^{1}H Nuclear Magnetic Resonance Study of *para*-Substituted Derivatives of Triphenylphosphine

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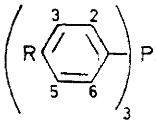
A ^{1}H n.m.r. investigation into *para*-substituted triarylphosphine derivatives is reported. For compounds showing a small chemical shift difference between *ortho*- and *meta*-protons, spectral analysis proved difficult owing to the relatively small number of observable transitions; in the cases of the tri-*para*-deuterio-derivative and the corresponding phosphonium salt, only approximate values of chemical shifts are reported. The electronic behaviour of the groups $\geqslant$P, $\geqslant$P(O), $\geqslant$P(S), and $\geqslant$P$^+$ interacting with a phenyl ring, derived from chemical shift measurements, is interpreted in terms both of substituent additivity constants and of Hammett substituent parameters. Long-range ^{31}P–^{1}H coupling constants are discussed in terms of hybridization at the phosphorus atom, *d*-orbital participation in $(p\text{–}d)_\pi$ conjugation, and molecular geometry by comparing the experimental results with semiempirically calculated values.

SEVERAL n.m.r. studies (both ^{1}H and ^{31}P) of derivatives of substituted triphenylphosphines and heteroaromatic phosphines have been reported.[1–7] Long-range proton–phosphorus coupling constants obtained from a large number of saturated, ethylenic, heterocyclic, and aromatic phosphorus derivatives were found to show sensitivity to hybridization at phosphorus.[1–6, 8–12] Appreciable changes in long-range $J(^{31}\text{P} \cdots \text{H})$ values are produced by phosphorus quaternization,[1,3,5,7–9,11–13] and the relative orientation of the phosphorus lone-pair and the relevant C–H bond in phosphines also seems[10,11,13] to be of considerable importance in determining the sign and magnitude of these coupling constants.

Experimental data for *para*-substituted triphenylphosphines are available only for a small number of substituents.[5,14] We have therefore synthesized a number of compounds containing a range of substituents with various electronic properties and have carried out ^{1}H n.m.r. measurements to investigate changes in electronic interactions between the phosphorus atom and the phenyl ring with various *para*-substituents. We have also attempted to obtain similar information for other series of compounds with different co-ordination at the phosphorus atom, resulting from replacing the lone-pair with oxygen or sulphur or by quaternization. The range of substituents selected is felt to be large enough for a definite behaviour to be assigned to each series.

RESULTS

The spectra of compounds (1)—(4) were recorded in various solvents and, in some cases, at various concentrations. Selected results are reported in Table 1. The



(1a–e) X = lone pair
(2a–f) X = O
(3a–e) X = S
(4a,b,d,and e) X = MeI

a; R = D
b; R = Cl
c; R = Br
d; R = OMe
e; R = Me
f; R = NMe$_2$

spectrum of triphenylphosphine was not taken into account, since, owing to the small chemical shift difference[14] between the three different types of protons, it is almost impossible to obtain information on the large number of n.m.r. parameters involved in determining the experimental spectrum. Instead we considered the 4-deuterio-derivative (1a), the spectrum of which differs, at first sight, from that of triphenylphosphine only insofar as the ratio of the two main peak[14] areas is 2 : 2 the *para*-proton signal disappears from the low-field band.

All the parameters reported in Table 1 were obtained by iterative analysis by use of the LAOCOON 3 program,[15] according to an AA′BB′X spin system. When the internal chemical shift, Δν, approximates to zero the

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[2] C. E. Griffin, *Tetrahedron*, 1964, **20**, 2399.

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[12] B. I. Ionin and T. N. Timofeeva, *Russ. Chem. Rev.*, 1972, **41**, 390.

[13] G. Mavel, ' Nouveaux apports de la RMN a la connaissance structurale des composes organo-phosphores,' Coll. nat. Centre nat. Res. sci., n. 182, Paris, 1970.

[14] G. Shaw, J. K. Becconsall, R. M. Canadine, and R. Murray, *Chem. Comm.*, 1966, 425.

