# Phosphorus-31 Nuclear Magnetic Resonance Chemical Shifts of Phosphorus Compounds

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THE NUCLEAR MAGNETIC resonance (NMR) chemical shifts of 140 phosphorus compounds are reported. These are listed (Table I) by classes of compounds so that relationships between chemical shifts and the substituent groups on phosphorus can be recognized. These data are useful for qualitative identification of these specific compounds and, to some extent, related compounds by extrapolation.

## EXPERIMENTAL

The NMR spectra were obtained on a Varian Model V-4300-2 high-resolution spectrometer with a radio frequency of 16.2 Mc. and a magnetic field of approximately 9400 gauss, using a Varian magnet, Model V-4012-A. Chemical shifts are reported in parts per million (p.p.m.) of the applied field using 85% $H_3PO_4$ as the reference standard (zero shift). Upfield shifts are denoted by a plus sign , downfield shifts by a minus sign. The samples were contained in a 15-mm. O.D. Pyrex glass tube with a narrow (1-2 mm.) tube containing the $H_3PO_4$ inserted concentrically through the stopper. Accuracy is approximately ± 0.5 p.p.m. The data were obtained with pure samples of isolated compounds, identified independently by physical constants or elemental analyses. The solvents used are reported, since, for some of the compounds, the chemical shifts varied for different solvents.

Spin-spin splitting is reported where observed under the instrument conditions described, with the number of peaks and the coupling constant in c.p.s. Chemical shifts for nonequivalent phosphorus nuclei in the same molecule are shown, with assignments to the respective $P_\alpha$, $P_\beta$, etc.

Correlations between structure and chemical shifts of the P-N compounds are discussed in a separate paper elsewhere (1).

Table I. Nuclear Magnetic Resonance Spectra of Phosphorus Compounds

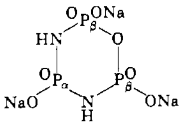
| Compound | Physical State | Chemical Shift, p.p.m. | Spin-Spin Splitting | |
|---|---|---|---|---|
| | | | No. Peaks | Coupling Constant, c.p.s. |
| Phosphines | | | | |
| $[C_6H_5P]$ n = 2 or 4 | In benzene | +4.6 | ... | ... |
| Aminophosphines, substituted | | | | |
| $(C_6H_5)_2NPCl_2$ | In toluene | −151.3 | ... | ... |
| Phosphites | | | | |
| $(C_6H_5CH_2O)_2P(O)H$ | Liquid | −7.9 | 2 | 713 |
| Halophosphate esters | | | | |
| $C_6H_5OP(O)Cl_2$ | Liquid | −1.8 | ... | ... |
| $(C_6H_5O)_2P(O)Cl$ | Liquid | +6.1 | ... | ... |
| $(C_6H_5CH_2O)_2P(O)Cl$ | Liquid | −4.7 | ... | ... |
| $(4\text{-}NO_2C_6H_4CH_2O)_2P(O)Cl$ | In $CHCl_3$ | −5.2 | ... | ... |
| Phosphoramidic chlorides | | | | |
| $[(CH_3)_2N]_2P(O)Cl$ | Liquid | −29.6 | ... | ... |
| $C_6H_5NHP(O)Cl_2$ | Liquid | −7.6 | ... | ... |
| $C_6H_5N(CH_3)P(O)Cl_2$ | Liquid | −13.6 | ... | ... |
| $(C_6H_5)_2NP(O)Cl_2$ | In dioxane | −8.2 | ... | ... |
| $(C_6H_5NH)_2P(O)Cl$ | In dioxane | −4.1 | ... | ... |
| $[(C_6H_5)_2N]_2P(O)Cl$ | In DME[a] | −8.1 | ... | ... |
| Miscellaneous chlorides | | | | |
| $C_6H_5(C_6H_5O)P(O)Cl$ | Liquid | −25.1 | ... | ... |
| $C_6H_5(CH_3)NP(O)(C_6H_5)Cl$ | Liquid | −36.7 | ... | ... |
| $C_6H_5(CH_3)NP(O)(NHC_6H_5)Cl$ | In THF[b] | −10.0 | ... | ... |
| $(C_6H_5O)_2P(O)N{=}PCl_3$ | Liquid | +12.0 | ... | ... |
| Miscellaneous pseudohalides | | | | |
| $(C_6H_5O)_2P(O)NCS$ | Liquid | +29.3 | ... | ... |
| Phosphates | | | | |
| $(C_2H_5O)_2P(O)OH$ | In water | 0.0 | ... | ... |
| $(C_2H_5O)_2P(O)ONH_4$ | In water | +0.5 | ... | ... |
| $(C_2H_5O)_2P(O)ONa$ | In water | −3.8 | ... | ... |
| $C_6H_5OP(O)(OH)_2$ | In water | +4.8 | ... | ... |
| $C_6H_5OP(O)(ONa)_2$ | In water | 0.0 | ... | ... |
| $C_6H_5OP(O)(OH)_2 \cdot C_6H_5NH_2$ | In pyridine | +4.6 | ... | ... |
| $C_6H_5OP(O)(OH)_2 \cdot C_6H_4(NH_2)_2\text{-}2$ | In DMF[c] | +6.2 | ... | ... |
| $(C_6H_5O)_2P(O)OH$ | In $CH_3OH$ | +12.7 | ... | ... |
| $(C_6H_5O)_2P(O)ONH_4$ | In water | +9.8 | ... | ... |
| $(C_6H_5O)_2P(O)ONa$ | In water | +9.0 | ... | ... |
| $(C_6H_5CH_2O)_2P(O)OH$ | In dioxane | +1.1 | ... | ... |

