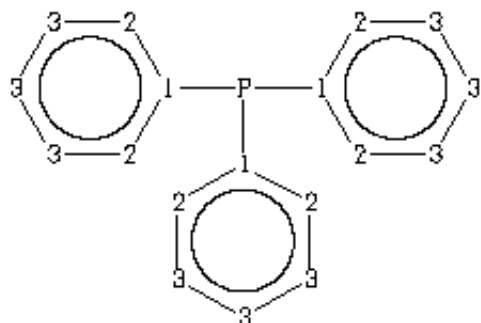
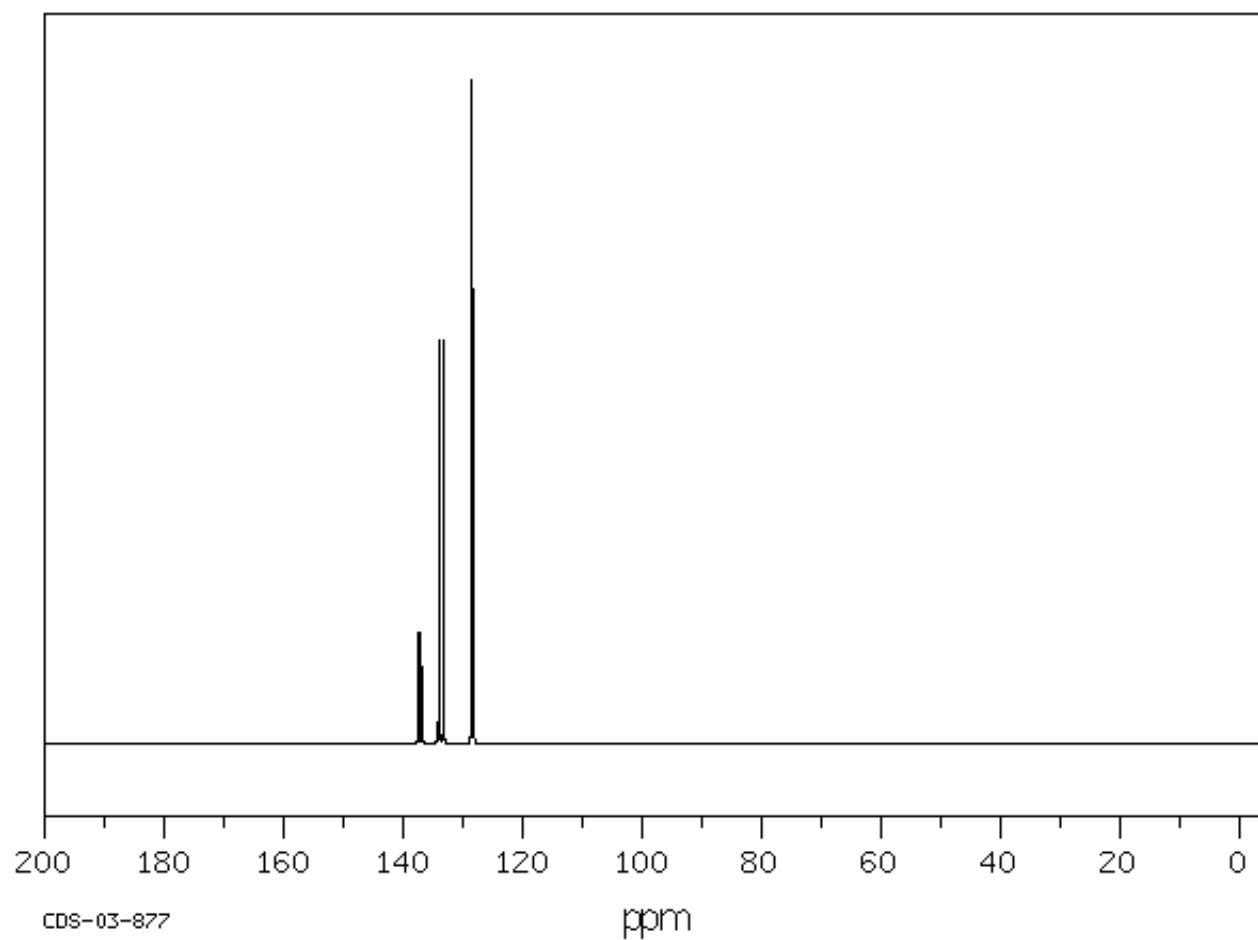