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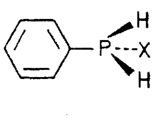
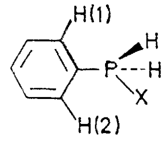
spectrum consists of two strong resonances, separated by *ca.* 4·3 Hz, and two sets of low-intensity transitions are located at their outer sides. These low-intensity resonances can be lost in the experimental spectrum if no strong magnification is employed; even so some of them may be obscured by noise. When $J(^{31}P \cdots H_o)$ or $J(^{31}P \cdots H_m)$ or both are set equal to 4 Hz, the calculated spectrum still consists of two strong peaks with a separation of about this amount, but the low-intensity transitions disappear. Iterative analysis of the experimental spectrum of (1a) was not possible owing to the small number of observed experimental transitions, and the output parameters are indeterminate. Direct inspection of the spectrum does not allow values of the order of 3·5—4 Hz to be conclusively assigned to $J(^{31}P \cdots H_o)$ and $J(^{31}P \cdots H_m)$, as previously reported.[14] By employing a Δν value of 0·6 Hz (*ortho*-protons at lower field) and a set of coupling constants very similar to those of the other *para*-substituted phosphines, a spectrum is obtained that is almost identical, even in the low-intensity transitions, with the experimental one, with the high-field band slightly broader (the transitions accumulated in this band differ from each other in frequency slightly more than those accumulated in the other band), as observed. For this reason, a small chemical shift difference between *ortho*- and *meta*-protons is reported in Table 1 for compound (1a). We feel, therefore, that in tris-*p*-deuteriophenylphosphine, and consequently in triphenylphosphine, $J(^{31}P \cdots H_o)$ and $J(^{31}P \cdots H_m)$ should not present anomalous values. Other evidence reported in the Discussion section supports this conclusion.



(a)



(b)

TABLE 1

Chemical shifts (δ values) and coupling constants (Hz) for *para*-substituted triphenylphosphine derivatives in various solvents at various concentrations; experimental error ±0·1 Hz

Compound	Solvent (molarity)	$\delta_2 = \delta_6$	$\delta_3 = \delta_5$	$J_{2.6}$	$J_{2,3} = J_{5,6}$	$J_{2,5} = J_{3,6}$	$J_{3,5}$	$J_{P,2} = J_{P,6}$	$J_{P,3} = J_{P,5}$	δ_{P+CH_3}	J_{P,CH_3}	Other resonances
(1a) *	CH_2Cl_2 (0·5)	7·29	7·28									
(1b)	$CDCl_3$ (0·5)	7·189	7·304	2·30	8·25	0·35	2·08	7·46	1·15			
(1c)	CH_2Cl_2 (0·5)	7·135	7·468	2·11	8·09	0·39	2·04	7·06	1·22			
(1d)	$CDCl_3$ (0·5)	7·261	6·870	2·20	8·30	0·41	2·59	7·63	1·14			$\delta_{OCH_3} = 3·773$
(1e)	$CDCl_3$ (1)	7·193	7·092	1·81	8·07	0·58	1·89	7·81	0·99			$\delta_{CH_3} = 2·316$
(2a)	CH_2Cl_2 (0·5)	7·650	7·438	1·22	7·62	0·60	1·73	12·13	2·67			
(2b)	$CDCl_3$ (0·5)	7·590	7·470	2·07	8·50	0·53	2·10	12·18	2·11			
(2c)	CH_2Cl_2 (0·5)	7·498	7·635	1·77	8·09	0·45	2·34	11·27	2·35			
(2d)	CH_2Cl_2 (0·5)	7·533	6·945	2·39	8·38	0·40	2·39	11·35	2·16			$\delta_{OCH_3} = 3·799$
(2e)	CH_2Cl_2 (0·5)	7·498	7·223	2·03	7·50	0·48	1·44	11·48	1·82			$\delta_{CH_3} = 2·375$
(2f)	CH_2Cl_2 (0·2)	7·398	6·678	2·31	8·52	0·45	2·52	11·17	2·20			$\delta_{N(CH_3)_2} = 2·961$
(3a)	CH_2Cl_2 (0·5)	7·696	7·436	1·78	8·15	0·73	1·58	13·56	3·96			
(3b)	CH_2Cl_2 (0·5)	7·632	7·435	2·04	8·08	0·39	2·37	12·86	2·64			
(3c)	CH_2Cl_2 (0·5)	7·543	7·616	2·07	8·32	0·46	2·07	12·02	3·52 †			
(3d)	$CDCl_3$ (0·5)	7·619	6·921	2·30	8·73	0·55	2·59	12·62	2·12			
(3e)	CH_2Cl_2 (1)	7·563	7·183	1·78	7·80	0·47	1·91	13·00	2·87			$\delta_{CH_3} = 2·356$
(4a) *	CH_2Cl_2 (0·5)	7·83	7·71							3·167	13·42	
(4b)	$CDCl_3$ (0·5)	7·872	7·683	2·26	8·61	0·49	2·12	13·07	2·73	3·323	13·67	
(4d)	$CDCl_3$ (0·5)	7·631	7·196	2·49	8·63	0·41	2·55	12·52	2·55	2·930	13·14	$\delta_{OCH_3} = 3·926$
(4e)	CH_2Cl_2 (0·5)	7·620	7·529	1·83	7·86	0·51	1·83	13·52	2·26 †	3·014	13·30	$\delta_{CH_3} = 2·487$