*(Continued on page 168)*

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

| Compound | Physical State | Chemical Shift, p.p.m. | Spin-Spin Splitting: No. Peaks | Spin-Spin Splitting: Coupling Constant, c.p.s. |
|---|---|---|---|---|
| $(4\text{-}NO_2C_6H_4O)_2P(O)OH$ | In acetone | +15.4 | ... | ... |
| $(4\text{-}NO_2C_6H_4CH_2O)_2P(O)OH$ | In DMF | +1.7 | ... | ... |
| $(4\text{-}NO_2C_6H_4CH_2O)_2P(O)ONa$ | In water | +1.0 | ... | ... |
| $(4\text{-}NO_2C_6H_4CH_2O)_3PO$ | In DMF | +0.7 | ... | ... |
| Phosphoric acid anhydrides | | | | |
| $(C_2H_5O)_2P(O)OP(O)(OC_2H_5)_2$ | Liquid | +13.4 | ... | ... |
| $(C_6H_5O)_2P(O)OP(O)(OC_6H_5)_2$ | Liquid | +23.9 | ... | ... |
| $(C_6H_5CH_2O)_2P(O)OP(O)(OCH_2C_6H_5)_2$ | In benzene | +12.6 | ... | ... |
| $(4\text{-}NO_2C_6H_4CH_2O)_2P(O)OP(O)(OCH_2C_6H_4NO_2)_2$ | In DMF | +14.5 | ... | ... |
| $(C_6H_5O)_2P_\alpha(O)OP_\beta(O)(OC_6H_5)OP(O)(OC_6H_5)_2$ | Liquid | $P_\alpha = +26.6$<br>$P_\beta = +35.6$ | 2<br>3 | 16<br>16 |
| Phosphonic acids, salts and esters | | | | |
| $CH_3P(O)(ONH_4)_2$ | In water | −19.3 | 4 | 11 |
| $CH_3P(O)(OC_3H_7)_2$ | Liquid | −27.4 | ... | ... |
| $CH_3P(O)(OC_6H_5)_2$ | Liquid | −24.1 | 4 | 9 |
| $C_6H_5P(O)(ONH_4)_2$ | In water | −10.8 | ... | ... |
| $C_6H_5P(O)(ONa)_2$ | In water | −13.8 | ... | ... |
| $C_6H_5P(O)(OCH_3)_2$ | Liquid | −21.4 | ... | ... |
| $C_6H_5P(O)(OC_6H_5)_2$ | In ethanol | −11.8 | ... | ... |
| $(C_6H_5O)_2P(O)\overline{N{-}CH{=}N{-}CH{=}C}H$ | In THF | +15.7 | ... | ... |
| Phosphoramidic acids, salts and esters | | | | |
| $(NaO)_2P(O)NH_2$ | In water | −8.9 | ... | ... |
| $(CH_3O)_2P(O)NH_2$ | In methanol | −15.2 | ... | ... |
| $(C_2H_5O)_2P(O)NH_2$ | In $CH_3COOC_2H_5$ | −11.1 | ... | ... |
| $(C_4H_9O)_2P(O)NH_2$ | Liquid | −12.1 | ... | ... |
| $C_5H_5O(NH_4O)P(O)NH_2$ | In water | −0.5 | ... | ... |
| $(C_6H_5O)_2P(O)NH_2$ | In DMSO[d] | −2.8 | ... | ... |
| $(C_6H_5CH_2O)_2P(O)NH_2$ | In ethanol | −12.0 | ... | ... |
| $HOP(O)(NH_2)_2$ | In water | +0.2 | ... | ... |
| $NaOP(O)(NH_2)_2$ | In water | −14.5 | ... | ... |
