tronegative elements bonded to the phosphorus. In the case of phosphorus connected to more than four atoms, the lower energy d-orbital(s) are already used in the σ-bond structure so that they are not available for π-bonding.

DAYTON, OHIO

[A JOINT CONTRIBUTION FROM THE MONSANTO CHEMICAL COMPANY AND VARIAN ASSOCIATES]

Principles of Phosphorus Chemistry. II. Nuclear Magnetic Resonance Measurements[1]

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The nuclear magnetic resonance spectra of nearly two hundred phosphorus compounds have been examined. The number and relative heights of the peaks obtained have been interpreted in terms of (1) the number and relative amounts of structurally different nuclei present in the sample, as well as (2) spin-spin splitting from interaction between nuclear moments within a molecule or molecule-ion. Large variations were observed in the chemical shifts of phosphorus atoms sharing electrons with three neighboring atoms, as compared to shifts of phosphorus atoms sharing electrons with four other atoms. Large, positive chemical shifts relative to orthophosphate were observed for phosphorus connected (1) to more than four other atoms and (2) through bent bonds. The observed data seem to fit into a qualitative picture based upon changes in hybridization and π-bond character of the phosphorus.

Interaction of a nucleus with its electronic environment, especially the valence electrons, influences the magnetic resonance absorption[3] of the nucleus. At resonance, a change in the electronic environment within the atom so as to reduce the magnetic field at the nucleus necessitates an increase in the applied magnetic field. Such an increase is called a positive chemical shift.[3,4] These shifts, which may be positive or negative, are measured in parts per million (p.p.m.) of the applied magnetic field relative to a chemical compound of the element arbitrarily chosen as a reference. Since the only naturally occurring isotope of phosphorus has a spin of one-half and a high magnetic moment,[5] this tool is especially appropriate for investigating phosphorus compounds, and nearly two hundred of these compounds have been looked at in the work reported here.

If a given sample contains phosphorus atoms in which the nuclei have different electronic environments, the nuclear magnetic spectrum of the sample will exhibit several resonance peaks, each corresponding to a different electronic environment of the nucleus. Conversely, if a given compound contains several phosphorus atoms in which the nuclei have the same electronic environments and hence are chemically equivalent, there will be only one resonance peak in its spectrum. More than one resonance peak can also come from spin-spin splitting,[6] which is due to interaction between nuclear moments within a molecule. Use of this spin-spin splitting in proving chemical structures is discussed in Paper III of this series.

Experimental Section

The measurements were made with a Varian Model V-4300B high resolution nuclear magnetic resonance spectrometer at a frequency of 12.3 Mc. and a magnetic field of approximately 7140 gauss. The samples were contained in 15 mm. cylindrical glass tubes. Three cc. of sample was sufficient, filling the tubes to a depth of approximately three cm. Sources and physical states of the samples are given in the Appendix. All measurements were carried out on either (1) relatively concentrated solutions, (2) liquid or molten samples, or, in a few cases, on (3) amorphous solid samples heated to the point where they begin to soften. The solutions were made as concentrated as was practically feasible.

Eighty-five per cent. orthophosphoric acid was used as the reference compound, and the procedure for determining the shift of the resonance of interest from the orthophosphoric acid resonance (in p.p.m. of the applied field) has been described earlier.[7] The chemical shifts[6] in p.p.m. are thus defined as $10^6 x(H_c - H_r)/H_r$ where H_c and H_r are the magnetic fields required for resonance in the sample and in a reference, respectively, at a fixed radio frequency (12.3 Mc.).

Results

All of the experimental data discussed here and in Paper III of this series are reported in the Appendix to this paper. These data, which we have determined, should be compared with the published information[8,9] on phosphorus compounds in order to get a full picture of the situation.

Several general observations can be made immediately upon inspection of the data. First, very large chemical shifts are found for the triply connected phosphorus atoms. The measured shifts cover a range of 500 p.p.m., as compared to a range of 100 p.p.m. (with the majority within 50 p.p.m.) for the quadruply connected phosphorus atoms studied. Secondly, large positive shifts with respect to the quadruply connected phosphorus are found for phosphorus atoms connected to more than

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(1) This paper was presented by C. F. Callis at the Phosphorus Symposium held on April 9, 1956, at the American Chemical Society Meeting in Dallas, Texas.

(2) Varian Associates, Palo Alto, California.

(3) E. R. Andrew, "Nuclear Magnetic Resonance," Univ. Press, Cambridge, 1955. J. E. Wertz, "Nuclear and Electronic Spin Magnetic Resonance," U. S. Air Force Report OSR-TN-55-203 [not classified and issued under Contract AF 18(600)-479] May, 1955. Also see refs. 6 and 8.

(4) In addition to chemical shifts, there are also shifts due to variations in the bulk magnetic susceptibility of the sample. For phosphorus, these shifts are small (of the order of magnitude of a few tenths p.p.m.) relative to most chemical shifts and hence can be neglected.

(5) W. H. Chambers and D. Williams, *Phys. Rev.*, **76**, 638 (1949); and M. F. Crawford and J. Levinson, *Can. J. Research*, **A27**, 156 (1949). See also "n-m-r Table," 3rd Edition, Varian Associates.

(6) H. S. Gutowsky, D. W. McCall and C. P. Slichter, *J. Chem. Phys.*, **21**, 279 (1953).

(7) B. P. Dailey and J. N. Shoolery, THIS JOURNAL, **77**, 3977 (1955).

(8) H. S. Gutowsky and D. W. McCall, *J. Chem. Phys.*, **22**, 162 (1954).

(9) Bro. Simon Peter, Ph.D. thesis under the direction of W. D. Knight, Univ. of California, Berkeley, 1953. (At the time of this study, available instrumentation gave much less accurate measurements than reported here and in ref. 8.)

four other atoms (+ *ca.* 100 p.p.m.)[10] and for bent bonds (*ca.* 150 p.p.m. shift per bent bond?).

Triply Connected Phosphorus.—As shown in Fig. 1, the various atoms or radicals attached to a triply connected phosphorus atom make a roughly constant contribution to the over-all shift, no matter what reference point is chosen from which to measure the shift. By using orthophosphoric acid as reference, the resonance shift contributions for the various substituent atoms or radicals are

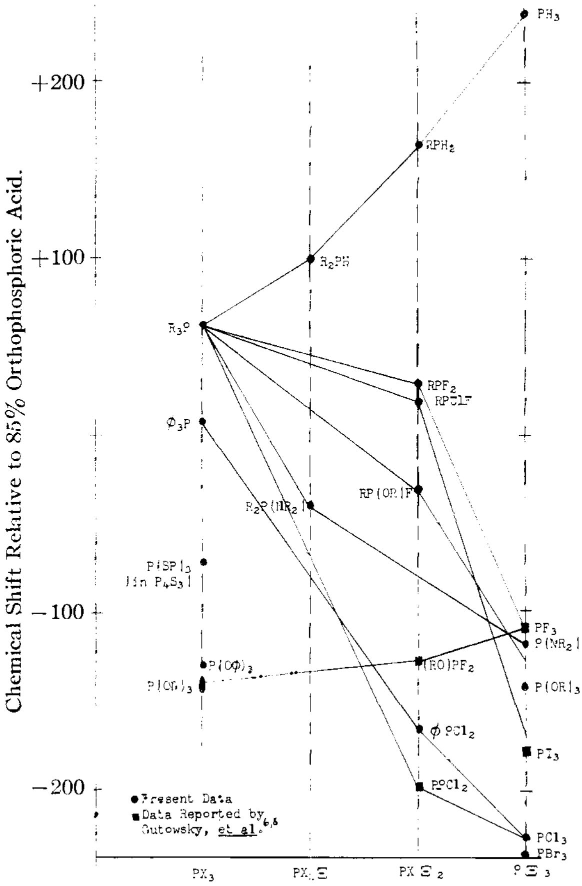
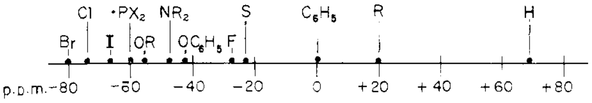


Fig. 1.—Chemical shifts for the triply connected phosphorus compounds.



