one non-ionized product and a strong base. In the unsymmetrical titration curves for this reaction it is significant that beyond the break in the curve the e.m.f. increases much less than would be expected from the dilution curves on the potassium halides. This would suggest that the excess titrant undergoes interaction with mercury(II) chloride, probably through ion-pair or ion-multiple formation, or through coördination of halide by mercury(II) to give products of the type K_nHgX_{2+n} (where n = 1, 2, . . .). However, the nature of the product of this interaction cannot be determined by the present experimental approach. It appears certain that the predominant product of the reaction between mercury(II) and halide in glacial acetic acid is molecular HgX_2.

Although it would be expected that the course of the reaction between mercury(II) acetate and a halogen acid could be followed with the glass electrode, it was not anticipated that this indicator electrode would be suitable for the titrations with the potassium halides. Experimentally, it is easily demonstrated that mercury(II) acetate undergoes no detectable neutralization reaction with perchloric acid nor with potassium acid phthalate, when titrated potentiometrically with the glass–calomel electrode pair. Likewise, it is notable that the magnitude of the break in the titration curve for potassium acid phthalate (a strong base) with hydrochloric acid (a moderately strong acid) is significantly smaller than that for the reaction between mercury(II) acetate and the same acid or the potassium halide. It is evident that the mercury(II) acetate–potassium halide reaction cannot be considered as a neutralization reaction involving a direct or indirect proton transfer mechanism. The glass electrode appears to respond as the indicator electrode toward changes in acetate concentration during the titration involving a nearly neutral acetate and the release of a strongly basic acetate. It has been suggested by Higuchi, Feldman and Rehm,[4] that measurements of acidity and basicity in glacial acetic acid with the glass electrode may be expressed in terms of acetate concentrations. Such an interpretation appears to be experimentally valid.

[4] T. Higuchi, J. Feldman and C. Rehm, *Anal. Chem.*, **28**, 1120 (1956).

WICHITA 13, KANSAS

[CONTRIBUTION FROM THE MONSANTO CHEMICAL COMPANY, RESEARCH DEPARTMENT, INORGANIC CHEMICALS DIVISION]

Principles of Phosphorus Chemistry. III. Structure Proofs by Nuclear Magnetic Resonance[1]

BY C. F. CALLIS, J. R. VAN WAZER, J. N. SHOOLERY[2] AND W. A. ANDERSON[2]

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Structure proofs based on nuclear magnetic resonance measurements are given for some oxyacids of phosphorus and several other phosphorus compounds. Indirect spin–spin coupling shows that essentially all of the primary and secondary phosphite esters, as well as the free acid and its salts, are present in the form in which one hydrogen is attached directly to the phosphorus. Structure proofs are given for the hypophosphate, isohypophosphate and diphosphite molecule-anions, as well as for P_4S_3 and $P_4O_6S_4$. Indirect spin–spin splitting in the tripoly- and tetrapolyphosphate anions shows that the P–O–P linkages are basically covalent; and all of the data indicate that the often postulated P^{+5} ion does not exist in the phosphates and related compounds.

Gutowsky, McCall and Slichter[3] have already shown that indirect spin–spin splitting of nuclear magnetic resonance peaks is a powerful tool for proving structures in the chemistry of phosphorus. Thus, these authors were able to demonstrate that the hydrogen and fluorine atoms are attached directly to the phosphorus by primarily covalent bonds in the following structures: PH_3, PF_3, $(CH_3O)PF_2$, $OPClF_2$, $OPCl_2F$ and the $F_2PO_2^-$, $H_2PO_2^-$, $HPO_3^{=}$ and PF_6^- ions. In this paper, structure proofs based on both indirect spin–spin splitting and chemical shifts will be presented along with a discussion of bonding in phosphorus compounds. The experimental procedure and the raw data are given in Paper II of this series. Unless otherwise designated, the data are P^{31} spectra. The majority of the measurements were made at 7140 gauss and 12.3 Mc. The chemical shifts relative to 85% orthophosphoric acid are defined as

$$\delta = \frac{H_{\text{sample}} - H_{H_3PO_4}}{H_{H_3PO_4}} \times 10^6$$

where H is the resonance field strength. The splittings given in cycles per second (c.p.s.) can be converted to parts per million (p.p.m.) of the applied field by dividing by the frequency of the rf probe in Mc., or to field units in gauss by multiplying the p.p.m. value by the field strength (times 10^{-6}) in gauss.

The simplest method of differentiating between chemical shifts and indirect spin–spin splittings is to make measurements at different field strengths. Thus, the separation between resonance peaks attributable to differently situated phosphorus atoms in a molecule or molecule-ion (the chemical shift) is found to be invariant with field strength when measured in p.p m. of the field. In other words, the separation divided by the field strength is a constant. On the other hand, the separation between multiplet peaks due to indirect spin–spin

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[1] Presented in part by C. F. Callis at the Phosphorus Symposium held on April 9, 1956, at the American Chemical Society Meeting in Dallas, Texas. Papers I and II in this series are published in THIS JOURNAL, **78**, 5709, 5715 (1956).

[2] Varian Associates, Palo Alto, California.

[3] H. S. Gutowsky, D. W. McCall and C. P. Slichter, *J. Chem. Phys.*, **21**, 279 (1953); H. S. Gutowsky and D. W. McCall, *ibid.*, **22**, 162 (1954).

coupling between a specific phosphorus atom and some other atom having nuclear spin is the same value in gauss or frequency units at any field. This method of determining whether a given set of lines is due to chemical shifts or spin–spin coupling was used in this study whenever there was some doubt in the matter.

Splitting by Directly Attached Atoms

Organic Phosphites.—Tertiary esters of phosphorous acid are quite universally represented with three atoms attached to the phosphorus, as shown by the formula $(RO)_3P$. However, the primary and secondary esters are depicted with either three or four atoms attached directly to the phosphorus.[4] This comes about by a shift of the hydrogen atom, as shown below for the secondary ester.

$$(RO)_2P(OH) = (RO)_2P(H)O \qquad (1)$$

The question of which of these two forms predominates has been argued for many years in the literature. However, Kosolapoff[4] and others have indicated recently that, because of hydrogen bonding between the phosphorus of one anion and the oxygen of another, both forms are simultaneously present, and the old question of which form predominates is simply semantics.

