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Principles of Phosphorus Chemistry. I. Some Generalities Concerning Multiple Bonding[1]

BY JOHN R. VAN WAZER

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Available data show that in those compounds in which the phosphorus atom shares electrons with four neighboring atoms, the atom-center distances between the phosphorus and the neighboring atoms are usually abnormally short, and the heats of formation of these compounds from monatomic gases in their spectroscopic ground states are abnormally large. These results are interpreted as showing an average of $^1/_4$ to $^1/_3$ π-bond per σ-bond leading from the phosphorus atom. By the same criteria, it is found that in the available compounds in which phosphorus shares electrons with three other atoms, π-bonding is generally small or non-existent. This lack of π-bonding is also true of those compounds in which, through the use of d-orbitals, more than four neighboring atoms share electrons with the phosphorus; and, indeed, in this latter case, there seems to be less than one σ-bond per atom connected to the phosphorus.

The purpose of this series of papers is to lay the groundwork for a comprehensive systematic chemistry of phosphorus and its compounds. Like carbon, phosphorus is covalently bound[2,3] to its neighboring atoms in all of its compounds, except perhaps for some metallic phosphides. Indeed, the chemistry of carbon and that of phosphorus is very closely connected, as would be expected from the diagonal relationship of these elements in the Periodic Table.

Probably the major difference between carbon and phosphorus is that the former element is quite closely restricted to the use of s- and p-orbitals, because of the relatively high energy of d-orbitals in the case of First Row elements; whereas, phosphorus, being a Second Row element, can use d-orbitals in bonding. For both carbon and phosphorus, the most common hybridization for σ-bonding is approximately the tetrahedral sp^3. However, in order to form π-bonds, carbon must go to lower hybrids: sp^2 and sp. Phosphorus, on the other hand, does not do this but can employ d-orbitals for π-bonding.[2] This difference between carbon and phosphorus in the mode of π-bond formation can be used to explain[4] why catenation is common in carbon compounds, while at the same time phosphorus compounds containing long chains of connected phosphorus atoms have not yet been synthesized.

Coördination of Phosphorus in its Compounds.—The known coördination numbers exhibited by phosphorus within the molecules or molecule-ions containing this element are 1, 3, 4, 5 and 6—which, to at least a first approximation, exhibit the symmetry of p, p^3, sp^3, sp^3d and sp^3d^2 hybridization, respectively. A very large number (several thousand in each case) of triply and quadruply connected[5] phosphorus compounds are known; but there are only a few compounds of higher coördination number in which d-orbitals are involved in the σ-bond

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[1] This paper was presented at the Phosphorus Symposium held on April 9, 1956, at the American Chemical Society Meeting in Dallas, Texas.

[2] J. R. Van Wazer, "Encyclopedia of Chemical Technology," edited by Kirk and Othmer, Interscience Publishers, New York, N. Y., 1953, Vol. X, pp. 403–510.

[3] According to most of the crystallographic and some of the chemical literature of the first half of the Twentieth Century, phosphorus compounds are considered to be made up of ions so that, for example, the sodium phosphates consist of P^{+5}, $O^{=}$ and Na^+ ions. This picture is untrue, as is demonstrated by the nuclear magnetic resonance data presented in Paper III of this series and by recent detailed X-ray studies. Such X-ray studies on phosphates, in which the electron density in the phosphorus and oxygen atoms is shown to correspond with P–O bonding through electron sharing, are given by C. Romers, J. A. A. Ketelaar and C. H. McGillavry, *Acta Cryst.*, **4**, 114 (1951), and S. Furberg, *Acta Chem. Scand.*, **9**, 1557 (1955).

[4] This idea is discussed for silicon *vs.* carbon by H. Gilman and G. E. Dunn, *Chem. Revs.*, **52**, 93 (1953).

[5] Because of the unwanted extra connotations of such words as "bond," "valence," "coördinated atom," etc., the term "connection" is often used in this series of papers to stand for the interaction between neighboring atoms held together by electron sharing, regardless of the number of σ-, π- or δ-bonds involved.

base structure. These are PF_5, PCl_5, PBr_5, PCl_2F_3, PBr_2F_3 and $(C_6H_5)_5P$,[6] in which the phosphorus is quintuply connected to its neighboring atoms, and the PF_6^- and PCl_6^- anions,[7] within which the phosphorus has a sixfold coördination. The singly connected phosphorus atoms appear only in compounds occurring at very high temperatures. Although singly connected phosphorus is not known under ordinary conditions, interpretation of diatomic spectra[8] has given considerable information about this normally unstable type of structure.

