Phosphorus-31 Nuclear Magnetic Resonance Spectra of Phosphorus Compounds

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DATA REPORTED in this paper represent a compilation of 200 new nuclear magnetic resonance (n.m.r.) chemical shifts of phosphorus compounds (Table I). A detailed discussion and evaluation of these P^{31} chemical shifts are available (2). The reported shifts constitute important information contributing to the field of organophosphorus chemistry and nuclear magnetic reasonance spectroscopy.

EXPERIMENTAL

All n.m.r. measurements were made on a Varian Model V-4300B high-resolution spectrometer with a radio frequency of 16.2 Mc. and a magnetic field of approximately 9395 gauss, using a Varian magnet, Model V-4012-HR. Chemical shifts are reported in parts per million of the applied field using 85% H_3PO_4 as a standard (zero shift). Upfield shifts are denoted by a plus sign and downfield shifts by a minus sign. The chemical shifts were determined by the concentric-tube technique, whereby a narrow tube containing the reference compound was inserted in the sample, giving an accuracy depending on the broadness of the peak of ca. ±0.5 p.p.m. for well-resolved reasonances. The few data obtained by the tube-interchange technique are marked by a superscript *b* and are accurate within ca. ±1.5 p.p.m. Most of the samples were contained in 15-mm. O.D. borosilicate glass tubes. When only a small quantity (as little as 100 mg.) of sample was available, either a 5-mm. O.D. tube was used with the proper probe insert or the tube in the sample holder was adjusted to a depth at which maximum response from the coil was obtained.

Most of the n.m.r. shifts have been obtained with pure samples. However, some of the compounds or phosphorus structure-building units have not been separated. In almost every case, compounds which were not isolated were contained in the reaction products of random reorganization reactions carried out in sealed borosilicate glass tubes.

Spin-spin splits, wherever observed, are also included and the respective coupling constants are reported in cycles per

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Table I. Nuclear Magnetic Resonance Spectra of Phosphorus Compounds

Structure	Physical State	Chemical Shift, P.P.M.	Obsd. Spin-Spin Splitting: No. peaks[a] expected	Obsd. Spin-Spin Splitting: Coupling constant, c.p.s.
Inorganic compounds				
POF_3[b]	Liquid under pressure	+35.5	4	1080
Na_3PS_4	In 3% Na_2S	−87.5	...	...
Na_3POS_3	In 3% Na_2S	−86.5	...	...
$Na_3PO_2S_2$	In 3% Na_2S	−61.9	...	...
Na_3PO_3S	In 3% Na_2S	−33.8	...	...
Phosphines				
$(CH_3)_2PH$[c]	In $(C_4H_9)_3PS$	+99.5	2	188
$(C_2H_5)_2PH$	In $(C_4H_9)_3PS$	+55.5	2	190
$(n\text{-}C_4H_9)_2PH$	In $(C_4H_9)_3PS$	+69.5	2	180
$(C_6H_5)_2PH$	Liquid	+41.1	2	214
$CH_3(C_2H_5)PH$	Liquid	+77.0	2	191
$CH_3(C_3H_7)PH$	Liquid	+87.0	2	196
$CH_3(C_4H_9)PH$	Liquid	+86.0	2	202
$CH_3(C_6H_5)PH$	Liquid	+72.3	2	222
$C_2H_5(C_6H_5)_2P$[d]	In $CHCl_3$	+13.5	...	...
$(C_2H_5)_2(C_6H_5)P$[e]	In $CHCl_3$	+15.1	...	...
$(C_6H_5)_2PCH_2P(C_6H_5)_2$	In CH_3COCH_3	+23.6	...	...
$CH_3(C_6H_5)_2P$	In $CHCl_3$	+28.0	...	...
Halophosphines				
CH_3PCl_2[f]	Liquid	−192.0	4	16
CH_2ClPCl_2	Liquid	−158.9	3	16
$C_2H_5PCl_2$	Liquid	−196.3	...	...
CH_3PClBr	Liquid	−190.0	...	...
CH_3PBr_2	Liquid	−184.0	4	24
$C_2H_5PBr_2$	Liquid	−194.0	...	...
$C_6H_5PBr_2$	Liquid	−152.0	...	...
$(C_2H_5)_2PCl$	Liquid	−119.0	...	...
$(C_6H_5)_2PCl$	Liquid	−81.5	...	...
$CH_3(C_2H_5)PCl$	Liquid	−105.2	...	...
$CH_3(C_6H_5)PCl$	Liquid	−83.4	...	...
$C_2H_5(C_6H_5)PCl$	Liquid	−97.0	...	...
$(CH_3)_2PBr$	Liquid	−87.9	...	...
$(C_2H_5)_2PBr$	Liquid	−116.2	...	...
$(C_6H_5)_2PBr$	[g]	−70.8	...	...
$CH_3(C_2H_5)PBr$	Liquid	−98.5	...	...
$CH_3(C_6H_5)PBr$	In $(C_4H_9)_3PS$	−77.0	...	...