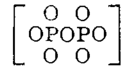
Nuclear magnetic resonance has shown that the question is not a semantic one. Indirect spin–spin splitting by the hydrogen attached directly to the phosphorus and the absence of other detectable peaks at field strengths where resonance is observed for the trisubstituted phosphites proves that approximately 95% or more of the primary and secondary esters, as well as the free acid, are present in the form in which one hydrogen is attached directly to the phosphorus. In other words, equation 1 is shifted far to the right. This means that the primary and secondary phosphites are more closely related[5] in structure to the phosphonates than they are to the tertiary esters, which can be considered as completely substituted phosphine derivatives. Whatever hydrogen bonding is present probably consists of a strong bond between the phosphorus and the hydrogen and a much weaker, secondary bond between the hydrogen and the oxygen atoms of neighboring molecules. The nuclear magnetic resonance data show that the hydrogen on the phosphorus atom is not readily exchanged whereas other experience[1,6] has shown that there should be considerable exchange of hydrogens on a given oxygen atom.

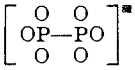
Substituted Phosphines.—Gutowsky has shown that phosphine, PH_3, gives the expected four peaks of relative areas 1–3–3–1, with a splitting between adjacent peaks of 170 c.p.s. Monomethyl- and dimethylphosphine give 1–2–1 and 1–1 patterns, respectively, with splittings of 205 c.p.s. Trimethylphosphine, as expected, gives only one peak (no splitting). In measuring these substituted phosphines, a relatively large field gradient of 0.05 gauss per cm. was used so that spin–spin splitting due to interaction of the phosphorus with the hydrogens on the methyl groups was not visible.

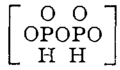
Ethyldifluorophosphine, $(C_2H_5)PF_2$, ethylchlorofluorophosphine, $(C_2H_5)(Cl)PF$, and ethylisopropoxyfluorophosphine, $(C_2H_5)(F)P(OC_3H_7)$ gave three, two and two peaks, respectively, with splitting in satisfactory agreement with that previously reported[3] for fluorine.

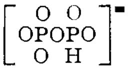
Splitting by Atoms Attached Directly and through an Intermediate Atom

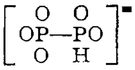
Oxyacids Containing Two P Atoms.—The historically known salts of the oxyacids of phosphorus containing two phosphorus atoms per anion are the (1) pyrophosphate, (2) hypophosphate and (3) pyrophosphite. Blaser[7] has described two more anions which he has called (4) "isohypophosphate" and (5) "diphosphite." The structures of the anions of these five acids—as determined from chemical evidence—are

(1)

$$\left[\begin{array}{c}\text{O O}\\ \text{OPOPO}\\ \text{O O}\end{array}\right]^{\equiv}$$

(2)

$$\left[\begin{array}{c}\text{O O}\\ \text{OP—PO}\\ \text{O O}\end{array}\right]^{\equiv}$$

(3)

$$\left[\begin{array}{c}\text{O O}\\ \text{OPOPO}\\ \text{H H}\end{array}\right]^{=}$$

(4)

$$\left[\begin{array}{c}\text{O O}\\ \text{OPOPO}\\ \text{O H}\end{array}\right]^{\equiv}$$

(5)

$$\left[\begin{array}{c}\text{O O}\\ \text{OP—PO}\\ \text{O H}\end{array}\right]^{=}$$

The P^{31} magnetic resonance spectra of the pyrophosphate (1) and hypophosphate (2) anions each show only one resonance peak. This proves that the structures, assuming two phosphorus atoms, are symmetrical and that no hydrogens are attached directly to the phosphorus. Up to now, the proof that the hypophosphate ion is symmetrical was weak, being based on crystal symmetry[8] from X-ray diffraction without assignment of atom positions. Interpretation of chemical data both for and against the symmetrical structure has appeared in the literature over the past century; of these, the most convincing[9] supports the incorrect isohypophosphate formula for the hypophosphate ion.

The chemical shift of the pyrophosphate anion, obtained from measurements on a solution of tetrasodium pyrophosphate in water, is +6 p.p.m. of the applied field (7140 gauss) relative to 85% orthophosphoric acid. The chemical shift of the hypophosphate anion obtained in the same way from an aqueous solution of disodium dihydrogen hypophosphate, is −9 p.p.m.

The pyrophosphite (3) anion exhibits two equal peaks, with the center of the two peaks shifted +5 p.p.m. of the applied field relative to 85% orthophosphoric acid. The separation of these peaks was found to be 630 c.p.s. at a field of 7140 gauss and 685 c.p.s. at a field of 9850 gauss. Since the difference between these two values is of the order of the experimental error involved, the two peaks undoubtedly arise from indirect spin–spin

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[4] *E.g.*, G. M. Kosolapoff, "Organophosphorus Compounds," John Wiley and Sons, New York, N. Y., 1950, pp. 192–199.

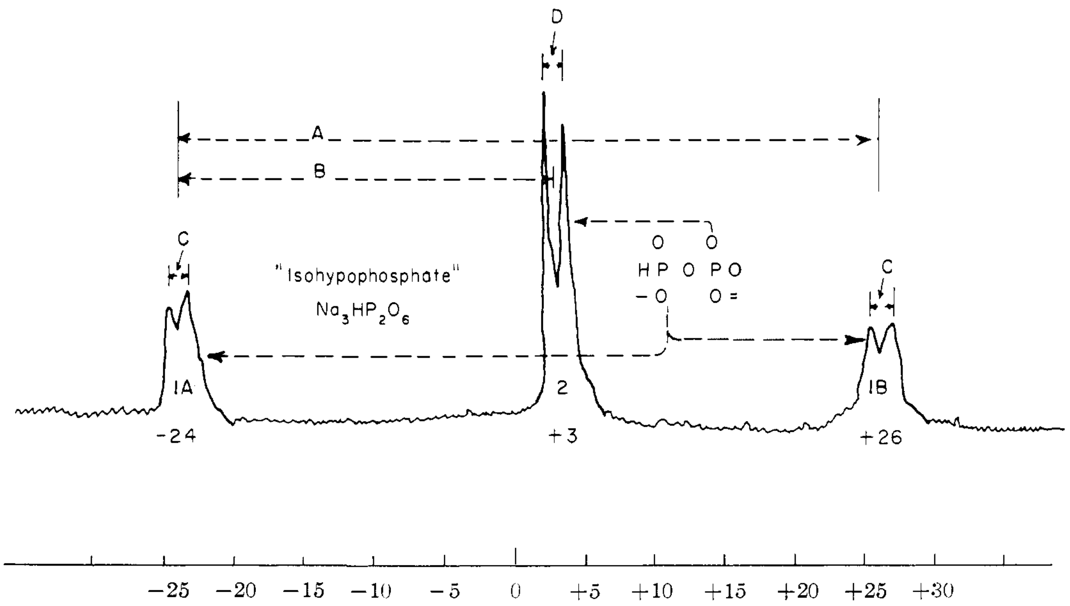
[5] G. M. Kosolapoff, also J. R. Van Wazer, "Encyclopedia of Chemical Technology," Vol. X, (Edited by Kirk and Othmer), Interscience Publishers, New York, N. Y., 1953, pp. 498 and 466.