By adding the appropriate shift contributions, the chemical shift of any triply connected phosphorus atom can usually be estimated to about ±(10–20) p.p.m. An exceptionally inaccurate case is found in RPClF, for which a shift of −85 p.p.m. was calculated from the above shift contributions, and the measured shift was +20 p.p.m.

Correlation of the measured shifts or of the shift contributions with electronegativity of the substituent atoms shows much scatter with a minimum shift contribution at an electronegativity of *ca.* 2.8 (Br). This means that for substituents of lower electronegativity than *ca.* 2.8, the shielding of the phosphorus decreases with increasing electronegativity of the substituent atom. This relationship has been observed for shifts measured in the fluorine atom[11] and is in the direction to be expected from consideration of bond polarities estimated from electronegativities alone, ignoring other factors involved in interactions between atoms. For substituent atoms having electronegativities greater than *ca.* 2.8, the effect is reversed, with more shielding of the phosphorus being associated with the higher electronegative constituents. Since the bond angles of the triply connected phosphorus compounds increase with increasing electronegativity of the substituent atoms, a simple theory correlation between bond angle and chemical shift in these compounds also cannot be set up.

Bent Bonds.—In the P_4 molecule there are three bent bonds per phosphorus, and the observed shift is +450 p.p.m.[8] By extrapolating on a plot similar to Fig. 1 from PI_3 through I_2PPI_2 (structure not well proven) to $P(P_3)$, we have estimated a value of −120 ± *ca.* 30 for the chemical shift of phosphorus connected to three like phosphorus atoms through unstrained bonds. This leads to a shift contribution of (450 + 120)/3 = 190 p.p.m. for each bent bond. A similar treatment of the P_3-ring[12] in phosphorus sesquisulfide (P_4S_3), using + 120 p.p.m. for this ring phosphorus and an extrapolated value of −110 for the $SP(P_2)$ unstrained structure, gives 115 p.p.m. for the shift contribution per bent bond.

Quadruply Connected Phosphorus Atoms.—Again, to a first approximation, each substituent atom or radical appears to make a given contribution to the over-all shift. This effect is best shown by the data of Table I, in which the shifts due to the substitution of oxygen by other atoms are reported. It should be noticed that replacement of oxygen by all of the elements listed (H, C, N, P, S, Cl, Se) leads to a negative shift, except for fluorine, which gives a positive shift. This means that replacement of oxygen by less electronegative elements gives less shielding and *vice versa.* Shielding by substituent elements is seen from the data of Table I to lie in the order: $Se < S < C_{aliphatic} < C_{aromatic} \approx P < N \approx Cl < H < O < F$—which, with the exception of hydrogen and phosphorus, is the order of increasing electronegativity. Again, the results are opposite to simple polar-bond theory (with other effects neglected) in that the shifts become more negative as the electronegativity of the substituents decrease. This is contrary to the case of triply connected phosphorus below an electronegativity of 2.8.

Comparison of the shifts found by substituting nitrogen for oxygen to those found by substituting sulfur for oxygen is of interest because of the closeness of these three elements in the Periodic Table, and because there are considerable data

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[10] Bro. Simon Peter[9] reports chemical shifts of +88 p.p.m. and +131 p.p.m. for PBr_5 and PCl_5, respectively (dissolved in carbon disulfide and measured relative to orthophosphoric acid). Gutowsky and McCall[8] give a chemical shift of +148 for HPF_6 (in solution, relative to orthophosphoric acid). In the present work, a shift of +80 ± 2 p.p.m. relative to orthophosphoric acid was found for PCl_5 dissolved in carbon disulfide (see Appendix).

[11] H. S. Gutowsky and C. J. Hoffman, *J. Chem. Phys.*, **19**, 1259 (1951).

[12] O. Hassel and A. Pettersen, *Tid. Kem. Berg. Met.*, **1**, 57 (1941). Also see Paper III of this series, unpublished.

TABLE I

CHEMICAL SHIFTS FOR QUADRUPLY CONNECTED PHOSPHORUS ON WHICH OXYGEN IS REPLACED BY ANOTHER SUBSTITUENT ATOM

No.	Element replacing oxygen	Original structure	Replaced structure	Total shift due to replacement (p.p.m.)	Shift per replaced atom (p.p.m.)
1	H	$C_6H_5PO(OH)_2$	$C_6H_5P(O)H(OH)$	− 4	− 4
2		$HOPO_3^=$	$HOPH(O)_2^-$	− 4	− 4
3		$HOPO_3^=$	$HOPH_2(O)$	−13	− 7
4		$PO_4^≡$	$H_2PO_2^-$	− 3	− 2
5		$(RO)_2PO_2^-$	$(RO)_2PH(O)$	− 8	− 8
6	C aliphatic	$PO_4^≡$	$RPO_3^=$	−22	−22
7		$HOPO_3^=$	$RPO_2(OH)^-$	−32	−32
8		$(R_2N)_3PO$	$(R_2N)_3PR^+$	−37	−37
9	C aromatic	$C_6H_5SPO(OR)_2$	$C_6H_5SPC_6H_5(O)(OR)$	−17	−17
10		$HOPH(O)_2^-$	$C_6H_5PH(O)_2^-$	−18	−18
11		$HOPO_3^=$	$HOPC_6H_5(O)_2^-$	−16	−16
12		$(RO)_2PO_2^-$	$(RO)_2PC_6H_5(O)$	−19	−19
13		$ROPO_3^=$	$ROP(C_6H_5)_2(O)$	−27	−14
14		$PO_4^≡$	$(C_6H_5)_3PO$	−18	− 6
15		$(R_2N)_3PO$	$(R_2N)_3PC_6H_5^{+a}$	(−23)	(−23)
16	N	$(HO)_2PO_2^-$	$(HO)P(NH_2)(O)_2^-$	− 3	− 3
17		$(C_6H_5O)_2P(OR)(O)$	$(C_6H_5O)_2P(NHR)(O)$	−13	−13
18		$-\!>POP(O)_2{}^-OP<\!-$	$-\!>PNP(O)_2NP<\!-$	−19	−10
19		$(RO)_3PO$	$(RO)P(NR_2)_2(O)$	−21	−11
20		$(RO)_2P(O)OP(O)(OR)_2$	$(R_2N)_2P(O)OP(O)(NR_2)_2$	−21	−11
21		$(RO)_3PO$	$(R_2N)_3PO$	−27	− 9
22		$RPO(OR)_2$	$RP(NR_2)_3^+$	−31	−10
23		$(X_3C)PO(OR)_2$	$(X_3C)P(NR_2)_3^+$	−37	−12
24		$RC_6H_5CH_2PO(OH)_2$	$(ClC_6H_5CH_2P(NR_2)_3^{+b}$	−30	−10
25	F	$ROPO_3^=$	$ROPF_2(O)$	+20	+10
26	P	$(HO)_2(O)POP(O)(OH)_2$	$(HO)_2(O)PP(O)(OH)_2$	−19	−19
27	S	$(RO)_2PO(OC_6H_5)$	$(RO)_2PO(SC_6H_5)$	−26	−26
28		$C_6H_5P(O)(OR)(OC_6H_5)$	$C_6H_5P(O)(OR)(SC_6H_5)$	−25	−25
29		$(RO)_3PO$	$(RO)_2P(SR)(O)$	−33	−33
30		$C_6H_5PO(Cl)_2$	$C_6H_5PS(Cl)_2$	−46	−46
31		Cl_3PO	Cl_3PS	−28	−28
32		$(RO)_2PO_2^-$	$(RO)_2P(S)(O)^-$	−57	−57
33		$(C_6H_5O)_3PO$	$(C_6H_5O)_3PS$	−71	−71
34		$(RO)_2PO(OC_6H_5)$	$(RO)_2PS(OC_6H_5)$	−46	−46
35	Cl	$-\!>PNP(O)_2{}^-NP<\!-$	$-\!>PNP(Cl)_2NP<\!-$	−20	−10
36		$(RO)PO_3^=$	$(RO)PCl_2(O)$	− 6	− 3
37		$ClCH_2PO(OR)_2$	$ClCH_2PO(Cl)_2$	−18	− 9
38		$C_6H_5PO_2(OH)$	$C_6H_5PO(Cl)_2$	−16	− 8
39		$PO_4^≡$	$OPCl_3$	0	0
40	Se	$(RO)_3PO$	$(RO)_3PSe$	−73	−73