Bond Shortenings and Excess Bond Energies.—In Table I, experimentally observed values of atom-center[9] distances in phosphorus compounds are compared with σ-bond distances, corrected for ionic effects, as taken from the tables of Schomaker and Stevenson[10a] and of Huggins.[10b] In general, it is found that the observed and calculated atom-center distances agree very well with each other in the case of triply connected phosphorus compounds. This is, of course, to be expected since the phosphorus contribution given in the bond-length tables[10] was obtained from the compounds having triply connected P atoms.

For the singly and quadruply connected phosphorus compounds, the measured atom-center distances are generally shorter than the calculated distances. In the quadruply connected compounds the observed distances are usually 10–20% shorter than was calculated. Following Pauling,[11,12] this shortening will be attributed to π-bonding. By use of a published relationship[12] between bond shortening and π-bond character, the number of π-bonds per σ-bond can be obtained. This is presented in the ninth and tenth columns of Table I. The total number of π-bonds per phosphorus atom is shown for each molecule in the last two columns of the table.

In the case of compounds in which phosphorus is connected to more than four neighboring atoms, some of the measured atom-center distances are slightly larger than the calculated ones. This is probably attributable to extreme ionic character in these compounds, so as to diminish the use of d-orbitals in the σ-bond base structure.

In a somewhat similar fashion, π-bonding can be estimated from enthalpy data. In Table II, the heats of formation from the monatomic gaseous elements are listed for those phosphorus compounds on which enthalpy measurements are readily available.[8,13] These experimental values are compared with values calculated from Huggins' table[10b] of bond-energy contributions. Again, it is seen that the observed and calculated values are in good agreement for the triply connected compounds. The two listed compounds in which phosphorus has a coördination number greater than four show a deficiency of energy over that calculated. Again, this is probably attributable to excess ionic character (apparently somewhat less than four complete σ-bonds plus five ionic contributions are spread over the five bond locations). The compounds based on singly and quadruply connected phosphorus atoms exhibit experimental values of the enthalpy which are considerably higher than the calculated values. This deviation is again attributed to π-bonding.

In order to calculate the amount of π-bonding, a value of 50 kcal. was more or less arbitrarily assigned to the bond energy of a π-bond. This assignment is based on the data given in Table III. This leads to an estimation of the average number of π-bonds per σ-bond in each molecule, as shown in the last column of Table II.

Discussion

In view of the rough approximations and insufficiently accurate data which were employed, the relatively good agreement between the amount of π-bonding estimated from internuclear distances and from enthalpy data is most gratifying. This good agreement does not, however, show that π-bonding is the common cause for the observed bond shortenings and excess enthalpies—rather, it merely demonstrates that energy values are closely related to atom-center distances, as would be expected. Justification for attributing the observed effects to π-bonding comes from a recent quantum mechanical calculation[14] in which it is shown that π-bonds involving a d_π-orbital of one atom and a p_π-orbital of another should be both common and important and that the strength of such bonds ought to be relatively independent of the difference in electronegativity between the bonded atoms.

From the available information, several generalities can be made concerning the phosphorus compounds which are stable under normal conditions:

1. In those compounds in which phosphorus shares electrons with three neighboring atoms, there are three σ-bonds, with little or no π-character, from the phosphorus.
2. In those compounds in which phosphorus shares electrons with four neighboring atoms, there are four σ-bonds, with an average of about one π-bond per P atom.
3. When electrons are shared with five or six neighboring atoms, there is less than one full σ-bond for each connection between the phosphorus and a neighboring atom with apparently very little π-bonding.

These generalities are obviously dependent to a considerable extent upon the specific atoms con-

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(6) Pentaphenyl phosphorus has been described by G. Wittig and M. Rieber, *Ann.*, **562**, 177, 187 (1949).