[6] J. T. Arnold, *Phys. Rev.*, **102**, 136 (1956).

[7] B. Blaser, *Ber.*, **68**, 1670 (1935); **86**, 563 (1953). Also paper given at the Phosphorus Symposium held on April 9, 1956, at the American Chemical Society Meeting in Dallas, Texas.

[8] B. Raistrick, *Sci. J. Roy Coll. Sci.*, **19**, 9 (1949); B. Raistrick and E. Hobbs, *Nature*, **164**, 113 (1949); R. Brooks and T. C. Alcock, *ibid.*, **166**, 435 (1950).

[9] B. Blaser and P. Halpern, *Z. anorg. Chem.*, **215**, 33 (1933). [The interpretation given in this paper does not represent Dr. Blaser's present views. He now supports the symmetric formula (no. 2 in the above text).]



Shift from peak for 85% H_3PO_4, measured in p.p.m. of the applied magnetic field.

Fig. 1.—P^{31} magnetic resonance spectrum of the isohypophosphate anion at 7140 gauss and 12.3 Mc.: A = 620 c.p.s.; B = 27 p.p.m. or 328 c.p.s.; C = 17 c.p.s.; D = 17 c.p.s.

coupling. This means that the structure is symmetrical, with one hydrogen attached to each phosphorus atom.

The spectrum of the isohypophosphate (4) anion is shown in Fig. 1. This anion gives a splitting of 620 c.p.s. for the hydrogen attached directly to one of the phosphorus atoms. The magnitude of this splitting (to give Peaks 1A and 1B) is approximately equal to that of the phosphite anion (590–690 c.p.s.), and of the dialkyl phosphites (670–700 c.p.s.). The area of peak 2 equals the area of Peaks 1A plus 1B as would be expected for the assignment of peak 2 to the phosphorus atom to which no hydrogen is attached. All three peaks show a splitting of 17 c.p.s. due to interaction of the two chemically different phosphorus atoms through the bridging oxygen. This amount of splitting is approximately equal to the splitting found for the interaction of end and middle groups in the phosphates (see Fig. 3). The observed spectrum is in agreement with the theoretical treatment of the system containing three coupled nuclei discussed in the following paragraph, if the reasonable assumptions are made that the coupling of the hydrogen to the adjacent phosphorus is much greater than the coupling of the hydrogen to the other phosphorus and also much greater than the coupling of the two phosphorus atoms. Thus, the structure proposed by Blaser on the basis of chemical evidence has been proven correct by this physical method.

The phosphorus spectrum of the diphosphite (5) anion is shown in Fig. 2b. This spectrum corroborates the mathematical treatment of a system consisting of three coupled nuclei of spin $^1/_2$. The Zeeman levels shown in the schematic diagram, Fig. 2a, were calculated from the following Hamiltonian[10] representing the total energy of the system, assuming that the spin-coupling of the hydrogen and either phosphorus is small compared to the chemical shift between the hydrogen and either phosphorus

$$\mathcal{H} = -\hbar\{\omega_{\mathrm{H}}I^0_{\mathrm{H}} + \omega_{\mathrm{P1}}I^0_{\mathrm{P1}} + \omega_{\mathrm{P2}}I^0_{\mathrm{P2}} + J_{\mathrm{HP1}}I^0_{\mathrm{H}}I^0_{\mathrm{P1}} + J_{\mathrm{HP2}}I^0_{\mathrm{H}}I^0_{\mathrm{P2}} + J_{\mathrm{P1P2}}[I^0_{\mathrm{P1}}I^0_{\mathrm{P2}} + {}^1/_2(I^+_{\mathrm{P1}}I^-_{\mathrm{P2}} + I^-_{\mathrm{P1}}I^+_{\mathrm{P2}})]\} \quad (2)$$

where $\mathcal{H}$ is the Hamiltonian operator, $\hbar$ the quantum of action divided by 2π, ω the unperturbed resonance frequency, I^0 the z-component of the spin operator chosen in the direction of the applied magnetic field, J the spin-coupling constant, and $I^\pm$ the complex spin operator in the plane perpendicular to the field. The subscripts H, P1 and P2 refer to the hydrogen nucleus, the phosphorus adjacent to the hydrogen, and the other phosphorus, nucleus respectively. The resonance frequencies of the phosphorus nuclei derived from equation 2 are

$$\omega_1 = \omega_{\mathrm{P2}} + {}^1/_2\delta + {}^1/_2(J' + {}_{\mathrm{P1P2}}) + {}^1/_2\sqrt{(\delta + J'')^2 + J^2_{\mathrm{P1P2}}} \quad (3)$$

$$\omega_2 = \omega_{\mathrm{P2}} + {}^1/_2\delta + {}^1/_2(J' - {}_{\mathrm{P1P2}}) + {}^1/_2\sqrt{(\delta + J'')^2 + J^2_{\mathrm{P1P2}}} \quad (4)$$

$$\omega_5 = \omega_{\mathrm{P2}} + {}^1/_2\delta - {}^1/_2(J' - J_{\mathrm{P1P2}}) + {}^1/_2\sqrt{(\delta - J'')^2 + J^2_{\mathrm{P1P2}}} \quad (5)$$

$$\omega_6 = \omega_{\mathrm{P2}} + {}^1/_2\delta - {}^1/_2(J' + J_{\mathrm{P1P2}}) + {}^1/_2\sqrt{(\delta - J'')^2 + J^2_{\mathrm{P1P2}}} \quad (6)$$