[a] The shift of $(R_2N)_3PC_6H_5^+$ was estimated from the measured value of $(R_2N)_3P^+CH_2$Cl, by use of Fig. 3. [b] A change of substituent in the *para*-position should affect the shift by no more than a few p.p.m. (see Fig. 3).

available. Although a wide variety of structures were employed in either case, the oxygen-to-nitrogen shift is quite constant at −11 ± 2 p.p.m. per atom (except for item 16 in Table I); whereas, the oxygen-to-sulfur shift varies from −25 to −71 p.p.m. per atom. This means that in most structures the nitrogen substitutes for oxygen in the same way each time; whereas, there is a variable change in bonding type when sulfur substitutes for oxygen. Inspection of the data indicates that the sulfur-for-oxygen shift is −25 to −30 p.p.m. for bridging positions (*e.g.*, C–O–P), and it is *ca.* −60 p.p.m. for the isolated position. In view of the differences between the amount of π-character in P–O and in P–S connections, as well as the effect in which π-bonding is concentrated in connections to isolated (non-bridging) atoms (both effects being described in Paper I of this series), such a difference between isolated and bridging positions is to be expected. As is pointed out later under General Remarks, this variation in π-bonding results in changes in the symmetry of the p-shell.

The data on quadruply connected phosphorus compounds show that the positive or negative charges due to ionization of atoms attached to the group consisting of phosphorus and its tetrahedron of four neighboring atoms has essentially no effect on the chemical shift. Moreover, as would be expected, the kind of counter ion balancing this charge also has no appreciable effect on the shift.

When a chain of atoms is attached to a phosphorus atom, the neighboring atom has the greatest effect on both the chemical shift and spin–spin splitting of the phosphorus with the atom next in line having the next most important effect and so forth. This is shown by the phosphate family of compounds which has been carefully investigated in this study.

In Fig. 2 the various phosphate structures are shown in relation to their chemical shifts. In this family of compounds, the phosphorus is always tetrahedrally surrounded by four oxygen atoms. Chemical shifts are caused by bonding other atoms to these oxygens. A small shift of +5 p.p.m. is found upon going from the $PO_4^{\equiv}$ ion (as in solutions of Na_3PO_4 and K_3PO_4) to the $HOPO_3^{=}$ ion. However, the mono-, di- and trihydrogen orthophosphates exhibit no shifts when going from one to another, so that we can conclude that the weakest hydrogen of orthophosphoric acid is held by a bond of some covalent character as compared to the mainly ionic bonding of the other two hydrogen ions. The absence of separate peaks (for each ion) in a given spectral pattern, with the relative heights of such peaks changing with the *p*H and concentration, indicates that bonding of any hydrogen to the PO_4 group exhibits considerable ionic character and that the rate of exchange between covalently bound and ionized hydrogen is fast with respect to these measurements.[13] It is, of course, possible that the postulated peaks for different ions lie close together and have not yet been resolved.

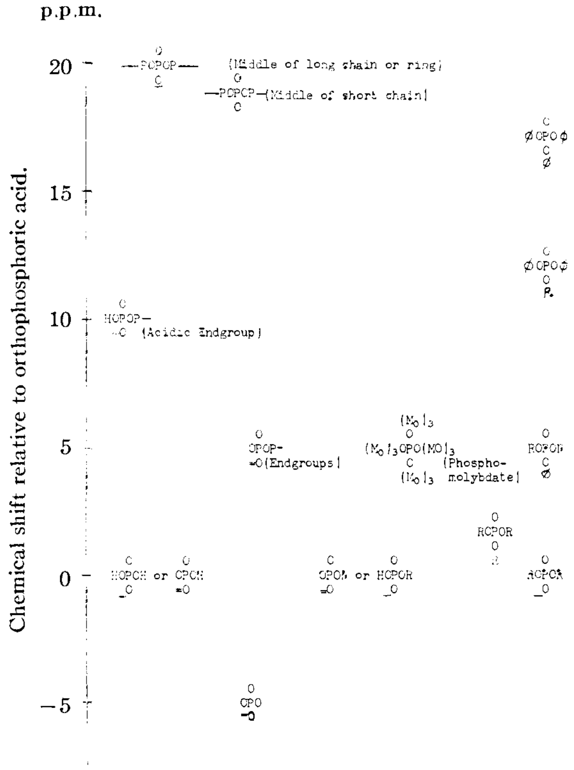

Fig. 2.—Chemical shifts of various phosphate structures.

A similar shift of +5 p.p.m. is found for end groups of chain phosphates, when going from alkaline to acid solutions. Presumably, this shift is due to the weakly acidic end-group hydrogen.[14] Lack of such a shift for middle PO_4 groups is attributable to the fact that there is one strongly acidic hydrogen for each phosphorus atom in any phosphate.[14]

As has been pointed out in a preliminary communication,[15] separate resonance peaks are found for (1) isolated (orthophosphate), (2) end, and (3) middle-PO_4 groups. The shift for the middle group ranges from +18 to +20 p.p.m. as measured from orthophosphoric acid, with the greatest shift being for middle groups in long chains or in rings.

Attempts to measure the resonance peak of a branching-point PO_4 group have not as yet been conclusive. Solid, amorphous ultraphosphates, in a high-resolution spectrometer, give no resonance peak until they are heated to temperatures where they begin to soften. Then, they show a broad peak at +31 p.p.m. with no evidence for the middle-group peak at + 20 p.p.m, even though middle groups must have been present in the structures.[16] Presumably, these ultraphosphates (Na_2O–P_2O_5 glasses for which the Na_2O/P_2O_5 mole ratio ranged from 0.42 to 0.82, as well as azeotropic phosphoric acid for which $H_2O/P_2O_5 = 0.69$) were undergoing random reorganization[17] at the temperatures needed for obtaining noticeable resonance peaks, so that the observed shift may correspond to an averaged reorganizing unit. The spectrum of the ethyl "metaphosphate" made from P_4O_{10} and excess ethyl ether[18] showed three peaks at +14, +29 and +41 p.p.m. with the signal amplitudes corresponding to 25, 72 and 3% of the total phosphorus, respectively. Tentatively (in view of Fig. 2), we have ascribed the first peak to end groups, the second to middle groups, and the third to a small amount of branching points. Whatever is the proper assignment of the peaks, one thing is certain—the structure given in the recent literature[19] for this reaction product is incorrect.

Systems other than the condensed phosphates in which chain and ring structures are found also exhibit separate resonance peaks for end and middle groups as well as for isolated groups, when known. Work is under way on studying such systems, for which approximate shifts can be estimated, in some cases, from Table I.

The phosphonic acids and the phosphonates offer a direct way to measure the relative electron-donating ability of organic radicals, since the carbon is attached directly to the phosphorus in these compounds. A graphic presentation of the measured shifts is given in Fig. 3, where it can be seen that, as in other cases of quadruply connected phosphorus, the stronger electron-donating groups cause the lesser shielding of the phosphorus nu-

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(13) Absence of spin–spin splitting supports these arguments.

(14) J. R. Van Wazer and K. A. Holst, This Journal, **72**, 639 (1950).

(15) J. R. Van Wazer, C. F. Callis and J. N. Shoolery, *ibid.*, **77**, 4945 (1955).

(16) J. R. Van Wazer and E. J. Griffith, *ibid.*, **77**, 6140 (1955).

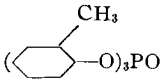
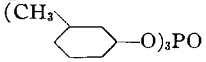
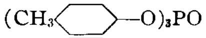
(17) J. R. Van Wazer, *ibid.*, **72**, 644 (1950).