* Owing to the small chemical shift difference between *ortho*- and *para*-protons, the spectrum does not have enough fine structure to allow an unequivocal iterative analysis. † For this parameter the probable error in the iterative analysis is high and we feel that it is largely undetermined.

It was not possible to obtain parameters from iterative analysis of the spectrum of compound (4a) either, owing to the small number of experimental transitions. The chemical shifts of *ortho*- and *meta*-protons reported in Table 1 were obtained as for compound (1a).

For compounds (1e—4e) the analysis was performed on the multiplets of aromatic protons decoupled from the methyl group, in order to simplify the spectrum.

Owing to solubility problems, we could not always employ the same concentration and the same solvent. However, a relatively small solvent effect is present and change in concentration, at least in methylene chloride solution, and within the range of concentrations employed (0·5—0·25M), has an irrelevant effect on n.m.r. parameters. Solvent effects on chemical shifts are more pronounced than on coupling constants, but are no higher than 2—3 Hz and do not alter the general features of the behaviour of the series of compounds examined. No specific studies on solvent–solute interactions were carried out, such investigations being considered outside the scope of the present work.

DISCUSSION

The degree of conjugation of the phosphorus atom with the aromatic π-electrons seems much less[16] than in the corresponding amine derivatives. This fact accounts for the low sp^3 character of the P–C bonds: it seems that the phosphorus atom retains much *p*σ

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[16] A. J. Kirby and S. G. Warren in ' Reaction Mechanism in Organic Chemistry,' eds. C. Eaborn and N. B. Chapman, Monograph 5, Elsevier, Amsterdam, 1967, ch. 1.

character, even in aromatic phosphines, and the lone-pair a high *s*-character. This implies that the electron-*donating* character of the phosphorus atom in arylphosphines is very weak and acts in the same direction as electrostatic effects, owing to the lower electronegativity of phosphorus relative to carbon. *d* Orbitals seem to be too diffuse[17] for significant overlap with $p\sigma$ or $p\pi$ orbitals of carbon. Interactions involving these orbitals could become relevant, as a result of contraction and stabilization,[18] when the phosphorus atom acquires a more positive character. This should affect, even if to different extents, the properties of P(O) and P(S) groups; the increased positive character of the phosphorus atom due to the higher electronegativity of the oxygen and sulphur atoms should confer on these groups a higher electrostatic electron-attracting and electron-withdrawing character owing to a major redisposition of *d* orbitals for $(d-p)_\pi$ bonding. In phosphonium salts this effect should be even greater.