$$\omega_3 = \omega_{\mathrm{P2}} + {}^1/_2\delta + {}^1/_2(J' + J_{\mathrm{P1P2}}) - {}^1/_2\sqrt{(\delta + J'')^2 + J^2_{\mathrm{P1P2}}} \quad (7)$$

$$\omega_4 = \omega_{\mathrm{P2}} + {}^1/_2\delta + {}^1/_2(J' - J_{\mathrm{P1P2}}) - {}^1/_2\sqrt{(\delta + J'')^2 + J^2_{\mathrm{P1P2}}} \quad (8)$$

$$\omega_7 = \omega_{\mathrm{P2}} + {}^1/_2\delta - {}^1/_2(J' - J_{\mathrm{P1P2}}) - {}^1/_2\sqrt{(\delta - J'')^2 + J^2_{\mathrm{P1P2}}} \quad (9)$$

$$\omega_8 = \omega_{\mathrm{P2}} + {}^1/_2\delta - {}^1/_2(J' + J_{\mathrm{P1P2}}) - {}^1/_2\sqrt{(\delta - J'')^2 + J^2_{\mathrm{P1P2}}} \quad (10)$$

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[10] W. A. Anderson, *Phys. Rev.*, **102**, 151 (1956).

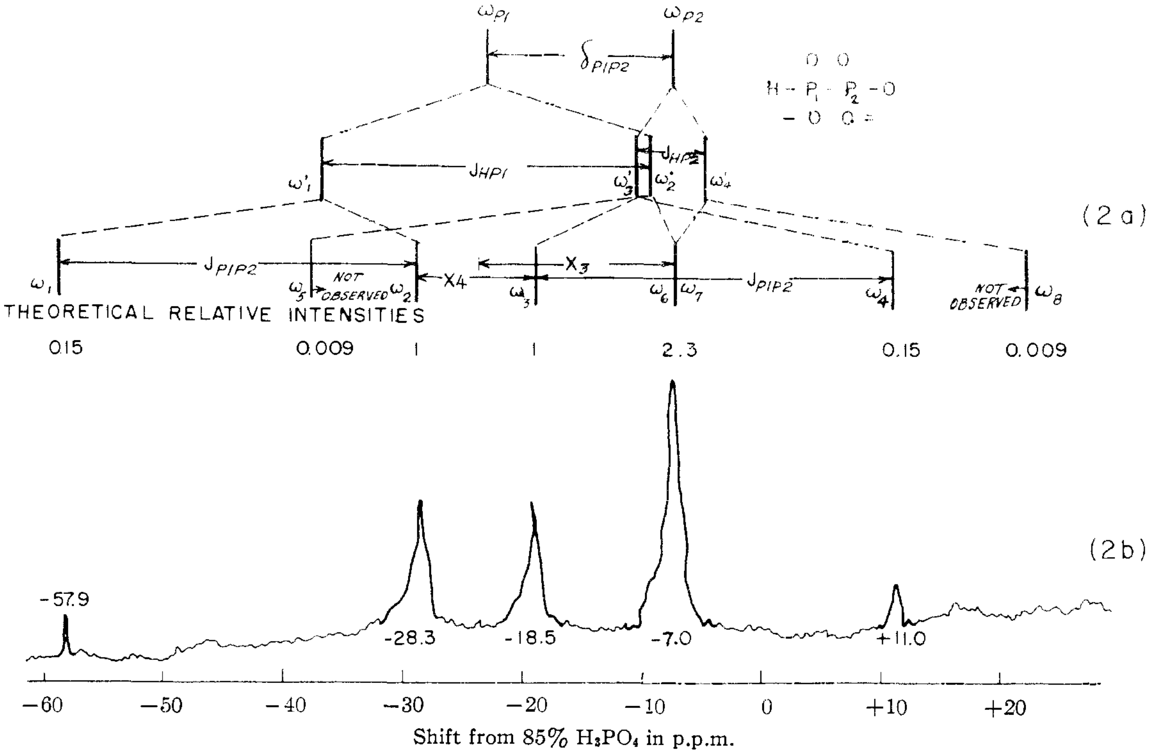

Fig. 2.—Zeeman levels and observed phosphorus spectrum for the diphosphite anion at a field of 9440 gauss. Because of saturation effects at the high rf field used to show up the small peaks, the peak areas are not strictly proportional to their predicted values. The measured values of X_3 and X_4 are 16.4 and 9.8 p.p.m. of the applied field as compared to the calculated values of 16.2 and 9.6 p.p.m., respectively. At the 7140 gauss field, the observed values of X_3 and X_4 are 21.9 and 9.5 p.p.m. compared to the calculated values of 21.6 and 10 p.p.m., respectively.

where δ is the chemical shift between the phosphorus nuclei, and

$$J' = \frac{1}{2}(J_{HP1} + J_{HP2}) \quad (11)$$

$$J'' = \frac{1}{2}(J_{HP1} - J_{HP2}) \quad (12)$$

Examination of the phosphorus spectrum does not yield sufficient information to compute the chemical shift of the phosphorus nuclei and all of the spin-coupling constants. Consequently, it was necessary to examine the hydrogen spectrum of the diphosphite anion dissolved in D_2O in order to obtain the phosphorus–hydrogen spin-coupling constants. Four lines were observed in the hydrogen spectrum (one masked by HDO resonance), which means that the hydrogen is strongly coupled to both of the phosphorus nuclei. Measurements of line spacings on these hydrogen spectra, and on the phosphorus spectra reproduced in Fig. 2b at two different fields permit the calculation of the quantities summarized in Table I. In these computations it was assumed that the resonance frequencies, ω_6 and ω_7, form an unresolved doublet.

The line intensities of the satellite lines, ω_1, ω_5, ω_4, and ω_8, relative to the parent line intensities are given by the ratios $[\sqrt{(\delta \pm J'')^2 + J^2_{P1P2}} - J_{P1P2}]/[\sqrt{(\delta \pm J'')^2 + J^2_{P1P2}} + J_{P1P2}]$. These relative values are included in Fig. 2a just below the schematic diagram. Two of the satellite lines, ω_1 and ω_4, were observed only under conditions of high rf power (some saturation) and their resonance frequencies are in agreement with those predicted from the mathematical treatment.