SDBS-¹³C NMRSDBS No. 2967CDS-03-877C₁₈ H₁₅ P**triphenylphosphine**

25.16 MHz

0.48 g : 1.5 ml CDCl₃

ppm	Int.	Assign.
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137.42	243	P 1
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136.97	243	P	1
134.04	897	P	2
133.25	897	P	2
128.53	471		3
128.53	1000	P	3
128.26	1000	P	3

SDBS No. 2967CDS-03-877

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Proton Magnetic Resonance and Electronic Spectra of Triphenylphosphine

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MAVEL¹ has found that the 25 Mc./sec. proton magnetic resonance spectrum of triphenylphosphine in cyclohexane solution is a single peak, whereas other workers²⁻⁴ using different solvents have observed two peaks of unequal height with a separation of about 4 c./sec. at 60 Mc./sec. In some cases^{3,4} the separation between these peaks has been assigned, incorrectly, to a chemical shift.

We have examined the proton magnetic resonance of triphenylphosphine in several organic solvents at 60 Mc./sec. (and at 32°C, except where stated otherwise). Relatively concentrated solutions give a single peak; for example, a 1.5M solution in deuteriochloroform gives an asymmetric peak at $\tau = 2.8$ p.p.m. with a half-width of about 3 c./sec. In dilute solutions ($<1M$) a doublet (splitting = 3.5 ± 0.2 c./sec.) is seen, in which the relative heights and widths of the two peaks are concentration-dependent, while the areas under them remain equal, within the limits of accuracy of our measurements. Spectra at four different concentrations in deuteriochloroform are shown in Figure 1. The ratio of the height of the up-field peak to the down-field peak is about 2:1 in a 0.72M solution, changing gradually to about 1:2 in a 0.09M solution.

The same phenomenon occurs over a similar range of concentrations in tetrahydrofuran, acetone, and carbon disulphide. In the two latter solvents each component of the doublet shows additional smaller, partly resolved, splittings.

The ratio of peak heights is also temperature-dependent: in a dilute solution in tetrahydrofuran at 60°C the relative height of the up-field peak is greater than at 32°C.

The equality of areas in the doublet under all conditions suggests that the 3.5 c./sec. splitting is due to proton-³¹P coupling, and this interpretation has been confirmed by heteronuclear spin decoupling experiments on the 40 Mc./sec. proton spectrum.⁵ In solutions in deuteriochloroform covering the concentration range 0.09–1.44M double irradiation at 16.2 Mc./sec. decouples the ³¹P nucleus; the proton resonance then collapses to a single peak with a half-width less than 2 c./sec.

We conclude from these results that each component of the doublet corresponds to one spin state of the ³¹P nucleus, and presumably each contains the resonances of the *ortho*-, *meta*-, and *para*-protons of the benzene rings. The suggested scheme is shown in Figure 2. The fine structure

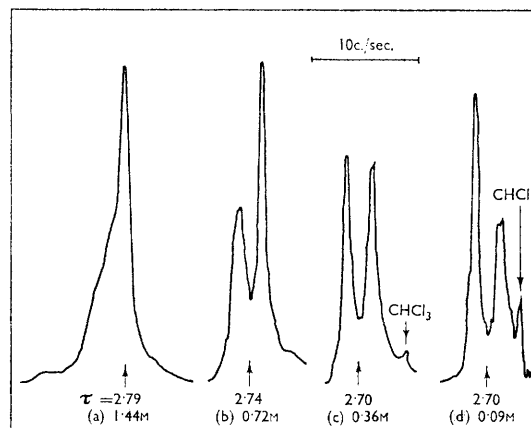


FIGURE 1

60 Mc./sec. ¹H n.m.r. spectrum of triphenylphosphine in CDCl₃

arising from chemical-shift differences, with additional multiplicity due to proton-proton coupling, is not resolved in practice and only two composite peaks are observed. The relative chemical shifts are expected to be dependent on concentration and temperature because of molecular interactions (magnetic anisotropy, electric reaction field, and van der Waals forces may all contribute), and this dependence would account for the observed changes in the peak widths. At relatively high concentrations (Figure 1a) the down-field peak is apparently so broad that it merges with the up-field peak.

