S.A.*, 1970, **65**, 19; F. J. Weigert, Ph.D. Thesis, California Institute of Technology, 1968.

[5] E. J. Boros, *et al.*, *J. Amer. Chem. Soc.*, 1966, **88**, 1140.