The theoretical splitting of the phosphorus lines resulting in resonance frequencies ω_1', ω_2', ω_3' and ω_4' can be obtained from equations 3–10 inclusive by setting J_{P1P2} equal to zero. It is interesting to note that the observed splitting of these lines is not symmetrical, and that the more asymmetric the split of the line, the greater the difference in relative line intensities—with the more intense line near the center of the pattern.

Table I

Nuclear Magnetic Resonance Constants of the Diphosphite Anion

Spin-spin couplings			P,P-Chemical shift in P spectrum		
			Value (p.p.m.)		
Notation	Cycles[a] per sec.	Value Gauss (spectrum)	Between nuclei	Shift of P2 relative to 85% H_3PO_4	Field (gauss)
J_{P1P2}	480 ± 10	0.28 (phosphorus)	15.4	−7.0	7140
J_{HP1}	444	.26 (phosphorus) .10 (hydrogen)	15.8		9440
J_{HP2}	94	.054 (phosphorus) .022 (hydrogen)			

[a] $\frac{\text{Spin-spin coupling in gauss}}{\text{Field strength in gauss}} \times$ frequency of probe.

The explanation for the observed spectra is in accord with the structure for the diphosphite anion given by Blaser. Other authors[11] have suggested that the substance called a "diphosphite" by Blaser is simply a tautomeric form of phos-

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(11) A. D. Mitchell, *J. Chem. Soc.*, **127**, 336 (1925); J. H. Kolitowska, *Z. anorg. allgem. Chem.*, **230**, 310 (1937).

phorous acid. However, the fact that the hydrogen nuclear resonance spectrum exhibits four peaks indicates that there are two phosphorus atoms in the structure. Furthermore, the magnitude of the splitting supports the idea that hydrogen and the two phosphorus atoms are directly bonded together, *viz.*, H–P–P. All in all, the nuclear magnetic resonance data lend strong support to the structure given by Blaser[7] if the sample of trisodium diphosphite (amorphous to X-ray diffraction) which he supplied to us represents a reasonably pure (> 95%) compound.

Splitting by Atoms Attached through Intermediate Atoms

In the case of magnetic resonance of the hydrogen nucleus in organic compounds, splitting due to the interaction of hydrogens separated from each other by two carbon atoms has been observed under high resolution conditions.[10,12] As shown here, phosphorus also can interact with hydrogen, fluorine, and chemically different phosphorus atoms separated from the phosphorus atom in question by one or two other atoms.

Polyphosphates.—The spectra of the pyro-, tripoly- and tetrapolyphosphate[13] anions are shown in Fig. 3. As previously described,[14] isolated (orthophosphate), end, and middle PO_4-groups resonate at measurably different external fields, with the end- and middle-group shifts being 5–10 and 18–21 p.p.m. with respect to 85% H_3PO_4, which contains the isolated PO_4-groups. In Fig. 3, the end-group resonance peaks are denoted by E, and the middle-group resonance peaks by M. Since the two phosphorus nuclei in the pyrophosphate ion are indistinguishable, internally and externally, *i.e.*, they are chemically equivalent, the indirect spin–spin coupling does not show up as observable splitting, although this coupling ought to be approximately equal to the coupling of the end and middle phosphorus atoms in the tripolyphosphate anion (J_{P1P2} in the pyrophosphate $\approx J_{P1P2} = J_{P2P3}$ in the tripolyphosphate). For the tripolyphosphate anion, the area under peak M is half the area under peak E, and the M peak is split into three parts, of approximate relative areas 1–2–1, whereas the E peak is split into two parts of equal area. Since the middle-group phosphorus is attached to two chemically different phosphorus atoms (in the two end groups), spin–spin splitting into a 1–2–1 triplet is to be expected. Likewise, attachment of the two end-group phosphorus atoms to the lone middle group gives spin-spin splitting into a 1–1 doublet. Measurements of the spectrum of tripolyphosphate at a higher field (9,850 gauss) offer additional verification of the accepted structure. The ratio of the separations, ($\delta_1/\delta_2 = 1.3$), of the pairs of multiplets at the two fields is in acceptable agreement with the ratio of the two fields ($H^6/H_2 = 9850/7140 = 1.4$), as expected for non-equivalent nuclei. The splitting in the multiplets (17 c.p.s.) is independent of field strength as was confirmed earlier[3] for several cases of multiplet splittings.

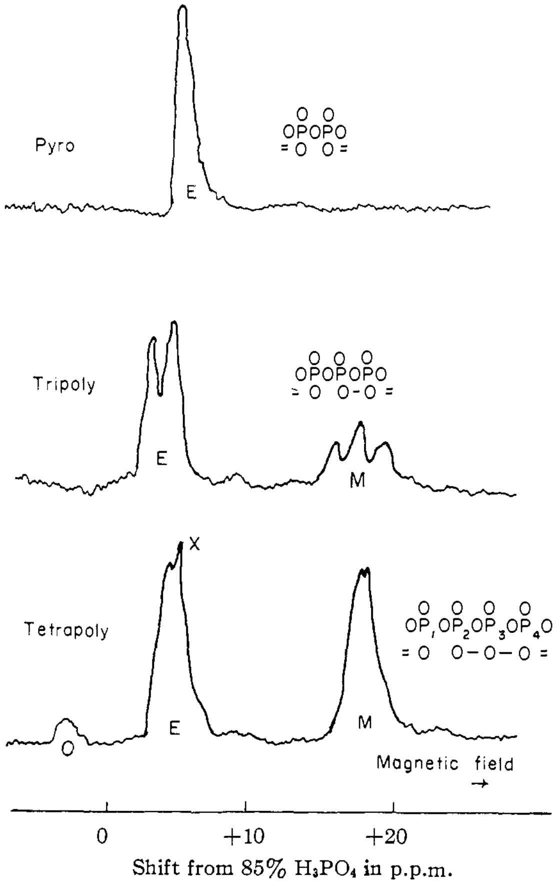

Fig. 3.—P^{31} magnetic resonance spectra of chain-phosphate anions at 7140 gauss and 12.3 Mc. as adjusted to the same scale. The end-group peaks are denoted by E, and the middle-group peaks by M. Orthophosphate impurity is denoted by O, and the extra height of the peak marked "X" is due to some pyrophosphate impurity.