| $NaOP(S)(NH_2)_2$ | In water | −54.2 | ... | ... |
| $C_6H_5OP(O)(NH_2)_2$ | In DMSO | −15.2 | ... | ... |
| $C_6H_5OP(S)(NH_2)_2$ | In methanol | −68.6 | ... | ... |
| N-substituted phosphoramidic acids, salts and esters | | | | |
| $(HO)_2P(O)NHC_6H_5$ | In DMF | +12.0 | ... | ... |
| $C_6H_5O(HO)P(O)NHC_6H_5$ | In DMF | +4.1 | ... | ... |
| $(C_6H_5O)_2P(O)NHCH_3$ | In DMF | +1.2 | ... | ... |
| $(C_6H_5O)_2P(O)NHC_6H_5$ | In DMF | +7.1 | ... | ... |
| $(C_6H_5O)_2P(O)NHC_6H_{11}$ | In $CHCl_3$ | +0.4 | ... | ... |
| $C_6H_5O(HO)P(O)(o\text{-}NHC_6H_4NH_2)$ | In 1-M-2-P[e] | +6.0 | ... | ... |
| $C_6H_5O\overline{P(O)NHC_6H_4N}H\text{-}2$ | In ethanol | −18.1 | 3 | 15 |
| $C_6H_5O\overline{P(O)NHC_6H_4N}H\cdot C_5H_5N$ | In pyridine | −17.8 | 3 | 13 |
| $C_6H_5OP(O)(NHC_6H_{11})_2$ | In ethanol | −10.7 | ... | ... |
| $NaOP(O)[N(C_6H_5)_2]_2$ | In DME | +3.8 | ... | ... |
| $C_6H_5OP(O)(NHCH_3)_2$ | In ethanol | −16.0 | ... | ... |
| $C_6H_5OP(O)(NHC_6H_5)_2$ | In DMF | +2.3 | ... | ... |
| $NaO\overline{P(O)NHC_6H_4N}H\text{-}2$ | In water | −21.2 | ... | ... |
| Phosphoric amides | | | | |
| $PO(NH_2)_3$ | In water | −22.0 | ... | ... |
| $PS(NH_2)_3$ | In water | −61.1 | ... | ... |
| $(CH_3)_2NP(O)(NHC_6H_5)_2$ | In dioxane | −6.4 | ... | ... |
| $(CH_3)_2NP(O)(NHC_6H_{11})_2$ | In benzene | −15.7 | ... | ... |
| $(CH_3)_2NP(O)[N(CH_3)C_6H_5]_2$ | Liquid | −25.5 | ... | ... |
| $(CH_3)_2NP(O)[N(C_6H_5)_2]_2$ | In $CHCl_3$ | −8.9 | ... | ... |
| $PO(NHC_6H_5)_3$ | In DME | +4.8 | 4 | 10 |
| $PO(NCH_3C_6H_5)_3$ | In DME | −13.0 | ... | ... |
| $PO[N(C_6H_5)_2]_3$ | In $CH_2Cl_2$ | −1.7 | ... | ... |
| $C_6H_5NHP(O)(NHC_6H_{11})_2$ | In ethanol | −8.0 | ... | ... |
| $C_6H_5N(CH_3)P(O)(NHC_6H_{11})_2$ | In benzene | −11.0 | ... | ... |
| $(C_6H_5)_2NP(O)(NHC_6H_{11})_2$ | In 1-M-2-P | −6.8 | ... | ... |
| Phosphonic amides | | | | |
| $CH_3P(S)(NHC_6H_{11})_2$ | In DMF | −65.4 | ... | ... |
| $C_6H_5P(O)(NH_2)_2$ | In *m*-cresol | −25.4 | ... | ... |
| $C_6H_5P(S)(NH_2)_2$ | In ethanol | −64.5 | ... | ... |
| $C_6H_5P(O)(NHC_6H_5)_2$ | In DMF | −8.4 | ... | ... |