(18) K. Langheld, *Ber.*, **43**, 1857 (1910); **44**, 2076 (1911); **45**, 3737, 3760 (1912).

(19) E. Thilo and H. Woggon, *Z. anorg. allgem. Chem.*, **277**, 17 (1954).

APPENDIX

NUCLEAR MAGNETIC RESONANCE SPECTRA OF PHOSPHORUS COMPOUNDS

Name	Source[a]	Structure	Physical state	Chemical shifts (p.p.m.) relative to 85% orthophosphoric acid	Spin-spin splitting[6] Line structure	Splitting in gauss[b]	Comments
A. Triply-connected compounds							
Ethyldifluorophosphine	W	$C_2H_5PF_2$	Liquid	+ 30 ± 3	1-2-1	0.57	
Trimethyl phosphite	MC	$P(OCH_3)_3$	Liquid	−141 ± 1			
Triethyl phosphite	VC	$P(OC_2H_5)_3$	Liquid	−139 ± 1			
Triisopropyl phosphite	VC	$P(OCH(CH_3)_2)_3$	Liquid	−138 ± 1			
Tributyl phosphite	VC	$P(OC_4H_9)_3$	Liquid	−139 ± 1			
Tris-(β-chloroethyl) phosphite	MC	$P(O(CH_2)_2Cl)_3$	Liquid	−139 ± 1			
Tris-(2-ethylhexyl) phosphite	VC	$P(OC_8H_{17})_3$	Liquid	−140 ± 1			
Triphenyl phosphite	F	$P(OC_6H_5)_3$	Liquid	−128 ± 1			
Ethylchlorofluorophosphine	W	C_2H_5PClF	Liquid	+ 20 ± 2	1-1	0.33	
Ethylfluoroisopropoxyphosphine	W	$C_2H_5P(OCH(CH_3)_2)F$	Liquid	− 29 ± 3	1-1	0.57	Small peak at +127 p.p.m. attributed to impurity
Phosphorous trichloride	F	PCl_3	Liquid	−220 ± 1			
Hexamethylphosphorous triamide	MB	$P(N(CH_3)_2)_3$	Liquid	−122 ± 2			Small peaks at −46 and 0 attributed to impurities
Hexaethylphosphorous triamide	MD	$P(N(C_2H_5)_2)_3$	Liquid	−118 ± 3			
Dichlorophenylphosphine	F	$C_6H_5PCl_2$	Liquid	−166 ± 1			
Phosphorus tribromide	F	PBr_3	Liquid	−229 ± 1			
Dimethylamidodimethylphosphine	B	$(CH_3)_2NP(CH_3)_2$	Liquid	− 39 ± 1			
Triphenylphosphine	F	$P(C_6H_5)_3$	Ether soln.	+ 8 ± 1			Peak broad
Trimethylphosphine	B	$P(CH_3)_3$	Liquid	+ 62 ± 1			
Dimethylphosphine	B	$HP(CH_3)_2$	Liquid	+ 98.5 ± 1	1-1	0.12	
Monomethylphosphine	Wa	H_2PCH_3	Liquid	+163.5 ± 1	1-2-1	0.12	
Phosphine	O	PH_3	Liquid at −90°	+238 ± 1	1-3-3-1	..	
Phosphorus sesquisulfide	F	$P(S)_3$ in P_4S_3	CS_2 soln	− 71 ± 1	1-3-3-1	..	1 of 2 major multiplets
B. Bent bonds							
Elemental phosphorus	M	P_4	Solid	1 broad peak at very high positive field			Gutowsky[8] gives a value of +450 p.p.m.
Phosphorus sesquisulfide	F	$SP(P)_2$ in P_4S_3	CS_2 soln.	+120 ± 1	1-1	0.05	1 of 2 major multiplets
C. Quadruply-connected compounds							
Organic Phosphates							
Tri-*o*-tolyl phosphate	F		Liquid	+17 ± 0.3			
Tri-*m*-tolyl phosphate	F		Liquid	+17 ± 0.5			
Tri-*p*-tolyl phosphate	F		Benzene soln.	+16 ± 0.5			
Tricresyl phosphate	MC		Liquid	+18 ± 1			
Triphenyl phosphate	F	$(C_6H_5O)_3PO$	Ether soln.	+18 ± 0.5			
p-Chlorophenyl diphenyl phosphate	F	$ClC_6H_4O(C_6H_5O)_2PO$	Liquid	+17.5 ± 0.5			

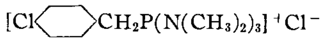
APPENDIX (*Continued*)

Name	Source[a]	Structure	Physical state	Chemical shifts (p.p.m.) relative to 85% orthophosphoric acid	Spin-spin splitting[a] Line structure	Spin-spin splitting[a] Splitting in gauss[b]	Comments
Butyl diphenyl phosphate	MD	$C_4H_9O(C_6H_5O)_2PO$	Liquid	+12 ± 1			
2-Ethylhexyl diphenyl phosphate	MC	$C_8H_{17}O(C_6H_5O)_2PO$	Liquid	+12 ± 1			
Ethyl diphenyl phosphate	MD	$C_2H_5O(C_6H_5O)_2PO$	Liquid	+12 ± 1			Smaller peaks at −2 and +10 attributed to other esters present
Dibutyl phenyl phosphate	MC	$(C_4H_9O)_2C_6H_5OPO$	Liquid	+ 4 ± 1			
Dibutyl phosphate	MD	$(C_4H_9O)_2HOPO$	Liquid	0 ± 0.5			
Triethyl phosphate	F	$(C_2H_5O)_3PO$	Liquid	+ 1 ± 1			
Tris-(*β*-chloroethyl) phosphate	MC	$(ClC_2H_4O)_3PO$	Liquid	+ 2 ± 1			
Tri-*n*-butyl phosphate	E	$(n\text{-}C_4H_9O)_3PO$	Liquid	− 1 ± 0.5			Fine structure indicated
Tri-butyl phosphate	Ba	$(C_4H_9O)_3PO$	Liquid	+ 1 ± 0.5			Fine structure indicated
Amyl octyl acid phosphate	MM	$(C_5H_{11}O)(C_8H_{17}O)HOPO$	Liquid	+ 1 ± 0.5			
Inorganic orthophosphates							
Trisubstituted orthophosphates		$PO_4^{\equiv}$ plus $3Na^+$ or $3K^+$	Aq. soln.	− 5			
Orthophosphate with 1 to 3 H/P		$PO_4H^{=}$	Aq. soln.	0			
Orthophosphoric acid (85%)	B & A	$(HO)_3PO$	Liquid (aq.)	0			
1:1 water diln. of 85% H_3PO_4	B & A	$(HO)_3PO$	Aq. soln.	− 1 ± 1			
Monosodium orthophosphate	Ba	NaH_2PO_4	Aq. soln.	0 ± 1			
Disodium orthophosphate	Ba	Na_2HPO_4	Aq. soln.	+ 3 ± 1			
Trisodium orthophosphate	Ba	Na_3PO_4	Aq. soln.	− 5 ± 1			
Monopotassium orthophosphate	Ba	KH_2PO_4	Aq. soln.	− 1 ± 1			
Dipotassium orthophosphate	Ma	K_2HPO_4	Aq. soln.	− 1 ± 1			
Tripotassium orthophosphate	F	K_3PO_4	Aq. soln.	− 6 ± 1			
Monoammonium orthophosphate	Mc	$NH_4H_2PO_4$	Aq. soln.	− 1 ± 1			
Diammonium orthophosphate	Mc	$(NH_4)_2HPO_4$	Aq. soln.	− 1 ± 1			
Phosphomolybdic acid	Mc		Aq. soln.	+ 5 ± 1			
Condensed phosphates							
End groups, doubly substituted		$-OPO_3^{=}$, plus $2Na^+$ or $2K^+$	Aq. soln.	+ 5 ± 1			
End groups, 1 to 2 H/P atom		$-OPO_3H^-$	Aq. soln.	+10 ± 1			
Tetrasodium pyrophosphate	Ba	$O_3POPO_3^{\equiv}$	Aq. soln.	+ 6 ± 1			
Sodium acid pyrophosphate	MW	$HO_3POPO_3H^{=}$	Aq. soln.	+10 ± 1			
Potassium acid pyrophosphate	MN	$HO_3POPO_3H^{=}$	Aq. soln.	+ 9 ± 1			
Ammonium pyrophosphate	MR	$O_3POPO_3^{\equiv}$	Aq. soln.	+ 8 ± 1			Resonance at −2 p.p.m. attributed to orthophosphate
Middle groups, short chains		$-OPO_2^-O-$	Aq. soln.	+18 ± 1			
Middle groups, long chains and rings		$-OPO_2^-O-$	Aq. soln.	+21 ± 1			
Sodium tripolyphosphate	MCa	$P_3O_{10}^{-5}$	Aq. soln. (supersatd.)	+ 4 ± 1 +18 ± 1	1-1 1-2-1	0.01 0.01	End-group and middle-group peaks are resolved