The differences in chemical shifts between ring protons are small, in striking contrast to phosphines of the type Ph₂RP and PhR₂P, where R is H or alkyl, and arylphosphine oxides. A similar effect is seen in the spectrum of triphenylarsine,

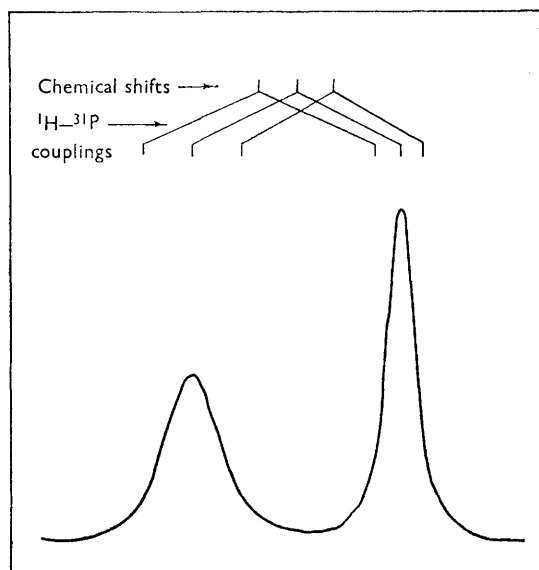


FIGURE 2

Schematic chemical shifts and couplings

where only a single peak of half-width 2 c./sec. is observed. The coupling constants between ^1H and all the ring protons are similar, with an average value of 3.5 c./sec. By contrast, in the ^{31}P spectra of Ph_2PH and PhPH_2 , Akitt *et al.*⁶ found $J_{\text{P-H}}(\text{ortho}) = 7.9$ and 6.6 c./sec. respectively. Similarly, in a series of triarylphosphine oxides with *para*-substituents, $J_{\text{P-H}}(\text{ortho})$ ranged from 10.5 to 11.5 c./sec., and $J_{\text{P-H}}(\text{meta})$ from 2.1 to 3.4 c./sec.⁷

In an attempt to find an explanation for these results, we have also recorded the electronic spectra of several arylphosphines, phosphine oxides, and arsines. For the trivalent phosphine and arsine compounds most workers⁸ have reported only one band in the region 230–270 $\text{m}\mu$. However, Cullen and Hochstrasser⁹ performed a Gaussian analysis on the spectra of the phenylarsines and found a second band hidden under the long-wavelength tail of the main absorption.

By a similar analysis we find a corresponding weak band in the spectra of the phenylphosphines (Table). Accepting Cullen and Hochstrasser's assignment of the weak band as a $\pi \rightarrow \pi^*$ transition and the intense band as an $n \rightarrow \pi^*$ or charge-transfer transition we propose a similar assignment for the phosphines. The low-intensity and small bathochromic shift of the second band indicates that the conjugation is not nearly as strong in arylphosphines as had been supposed. The spectra indicate, however, that conjugation in triphenylphosphine, although small, is larger than in the other arylphosphines.

TABLE. Electronic spectra of phosphines and phosphine oxides in ethanol

Compound	$\lambda_{\text{max}}(\text{m}\mu)$	ϵ_{max}	$\lambda_{\text{max}}(\text{m}\mu)$	ϵ_{max}
PhEt_2P	252.8	3300	273.2	140
Ph_2EtP	251.3	8090	277.8	950
Ph_3P	261.4	11,000	281.7	1250
Ph_2EtPO			265.0	1370

These n.m.r. and spectral results can be explained if it is assumed that the key mechanism is the interaction of the phosphorus $p(\pi)$ -orbitals with the π -orbital systems of the benzene rings. In triphenylphosphine the molecular geometry¹⁰ prevents rotation of the benzene rings about the C–P bond. The rings are therefore held in positions where a small but appreciable overlap occurs between the π -orbitals of the benzene rings and the phosphorus lone-pair orbitals. It seems possible that this interaction, acting in opposition to the inductive effect, causes the chemical shift differences to be less in triphenylphosphine than in mono- or di-phenylphosphines where relatively free rotation of the rings is possible and p – π orbital overlap becomes negligible. It also seems likely that proton– ^{31}P coupling in triphenylphosphine occurs mainly through a mechanism involving the π -orbital system of the benzene rings, whereas in the other phosphines (Ph_2RP , PhR_2P) and phosphine oxides the dominant effect is one involving σ -orbitals.

(Received, May 25th, 1966; Com. 353.)

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