For the tetrapolyphosphate anion, the E and M peaks are of approximately equal area (after correction for pyrophosphate, a known impurity), and are both split into doublets of intensity 1–1. Such a picture is in accord with the published analysis[15] for the case of four coupled nuclei in a molecule with a plane of symmetry and two pairs of non-equivalent nuclei.[16] If we let $J_{P1P2} = J_{P3P4}$ be the spin coupling between adjacent end and middle phosphorus nuclei, and J_{P2P3} be the spin coupling between the central nuclei, a similar analysis can be made for various values of the ratio of $J_{P2P3}/J_{P1P2} = J_{P3P4}$. For this ratio equal to zero, a simple doublet with spacing $J_{P1P2} = J_{P3P4}$ is predicted for each phosphorus group. For the above ratio equal to one, two lines with spacing $J_{P1P2} = J_{P3P4}$ are still predicted for each phosphorus group, but in addition two slightly weaker lines are predicted closer to the center of each

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[12] *E.g.*, see the spectrum shown by B. P. Dailey and J. N. Shoolery, THIS JOURNAL, **77**, 3977 (1955).

[13] See O. T. Quimby, *J. Phys. Chem.*, **58**, 603 (1954); R. K. Osterheld and R. P. Langguth, *ibid.*, **59**, 76 (1955), for information about the tetrapolyphosphate.

[14] J. R. Van Wazer, C. F. Callis and J. N. Shoolery, THIS JOURNAL, **77**, 4945 (1955).

[15] H. H. McConnell, A. D. McLean and C. A. Reilly, *J. Chem. Phys.*, **23**, 1152 (1955).

[16] J. R. Van Wazer, M. Goldstein and E. Farber, THIS JOURNAL, **75**, 1563 (1953); C. F. Callis, J. R. Van Wazer and P. G. Arvan, *Chem. Revs.*, **54**, 777 (1954).

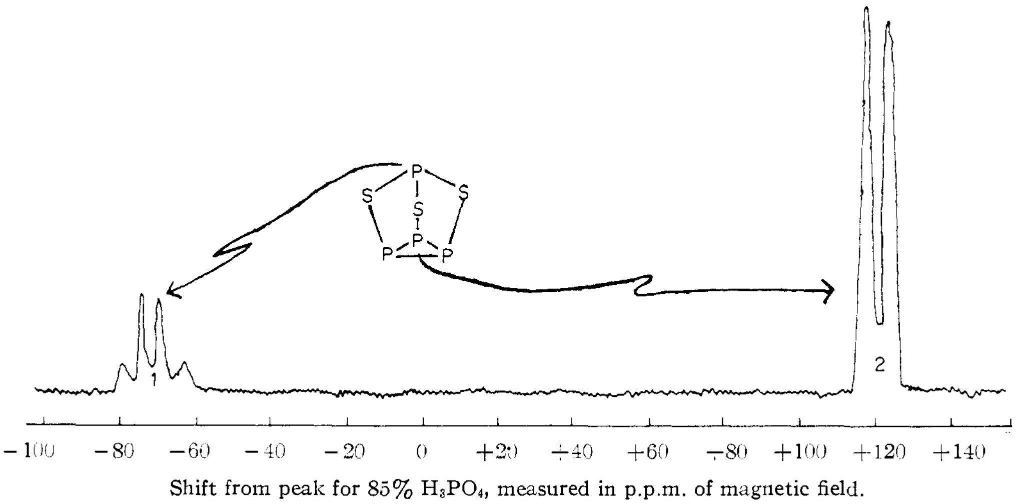

Fig. 4.—P^{31} magnetic resonance spectrum of phosphorus sesquisulfide at 7140 gauss and 12.3 Mc.

doublet, and two considerably weaker satellites should be found farther from the center of each doublet. Presently available signal-to-noise and resolution does not permit us to choose between these two ratios, but the observed spectrum is not compatible with a value of $J_{P2P3}/J_{P1P2} = J_{P3P4}$ greater than *ca.* 1.2.

The nuclear magnetic resonance data based on the shifts, the areas under the peaks, and the indirect spin–spin splitting give a unique physical proof for the structures (shown in Fig. 3) of the tripoly- and tetrapolyphosphates, for which only chemical structure proofs have heretofore been available.[17]

Phosphorus Sulfides.—The most interesting member of this class of compounds which we have studied is phosphorus sesquisulfide, P_4S_3, the nuclear magnetic spectrum of which is shown in Fig. 4. In accord with the structure of this compound as determined by X-ray diffraction[18] and shown in Fig. 4, there are two major peaks. Peak 1, which is a 1–3–3–1 quadruplet, corresponds to the phosphorus atom connected through three sulfur atoms to the other three, chemically different phosphorus atoms. Peak 2, a 1–1 doublet exhibiting a total area which is three times that of peak 1, is attributable to the three phosphorus atoms in a ring. Splitting of this peak is due to interaction with the lone phosphorus atom. Presumably, the relatively large splitting (86 c.p.s.) in the case of this sulfide as compared to the splitting (17 c.p.s.) in compounds in which the chemically different phosphorus atoms are separated by oxygens is attributable to the fact that the phosphorus atoms are triply connected[19] in the sulfide (also bent bonds) and is not due to a difference between oxygen and sulfur in transmitting the interaction between the phosphorus atoms.

The existence of one peak in the spectrum of phosphorus sulfoxide, $P_4O_6S_4$, is in agreement with a symmetrical structure[20] in which the four phosphorus atoms are identical.

Splitting by Hydrogen and Fluorine Atoms.—Hydrogen and fluorine interacting with phosphorus through an intermediate atom or atoms cause spin–spin splitting as well as do phosphorus atoms which are chemically different. An example of such behavior is found in dichlorofluoromethyl-tris-(dimethylamido)-phosphonium chloride, $[Cl_2FCP(N(CH_3)_2)_3]^+ Cl^-$, in which the fluorine attached to the carbon atom causes a splitting of 85 c.p.s. of the phosphorus peak.

Splitting is not recorded in the Appendix of Paper II for the compounds containing P–C linkages (such as the phosphonates) because the spectra of these compounds were observed with insufficient resolution to show up splitting of the order of magnitude of *ca.* 20 c.p.s. However, a recent spectrum of trimethylphosphite, $P(OCH_3)_3$, has been taken under conditions of extremely high resolution and shows spin–spin splitting due to the hydrogens acting on the phosphorus through the carbon *and* oxygen atoms. This spectrum, shown in Fig. 5, clearly exhibits eight of the ten peaks (two of which are too small to show over the background) for the 1–9–36–84–126–126–84–36–9–1 splitting expected for coupling with nine other atoms—the nine hydrogens in the molecule. In comparison, it was found that at the same resolution no fine structure showed up in the peak observed for triphenyl phosphite. Presumably this lack of fine structure is due to the fact that in the triphenyl phosphite the nearest hydrogen is separated from the phosphorus by three intermediate atoms (–C–C–O–) as compared to the two intermediate atoms (–C–O–) in the trimethyl compound.