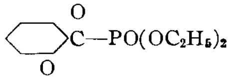
APPENDIX (*Continued*)

Name	Source[a]	Structure	Physical state	Chemical shifts (p.p.m.) relative to 85% orthophosphoric acid	Spin–spin splitting[6]		Comments
					Line structure	Splitting in gauss[b]	
Potassium tripolyphosphate	MA	$P_3O_{10}^{-5}$	Aq. soln.	$+6 \pm 1$ $+19 \pm 1$			Peak at −3 p.p.m. attributed to orthophosphate. Sample also contains pyrophosphate as impurity
Ammonium tripolyphosphate	MR	$P_3O_{10}^{-5}$	Aq. soln.	$+8 \pm 1$ $+22 \pm 1$			Peak at −2 p.p.m. attributed to orthophosphate impurity
Sodium phosphate glass n = *ca.* 4[c]	MCa	$P_4O_{13}^{-6}$	Aq. soln.	$+3 \pm 1$ $+18 \pm 1$			
Sodium phosphate glass, n = 5.4	MCa	$^{-}O_3POP\bar{O}_2O\text{---}OP\bar{O}_2OPO_3^{-}$	Aq. soln.	$+5 \pm 1$, $+21 \pm 1$			
Sodium phosphate glass, n = 6.8	MCa	$^{-}O_3POP\bar{O}_2O\text{---}OP\bar{O}_2OPO_3^{-}$	Aq. soln.	Two peaks not ref'd.			
Sodium phosphate glass, n = 14	MCa	$^{-}O_3POP\bar{O}_2O\text{---}OP\bar{O}_2OPO_3^{-}$	Aq. soln.	$+6 \pm 1$, $+20 \pm 1$			
Sodium phosphate glass, n = 25	MG	$^{-}O_3POP\bar{O}_2O\text{---}OP\bar{O}_2OPO_3^{-}$	Aq. soln.	$+5 \pm 1$, $+19 \pm 1$			
Sodium phosphate glass, n = 80	MG	$^{-}O_3POP\bar{O}_2O\text{---}OP\bar{O}_2OPO_3^{-}$	Aq. soln.	$+19 \pm 1$			Indication of resonance at + 5 p.p.m.
Sodium phosphate glass, n = 230	MG	$^{-}O_3POP\bar{O}_2O\text{---}OP\bar{O}_2OPO_3^{-}$	Aq. soln.	$+21 \pm 1$			
Sodium trimetaphosphate	MMH	$(NaPO_3)_3$, ring structure	Aq. soln.	$+21 \pm 1$			
Sodium tetrametaphosphate	MG	$(NaPO_3)_4$, ring structure	Aq. soln.	$+21 \pm 1$			
Ammonium tetrapolyphosphate	We	$(NH_4)_6P_4O_{13}$	Aq. soln.	$+9 \pm 1$ $+22 \pm 1$	Both lines are doublets	0.01	Small peak at 0 ± 1 attributed to orthophosphate impurities
Sodium ultraphosphate, Na_2O/P_2O_5 = 0.82	MCa	Theor. highly branched	Heated to soften	+31			Peak broad
Sodium ultraphosphate, Na_2O/P_2O = 0.50	MCa	Theor. highly branched	Heated to soften	+31			Peak broad
Sodium ultraphosphate, Na_2O/P_2O = 0.42	MCa	Theor. highly branched	Heated to soften	+30			Peak broad
$H_2O \cdot P_2O_5$ azeotropic acid	MG	Theor. highly branched	Heated to soften	+34			Peak broad
Sodium ultraphosphate, Na_2O/P_2O_5 = 0.96	MG	No branching points expected	30 min. after dissoln. in water	+14			Low signal to noise ratio. Peak at lower field possible
Trisodium isohypophosphate tetrahydrate	Bl	$Na_2O_3POPHO_2Na$	Aq. soln.	$+1 \pm 0.5$ $+3 \pm 0.5$	1–1 (each a doublet) 1–1	0.36 0.01	Both lines split into doublets by phosphorus spin–spin interaction
Hexaphenyl bis-(diethyleneglycol) tetraphosphate	MD	$((C_6H_5O)_2OPOC_2H_4OC_2H_4OP\text{-}(OC_6H_5)_2O\text{–})_2$	Liquid	$+7.5 \pm 1$ $+12.5 \pm 1$			Peaks of equal area
Pentaphenyl bis-(diethyleneglycol) triphosphate	MD	$(C_6H_5O)_2OPOC_2H_4OC_2H_4OP(O\text{-}C_6H_5)_2O\text{–}C_2H_4OC_2H_4OPO(OC_6H_5)_2$	Liquid	$+7 \pm 1$ $+13 \pm 1$			+7 peak is smaller than the +13 peak
Phosphorus pentoxide–ethyl ether reaction product	MCa	......	Viscous liquid	$+14 \pm 1$ $+29 \pm 1$ $+41 \pm 1$			+41 peak small compared to other peaks

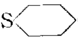
APPENDIX (*Continued*)