(7) Crystalline phosphorus pentachloride has the structure: $(PCl_4)^+(PCl_6)^-$, according to D. Clark, H. M. Powell and A. F. Wells, *J. Chem. Soc.*, 642 (1942). However, the PCl_6^- anion is not otherwise known and is not found in solution as is the PF_6^- anion.

(8) *E.g.*, see G. Herzberg, "Molecular Spectra and Molecular Structure. I. Diatomic Molecules," Prentice-Hall, New York, N. Y., 1939, pp. 482–494. Also see H. Sponer, "Molekülspektren," Julius Springer, Berlin, 1935, Tabellen; and W. Jevons, "Band Spectra of Diatomic Molecules," Univ. Press, Cambridge, 1932, pp. 272–290.

(9) The term "atom-center distance" is used here to describe the distance between the effective centers of the electron clouds of the two atoms. It is synonymous with the less precise term "interatomic distance" and is not necessarily equivalent to the internuclear distance.

(10) (a) V. Schomaker and D. P. Stevenson, THIS JOURNAL, **63**, 37 (1941); (b) M. L. Huggins, *ibid.*, **75**, 4123, 4126 (1953).

(11) L. Pauling, "The Nature of the Chemical Bond," 2nd Ed., Cornell Univ. Press, Ithaca, N. Y., 1940, pp. 160–178.

(12) L. Pauling, *J. Phys. Chem.*, **56**, 361 (1952).

(13) Data are taken from W. M. Latimer, "Oxidation Potentials," 2nd Ed., Prentice-Hall, New York, N. Y., 1952, and are generally in accord with the values in Circular 500 of the National Bureau of Standards.

(14) D. P. Craig, A. Maccoll, R. S. Nyholm, L. E. Orgel and L. E. Sutton, *J. Chem. Soc.*, 332 (1954).