The effect of substituents on an aromatic ring can be checked by employing ^{1}H n.m.r. data in the context of additivity rules.[18] This empirical treatment assigns to a given substituent a parameter *S* typical of the interaction of the substituent with a particular position of the phenyl ring; deviations from additivity in polysubstituted benzenes indicate conjugative interactions between substituents. By employing the additivity constants reported[19] and the chemical shift values of Table 1 (preferably values measured for 0·5M-solutions in $CDCl_3$; δ 7·27 for benzene), the following additive constants were obtained for phosphorus groups in arylphosphine derivatives:

	S_o	S_m
$\geqslant$P	−0·03 ± 0·04	+0·03 ± 0·03
$\geqslant$P(O)	−0·35 ± 0·03	−0·15 ± 0·01
$\geqslant$P(S)	−0·42 ± 0·01	−0·11 ± 0·03
$\geqslant$P$^+$	−0·51 ± 0·04	−0·39 ± 0·04

The small interval of indeterminacy for the substituent constants *S* shows that conjugative interactions between phosphorus groups and the other substituents here examined are small. The conjugative effect of trivalent phosphorus seems almost absent, for S_o and S_m are nearly zero, in accord with the high *s*-character of the phosphorus lone-pair; also the inductive effect does not operate to any noticeable extent.

For the P(O) group electron-withdrawing properties are evident. The *S* values indicate that for the *ortho*-position the electron-withdrawing effect of the P(O) group is between those of the substituents C=O and Br, and for the *meta*-position the effect is close to that of the C=O group. These findings reflect the fact that C=O and P=O bonds have similar polarity,* but the electrostatic effect contributed by the positive character of the phosphorus atom is accompanied by an electron migration from the phenyl ring due to a $(p-d)_\pi$ conjugation smaller than that present in carbonyl compounds originating from $(p-p)_\pi$ interactions.

For the P(S) group a slightly higher low-field shift is observed for *ortho*-protons than in the case of the P(O) group, whereas comparable *S* values are found for *meta*-positions. The results suggest a similarity in behaviour for these two groups, which show substantial electron-withdrawal from unsaturated systems.[22]

The electron-withdrawing effect of $\geqslant$P$^+$ in phosphonium salts is higher, as expected in view of the more positive character of the phosphorus atom, and $(d-p)_\pi$ conjugation should be enhanced with respect to the substituents previously discussed, as shown by the higher S_o and S_m values. For the *ortho*-positions the *S* value is lower than those of the substituents NO_2 and CO_2Me,[19] whereas for the *meta*-position it is higher; no doubt in the *ortho*-position effects other than inductive or mesomeric influence the proton chemical shift.[2]

A further test of substituent properties of the groups $\geqslant$P, $\geqslant$P(O), $\geqslant$P(S), and $\geqslant$P$^+$ in the phenyl ring has been performed in terms of Hammett's σ constants. By employing differently substituted *p*-tolyl derivatives, a linear correlation can be obtained between methyl proton chemical shifts and σ constants $[\delta_{CH_3} = (0·18 \pm 0·04) + (2·32 \pm 0·02)]$. By using this equation and the methyl chemical shifts of Table 1 for compounds (1)—(4) the following σ_p values are obtained: $\geqslant$P, −0·02; $\geqslant$P(O), +0·26; $\geqslant$P(S), +0·20; $\geqslant$P$^+$, +0·93. These values do not contradict the conclusions regarding the electronic effects of these groups drawn from *S* values.

Even the ^{1}H chemical shift of the methyl group bonded to phosphorus in phosphonium salts is linearly related to σ_p ($r = 0·996$) and this reveals that no strong interactions between *para*-substituents occur, as indicated by the additivity behaviour previously discussed.

Long-range ^{31}P · · · H coupling constants can indicate the degree of hybridization at the phosphorus atom provided that the electronegativities of the groups bonded to phosphorus are not too different.[9] Hence it is not safe to compare $J(^{31}P \cdots H)$ values of phosphines, phosphine oxides, phosphine sulphides, and phosphonium salts in order to obtain information concerning hybridization at the phosphorus atom. For various substituents in the phenyl ring, and within the same series of phosphorus derivatives, $J(^{31}P \cdots H_o)$ varies over a small range with no apparent regular behaviour. The following mean values can be deduced from data for the *para*-

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* The P=O bond moment is 39% of the $e \times r_{P=O}$ value;[21] for the C=O bond this quantity amounts to 41% ($\mu_{C=O}$ 2·4 D; $d_{C=O}$ 1·22 Å).