Name	Source[a]	Structure	Physical state	Chemical shifts (p.p.m.) relative to 85% orthophosphoric acid	Spin–spin splitting[b]		Comments
					Line structure	Splitting in gauss[b]	
Organic phosphites							
Dimethyl phosphite	MC	$(CH_3O)_2HPO$	Liquid	−11 ± 1	1-1	0.41	
Diethyl phosphite	MC	$(C_2H_5O)_2HPO$	Liquid	− 8 ± 1	1-1	0.39	
Dibutyl phosphite	MC	$(C_4H_9O)_2HPO$	Liquid	− 8 ± 1	1-1	0.39	
Bis-(2-ethylhexyl) phosphite	MC	$(C_8H_{17}O)_2HPO$	Liquid	− 7 ± 1	1-1	0.39	
Inorganic phosphites							
Phosphorous acid	Ba	$(HO)_2HPO$	30% aq. soln.	− 5 ± 2	1-1	0.40	
Phosphorous acid	MH	$(HO)_2HPO$	13.1 *M* aq. soln. prepd. from cryst. acid	− 8 ± 2	1-1	0.40	
Monosodium phosphite	M	$NaO(HO)HPO$	Aq. soln.	− 4 ± 2	1-1	0.36	
Disodium phosphite	F	$(NaO)_2HPO$	Aq. soln.	− 4 ± 2	1-1	0.34	
Other lower oxidation states							
Sodium hypophosphate	MP	$HO(NaO)POPO(ONa)OH$	Aq. soln.	− 9 + 1			
Hypophosphorous acid	Ba	$H_2PO(OH)$	50% aq. soln.	−13 ± 2	1-2-1	0.33	
Calcium hypophosphite	Ol	$H_2PO(OCa)$	Aq. soln.	− 8 ± 2	1-2-1	0.31	
Sodium hypophosphite	Ol	$H_2PO(ONa)$	Aq. soln.	− 8 ± 2	1-2-1	0.31	
Potassium hypophosphite	Ol	$H_2PO(OK)$	Aq. soln.	− 6 ± 2	1-2-1	0.31	
Nitrogen-substituted compounds							
Monosodium phosphoramidate	MNi	$NaOPO(OH)NH_2$	Aq. soln.	− 3 ± 1			Structure verified by X-ray
Phosphorodiamidic acid	MNi	$HOPO(NH_2)_2$	Aq. soln.	+ 3.5(?)			{Also minor peaks at +10 and +25. Compd. dec. as verified by X-ray exam.}
Sodium salt of trimeric phosphoronitridic acid	MNi	$(NaPO_2NH)_3$, ring structure	Aq. soln.	+ 1 ± 2			Structure verified by X-ray.
Hexamethylphosphoramide	MRu	$((CH_3)_2N)_3PO$	Liquid	−27 ± 1			Peak broad
Hexamethylphosphoramide	MD	$((CH_3)_2N)_3PO$	Liquid	−26.5 ± 0.5			
Hexa-*n*-butylphosphoramide	MD	$((n\text{-}C_4H_9)_2N)_3PO$	Liquid	−23 ± 1			
Ethyl tetramethylphosphorodiamidate	MD	$C_2H_5OPO(N(CH_3)_2)_2$	Liquid	−18 ± 1			Peak broad
Octamethylpyrophosphoramide	MD	$((CH_3)_2N)_4P_2O_3$	Liquid	−12 ± 1			{Different preparations}
Octamethylpyrophosphoramide	MD	$((CH_3)_2N)_4P_2O_3$	Liquid	−11 ± 1			
Phosphonitrilic chloride trimer	M	$(PNCl_2)_3$, ring structure	Benzene soln.	−19 ± 1			
Phosphonitrilic chloride polymer	MK	$(PNCl_2)_x$ chain	Benzene soln.	−20 ± 1, +7 ± 1			−20 peak the larger
Diphenyl dodecylphosphoramide	MK	$(C_6H_5O)_2PO(NHR)$	Benzene soln.	− 1 ± 1			
n-Butyl tris-(dimethylamido)-phosphonium bromide	MD	$[n\text{-}C_4H_9P(N(CH_3)_2)_3]^+Br^-$	Liquid	−62 ± 1			3 minor peaks at −27, −3 and +23 attrib. to impurities
Chlorobenzyl tris-(dimethylamido)-phosphonium chloride	MD	 $[Cl$ $CH_2P(N(CH_3)_2)_3]^+Cl^-$	Alcohol soln.	−55.5 ± 1			
Dichlorofluoromethyltris-(dimethylamido)-phosphonium chloride	MD	$[Cl_2FC\text{–}P(N(CH_3)_2)_3]^+Cl^-$	Alcohol soln.	−44 ± 1	1-1	0.05	Fluorine splitting

APPENDIX (*Continued*)

Name	Source[a]	Structure	Physical state	Chemical shifts (p.p.m.) relative to 85% orthophosphoric acid	Spin–spin splitting[c]		Comments
					Line structures	Splitting in gauss[b]	
Other quadruply-connected compounds							
Triethyl selenophosphate	MD	$(C_2H_5O)_3PSe$	Liquid	−71 ± 1			4 small peaks at −100, −35, 0 and +20 attrib. to imp.
(Chloromethyl)-phosphonic dichloride	M	$ClCH_2POCl_2$	Liquid	−38 ± 2			Minor peak at −23 attributed to impurity
Compounds with P–C linkages							
Phenylphosphonic acid	F	$C_6H_5PO(OH)_2$	Acetone soln.	−17.5 ± 1			
p-Chlorophenylphosphonic acid	MK	$ClC_6H_4PO(OH)_2$	Acetone soln.	−14 ± 1			
p-Ethylbenzylphosphonic acid	MK	$(C_2H_5{\cdot}C_6H_4{\cdot}CH_2)PO(OH)_2$	Acetone soln.	−26 ± 2			
3-Bromopropylphosphonic acid	MD	$(Br\text{-}C_3H_6)PO(OH)_2$	Acetone soln.	−30 ± 2			
n-Butylphosphonic acid	MK	$(C_4H_9)PO(OH)_2$	Acetone soln.	−32.5 ± 1			
n-Pentylphosphonic acid	MK	$(C_5H_{11})PO(OH)_2$	Aqueous soln.	−33 ± 1			
β-Styrenephosphonic acid	MK	$C_6H_5CH{=}CHPO(OH)_2$	Acetone soln.	−18 ± 1			Evidence of fine structure
Dibutyl ethylphosphonate	MK	$C_2H_5PO(OC_4H_9)_2$	Liquid	−31 ± 2			
Dibutyl butylphosphonate	V-C	$C_4H_9PO(OC_4H_9)_2$	Liquid	−32 ± 1			
Dibutyl nonylphosphonate	MK	$C_9H_{19}PO(OC_4H_9)_2$	Liquid	−31 ± 1			
Di-*n*-butyl decylphosphonate	M	$C_{10}H_{21}PO(OC_4H_9)_2$	Liquid	−32 ± 1			
Diethyl methylphosphonate	MB	$CH_3PO(OC_2H_5)_2$	Liquid	−30 ± 1			
Diethyl ethylphosphonate	V-C	$C_2H_5PO(OC_2H_5)_2$	Liquid	−32.5 ± 1			
Bis-(2-ethylhexyl) 2-ethylhexylphosphonate	V-C	$C_8H_{17}PO(OC_8H_{17})_2$	Liquid	−32 ± 1			
Sodium decylphosphonate	MK	$C_{10}H_{21}PO(ONa)_2$	Aq. soln.	−27 ± 2			
Bis-(*β*-chloroethyl) vinylphosphonate	MC	$H_2C{=}CH_2PO(OC_2H_4Cl)_2$	Liquid	−22 ± 1			
Dibutyl amylnaphthylphosphonate	MK	$C_5H_{11}{-}C_{10}H_6PO(OC_4H_9)_2$	Liquid	−26.5 ± 1			
Bis-(2-butoxyethyl) phenylphosphonate	MD	$C_6H_5PO(OC_2H_4OC_4H_9)_2$	Liquid	−19 ± 0.5			
Diethyl trichloromethylphosphonate	MD	$Cl_3CPO(OC_2H_5)_2$	Liquid	− 6.5 ± 0.5			
Diethyl acetylphosphonate	MB	$CH_3COPO(OC_2H_5)_2$	Liquid	+ 2 ± 1			Minor peak at −20 attributed to impurity
Diethyl benzylthiomethylphosphonate	MB	$C_6H_5CH_2SCH_2PO(OC_2H_5)_2$	Liquid	−24 ± 1			
Diethyl chloromethylphosphonate	MB	$ClCH_2PO(OC_2H_5)_2$	Liquid	−20 ± 2			
Diethyl benzoylphosphonate	MB		Liquid	+ 2 ± 1			Minor peak at −16 attributed to impurities
Diethyl dimethylcarbamylphosphonate	MB	$Me_2NC{-}PO(OC_2H_5)_2$	Liquid	0 ± 0.5			
2,4,6-Tris-(diethylphosphonyl)-1,3,5-triazine	MB	$N_3C_3(PO(OC_2H_5)_2)_3$, C–N ring	Liquid	0 ± 1			
Phenylphosphonous acid	F	$C_6H_5PO(H)(OH)$	Aq. soln.	−23 ± 1	1–1	0.33	
Phenylphosphonous acid	F	$C_6H_5PO(H)(OH)$	Acetone soln.	−20 ± 1	1–1	0.33	
Sodium 2-methyl-4-dimethylaminophenylphosphonite	M	$(Me_2N)(CH_3)C_6H_3PO(H)ONa$	Aq. soln.	−20 ± 5	1–1	0.29	

APPENDIX (*Continued*)