TABLE I

AMOUNT OF MULTIPLE BONDING IN VARIOUS PHOSPHORUS COMPOUNDS

Compound	Ref	Bond	Calcd. σ-bond distance cor. for ionic effects		Obsd. atom-center Distance	Bond shortening		Calcd. no. of π-bonds/σ-bond		π-Bonds per P atom	
			S and S[q] (Å.)	H[v] (Å.)		S and S (Å.)	H (Å.)	S and S (Å.)	H (Å.)	S and S	H
Singly connected phosphorus											
P_2	8	P–P	2.20	2.21	1.890	0.31	0.32	2.2	2.4	*ca.* 2	*ca.* 2
PN	8	P–N	1.76	1.76	1.491	.27	.27	1.7	1.7	*ca.* 2	*ca.* 2
PO	8	P–O	1.71	1.69	1.447	.26	.24	1.3	1.1	*ca.* 1	*ca.* 1
PC	8	P–C	1.83	1.87	1.5622	.27	.31	1.7	2.2	*ca.* 2	*ca.* 2
PH	8	P–H	1.46	1.43	1.429	.03	.00	0.0	0.0	0.0	0.0
Triply connected phosphorus (primarily p^3-bonding)											
PH_3	10b	P–H	1.46	1.43	1.424	0.06	0.01	0.1	0.1	0.3	0.3
PF_3	10b	P–F	1.65	1.61	1.52 ± 0.04	.13	.09	.3	.2	.9	.6
		P–F	1.65	1.61	1.55 ± .03	.10	.06	.2	.1}	.2	.1
$PFCl_2$	*a*	P–Cl	2.01	2.03	2.02 ± .02	.01	− .01	.0	.0}		
PCl_3	10b	P–Cl	2.01	2.03	2.00 ± .02	.01	.02	.0	.1	.0	.3
PBr_3	10b	P–Br	2.18	2.19	2.23 ± .01	− .05	− .04	..	..	.0	.0
PI_3	10b	P–I	2.40	2.42	2.52 ± .01	.12	.10	.3	.2	.9	.6
P_4O_6	10b	P–O	1.71	1.69	1.67 ± .03	.04	.02	.1	.0	.3	.2
					1.65 ± .02	.06	.04	.1	.1		
$P(CH_3)_3$	10b	P–C	1.83	1.87	1.87 ± .02	.04	.00	.1	.0	.3	.0
Cryst. P_4	10b	P–P	2.20	2.21	2.205	.00	.00	.0	.0	.0	.0
P_4 liquid	*b*	P–P	2.20	2.21	2.25 ± .08	− .05	− .04	..	..	.0	.0
Amorph. red P	*b*	P–P	2.20	2.21	2.29 ± .08	− .09	− .08	..	..	.0	.0
Cryst. black P	10b	P–P	2.20	2.21	2.18 ± .02	.02	.03	.0	.0	.0	.0
Amorph. black P	*b*	P–P	2.20	2.21	2.27 ± .03	− .07	− .06	..	..	.0	.0
P_4S_3	*x*	P–P	2.20	2.21	2.15 ± .05	.05	.06	.1	.1	.2	.2
		P–S	2.10	2.12	2.15 ± .05	− .05	− .03	..	.0		
P_4S_7	*u*	P–P	2.20	2.21	2.35 ± .01	− .16	− .15	..	..	.0	.2
		P–S	2.10	2.12	2.08 ± .01	.02	.04	.0	.1		
						+0.01	+0.02			0.2 ± 0.2	0.2 ± 0.1
Quadruply connected phosphorus (primarily sp^3 bonding)					Av.	±0.05	±0.03				
$PO_4^{\equiv}$ in H_3PO_4	*c*	P–O	1.71	1.69	1.57 ± 0.02	0.14	0.12	0.3	0.3	1.5	1.4
		P–O			1.52 ± .02	.19	.17	.6	.5		
$PO_4^{=}$ in KH_2PO_4	*d*	P–O	1.71	1.69	1.56 ± .01	.15	.13	.4	.3	1.6	1.2
					1.53–1.58 ± 0.01[y]	.18–0.13	.16–0.11	.3–0.5	.2–0.4	1.6	1.2
$PO_4^{\equiv}$ in $NH_4H_2PO_4$	*e*	P–O	1.71	1.69	1.50 ± .01	.21	.19	.7	.6	2.8	2.4
					1.49–1.59 ± 0.01[y]	.22–0.12	.20–0.10	.3–0.7	.2–0.6	2.0	1.6
$PO_4^{\equiv}$ in $\beta Ca_3(PO_4)_2$	*f*	P–O	1.71	1.69	1.56 ± .02	.15	.13	.4	.3	1.6	1.2
$PO_4^{\equiv}$ in BPO_4	*g*	P–O in P–O–B	1.71	1.69	1.55 ± .02	.16	.14	.4	.3	1.6	1.2
$PO_4^{\equiv}$ in $AgPO_4$	*h*	P–O in P–O–Ag	1.71	1.69	1.61 ± .03	.10	.08	.2	.2	0.8	0.8

Table I (*Continued*)