Table I. (*Continued*)

Structure	Physical State	Chemical Shift, P.P.M.	Obsd. Spin-Spin Splitting: No. peaks[a] expected	Obsd. Spin-Spin Splitting: Coupling constant, c.p.s.
Aminophosphines				
$[(CH_3)_2N]_3P$[b]	Liquid	−123.0	...	...
$[(C_2H_5)_2N]_3P$[c]	Liquid	−119.0	...	...
$[(CH_3)_2N]_2PCH_3$	Liquid	−86.4	...	...
$[(C_2H_5)_2N]_2PCH_3$	Liquid	−80.4	...	...
$[(CH_3)_2N]_2PCl$	Liquid	−160.0	...	...
$[(C_2H_5)_2N]_2PCl$	Liquid	−154.0	...	...
$(CH_3)_2N(CH_3)PCl$	Liquid	−150.7	...	...
$(C_2H_5)_2N(CH_3)PCl$	Liquid	−143.0	...	...
$(CH_3)_2N(CH_3)PBr$	Liquid	−161.1	...	...
$(CH_3)_2NPCl_2$	Liquid	−166.0	...	...
$(C_2H_5)_2NPCl_2$	Liquid	−162.0	5	12
Diphosphines				
$(CH_3)_2P\text{-}P(CH_3)_2$	In $(C_4H_9)_3PS$	+59.5	...	...
$(C_2H_5)_2P\text{-}P(C_2H_5)_2$	In $(C_4H_9)_3PS$	+34.3	...	...
$CH_3(C_2H_5)P\text{-}P(C_2H_5)CH_3$[d]	Liquid	+44.7	...	...
		+46.1	...	...
$CH_3(C_6H_5)P\text{-}P(C_6H_5)CH_3$[d]	In $(C_4H_9)_3P$	+38.2	...	...
		+41.9	...	...
Dialkylphosphite salts				
$LiOP(OC_4H_9)_2$	In diglyme	−145.0	...	...
$KOP(OC_2H_5)_2$	In diglyme	−152.3	...	...
$KOP(OC_4H_9)_2$	In diglyme	−152.0	...	...
$NaOP(OC_2H_5)_2$	In diglyme	−153.0	...	...
$NaOP(OC_4H_9)_2$	In diglyme	−153.5	...	...
$NaOP(OC_6H_5)_2$	In diglyme	−146.7	...	...
Alkylthio dihalophosphites				
$(CH_3S)PCl_2$	Liquid	−206.0	...	...
$(C_2H_5S)PCl_2$	"	−210.7	...	...
$(n\text{-}C_3H_7S)PCl_2$	"	−212.6	...	...
$(C_5H_{11}S)PCl_2$	"	−210.4	...	...
$(C_7H_{15}S)PCl_2$	Liquid	−211.0	...	...
$[(CH_3)_2CHS]PCl_2$	"	−211.0	...	...
$(CH_2{=}CH\text{-}CH_2S)PCl_2$	"	−210.1	...	...
$(C_6H_5S)PCl_2$	Liquid	−204.2	...	...
$(C_6H_5CH_2S)PCl_2$	"	−205.5	...	...