Name	Source[a]	Structure	Physical state	Chemical shifts (p.p.m.) relative to 85% orthophosphoric acid	Spin–spin splitting[6]		Comments
					Line structure	Splitting in gauss[b]	
Ethyl bis-(*p*-chlorophenyl)-*sec*-phosphonate	MD	$(ClC_5H_4)_2PO(OC_2H_5)$	Liquid	−27 ± 1			
Tris-(*p*-chlorophenyl)-phosphine oxide	M	$(ClC_6H_4)_3PO$	Benzene soln.	−23 ± 1			
Sulfur substitution for oxygen							
Phosphorus sulfoxide	MCr	$P_4S_4O_6$	CS_2 soln.	−16 ± 1			
Phosphorus oxychloride	F	$POCl_3$	Liquid	− 4 ± 1			
Dichlorophenylphosphine oxide or phenylphosphonic dichloride	F	$C_6H_5POCl_2$	Liquid	−34 ± 1			
Dichlorophenylphosphine sulfide or phenylphosphonothionic dichloride	F	$C_6H_5PSCl_2$	Liquid	−80 ± 1			
Tri-*p*-tolyl thiophosphate	F	$(CH_3C_6H_5O)_3PS$	Benzene soln.	−53.5 ± 1			
O,O-Dimethyl S-propyl phosphorothioate	MB	$(CH_3O)_2PO(SC_3H_7)$	Liquid	−31 ± 1			Minor peaks at −73 and −3 attributed to impurities
O,O-Diethyl S-(*p*-chlorophenyl)-phosphorothioate	MB	$(C_2H_5O)_2PO(SC_6H_4Cl)$	Liquid	−21 ± 1			Minor peaks at −14 and +3 attributed to impurities
O,O-Diethyl O-(*p*-nitrophenyl)-phosphorothioate	MB	$(C_2H_5O)_2PS(OC_6H_4NO_2)$	Liquid	−42 ± 1			
O,O-Diethyl S-phenyl phosphorothioate	MB	$(C_2H_5O)_2PO(SC_6H_5)$	Liquid	−22 ± 1			Minor peak at +1 attributed to impurity
O-Ethyl S-(*p*-chlorophenyl)-phenylphosphorothioate	MB	$C_6H_5PO(OC_2H_5)(SC_6H_4Cl)$	Liquid	−39 ± 1			Minor peaks at −17 and −9 attributed to impurities
Sodium diethylthiophosphate	MD	$(C_2H_5O)_2PS(ONa)$	Alcohol soln.	−57 ± 1			
O,O-Diisopropyl S-(*p*-chlorophenyl)-peroxyphosphorotrithioate	MB	$(i\text{-}C_3H_7O)_2PS(SS$  $Cl)$	Liquid	−74 ± 2			
		D	**More than four atoms**				
Phosphorus pentachloride	F	PCl_5	CS_2 soln.	+80 ± 2			

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[a] Key to the symbols used for acknowledging the sources of these phosphorus compounds: W, synthesized by Professor Eugene E. Weaver of Wabash College, Crawfordsville, Indiana; MC, supplied through the courtesy of Dr. D. H. Chadwick of the Organic Chemicals Division, Monsanto Chemical Company; VC, commercial samples from the Virginia–Carolina Chemical Company; F, commercial samples from the Fisher Scientific Company; MB, synthesized by Dr. Gail H. Birum of the Research and Engineering Division, Monsanto Chemical Company; MD, synthesized by Dr. W. T. Dye, Monsanto Chemical Company; B, samples obtained from Dr. A. B. Burg of the University of Southern California; Wa, sample obtained from Dr. R. W. Wagner of the American Potash and Chemical Corporation; O, sample obtained from Dr. R. A. Ogg, Jr., of Stanford University; E, commercial samples from the Eastman Kodak Company; Ba, commercial samples from the Baker Chemical Company; MM, sample obtained from R. Marotta of the Inorganic Chemicals Division, Monsanto Chemical Company, Everett, Mass.; MK, synthesized by Dr. G. M. Kosolapoff in the Monsanto Chemical Company laboratories; B&A, commercial samples from the General Chemical Division of Allied Chemical and Dye Corporation; Ma, commercial samples from the Mallinckrodt Chemical Company; Me, commercial samples from the Merck Chemical Company; MCa, prepared by C. F. Callis; MG, prepared by Dr. E. J. Griffith of the Inorganic Chemicals Division, Monsanto Chemical Company; Bl, samples obtained from Dr. Bruno Blaser of Henkel u. Cie.; MW, prepared by Felix Wright, Inorganic Chemicals Division, Monsanto Chemical Company; MN, prepared by G. D. Nelson, Inorganic Chemicals Division, Monsanto Chemical Company; MR, prepared by Dr. R. Rebertus in the Monsanto Chemical Company laboratories; MA, prepared by Dr. P. G. Arvan, Inorganic Chemicals Division, Monsanto Chemical Co.; MMH, prepared by John McCullough of the Inorganic Chemicals Div., Monsanto Chemical Co.; We, obtained from Dr. A. E. R. Westman of the Ontario Research Foundation; MNi, prepared by Dr. Morris Nielson of the Research & Eng. Div., Monsanto Chemical Co.; M, experimental sample of the Monsanto Chemical Company; MRu, obtained by Dr. R. Ruhrwein of the Research & Eng. Div., Monsanto Chemical Co.; MH, prepared by R. B. Hudson, Inorganic Chemicals Division, Monsanto Chemical Co.; MP, prepared by Dr. J. H. Payne, Inorganic Chemicals Div., Monsanto Chemical Co.; MOl, commercial samples from Oldbury Chemical Company; MCr, prepared by J. W. Cross, Inorganic Chemicals Division, Monsanto Chemical Co , Everett, Mass. [b] Average value between adjacent peaks. [c] All chain lengths given in this group were determined by end-group titration methods.

