U. D. C. 538.27 : 546.18

Application of Proton Magnetic Resonance to the Investigation of Organophosphorus Compounds

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Methods of analysing the p.m.r. spectra of organophosphorus compounds are examined, the chief features of the chemical shifts of protons and the proton-proton and proton-phosphorus spin-spin interaction constants are summarised, and the main lines of investigation of organophosphorus compounds by the p.m.r. method are discussed. A list of 167 references is included.

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I. INTRODUCTION

The vigorous development of nuclear magnetic resonance (n.m.r.) spectroscopy, especially of proton magnetic resonance (p.m.r.) spectroscopy, is due to the wide possibilities for its application in chemistry both for structural and physicochemical investigations and for a more thorough understanding of the electronic structure of complicated organic molecules. The fundamental difference between n.m.r. and other widely used spectroscopic methods is the presence in the spectra of two groups of cross parameters—the chemical shifts of equivalent nuclei and the spin–spin coupling constants between magnetically non-equivalent nuclei—which leads to a significant enhancement of the reliability and the concreteness of the information obtainable. During the past decade the n.m.r. method has rightly occupied a leading position among spectroscopic methods for investigating organic compounds, and in fact now constitutes an independent branch of science.

The n.m.r. method is especially useful in the investigation of organophosphorus compounds because the stable phosphorus-31 isotope (natural content 100%) possesses a magnetic moment and a nuclear spin of $\frac{1}{2}$, which enables additional parameters—chemical shifts of phosphorus δP and spin–spin coupling constants of phosphorus with protons and other magnetic nuclei of the molecule—to be obtained. Interest in these parameters had already appeared in the first fundamental n.m.r. investigations[1,2]. The modern n.m.r. technique enables chemical shifts of phosphorus to be obtained both by direct resonance at ^{31}P nuclei (^{31}P n.m.r.) and by use of double nuclear resonance methods ($^{1}H-\{^{31}P\}$ and $^{19}F-\{^{31}P\}$ d.n.m.r.).[3-5] As a consequence of the accumulation of comprehensive experimental results on chemical shifts of phosphorus[2,4-11] combined with theoretical analysis[11-15], this parameter can be used widely with the various phosphorus compounds investigated.

At the same time the investigation of organophosphorus compounds by single resonance on protons (p.m.r.) retains its value, since proton resonance is accompanied with the simplest of apparatus, accessible to a wide circle of investigators, and will reveal most parameters of the spectrum. Besides the investigation of the effect of phosphorus-containing groups on the proton chemical shifts δ_H and the proton–proton interaction constants J_{HH}, the p.m.r. method will usually yield the spin–spin coupling constants of protons and phosphorus J_{HP}, and in isolated cases also the spin–spin coupling constants between the phosphorus nuclei J_{PP}. In his excellent reviews Mavel[16,17] has carefully collected the literature on this problem up to 1965 inclusive; the subsequent voluminous literature has described the application of p.m.r. both for the identification of organophosphorus compounds and to reveal the main features of the spectra. The chief purpose of the present Review is to summarise these regularities, and also to examine features of the analysis of p.m.r. spectra applied to those of organophosphorus compounds. For this reason the Review does not claim to cover exhaustively all papers on the proton magnetic resonance of organophosphorus compounds. However, it does consider the results of some of the most comprehensive investigations outside the scope of the actual p.m.r. of these compounds.

II. ANALYSIS OF COMPLEX p.m.r. SPECTRA OF ORGANOPHOSPHORUS COMPOUNDS

The relation between the position and intensity of lines and the parameters of the p.m.r. spectra of organophosphorus compounds conforms to the general rules of nuclear magnetic resonance[18]. The main difficulty in the analysis is that single resonance of protons leaves transitions in the resonance range of phosphorus outside the spectrum. Nevertheless, the use of special procedures enables most of the spectral parameters to be determined in individual cases when the molecules contain a small number of ^{31}P nuclei (one or two).