$(CH_3S)PBr_2$	"	−203.5	4	ca. 7
$(C_6H_5S)PBr_2$	"	−203.5	...	...
Dialkylthio halophosphites				
$(CH_3S)_2PCl$[b]	"	−188.2	7	11
$(C_2H_5S)_2PCl$[b]	"	−186.2	5	ca. 11
$(n\text{-}C_3H_7S)_2PCl$[b]	"	−189.4	5	ca. 13
$(C_5H_{11}S)_2PCl$[b]	"	−187.2	5	ca. 11
$(C_7H_{15}S)_2PCl$[b]	"	−187.7	...	...
$[(CH_3)_2CHS]_2PCl$[b]	"	−181.6	...	...
$(CH_2{=}CH\text{-}CHS)_2PCl$[b]	"	−185.1	...	...
$(C_6H_5S)_2PCl$[b]	"	−182.7	...	...
$(C_6H_5CH_2S)_2PCl$[b]	"	−180.3	5	ca. 11
$(C_6H_5S)_2PBr$[b]	"	−184.2	...	...
Thiophosphite esters				
$(CH_3S)_3P$[b]	Liquid	−125.6	10	12
$(C_4H_9S)_3P$	In $(C_4H_9)_3PS$	−116.1	...	...
$(C_6H_5S)_3P$[b]	Liquid	−130.5	...	...
Various triply connected organic phosphorus compounds				
$ClCH_2P(OC_6H_5)_2$	Liquid	−153.6	...	...
$C_6H_5P(OC_6H_5)_2$	Liquid	−164.9	...	...
$[(CH_3)_2PBH_2]_{3\text{ or }4}$	In CH_3OH	+47.0	Multiple	...
Phosphine oxides				
$(C_6H_5)_3PO$	In $CHCl_3$	−27.0	...	...
$(CH_2Cl)_3PO$	In C_2H_5OH	−38.1	...	...
$(CH_2OH)_3PO$	In H_2O	−45.4	...	...
$CH_2Cl(C_6H_5)_2PO$	In $CHCl_3$	−30.4	...	...
$CH_2Cl(CH_3)_2PO$	In $CHCl_3$	−42.0	...	...
$CH_3(CH_2Cl)(C_2H_5)PO$	In $CHCl_3$	−48.0	...	...
$CH_3(CH_2Cl)(C_6H_5)PO$	In $CHCl_3$	−47.2	...	...
$(C_6H_5)_2(O)PCH_2P(O)(C_6H_5)_2$	In C_2H_5OH	−26.4	...	...
$(C_6H_5)_2PHO$	In diglyme	−22.9	2	490
Phosphine sulfides				
$(CH_3)_3PS$		−59.1	...	...
$(C_4H_9)_3PS$	In $CHCl_3$	−48.0	...	...
$(C_6H_5)_3PS$	In $CHCl_3$	−42.6	...	...
$(CH_3)_2(C_2H_5)PS$	In $CHCl_3$	−57.0	...	...
$CH_3(C_2H_5)_2PS$	In $CHCl_3$	−57.0	...	...
$(C_2H_5)_2(C_6H_5)PS$	In $CHCl_3$	−52.0	...	...
$(CH_3)_2(S)P\text{-}P(S)(CH_3)_2$	In $CHCl_3$	−34.7	...	...