Compound	Ref.	Bond	Calcd. σ-bond distance cor. for ionic effects		Obsd. atom-center distance	Bond shortening		Calcd. no. of π-bonds/σ-bond		π-Bonds per P atom	
			S and S^g (Å.)	H^p (Å.)		S and S (Å.)	H (Å.)	S and S (Å.)	H (Å.)	S and S	H
$OPO_3^{=}$ in ZrP_2O_7	*i*	P–O in P–O–P	1.71	1.69	1.56 ± .04	.15	.13	.4	.3	1.6	1.2
		P–O isolated	1.71	1.69	1.52 ± .04	.19	.17	.6	.5		
$OP(O)_2^-$ O in $(NH_4)_4P_4O_{12}$	*i*	P–O in P–O–P	1.71	1.69	1.59–1.63 ± 0.01	.12–0.08	.10–0.06	.2–0.3	.1–0.2	2.1	1.8
		P–O isolated			1.44–1.51 ± .01	.27–0.20	.25–0.18	.6–1.0	.5–1.0		
P_4O_{10}	*k*	P–O in P–O–P	1.71	1.69	1.62 ± .02	.09	.07	.2	.1	2.5	1.7
		P–O isolated	1.71	1.69	1.39 ± .02	.32	.30	1.9	1.4		
$P_4O_6S_4$	*z*	P–O	1.71	1.69	1.61 ± .02	.10	.08	0.2	0.2	1.6	1.7
		P–S	2.10	2.12	1.85 ± .02	.25	.27	1.0	1.1		
P_4S_{10}	*u*	P–S in P–S–P	2.10	2.12	2.09 ± .03	.01	.03	0.0	0.1	0.3	0.7
		P–S isolated	2.10	2.12	1.96 ± .03	.14	.16	.3	.4		
P_4S_7	*u*	P–S in P–S–P	2.10	2.12	2.07 ± .02	.03	.05	.1	.1	0.7	0.8
		P–S isolated	2.10	2.12	1.95 ± .02	.15	.17	.4	.5		
$(PNCl_2)_3$	*l*	P–N	1.76	1.76	1.65 ± .04	.11	.11	.2	.2	.6	.6
		P–Cl	2.01	2.03	1.97 ± .03	.04	.06	.1	.1		
$(PNCl_2)_4$	*m*	P–N	1.76	1.76	1.67 ± .03	.09	.09	.2	.2	.4	.6
		P–Cl	2.01	2.03	1.99 ± .03	.02	.04	.0	.1		
POF_3	*a*	P–O	1.71	1.69	1.56 ± .03	.15	.13	.4	.3	1.3	.9
		P–F	1.65	1.61	1.52 ± .02	.13	.09	.3	.2		
POF_2Cl	*a*	P–O	1.71	1.69	1.55 ± .03	.16	.14	.4	.3	1.0	.7
		P–F	1.65	1.61	1.51 ± .03	.14	.10	.3	.2		
		P–Cl	2.01	2.03	2.01 ± .04	.00	.02	.0	.0		
$POFCl_2$	*a*	P–O	1.71	1.69	1.54 ± .03	.17	.15	.5	.4	0.9	.8
		P–F	1.65	1.61	1.50 ± .03	.15	.11	.4	.2		
		P–Cl	2.01	2.03	1.99 ± .04	.02	.04	.0	.1		
$POCl_3$	*o*	P–O	1.71	1.69	1.45 ± .05	.26	.24	1.0	.9	1.0	1.2
		P–Cl	2.01	2.03	1.99 ± .02	.02	.04	0.0	.1		
$POBr_3$	*n*	P–O	1.71	1.69	1.44 ± .10	.27	.25	1.1	1.0	2.0	1.9
		P–Br	2.18	2.19	2.06 ± .03	.12	.13	0.3	0.3		
PSF_3	*r*	P–S	2.10	2.12	1.85 ± .02	.25	.27	1.0	1.1	1.9	1.7
		P–F	1.65	1.61	1.51 ± .02	.14	.10	0.3	0.2		
$PSCl_3$	*p*	P–S	2.10	2.12	1.94 ± .03	.16	.18	.4	.5	0.4	0.5
		P–Cl	2.01	2.03	2.01 ± .02	.00	.02	.0	.0		
PSF_2Br	*n*	P–S	2.10	2.12	1.87 ± .05	.23	.25	.8	1.0	2.1	1.9
		P–F	1.65	1.61	1.45 ± .08	.20	.16	.6	0.4		
		P–Br	2.18	2.19	2.14 ± .04	.04	.05	.1	.1		
$PSFBr_2$	*n*	P–S	2.10	2.12	1.87 ± .05	.23	.25	.8	1.0	1.2	1.2
		P–F	1.65	1.61	1.50 ± .10	.15	.11	.4	0.2		
		P–Br	2.18	2.19	2.18 ± .03	.00	.01	.0	.0		

TABLE I (*Continued*)