In the case of compounds containing one phosphorus atom the *method of subspectra* provides a such procedure. The complete proton spectrum of these compounds $(A_mB_nC_kX)$† can be regarded as the superimposition of two simpler subspectra $(A_mB_nC_k)'$ and $(A_mB_nC_k)''$,

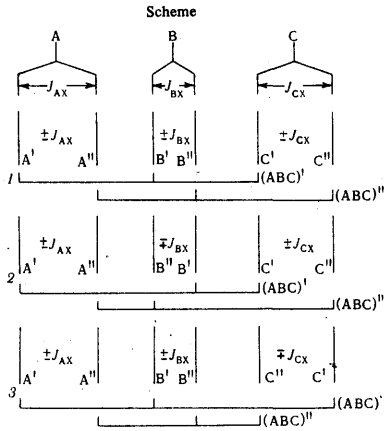
†The letters A–C denote protons, and X is a phosphorus nucleus. The symbol ν_K indicates the chemical shift (in c/s) of the K nucleus with respect to a reference point.

defined by the spin–spin coupling constants *only* between protons and the so called *effective shifts*, which are connected with the true proton chemical shifts and proton–phosphorus spin–spin coupling constants by the simple relations[19]

$$\nu'_A = \nu_A + \frac{1}{2}J_{AX};\ \nu'_B = \nu_B + \frac{1}{2}J_{BX};\ \nu'_C = \nu_C + \frac{1}{2}J_{CX}\ldots$$

$$\nu''_A = \nu_A - \frac{1}{2}J_{AX};\ \nu''_B = \nu_B - \frac{1}{2}J_{BX};\ \nu''_C = \nu_C - \frac{1}{2}J_{CX}\ldots$$

Subspectra provide a very graphic method of determining the relative signs of the constants J_{HP}. Indeed, the lines of the complete spectrum should be distributed between the subspectra according to the relative signs of J_{AX}, J_{BX}, and J_{CX}:.



where in (1) the three constants have the same sign, in (2) the constant J_{BX} is opposite in sign in sign to J_{AX}, and in (3) the constant J_{CX} is opposite to sign to J_{AX} and J_{BX}. If the experimental spectrum enables lines to be assigned unambiguously between subspectra, it is possible also to choose the relative signs of the spin–spin coupling constants.

Fig. 1 shows the experimental and theoretical spectra of the ethylenic protons in vinylphosphonic bisdimethylamide[20]. It is readily seen that the relative intensities agree well with the distribution among subspectra assumed to correspond to constants J_{AX}, J_{BX}, and J_{CX} having the same sign. The spectra of allenic derivatives having a three-coordinated (Fig. 2) or a four-coordinated (Fig. 3) phosphorus atom[21] clearly show how the line intensity ratio varies with the signs of the constants. Thus in the p.m.r. spectrum of propadienylphosphonous bisdimethylamide the constants have the same sign, whereas in the spectrum of propadienylphosphonic bisdimethylamide the signs are different. Most of the parameters in the spectra can be obtained by direct measurement.

If, however, the subspectrum is highly symmetrical (e.g. the AB subspectrum in ABX, or AA'BB' in AA'BB'X[21]), unambiguous distribution of lines among subspectra is impossible. Complete analysis of the spectrum then requires a change in the relation between chemical shifts and spin–spin coupling constants, which can be achieved by using a spectrometer having a different working frequency[23] or by the employment of specific solvents to change the chemical shifts of individual protons[24].

Subspectra can be analysed in various ways depending on their complexity—manually[23] and by the use of previously calculated standard data[25], e.g. Corio's tables[26] (also Ref. 27, p. 587) or tables taking into account the resolving power of the spectrometers[28], and also with the application of electronic computers and special programmes[20,24,29,30].

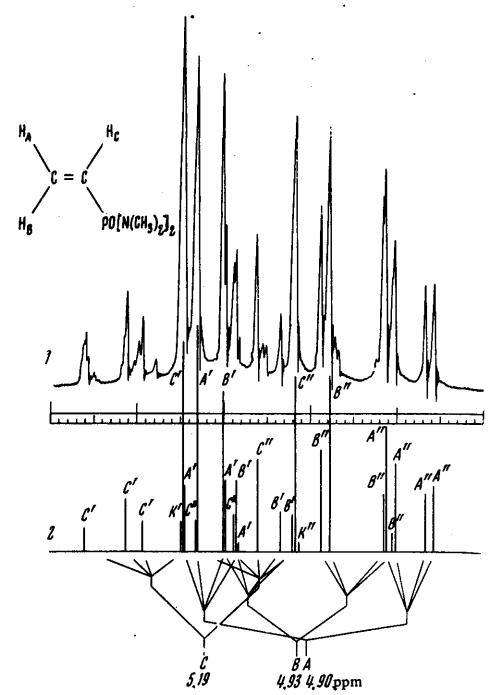


Figure 1. Proton magnetic resonance spectrum of ethylenic protons of vinylphosphonic bisdimethylamide (spectrum of type ABCX, with J_{CX} = 30.9, J_{BX} = 28.6, J_{AX} = 58.0, J_{AB} = 1.25, J_{BC} = 18.25, and J_{AC} = 12.35 c/s): 1) experimental spectrum at 100 Mc/s; 2) theoretical spectrum.