Table I. Nuclear Magnetic Resonance Spectra of Phosphorus Compounds (*Continued*)

Structure	Physical State	Chemical Shift, P.P.M.	Obsd. Spin-Spin Splitting	
			No. peaks[a] expected	Coupling constant, c.p.s.
$(C_2H_5)_2(S)P\text{-}P(S)(C_2H_5)_2$	In CH_3COCH_3	−49.4	...	...
$CH_3(C_2H_5)(S)P\text{-}P(S)(C_2H_5)CH_3$	In $CHCl_3$	−44.5	...	...
$CH_3(n\text{-}C_3H_7)(S)P\text{-}P(S)(n\text{-}C_3H_7)CH_3$	In $CHCl_3$	−40.1	...	...
$CH_3(C_6H_5)(S)P\text{-}P(S)(C_6H_5)CH_3$	In $CHCl_3$	−37.0	...	...
Phosphinic chlorides				
$(CH_3)_2POCl$	In CCl_4	−62.8	7	19
$(CH_2Cl)_2POCl$	Liquid	−49.3	5	12
$(C_2H_5)_2POCl$	In CCl_4	−76.7	...	...
$(C_6H_5)_2POCl$	Liquid	−42.7	...	...
$CH_3(CH_2Cl)POCl$	Liquid	−57.0	...	...
$CH_3(C_2H_5)POCl$[a]	In CCl_4	−67.9	...	...
$CH_3(C_6H_5)POCl$	In CCl_4	−52.0	...	...
$CH_2Cl(C_6H_5)POCl$	Liquid	−44.4	...	...
$C_2H_5(C_6H_5)POCl$	In CCl_4	−59.0	...	...
Thionophosphinic chlorides				
$(CH_3)_2PSCl$	Liquid	−87.3	...	...
$(C_2H_5)_2PSCl$	Liquid	−108.3	...	...
$(C_6H_5)_2PSCl$	Liquid	−79.5	...	...
$CH_3(CH_2Cl)PSCl$	Liquid	−85.0	...	...
$CH_3(C_2H_5)PSCl$	Liquid	−98.0	...	...
$CH_3(n\text{-}C_3H_7)PSCl$	Liquid	−95.3	...	...
$CH_3(n\text{-}C_4H_9)PSCl$	Liquid	−96.5	...	...
$CH_3(C_6H_5)PSCl$	Liquid	−81.0	...	...
$C_2H_5(CH_2Cl)PSCl$	Liquid	−95.6	...	...
$C_2H_5(C_6H_5)PSCl$	Liquid	−93.7	...	...
$C_6H_5(CH_2Cl)PSCl$	Liquid	−77.0	...	...
Thionophosphinic bromides				
$(CH_3)_2PSBr$	In $CHCl_3$	−63.2	...	...
$(C_2H_5)_2PSBr$[b]	Liquid	−98.3	...	...
$(C_4H_9)_2PSBr$[b]	Liquid	−91.2	...	...
$CH_3(C_2H_5)PSBr$	Liquid	−85.0	...	...