[17] D. P. Craig, A. Maccoll, R. S. Nyholm, L. E. Orgel, and L. E. Sutton, *J. Chem. Soc.*, 1954, 332; H. H. Jaffé, *J. Chem. Phys.*, 1953, **21**, 258.

[18] J. S. Martin and B. P. Dailey, *J. Chem. Phys.*, 1963, **39**, 1722.

[19] J. W. Emsley, J. Feeney, and L. H. Sutcliffe, 'High Resolution Nuclear Magnetic Resonance Spectroscopy,' Pergamon, Oxford, 1966, vol. 2, p. 737; for the $N(CH_3)_2$ group *S* values were obtained from the chemical shifts of *NN*-dimethylaniline:[20] $S_o = 0·74$, $S_m = 0·14$.

[20] K. Hayamizu and O. Yamamoto, *J. Mol. Spectroscopy*, 1968, **25**, 422.

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[22] R. F. Hudson in 'Structure and Mechanism in Organophosphorus Chemistry,' ed. A. T. Blomquist, Academic Press, London, 1965, p. 73.

substituted derivatives here considered: $J(^{31}\text{P}\cdots\text{H}_o)$ $7{\cdot}4 \pm 0{\cdot}4$; $J[^{31}\text{P(O)}\cdots\text{H}_o]$ $11{\cdot}5 \pm 0{\cdot}4$; $J[^{31}\text{P(S)}\cdots\text{H}_o] = 12{\cdot}7 \pm 0{\cdot}4$; $J[^{31}\text{P}^+\cdots\text{H}_o]$ $12{\cdot}9 \pm 0{\cdot}3$. A similar order is found for $J[^{31}\text{P(X)}\cdots\text{H}_m]$. No doubt part of the increase in these coupling constants, which are positive for aryl phosphines[5] and become more positive as the valency of the phosphorus atom increases,[5] is due to an increase in *s*-character of the P–C bond, as can be deduced from molecular geometries.[21]

Insight into the electronic mechanism acting on spin–spin coupling constants in a given class of molecules can be gained at a semiempirical level by calculating the contribution due to the contact term on the basis of the Pople–Santry expression.[23] The extended Huckel method (EHMO) was employed to obtain MO wave functions with Clementi orbitals[24] as basis sets.* In order to simplify calculations and to ensure that computer times were not excessive, the molecules employed were of the type PhP(X)H_2. Molecular geometries were deduced from those of related compounds.[21] Charge-iteration[27] was also employed but only small changes were produced on computed coupling constants without changing the general trend.† The results show that for different conformations of the compounds, *i.e.* (*a*) and (*b*), different sets of ^{31}P–^{1}H coupling constants are obtained. For $^3J(^{31}\text{P}\cdots\text{H}_o)$ the calculated values on changing the nature of X follow qualitatively the trend of experimental values in any possible conformation. An analysis of the dependence of the EHMO energy pattern on the torsion angle formed by the phosphorus lone-pair (or equivalent substituent X) and the ring plane shows that the energy minimum corresponds to an angle of 90° [conformation (*a*)] in all cases except those of phosphine oxides, where it is 0° [conformation (*b*)]. This seems to be generated by a non-repulsive interaction between the oxygen atom and the *ortho*-protons. By averaging the coupling constants for all possible conformations (weight-averaging) and employing EHMO energies, the following values are obtained for $^3J[^{31}\text{P(X)}\cdots\text{H}_o]$: P, 3·9; P(O), 4·3; P(S), 6·5; P^+, 7·0. These values agree in sign and quality with the trend of observed values, but this is all that one can expect from this kind of calculation. The same result is obtained for direct couplings $^1J(^{31}\text{P–H})$, for which positive values in the order $\text{P} < \text{P(O)} < \text{P(S)} < \text{P}^+$ are found, with a trend similar to that of experimental results[9,12] for similar compounds, although the value for phosphine is an overestimate and those for the other compounds are underestimates. No agreement is found for $^4J(^{31}\text{P}\cdots\text{H}_m)$, for which small and negative values are calculated. For coupling constants extending over more than one carbon–carbon bond in a π-system the contribution given by the Pople–Santry expression for spin–spin contact contribution and the MO wave function employed does not provide accurate predictions.[28] For the P–C–H coupling constant in phosphonium salt a value of −10·1 Hz is calculated as against an experimental value of 13·1—13·6 Hz, reported with absolute negative sign.[9,10] The calculated $^3J_{\text{HH}}$ for *ortho*-protons is in the range 8·0—8·6 Hz, very close to the experimental values.