Compound	Ref.	Bond	Calcd. σ-bond distance cor. for ionic effects S and S[a] (Å.)	H[b] (Å.)	Obsd. atom-center distance	Bond shortening S and S (Å.)	Bond shortening H (Å.)	Calcd. no. of π-bonds/σ-bond S and S (Å.)	Calcd. no. of π-bonds/σ-bond H (Å.)	π-Bonds per P atom S and S	π-Bonds per P atom H
$PSBr_3$	*n*	P–S	2.10	2.12	1.89 ± .06	.21	.23	.7	.8	1.0	1.1
		P–Br	2.18	2.19	2.13 ± .03	.05	.06	.1	.1		
$(PCl_4)^+$	*s*	P–Cl	2.01	2.03	1.98 ± .01	.03	.05	.0	.1	0.0	0.4
					Av.	+0.13 ± 0.06	+0.12 ± 0.06			1.2 ± 0.5	1.0 ± 0.5
More than four connections (involving d-orbitals)											
PF_5	*a*	P–F apical	1.65	1.61	1.57 ± 0.02	0.08	0.04	0.2	0.1	0.8	0.3
		P–F	1.65	1.61	1.59 ± .03	.06	.02	.1	.0		
PF_3Cl_2	*a*	P–F	1.65	1.61	1.59 ± .03	.08	.04	.2	.1	0.6	0.3
		P–Cl	2.01	2.03	2.05 ± .03	−.04	−.02	.0	.0		
PCl_5	*t*	P–Cl apical	2.01	2.03	2.01 ± .05	.00	.02	.0	.0	0.0	0.0
		P–Cl	2.01	2.03	2.07 ± .05	−.06	−.04	..	..		
$(PCl_6)^-$	*s*	P–Cl apical	2.01	2.03	2.04 ± .02	−.03	−.01	.0	.0		
		P–Cl	2.01	2.03	2.08 ± .01	−.07	−.05	..	..	0.0	0.0
					Av.	0.00 ± 0.06	0.00 ± 0.03			0.3 ± 0.4	0.2 ± 0.1

[a] L. O. Brockway and J. Y. Beach, THIS JOURNAL, **60**, 1836 (1938). [b] C. D. Thomas and N. S. Gingrich, *J. Chem. Phys.*, **6**, 659 (1938). [c] S. Furberg, *Acta Chem. Scand.*, **9**, 1557 (1955); J. P. Smith, W. E. Brown and J. R. Lehr, THIS JOURNAL, **77**, 2728 (1955). [d] J. West, *Z. Krist.*, **74**, 306 (1930); B. C. Frazer and R. Pepinsky, *Acta Cryst.*, **6**, 273 (1953). [e] R. O. Keeling, Ph.D. thesis under the direction of R. Pepinsky, Pennsylvania State University, State College, Pa., 1954. [f] A. L. Mackay, *Acta Cryst.*, **4**, 477 (1951). [g] G. E. R. Schulze, *Z. Physik. Chem.*, **B24**, 215 (1934). [h] L. Helmholz, *J. Chem. phys.*, **4**, 316 (1936). [i] G. R. Levi and G. Peyronel, *Z. Krist.*, **92**, 190 (1935); G. Peyronel, *ibid.*, **94**, 311 (1936). [j] C. Romers, J. A. A. Ketelaar and C. H. McGillavry, *Acta Cryst.*, **4**, 114 (1951). [k] G. C. Hampson and A. J. Stosick, THIS JOURNAL, **60**, 1814 (1938). [l] K. O. Brockway and W. M. Bright, *ibid.*, **65**, 1551 (1943). [m] J. A. A. Ketelaar and T. A. de Vries, *Rec. trav. chim.*, **58**, 1081 (1939). [n] J. H. Secrist and L. O. Brockway, THIS JOURNAL, **66**, 1941 (1944). [o] G. R. Badgley and R. L. Livingston, *ibid.*, **76**, 261 (1954). (Data given in ref. *n* are incorrect). [p] J. Y. Beach and D. P. Stevenson, *J. Chem. Phys.*, **6**, 75 (1938). [q] Schomaker and Stevenson, ref. 9. [r] D. P. Stevenson and H. Russell, THIS JOURNAL, **61**, 3264 (1939). [s] D. Clark, H. M. Powell and A. F. Wells, *J. Chem. Soc.*, 642 (1942). [t] M. Rouault, *Ann. Phys. Leipzig*, **14**, 78 (1940); *Compt. rend.*, **207**, 620 (1938). [u] A. Vos and E. H. Wiebenga, *Acta Cryst.*, **8**, 217 (1955); **9**, 92 (1956). [v] Huggins, ref. 10a. [x] O. Hassel and A. Pettersen, *Tidd. Kem. Berg. Met.*, **1**, 57 (1941); S. van Houten, A. Vos and G. A. Wregers, *Rec. trav. chim.*, **74**, 1167 (1955); also see Y. C. Leung, J. Wasser, and L. R. Roberts, *Chem. & Ind.*, **1955**, 948. [y] At a temperature below the ferroelectric transition. [z] A. J. Stosick, THIS JOURNAL, **61**, 1130 (1939). Also see P. W. Allen and L. E. Sutton, *Acta Cryst.*, **3**, 46 (1950), for a review of electron diffraction data.