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

| Compound | Physical State | Chemical Shift, p.p.m. | Spin-Spin Splitting | |
|---|---|---|---|---|
| | | | No. peaks | Coupling constant, c.p.s. |
| $C_6H_5P(O)(NHC_6H_{11})_2$ | In methanol | −20.5 | ... | ... |
| $C_6H_5P(O)[N(CH_3)_2]_2$ | In benzene | −28.1 | ... | ... |
| $C_6H_5P(O)[N(C_2H_5)_2]_2$ | Liquid | −38.3 | ... | ... |
| $C_6H_5P(O)[N(CH_3)C_6H_5]_2$ | In benzene | −21.0 | ... | ... |
| $C_6H_5P(O)[N(C_6H_5)_2]_2$ | In DME | −14.8 | ... | ... |
| $C_6H_5P(O)(NHC_6H_{11})N(CH_3)C_6H_5$ | In methanol | −22.0 | ... | ... |
| $C_6H_5P(O)(OH)NH(CH_2)_3NH_2$ | In water | −18.2 | ... | ... |
| $C_6H_5P(O)(OH)NHCH_2CH(OH)CH_2NH_2$ | In water | −18.7 | ... | ... |
| $C_6H_5P(O)N(C_2H_5)C_2H_4NC_2H_5$ | Liquid | −24.0 | ... | ... |
| $C_6H_5P(O)NHC_6H_4NH\text{-}2$ | In DMF | −23.0 | ... | ... |
| $C_6H_5P(O)N(CH_3)C_6H_4NCH_3\text{-}2$ | In benzene | −26.6 | ... | ... |
| Phosphine oxides, substituted | | | | |
| $PO(-N-CH=N-CH=CH)_3$ | In 1-M-2-P | +16.3 | ... | ... |
| $C_6H_5P(O)(-N-CH=CH-CH=CH)_2$ | In DMF | −11.4 | ... | ... |
| $C_6H_5P(O)(-N-CH=N-CH=CH)_2$ | In DME | −6.0 | ... | ... |
| $C_6H_5P(O)[N(CH_3)C_6H_5]N-CH=N-CH=CH$ | In $CHCl_3$ | −16.6 | ... | ... |
| $C_6H_5P(O)[N(C_6H_5)_2]N-CH=N-CH=CH$ | In $CHCl_3$ | −13.0 | ... | ... |
| Phosphinic amides | | | | |
| $(C_6H_5)_2P(O)NH_2$ | In methanol | −25.5 | ... | ... |
| $C_6H_5(ClCH_2)P(O)NHC_6H_5$ | In 1-M-2-P | −20.0 | ... | ... |
| $(C_6H_5)_2P(O)NHC_6H_5$ | In methanol + DMF | −18.8 | ... | ... |
| $(C_6H_5)_2P(O)N(C_6H_5)_2$ | In $CHCl_3$ | −25.8 | ... | ... |
| $C_6H_5N(CH_3)P(O)(-N-CH=N-CH=CH)_2$ | In DMF | +7.6 | ... | ... |
| Phosphinic imides | | | | |
| $(CH_3)_2P(O)NHP(O)(CH_3)_2$ | In $CHCl_3$ | −43.4 | ... | ... |