The presence of two phosphorus atoms in a molecule may produce considerable complication of the spectrum. Nevertheless, partial or complete analysis is possible in individual cases without the use of computers. Harris[31] used certain symmetry properties of the $A_nXX'A_n$ system to show that all parameters governing the form of such a spectrum can be obtained by direct measurement and simple calculation. If the spin–spin coupling constant between two groups of protons $J_{AA'} = 0$, the spectrum theoretically contains $2n + 1$ pairs of lines symmetrically arranged about $\nu_{A'}$, the chemical shift of $2n$ chemically equivalent protons. Since the nuclei are magnetically equivalent within each group of protons A and A', the spin–spin coupling constant between protons within a group does not affect the form of the spectrum, and therefore cannot be determined. The three remaining parameters of the spectrum J_{AX}, $J_{AX'}$, and J_X are elucidated by means of the relations

$$N = |J_{AX} + J_{AX'}|;\ L = |J_{AX} - J_{AX'}|\ .$$

The parameter N is easily determined from the distance between the pair of most intense lines in the spectrum (Fig. 4), representing half the total intensity. The remaining lines can be grouped into quartets, each corresponding to a definite value of the parameter χ, which assumes

integral values from 1 to n. The distance between the more intense inner lines of a quartet is connected with the parameters of the spectrum by the relation

$$S_{\text{inn}}(\chi) = (\chi^2 L^2 + J_X^2)^{1/2} - [(\chi - 1)^2 L^2 + J_X^2]^{1/2}.$$

The outer lines of the quartet are weak; the distance between them is determined by the similar expression

$$S_{\text{out}}(\chi) = (\chi^2 L^2 + J_X^2)^{1/2} + [(\chi - 1)^2 L^2 + J_X^2]^{1/2}.$$

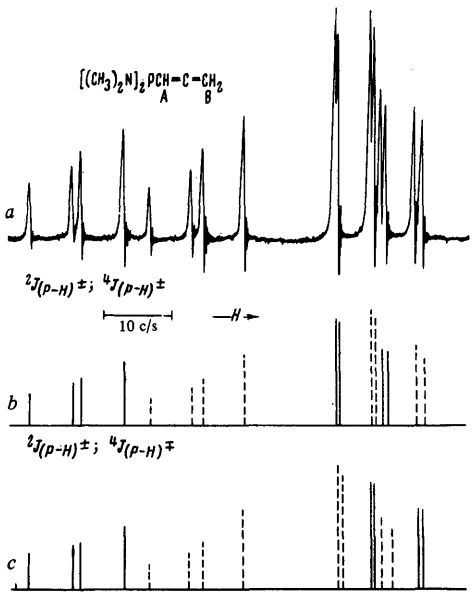


Figure 2. Proton magnetic resonance spectrum of allenic protons of propadienylphosphonous bisdimethylamide (spectrum of type AB_2X): *a*) experimental spectrum at 60 Mc/s; *b*) theoretical spectrum with the constants $^2J_{HP}$ and $^4J_{HP}$ having the same sign; *c*) theoretical spectrum with the constants having opposite signs.

The distance between the inner lines of the quartets increases with increase in χ, but does not exceed L, so that the latter can be determined roughly from the spectrum by finding the limit to which values of S_{inn} converge. At the same time the intensity of these lines drops rapidly. This applies also to the outer lines of the quartet, which diverge from the value $2L$. Since these lines are in general weak, in some cases only the first pair of lines ($\chi = 1$) can be observed. The constant $|J_X|$ is then determined by direct measurement from the distance between outer and inner lines of the first quartet ($\chi = 1$); from the results the parameter L is readily determined by means of the above formulae. If the outer lines cannot be observed, $|J_X|$ and L can be determined only from the inner lines of the first and second quartets, but the accuracy is considerably lower.