TABLE II

ESTIMATION OF π BONDING FROM EXCESS ENTHALPY OVER THE BOND ENERGY SUMMATION

Compd. in gaseous state	Exptl. (kcal./mole)	Calcd. for σ-bonds with ionic character (kcal./mole)	Excess energy per bond to P (kcal./mole)	Estimated av. no. of π-bonds[a] per σ-bond
Singly connected phosphorus				
P_2	116.6	50	67	1.3
PN	181.0	50	131	2.6
PO	144.1	84	60	1.2
Triply connected phosphorus (primarily p^3-bonding)				
PH_3	229.3	231	1/2	0.0
PCl_3	235.4	231	1	.0
PBr_3	191.2	189	1	.0
PI_3	147[b]	144	1	.0
P_2I_4	254[b]	146	1	.0
P_4	287.7	277[c]	2	.0
		Av.	1	0.0
Quadruply connected phosphorus (primarily sp^3-bonding)				
$POCl_3$	362.9	315	12	0.2
$POBr_3$	315[b]	273	11	.2
H_3PO_2	480[b]	430	13	.3
H_3PO_3	625[b]	545	20	.4
H_3PO_4	757[b]	666	23	.5
$H_4P_2O_7$	1281[b]	1104	22	.4
P_4O_{10}	1612.3	1344	17	.3
		Av.	17 ± 4	0.3 ± 0.1
More than four connections (involving d-orbitals)				
PCl_5	305.6	385(331[d])	−16	0.0
PBr_5	256[b]	315(267[d])	−12	.0

[a] Calculated on the assumption that the heat of formation of a π-bond from monoatomic gases is 50 kcal./mole. [b] Heats of fusion plus vaporization estimated as follows: PI_3, 16; P_2I_4, 18; $POBr_3$, 14; H_3PO_2, 15; H_3PO_3, 16; H_3PO_4, 18; $H_4P_2O_7$, 30; and PBr_5, 19 kcal. [c] Corrected for strain of 3.8 kcal./bond because of bent bonds. [d] Calculated on assumption of four non-polar σ-bonds and five ionic bond contributions.

TABLE III

ESTIMATION OF THE ENERGY PER π-BOND

Compound	Bond	Assumed no. of π-bonds per σ-bond	Over-all as measured (kcal./mole)	For σ-bond(s) with ionic contribution (kcal./mole)	Energy per π-bond (kcal./mole)
C_6H_6	C–C	$^1/_2$	95	64	62
C_2H_4	C–C	1	107	64	43
C_2H_2	C–C	2	143	64	40
CS_2	C–S	1	109	57	52
HCN	C–N	2	154	53	50
N_2	N–N	2	171	32	70
P_2	P–P	2(?)	117	50	33
				Av.	50 ± 10

nected to the phosphorus and, indeed, it is possible that the observed differences between the triply and quadruply connected phosphorus atoms may be attributed primarily to the individual ligands. Fluorine appears to contribute nearly as much shortening (assuming that the tabulated values[10] for the fluorine bond length are correct) to the P–F connection in the triply connected as in the quadruply connected phosphorus compounds. On the other hand, chlorine shows essentially no shortening, whether attached to either triply or quadruply connected phosphorus.

Several interesting family relationships appear among the quadruply linked phosphorus compounds listed in Table I. Perhaps the most important of these is found in the phosphates. In the orthophosphates in which the PO_4 group is not bonded to other atoms or groups in the crystal, all four P–O distances are equal and correspond to 0.3–0.4 π-bond/σ-bond. In a terminal PO_4 group,[15] the three connections to isolated oxygen atoms show a little more π-character, 0.5–0.6 π-bond/σ-bond. In a middle PO_4 group, the two connections to isolated oxygen atoms show even more π-character; while the two connections to the bridging oxygens exhibit less π-character (0.1–0.3 π-bonds/σ-bond) than the P–O connections in the orthophosphate group. Finally, in P_4O_{10}, the branching-point PO_4 groups show an extreme unbalance in the distribution of π-character among the four P–O connections. In this case, the one connection to the single isolated oxygen atom is alleged to have 1.4–1.9 π-bonds/σ-bond, while the three connections to bridging oxygens exhibit practically no π-character (0.1–0.2 π-bonds/σ-bond). These data give a reason for the "Antibranching Rule"[15] in phosphates.