| $(C_6H_5)_2P(O)NHP(O)(C_6H_5)_2$ | In aniline | −14.5 | ... | ... |
| Imidophosphate salts and esters | | | | |
| $Na_4P_2O_6NH$ | In water | −2.7 | ... | ... |
| $(CH_3O)_2P(O)NHP(O)(OCH_3)_2$ | Liquid | 0.0 | ... | ... |
| $(C_2H_5O)_2P(O)NHP(O)(OC_2H_5)_2$ | In $CHCl_3$ | −2.5 | ... | ... |
| $C_6H_5O(NaO)P(O)NHP(O)(ONa)_2$ | In water | 0.0 | ... | ... |
| $(C_6H_5O)_2P_\alpha(O)NHP_\beta(O)(OH)_2$ | In methanol | $P_\alpha = +8.1$<br>$P_\beta = +2.5$ | 4 | 14 |
| $(C_6H_5O)_2P_\alpha(O)NHP_\beta(O)(OK)_2$ | In methanol | $P_\alpha = +3.3$<br>$P_\beta = +2.1$ | 4 | 8 |
| $(C_6H_5O)_2P_\alpha(O)NHP_\beta(O)(OC_2H_5)OH$ | In $CHCl_3$ | $P_\alpha = +8.6$<br>$P_\beta = +1.1$ | ... | ... |
| $(C_6H_5O)_2P(O)NHP(O)(OC_6H_5)OH$ | In methanol | +9.7 | ... | ... |
| $(C_6H_5O)_2P(O)NHP(O)(OC_6H_5)_2$ | In benzene | +10.7 | ... | ... |
| $Na[(C_6H_5O)_2P(O)NP(O)(OC_6H_5)_2]$ | In benzene | +8.0 | ... | ... |
| $(C_6H_5O)_2P(O)N(CH_3)P(O)(OC_6H_5)_2$ | In benzene | +7.3 | ... | ... |
| $(CH_3C_6H_4O)_2P(O)NHP(O)(OC_6H_4CH_3)_2$ | In benzene | +11.6 | ... | ... |
| | Liquid | +11.0 | ... | ... |
| $(C_6H_5O)_2P_\alpha(O)NHP_\beta(O)(OC_6H_5)NH_2$ | In DMSO | $P_\alpha = +8.4$<br>$P_\beta = -3.8$ | 2<br>2 | 12<br>12 |
| $(C_6H_5O)_2P_\alpha(O)NHP_\beta(O)(OC_6H_5)NHP(O)(OC_6H_5)_2$ | In dioxane | $P_\alpha = +12.5$<br>$P_\beta = +5.9$ | 2<br>3 | 13<br>13 |
| $(C_6H_5O)_2P_\alpha(O)NHP_\beta(O)(OC_6H_5NHP_\gamma(O)(OC_6H_5)NH_2$ | In DMSO | $P_\alpha = +8.4$<br>$P_\beta = +6.3$<br>$P_\gamma = -0.8$ | 4<br>Multiple<br>4 | 14<br>8<br>8 |
| $(NaO)_2P(O)NHP(O)(ONa)NHP(O)(ONa)_2$ | In water | −1.6 | ... | ... |
| $Na_3P_3O_7(NH)_2$  | In water | $P_\alpha = +4.2$<br>$P_\beta = +7.9$<br>Ratio 1:2 | 3<br>2 | 7<br>7 |