$CH_3(C_6H_5)PSBr$	In CCl_4	−61.0	...	...
$CH_3(C_6H_5CH_2)PSBr$	In CCl_4	−73.7	...	...
Phosphonic and thionophosphonic halides				
CH_3POCl_2	In THF	−43.5	...	...
$CHCl_2POCl_2$	Liquid	−10.3	...	...
$ClCH_2CH_2POCl_2$	Liquid	−41.9	...	...
$CH_2(POCl_2)_2$	In petrol. ether	−24.4	...	...
$CH_2ClPOClF$[b]	[c]	−32.0	2	1180
CH_2ClPOF_2[b]	[c]	−11.5	3	1140
$CH_2ClPSCl_2$	Liquid	−73.0	...	...
$C_6H_5CH_2PSCl_2$	[c]	−85.3	...	...
$CH_3PSClBr$	Liquid	−51.0	4	13
CH_3PSBr_2	Liquid	−20.5	4	13
$CH_2BrPSBr_2$	Liquid	−20.0	...	...
$C_6H_5PSBr_2$[b]	[c]	−20.2	...	...
Phosphonic acids				
$CH_3PO(OH)_2$	In water	−29.8	4	15
$CH_2ClPO(OH)_2$	In water	−17.8	3	11
$HOCH_2PO(OH)_2$	In water[d]	−23.5	...	...
$C_{12}H_{25}PO(OH)_2$	In THF	−29.9	...	...
$C_6H_5PO(OH)_2$	In water	−18.5	...	...
$CH_3C_6H_4PO(OH)_2$[b]	In water[d]	−19.5	...	...
$NH[CH_2PO(OH)_2]_2$	In water	−9.8	3	10
$N[CH_2PO(OH)_2]_3$	In water	−9.5	3	12
Diphosphonic acids				
$CH_2[PO(OH)_2]_2$	In water	−16.7	...	...
$(CH_2)_2[PO(OH)_2]_2$	In water	−27.4	...	...
$(CH_2)_3[PO(OH)_2]_2$	In water	−28.2	...	...
$(CH_2)_4[PO(OH)_2]_2$	In water	−31.6	...	...
$(CH_2)_5[PO(OH)_2]_2$	In water	−31.9	...	...
$(CH_2)_6[PO(OH)_2]_2$	In water	−30.6	...	...
$(CH_2)_{10}[PO(OH)_2]_2$	In THF	−28.6	...	...
Thiophosphate esters				
$(n\text{-}C_3H_7S)_3PS$	Liquid	−93.1	7	17
$(n\text{-}C_4H_9S)_3PS$	Liquid	−92.6	7	17
$(C_6H_5S)_3PS$	In toluene	−91.1	...	...
$(C_2H_5O)_3PS$	Liquid	−68.1	7	8
Halophosphate esters				
$(C_2H_5O)_2POCl$	Liquid	−3.3	...	...
$(CH_3O)POCl_2$	Liquid	−5.6	...	...
$(C_2H_5O)POCl_2$	Liquid	−3.4	...	...