In $P_4O_6S_4$, the oxygen atoms are all in bridging positions and show 0.2 π-bond/σ-bond, while the connections to the isolated sulfur atoms exhibit 1.0–1.1 π-bonds/σ-bond. In P_4S_{10}, the same unbalanced distribution of π-character in the PS_4 group is found as in the PO_4 group of P_4O_{10}. However, the measurements indicate less π-bonding per tetrahedron in the sulfide than in the oxide. In the monopotassium and monoammonium orthophosphates in their ferro-electric phases, there is unbalancing of the π-bonding within a PO_4 group because of coupling between groups through hydrogen bonds. In silver orthophosphate, the total π-character per PO_4 group is reduced, presumably because of π-bonding of all four of the oxygen atoms with the silver which is tetrahedrally coördinated. In all of the cases noted here, bonds from the phosphorus to bridging atoms have less π-character than the bonds to like atoms in isolated (non-bridging) positions, and the total π-bonding per phosphorus tends to remain nearly constant by increase of π-character in the bonds to non-bridging atoms connected to the phosphorus.

Pauling has shown that the shortening in internuclear distances which he attributes to π-bonding is found in the silicates, sulfates and perchlorates to about the same amount as in the phosphates.[12] Moreover, Stone and Seyferth[16] have produced evidence to show that π-bonding occurs quite universally in the quadruply connected silicon compounds. Presumably, such π-bonding, in which d-orbitals are employed, is generally found for elements below the First Row of the Periodic Table when these elements exhibit a base σ-bond structure approximating sp^3 hybridization.

Pauling[12] has given an elementary explanation of the existence of considerable π-bonding in the oxyacids as being a mechanism for reducing the positive charge on the central atom (P in this case) which would be expected from the electronegativity difference between it and the atoms connected to it. This explanation appears to hold, to at least a first approximation, for the quadruply connected phosphorus compounds, but further explanation is needed to justify the lack of π-bonding in the compounds in which the phosphorus is connected to other than four neighboring atoms, even though these atoms be highly electronegative. It should be noted that the bonds in the compounds in which phosphorus is connected to three[17] and to more than four atoms appear to be highly ionic, as Pauling's idea would predict for the absence of π-bonding.

My rough picture of the situation is that, in the triply connected structures, the π-bonding is made unnecessary by the presence of the fourth "abortive" bond, which appears[18] as the hybridization goes from nearly pure p^3 (for elements, such as H, having about the same electronegativity as phosphorus) to a mixed hybrid exhibiting considerable sp^3 character (for highly electronegative elements, such as F). Increasing the electronegativity of the substituent elements thus leads to the "abortive" bond which belongs entirely to the phosphorus and hence balances out the charge shift to the more elec-

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(15) For definition of various PO_4 groups, see J. R. Van Wazer and K. A. Holst, THIS JOURNAL, **72**, 639 (1950); J. R. Van Wazer, *ibid.*, **72**, 644 (1950); and J. R. Van Wazer and E. J. Griffith, *ibid.*, **77**, 6140 (1955).

(16) F. G. A. Stone and D. Seyferth, *J. Inorg. Nuclear Chem.*, **1**, 112 (1955).

(17) B. P. Dailey, *J. Phys. Chem.*, **57**, 490 (1953), has demonstrated pronounced ionic character in the bonds of NH_3, NF_3 and AsF_3 by measuring nuclear quadruple coupling constants. Also see R. Livingston, *ibid.*, **57**, 496 (1953), and D. W. McCall and H. S. Gutowsky, *J. Chem. Phys.*, **21**, 1300 (1953).

(18) C. A. Coulson, "Valence," Clarendon Press, Oxford, 1952, pp. 209–211.

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]

BY JOHN R. VAN WAZER, CLAYTON F. CALLIS, JAMES N. SHOOLERY[2] AND ROBERT C. JONES[2]

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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

[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.)