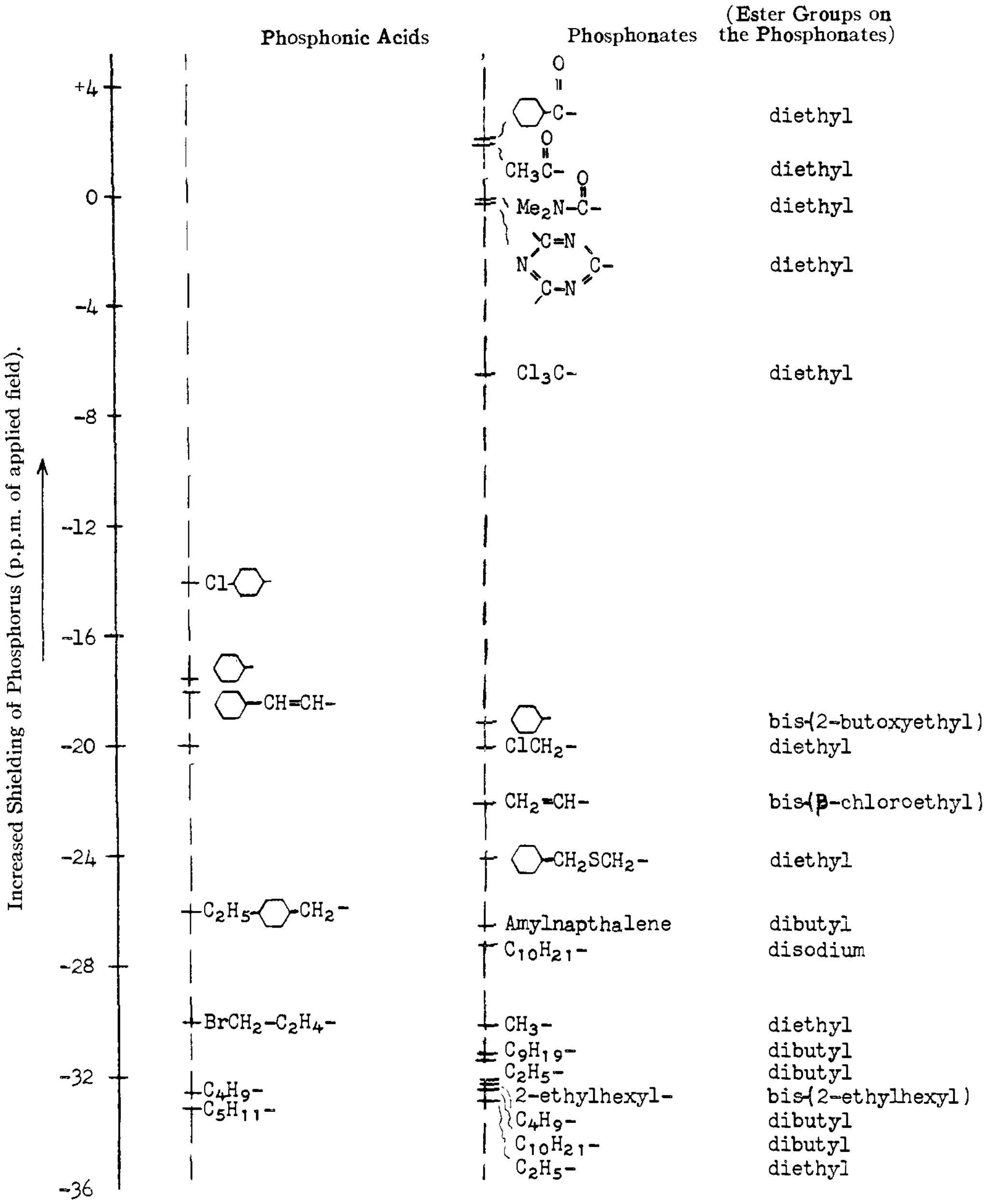

Fig. 3.—Relative electron-donating ability of organic radicals directly connected to the phosphorus, as measured by n-m-r shielding.

cleus. This technique offers the organic chemist a rapid method of determining the electron-donating ability of various radicals. The order in which the radicals are listed follows the accepted series[20] given for inductive effects for these radicals for which comparative information is given, except for hydrogen.

General Remarks.—The theoretical expression for magnetic shielding developed by Ramsey[3] divides the magnetic shielding of nuclei in molecules into two parts, a diamagnetic term which is essentially the Lamb correction[21] and a second-order paramagnetic term resulting from orbital angular momentum. Saika and Slichter[21] have calculated the chemical shift between F_2 and F^- based on this general theory. They have shown that the major contribution to the chemical shifts of fluorine are the fluctuating fields due to various instantaneous configurations of the p- (or d) orbitals in the valence shell.

Although a quantitative explanation of chemical shifts has not yet been developed for phosphorus, the observed data seem to fit the following qualitative picture. The large variations in the triply connected phosphorus compounds seem to be due to a simultaneous increase in bond angle and in s-contributions to the bonding hybrid which probably ranges from nearly pure p^3 for PH_3 to a hybrid near sp^3 for PF_3. The large positive shift for PH_3

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[20] H. Gilman, Ed., "Organic Chemistry, An Advanced Treatise," 2nd Ed., Vol. II, John Wiley and Sons, Inc., New York, N. Y., Chapter 25.

[21] A. Saika and C. P Slichter, *J. Chem. Phys.*, **22**, 26 (1954).

is thus attributed to the over-all asymmetry due to the p^3-bonds. With increasing electronegativity of the substituent atoms, this asymmetry appears to be counterbalanced by the "abortive bond" resulting from the increasing s-character of the hybrid. Finally, the "abortive bond" seems to overpower the real bonds to again cause an increase in shielding for PF_3 as compared to PBr_3.

The smaller chemical shifts found for the quadruply connected phosphorus atoms are probably due in great part to variations in the distribution of π-bonds among the four σ-bonds. The observed action of electron-donating substituents in causing less shielding of the phosphorus nucleus is thus explained by the action of these substituents in shifting π-bonds within the σ-bonded sp^3-hybrid structure so as to upset the electronic symmetry of the system. It appears that the variations from one individual compound to another in interatomic distances, as discussed in Paper I of this series, are reflected in the minor variations noted in nuclear magnetic resonance shifts. Since the purpose of Papers I and II is to establish broad generalities, peculiarities in the bonding in specific compounds are not elaborated upon here.

The large positive shifts due to more than four atoms connected to the phosphorus are probably attributable to the change in hybridization, with use of d-orbitals in the σ-bond base structure, and the similar shifts for bent bonds must be attributed to the poor overlapping of the orbitals and the resulting change in p-shell symmetry.

Acknowledgment.—The authors are indebted to the several individuals, designated in the Appendix, who generously donated many of the samples, and to Mr. John R. Parks of the Inorganic Chemicals Division of Monsanto for a number of helpful discussions.

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[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY, UNIVERSITY OF PENNSYLVANIA]

The Lower Hydrides of Phosphorus. I. The Thermal Decomposition of Biphosphine[1]

BY E. CHARLES EVERS AND EVAN H. STREET, JR.[2]

RECEIVED JUNE 4, 1956

At room temperature under strictly anhydrous conditions biphosphine decomposes in a sealed system eliminating phosphine to form a yellow solid hydride which corresponds closely in composition to P_9H_4. Yellow products having a higher H/P ratio appear to contain biphosphine. There is no evidence for the formation of Stock's $P_{12}H_6$ under these conditions.[6] But when biphosphine is decomposed in the presence of moisture substances are formed which correspond closely to $P_{12}H_6$. On heating it would appear that non-stoichiometric solid hydrides of practically any composition below P_9H_4 may be realized by employing the proper decomposition schedules. Vapor pressure and molecular weight data are recorded for biphosphine.

Introduction

Apart from some very early observations[3] four lower hydrides of phosphorus of apparently definite composition have been reported in the literature. One, biphosphine, H_4P_2, is a clear, water-white liquid, which has been characterized fairly well physically.[4,5] The other three are yellow to red colored solids which have been represented by the empirical formulas P_2H, P_9H_2 and P_5H_2, respectively.

The yellow solid hydride, P_2H, has been studied fairly extensively by Stock, *et al.*[6] It is said to be formed during the decomposition of metallic phosphides by water and in other reactions yielding phosphine or biphosphine or by thermally decomposing biphosphine. . According to Schenck and Buck,[7] the molecular weight in molten yellow phosphorus corresponds to the molecular formula, $P_{12}H_6$.

The substance P_9H_2, a red solid, was first reported by Stock and co-workers,[6] who obtained it by the thermal decomposition of P_2H in the temperature range from 100 to 220°.

Finally, the substance P_5H_2 was reportedly obtained by Hackspill[8] on hydrolysis of alkali metal phosphides of the type M_2P_5. Hackspill also reported that a solid having the composition H_2P_5 could be prepared by heating Stock's[6] P_2H to 80°. Therefore he questioned the existence of P_2H, stating that Stock's result might be explained by the presence of biphosphine stabilized by adsorption on P_5H_2.

More recently Royen and Hill[4] and Royen[9] have repeated certain of the earlier investigations on these substances and have cast some doubt as to the existence of the solid hydrides as true chemical entities. Their investigations indicated that solids of variable composition, amorphous to X-rays, were formed when biphosphine was decomposed thermally under various conditions. . They also reported that substances of similar composition and properties could be formed by the direct reaction of white phosphorus and phosphine, and concluded that the solid forms were "absorbates" of phosphine on an allotropic modification of phosphorus.

Our present investigation was undertaken primarily in an attempt to resolve the question of the stoichiometry of products obtained by decomposing biphosphine thermally. We were particularly concerned with the reliability of certain previous data

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[2] Taken from a Thesis by Evan H. Street, Jr., presented in partial fulfillment of the requirements for the Ph.D. degree, June, 1955.

[3] J. W. Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Longmans, Green and Co., New York, N. Y., 1923, p. 802.

[4] P. Royen and K. Hill, *Z. anorg. allgem. Chem.*, **229**, 97 (1936).

[5] Recent molecular structure studies have been carried out by E. R. Nixon, *J. Chem. Phys.*, in press.

[6] A. Stock, W. Böttcher and W. Langer, *Ber.*, **42**, 2630, 2847, 2853 (1909).

[7] R. Schenck and E. Buck, *ibid.*, **37**, 915 (1904).

[8] L. Hackspill, *Compt. rend.*, **156**, 1466 (1913).

[9] P. Royen, *Z. anorg. allgem. Chem.*, **229**, 112 (1936).