Dimethyl phosphite shows two major peaks, with a splitting of 710 c.p.s., because of the hydrogen atom directly attached to the phosphorus. Under super high resolution conditions, both of these

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(17) The previously available structure proofs for these two anions have been (1) proximate analysis, (2) *p*H titration, (3) cryoscopy in $Na_2SO_4 \cdot 10H_2O$, (4) paper chromatography, and (5) interpretation of hydrolysis data.

(18) O. Hassel and A. Pettersen, *Tid. Kem. Berg. Met.*, **1**, 57 (1941).

(19) J. R. Parks, This Journal, **79**, 757 (1957), has shown that the chemical shift of triply connected phosphorus compounds can be related to the electronegativity of the ligands and the bond angles. This reference gives a more quantitative picture of the idea presented here.

(20) A. J. Stosick, *ibid.*, **61**, 1130 (1939).

major peaks are split into seven subpeaks of relative heights 1–6–15–20–15–6–1 by the six hydrogens attached to the carbon atoms. This secondary splitting corresponds to *ca.* 14 c.p.s.

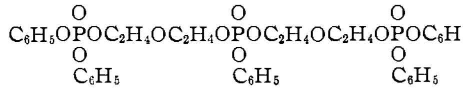
When the spectrum of orthophosphoric acid was run at the same resolution as was used in showing the fine structure of trimethyl phosphite in Fig. 5, there was no sign of fine structure due to interaction of the weakly acidic hydrogens through the oxygen atoms on the phosphorus. This means that the average frequency of the exchange process of the weakly acidic hydrogen from one phosphate to another or from phosphate to water and *vice versa* must exceed the splitting frequency, and thus collapse the spin–spin coupling to a single resonance line. As was noted in Paper II of this series, removal of the third, extremely weakly acidic hydrogen from the orthophosphate ion causes a slight negative shift which probably indicates covalent bonding of this hydrogen, with concomitant rapid exchange.

Structures from Chemical Shifts

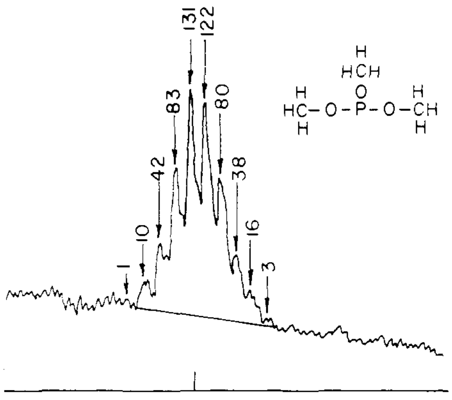
By utilizing shift contributions, as described in Paper II, an approximation can be made to the positions of resonance peaks to be found for phosphorus atoms attached to various given atoms. Likewise, a good estimation can be made of the amount of spin–spin splitting to be observed. Examples of this type of structure analysis are found for the isohypophosphate anion and phosphorus sesquisulfide in this paper and for ethyl "metaphosphate" in Paper II.

Estimation of the average number of phosphorus atoms in a mixture of chain phosphates also exemplifies the use of chemical shifts to determine structures. It is found that the relative areas of the end-group (A_E) and middle-group (A_M) peaks for a solution of a vitreous sodium phosphate gives the number average chain length, $\bar{n}$, as expected from the equation $\bar{n} = 2(A_E + A_M)/A_E$.

As shown in Fig. 2 of Paper II in this series, attachment of phenyl groups to a phosphate moiety causes a significant positive shift—with a shift of +5 p.p.m. (with respect to 85% H_3PO_4) for one phenyl group and +12 p.p.m. for two phenyl groups in a 7140 gauss field. Therefore, if pentaphenyl bis-(diethylene glycol) triorthophosphate and hexaphenyl tris-(diethylene glycol) tetraorthophosphate exhibit structures in which isolated PO_4-groups are separated by organic radicals so that two phenyl groups are attached to the PO_4^- groups at the end of the resulting chains and one phenyl group is attached to the PO_4-group(s) away from the ends, they will have peaks at the positions found for the corresponding monomers. Moreover, the hexaphenyl compound should exhibit two peaks of equal area and the pentaphenyl compound a peak at +5 p.p.m., which is half the size of the peak at +12 p.p.m. The observed spectra showed two equal sized peaks at +7.5 and +12.5 p.p.m. for the hexaphenyl compound and one peak at +7.0 p.p.m. and another twice as large at +13 p.p.m. for the pentaphenyl compound. These results demonstrate that the organic chemist who synthesized these compounds most probably attributed the proper structure to them. At least the compounds give nuclear magnetic resonance spectra as predicted from his structures. The structure for the pentaphenyl compound is thus



$$\begin{array}{c}\mathrm{O}\mathrm{O}\mathrm{O}\\ C_6H_5O\mathrm{P}OC_2H_4OC_2H_4O\mathrm{P}OC_2H_4OC_2H_4O\mathrm{P}OC_6H_5\\ \mathrm{O}\mathrm{O}\mathrm{O}\\ C_6H_5\qquad\qquad C_6H_5\qquad\qquad C_6H_5\end{array}$$



−141 ± 1 p.p.m. from peak for 85% H_3PO_4

Magnetic field→

Fig. 5.—The P^{31} magnetic resonance spectrum of trimethyl phosphite at 7140 gauss and 12.3 Mc. showing the fine structure due to spin–spin splitting of the phosphorus by the hydrogen atoms on the three methyl groups. The measured heights are listed (on a relative basis) over each peak. The random-noise height is somewhat less than *ca.* ±4 units. Theoretical splitting for nine attached atoms is 1-9-36-84-126-126-84-36-9-1.