In spite of the failure to produce quantitative estimates of coupling constants or even a trend for those couplings extending over four bonds, useful and instructive conclusions may be drawn from this kind of calculation and can be summarized as follows. (i) Inclusion of *d*-orbitals in the valence shell of phosphorus causes changes in the computed $J(^{31}\text{P}\cdots\text{H})$ values for all the compounds except the phosphine derivatives, in agreement with expectation if contraction and stabilization of *d*-orbitals occurs only when the phosphorus atom acquires positive character. (ii) Changes in the *s*-character of the P–C bond produce remarkable changes in $J(^{31}\text{P–H})$ and $^3J(^{31}\text{P}\cdots\text{H}_o)$ in phenylphosphines: for a geometry which assigns a tetrahedral structure to the molecule, the calculated value of $^3J(^{31}\text{P}\cdots\text{H}_o)$ amounts to 6·0 Hz. (iii) The increase in calculated $J(^{31}\text{P}\cdots\text{H})$ on passing from phosphines to the other phosphorus derivatives, which is partly related to the increased *s*-character of the P–C bond, is in accord with the experimental trend. (iv) The behaviour of $^3J(^{31}\text{P}\cdots\text{H}_o)$ in terms of the possible conformations for the molecules examined is justified by experimental results for phosphorus compounds. In fact, for phenylphosphines it is found that $^3J(^{31}\text{P}\cdots\text{H}_o)$ is dependent on the torsion angle between the phosphorus lone-pair and the C–H bond, where the maximum is at 0° and the minimum at 180°, and a plot is obtained which resembles that deduced by Mavel[10] for $^2J(^{31}\text{P}\cdots\text{H})$ in various phosphorus compounds. Only recently[11] it was argued from experimental results that, for $^2J(^{31}\text{P}\cdots\text{H})$ in vinylphosphines and related phosphonium salts, this constant for a conformation where the proton is *trans* to the phosphorus lone-pair is small and increases on going from $\geqslant\text{P}$ to $\geqslant\text{P}^+$, whereas the reverse holds for the eclipsed situation. In phenylphosphines, both geometrical situations are present in conformation (*b*), and the behaviour of $^3J(^{31}\text{P}\cdots\text{H}_o)$ for protons H(1) and H(2) fully reflects [P,H(1) 0·05; P,H(2) 10·2; P^+,H(1) 4·1; P^+,H(2) 7·3 Hz] the behaviour described for $^2J(^{31}\text{P}\cdots\text{H})$.‡

EXPERIMENTAL

^{1}H N.m.r. spectra were run on a JEOL JNM-C-60HL spectrometer, operating at 60 MHz in the internal lock mode.

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* For phosphorus and sulphur, a 3*d* hydrogen-like wave function was employed. Ionization potentials were mostly obtained from the work of Basch;[25] those relative to 3*d* orbitals of phosphorus and sulphur were taken from Cusachs' results.[26]

† A detailed comparison of MO coupling constants in different molecules containing elements of the third period will be reported in a future paper.

‡ After this paper was submitted, long range ^{1}H–^{31}P coupling constants in triphenylphosphine were reported (L. Radics, E. Baitz-Gács, and A. Neszmélyi, *Org. Magnetic Resonance*, 1974, **6**, 60) which confirm our conclusions.

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[24] E. Clementi, *I.B.M. J. Res. Develop. Suppl.*, 1965, **9**, 2.

[25] H. Basch, A. Viste, and H. B. Gray, *Theor. Chim. Acta*, 1965, **3**, 458.

[26] L. C. Cusachs and J. R. Linn, jun., *J. Chem. Phys.*, 1967, **46**, 2919.

[27] S. Polezzo, P. Cremaschi, and M. Simonetta, *Chem. Phys. Letters*, 1967, **1**, 357.