Table I. (*Continued*)

Structure	Physical State	Chemical Shift, P.P.M.	Obsd. Spin-Spin Splitting: No. peaks[a] expected	Obsd. Spin-Spin Splitting: Coupling constant, c.p.s.
$(C_2H_5O)POF_2$	Liquid	+21.2	3	1010
$(CH_3O)_2PSCl$	Liquid	−72.9	...	...
$(C_2H_5O)_2PSCl$	Liquid	−67.7	...	...
Phosphonic esters				
$CH_3PO(OCH_3)_2$	Liquid	−32.3	...	...
$CH_2ClPO(OCH_3)_2$	Liquid	−18.5	...	...
$CH_2ClPO(OC_2H_5)_2$[b]	Liquid	−18.1	Multiple	...
$CH_2ClPO(OC_6H_5)_2$	Liquid	−12.3	...	...
$CH_2IPO(OC_2H_5)_2$	Liquid	−19.8	...	...
$CH_3CHClPO(OC_2H_5)_2$	Liquid	−20.2	...	...
$ClCH_2CH_2PO(OC_2H_5)_2$	Liquid	−24.4	...	...
$BrCH_2CH_2PO(OC_2H_5)_2$	Liquid	−28.5	...	...
$ClCH_2CH_2PO(OCH_2CH_2Cl)_2$	Liquid	−27.0	...	...
$C_6H_5PO(OC_2H_5)_2$	Liquid	−16.9	...	...
$C_{12}H_{25}PO(OC_2H_5)_2$	Liquid	−29.9	...	...
$CH_2ClPO(Cl)(OC_6H_5)$[b]	[g]	−26.8	...	...
$NH[CH_2PO(OC_2H_5)_2]_2$	Liquid	−23.3	...	...
$N[CH_2PO(OC_2H_5)_2]_3$	Liquid	−22.6	...	...
Diphosphonic esters				
$CH_2[PO(OC_2H_5)_2]_2$	Liquid	−19.0	Multiple	...
$(CH_2)_2[PO(OC_2H_5)_2]_2$	Liquid	−26.8	...	...
$(CH_2)_3[PO(OC_2H_5)_2]_2$	Liquid	−29.3	...	...
$(CH_2)_4[PO(OC_2H_5)_2]_2$	Liquid	−31.5	...	...
$(CH_2)_5[PO(OC_2H_5)_2]_2$	Liquid	−30.8	...	...
$(CH_2)_6[PO(OC_2H_5)_2]_2$	Liquid	−29.6	...	...
$(CH_2)_{10}[PO(OC_2H_5)_2]_2$	Liquid	−30.9	...	...
Phosphate-phosphonates				
$(C_2H_5O)_2OP\text{-}O\text{-}CH(CH_3)PO(OC_2H_5)_2$	Liquid	−21.1	...	...
		+1.7	...	...
$(C_2H_5O)_2OP\text{-}O\text{-}CH(C_6H_5)PO(OC_2H_5)_2$	Liquid	−16.3	...	...
		+1.4	...	...
Phosphinic acids and esters				
$(CH_3)_2POOH$	In C_6H_6	−48.6	...	...
$(CH_2Cl)_2POOH$	In H_2O	−32.0	...	...
$(C_6H_5)_2POOH$	In C_2H_5OH	−25.5	...	...
$CH_3(CH_2Cl)POOH$	In H_2O	−50.7	...	...
$C_6H_5(CH_2Cl)POOH$	In THF	−36.3	...	...
$(CH_2Cl)_2PO(OC_2H_5)$	In Liquid	−39.7	...	...
Phosphinic acid anhydrides				
$O[OP(CH_3)_2]_2$	In THF	−52.6	...	...
$O[OP(CH_2Cl)_2]_2$	In THF	−37.3	...	...
$O[OP(C_6H_5)_2]_2$	In $CHCl_3$	−33.1	...	...
$O[OP(CH_2Cl)(CH_3)]_2$	Liquid	−45.9	...	...
$O[OP(CH_2Cl)(C_6H_5)]_2$	Liquid	−30.9	...	...
Miscellaneous quadruply connected compounds				
$(CH_3)_2NP(O)Cl_2$[b]	Liquid	−16.1	7	15
$(C_2H_5)_2NP(O)(Cl)CH_2Cl$	Liquid	−35.6	...	...
$[(CH_3)_3PH]Cl$	Liquid	+2.8	2	495
$[(HOCH_2)_4P]Cl$	In water	−25.2	...	...
$[(C_6H_5)_3CH_3P]I$	In ethanol	−21.0	...	...
Phosphonic acid anhydrides				
$[CH_3P(O)O]_n$	Liquid	−13.8	...	...
$[CH_2ClP(O)O]_n$	Liquid	−1.4	...	...
$[C_6H_5P(O)O]_n$	Liquid	0	...	...
Quintuply connected phosphorus compounds				
PCl_5[m]	At 170° C.	+78.6	...	...
PF_5	Liquid under pressure	+35.1	6	1010

[a] Relative intensity of peaks. 1-1 for doublet, 1-2-1 for triplet, 1-3-3-1 for quadruplet, etc. (binomial series). [b] Chemical shift determined by tube interchange technique. [c] Reported +98.5 (*4*). [d] Reported +12.0 (*3*). [e] Reported +16.0 (*3*). [f] Reported −191.2 (*1*). [g] Resonance identified in spectrum of mixture of phosphorus compounds (*2*). [h] Reported −122 ± 2 (*4*). [i] Reported −118 ± 3 (*4*). Two different resonance peaks as a result of two possible different steric isomeric structures. [k] Reported −72.0 (*1*). [l] Reported −20 ± 2 (*4*). [m] Reported +80 ± 2 (*4*).

second. The number of peaks expected in such splits is given and their relative expected intensities are 1-1, 1-2-1, 1-3-3-1, etc. (binomial series), for doublets, triplets, quadruplets, etc., respectively.

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