(*Continued on page 170*)

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

| | | | Spin-Spin Splitting | |
|---|---|---|---|---|
| Compound | Physical State | Chemical Shift, p.p.m. | No. peaks | Coupling constant, c.p.s. |
| $(NaO)_3[PONH]_3$ | In water | +1.5 | ... | ... |
| $(C_2H_5O)_3[PONC_2H_5]_3$ | In $CCl_4$ | −5.3 | ... | ... |
| $(KO)_4[PONH]_4$ | In water | +3.7 | ... | ... |
| Phosphonitrilic derivatives | | | | |
| $[PN(OC_2H_5)_2]_3$ | In $CHCl_3$ | −17.9 | ... | ... |
| $[PN(OC_2H_5)_2]_4$ | Liquid | +0.6 | ... | ... |
| $[PN(NCS)_2]_3$ | In $CCl_4$ | +26.8 | ... | ... |
| $[PN(NCS)_2]_4$ | In $CCl_4$ | +49.1 | ... | ... |
| $\{PN[NHC(S)NH_2]_2\}_3$ | In methanol | +10.8 | ... | ... |
| $\{PN[NHC(S)NH_2]_2\}_4$ | In methanol | +21.2 | ... | ... |
| $\{PN[NHC(S)NHC_6H_5]_2\}_3$ | In DMF | +2.2 | ... | ... |
| $\{PN[NHC(S)NHC_6H_5]_2\}_4$ | In DMF | +23.2 | ... | ... |
| Miscellaneous P-N compounds | | | | |
| $[C_6H_5NH\underset{\mid}{P}\underset{\mid}{N}C_6H_5]_2$ | In $CHCl_3$ | $\begin{cases}-113.6\\-109.2\end{cases}$ | ...<br>... | ...<br>... |
| $[C_6H_5NH\underset{\mid}{P}(O)\underset{\mid}{N}C_6H_5]_2$ | In 1-M-2-P | +12 | ... | ... |

[a] DME = dimethoxyethane. [b] THF = tetrahydrofuran. [c] DMF = dimethylformamide.
[d] DMSO = dimethylsulfoxide. [e] 1-M-2-P = 1-methyl-2-pyrrolidinone.

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# Solid State Reaction Study of Hydrated Iron Oxide with Hydrated Nitrates of Nickel and Cobalt

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**Pure $Ni(NO_3)_2 \cdot 6H_2O$ and pure $Co(NO_3)_2 \cdot 6H_2O$ were heated with hydrated iron oxide at 315–1200° C. Dehydration was complete at 315° C. In the Ni experiments, $NiFe_2O_4$ was formed at 480° C. At 650° C., $NiFe_2O_4$ was the major constituent. In the Co experiments, $CoFe_2O_4$ did not form at 480° C., but appeared as the major constituent at 650° C. Both reactions were complete at 1200° C.**

THE NEED CONTINUES for a better understanding of the transformation and reactions that occur in the preparation and application of catalysts and catalyst carriers. Chemical and physical changes occurring in mixtures of hydrated iron oxide with hydrated nitrates of nickel and cobalt are of both academic and industrial importance.

Similar information of the solid state reaction study of hydrated and $\alpha$-aluminas with the hydrated nitrates of nickel and cobalt has been reported (*4*). In the nickel experiments, nickel aluminate was formed at 870° C. with hydrated alumina but not with $\alpha$-alumina. At 1200° C. nickel aluminate was formed in each case, but to a lesser extent with $\alpha$-alumina. In the cobalt experiments, cobalt