Discussion

During the first half of the Twentieth Century, much of the discussion of the structure of oxyacids in the chemical and mineralogical literature was in terms of completely ionized atoms. According to this picture, a solid sodium phosphate would be made up of P^{+5}, $O^{=}$ and Na^+ ions, so arranged as to give close packing of spheres (the ions) with alternation of positive and negative charges in such a manner as to result in electroneutrality over even relatively short distances within the array. Application of this idea was usually confined to solids, although one would have to infer that, for example, condensed phosphate molecule-ions in solution were merely aggregates of P^{+5} and $O^{=}$ ions. The existence of spin–spin splitting in the tripoly- and tetrapolyphosphates indicates that this ionic picture is false and that a better picture consists of covalently bonded phosphorus and oxygen atoms making up the phosphate molecule-anions, the negative charges of which are balanced by the counter ions, *e.g.*, Na^+, some of which may be tightly affixed to the oxygens of the molecule-anions. If these condensed phosphate anions were merely a collection of ionized atoms, the rate of exchange (say, between the oxygens of the P–O–P linkages and the water) would be so rapid that no indirect spin–spin coupling could be observed.

Although complete X-ray structure analyses[21]

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[21] *E.g.*, see C. Romers, J. A. A. Ketelaar and C. H. MacGillavry, *Acta Cryst.*, **4**, 114 (1951); S. Furberg, *Acta Chem. Scand.*, **9**, 1557 (1955).

in which detailed electron density projections are employed do show that the atoms in the anions of phosphates and other similar oxyacids share electrons, occasional reports[22] purporting to demonstrate the existence of such highly charged ions as P^{+5} occasionally appear in the crystallographic literature. Publication of such results is to be deplored unless it is definitely demonstrated that a covalent picture cannot explain the data[23] or unless it is stated that ionic structure factors are used for convenience and do not necessarily indicate that the real structure is ionic.

It is believed that the detailed electron density projections[21] along with the indirect spin–spin splitting and other nuclear magnetic resonance data reported here and in Paper II of this series demonstrate that an ionic representation[24] of phosphorus in its compounds must be considered absurd unless one is equally ready to represent carbon in organic compounds as being ionized, *e.g.*, C^{+4} in CCl_4 or C^{-4} in CH_4.

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[22] *E.g.*, see R. Brill and A. P. de Bretteville, *Acta Cryst.*, **8**, 567 (1955). In recent private communication, Dr. R. Brill made the following statement concerning this reference: "The results primarily indicate only that the scattering powers of Al and P are equal at the third order of the basis reflections. This would be expected for the ions Al^{+3} and P^{+5}. However, this would also be the case if Al and P contain the same number of electrons and the distribution of electrons around both atoms would not differ too much."

[23] We believe this to be impossible for the phosphates, at least.

[24] For recent extreme ionic views, see W. A. Weyl, "The Screening of Cations as a Basic Principle of Inorganic Chemistry," Office of Naval Research, Technical Report No. 52, Contract No. N6onr 269 Task Order 8, Pennsylvania State College, July, 1952.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, IOWA STATE COLLEGE]

The Molecular Structure of $B_{10}H_{12}I_2$[1]

BY RILEY SCHAEFFER

RECEIVED FEBRUARY 4, 1957

The structure of $B_{10}H_{12}I_2$, obtained from $B_{10}H_{14}$ by treatment with I_2, has been determined by X-ray diffraction techniques. The unique space group D_{2h}^{10}Pccn and the presence of four molecules per unit cell requires the molecule to possess a twofold axis and makes possible the unambiguous determination of the intramolecular iodine–iodine distance. This observed distance is in agreement with that expected if substitution has occurred at the apices of the two pentagonal pyramids which share a common edge in the $B_{10}H_{14}$ structure.

Introduction

Although substituted diboranes ($B_2H_2R_4$) and borines (HBR_2) have been known for many years and present few structural problems, only two substitution derivatives of higher boranes have been described. Both $B_{10}H_{12}I_2$ and $B_{10}H_{12}Br_2$ were prepared by Stock by direct action of the halogen on $B_{10}H_{14}$.[2] Although many isomeric dihalides of decaborane are possible, the nature of the products obtained by Stock indicates that a single isomer was obtained at least in large part. Apparently, effects are operative in determining the mechanism of substitution which have not as yet been adequately assessed and it was consequently of considerable interest to determine which of the isomers was formed.

Experimental

A sample of $B_{10}H_{12}I_2$ crystallized from benzene as flat plates was available. Several crystals were selected, mounted, coated with Krylon and examined by X-ray diffraction. The crystals were not well formed but one showed only a small amount of extraneous scattering, which did not interfere with indexing, and was used for further study. Weissenberg and rotation photographs taken with filtered Cu radiation and precession photographs taken with filtered Mo radiation showed orthorhombic symmetry and gave the following unit cell dimensions: a = 13.13, b = 7.26, c = 12.00 Å.

Comparison of the unit cell dimensions with those of the disordered unit of $B_{10}H_{14}$ strongly suggested that only four molecules were present per unit cell. Indexing of the reflections on the basis of this unit cell led to the criteria for systematic extinction

$$hkl \text{ present in all orders} \qquad (1)$$

$$0kl \text{ present only for } l = 2n \qquad (2)$$

$$hk0 \text{ present only for } h + k = 2n \qquad (3)$$

$$h0l \text{ present only for } l = 2n \qquad (4)$$

The space group was thus uniquely established as D_{2h}^{10}-Pccn.

Sets of precession pictures of varying intensity were obtained by timed exposures of the $h0l$ and $hk0$ zones and the intensities of individual spots estimated visually with the aid of a standard scale prepared from the same crystal. Values of F_{hkl}^2 (on an arbitrary scale) were calculated from the observed intensities by application of the Lorentz and polarization factors.

Iodine positions were located readily by analytical interpretation of the Patterson function. Since the general positions of the space group are eightfold and only four molecules are present, the molecules must possess a center of symmetry or lie on a twofold axis. If the molecule is structurally derived from $B_{10}H_{14}$ it cannot possess a center of symmetry and must consequently have iodines substituted in one of the five sets of positions equivalent under twofold rotation (see Fig. 1). The intramolecular iodine–iodine distance could then be determined readily from the $hk0$ projection of the iodine

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[1] Presented at the American Chemical Society Meeting in Cincinnati, Ohio, in April, 1955. This work was supported in part by a Summer Research Grant to Iowa State College in 1954 by E. I. du Pont de Nemours and Company which is gratefully acknowledged.

[2] A. Stock, "Hydrides of Boron and Silicon," Cornell University Press, Ithaca, N. Y., 1933, pp. 120–122.