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Experimental errors in line position are probably within ±0·2 Hz. Sample solutions were always obtained from freshly prepared compounds and immediately subjected to n.m.r. analysis. Spectral computations and semiempirical MO calculations were performed on a CDC 6600 computer.

Compounds.—Tris-*p*-deuteriophenyl- [29] (1a), tris-*p*-chlorophenyl- [30] (1b), tris-*p*-methoxyphenyl- [31] (1d), and tri-*p*-tolyl-phosphine [32] (1e), obtained by known methods, were purified by crystallization from ethanol after column chromatography on silica gel (eluant light petroleum). Tris-*p*-bromophenylphosphine (1c) was prepared from *p*-bromophenylmagnesium bromide [33] and phosphorus trichloride in dry diethyl ether, by the procedure employed for the synthesis of the corresponding *p*-chloro-derivative.[30] The compound was purified as described for the other phosphines. Tris-*p*-methoxyphenylphosphine oxide [31] (2d) was obtained by oxidation of compound (1d) with hydrogen peroxide in acetone solution. This method was also employed for obtaining tris-*p*-deuteriophenyl- (2b), tris-*p*-bromophenyl- (2c), and tri-*p*-tolyl-phosphine oxide (2e). The compounds were crystallized by adding light petroleum to solutions in benzene. Tris-*p*-dimethylaminophenylphosphine oxide (2f) was obtained as described in the literature.[34] Tris-*p*-deuteriophenyl- (3a) and tris-*p*-bromophenyl-phosphine sulphide (3c) were obtained by the method described for the synthesis of tris-*p*-chlorophenyl- [35] (3b), tris-*p*-methoxyphenyl- [36] (3d), and tri-*p*-tolyl-phosphine sulphide [37] (3e). The compounds were purified as follows: elemental sulphur was separated from the crude material by column chromatography on silica gel with light petroleum as eluant; further elution with light petroleum–benzene (70 : 30 v/v) gave the sulphides (3a) and (3c), which were recrystallized from methanol. Methyl (tris-*p*-deuteriophenyl)phosphonium iodide (4a) was obtained as described for methyl (tris-*p*-chlorophenyl)- [35] (4b), methyl (tris-*p*-methoxyphenyl)- [35] (4d), and methyl (tri-*p*-tolyl)-phosphonium iodide [32] (4e), and purified by crystallization from acetonitrile–ether.

TABLE 2

Physical and analytical data

			Found (%)					Required (%)				
Compound	M.p. (°C)	Formula	C	H	Hal	P	S	C	H	Hal	P	S
(1c)	163—164	$C_{18}H_{12}Br_3P$	43·6	2·4	47·9	6·5		43·3	2·4	48·1	6·2	
(2a)	159—160 [a]	$C_{18}H_{12}D_3OP$	76·7	*b*		11·2		76·8	*c*		11·0	
(2b)	177—178 [d]	$C_{18}H_{12}Cl_3OP$	57·3	3·3	27·5	8·1		56·7	3·2	27·9	8·1	
(2c)	179—180	$C_{18}H_{12}Br_3OP$	42·1	2·3	46·8	6·3		42·0	2·4	46·6	6·0	
(2e)	145—146 [e]	$C_{21}H_{21}OP$	78·0	6·7		9·6		78·7	6·6		9·7	
(3a)	164—165	$C_{18}H_{12}D_3PS$	72·8	*f*		10·3	10·7	72·7	*g*		10·4	10·8
(3c)	182—183	$C_{18}H_{12}Br_3PS$	40·5	2·4	45·4	5·7	5·9	40·7	2·3	45·2	5·8	6·0
(4a)	189—190	$C_{19}H_{15}D_3IP$	56·0	*h*	31·6	7·6		56·0	*i*	31·2	7·6	

[a] Lit.,[29] 154—155°. [b] ($H_2O + D_2O$), 48·8%. [c] ($H_2O + D_2O$), 49·1%. [d] Lit.,[35] 170—175°. [e] Lit.,[38] 143—144°. [f] ($H_2O + D_2O$), 46·0%. [g] ($H_2O + D_2O$), 46·4%. [h] ($H_2O + D_2O$), 40·3%. [i] ($H_2O + D_2O$), 40·5%.

Physical and analytical data of new compounds are presented in Table 2.

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