It is significant that, in spectra of this type, the form of the quartets depends only on the two parameters L and $|J_X|$, so that their appearance is completely determined by the ratio $L/|J_X|$. Fig. 4 shows the variation in the spectrum of $A_3XX'A_3'$ with change in this ratio. The general pattern is preserved in the spectra of compounds having a different number of protons [32].

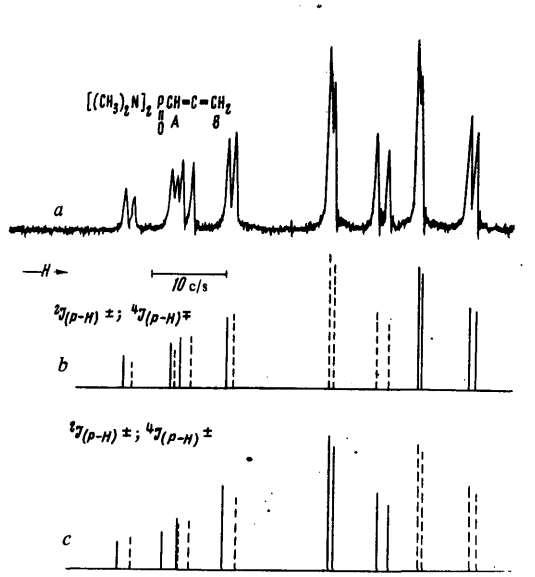


Figure 3. Proton magnetic resonance spectra of propadienylphosphonic bisdimethylamide.

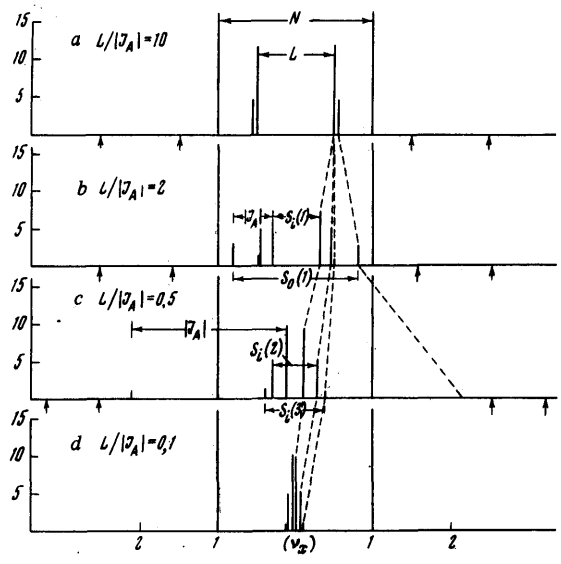


Figure 4. Theoretical spectra of the $A_3XX'A_3'$ system.

Complete analysis of the $A_nXX'A_n'$ spectrum enables only the absolute magnitude of the constant J_X to be determined. However, the relative signs of J_{AX} and $J_{AX'}$ can be ascertained: if any of the inner lines of the quartets lie outside the doublet N, these two constants are opposite

in sign; otherwise, they have the same sign. If the constant J_A is not zero, it is small, the general appearance of the spectrum is preserved, and each line in the quartets is split further; J_A can be evaluated from the magnitude of this splitting, although the calculation is fairly complicated[33]. A particular case is the simple AA'XX' spectrum: its complete analysis involves no theoretical difficulties, and all four spin–spin coupling constants can be determined without the use of tables or electronic computers[34].

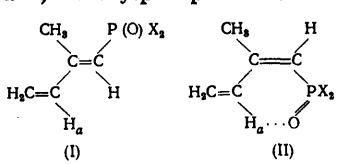
The present Section has considered ways of analysing the complicated p.m.r. spectra of organophosphorus compounds. It is noteworthy that in many cases the p.m.r. spectra are simple, first-order spectra not requiring special analysis. However, additional methods can be used for the analysis, in particular homonuclear and heteronuclear double and triple resonance, the method of two-quanta transitions[35–37], and also replacement of the magnetic nuclei by isotopes with analysis of the signals of ^{13}C satellites, but discussion of these aspects lies outside the scope of the present Review.

III. CHEMICAL SHIFTS OF PROTONS

According to Pauling (see 2.I in Ref. 38) the electronegativity of phosphorus coincides with that of hydrogen, and the chemical shift of the methyl protons in trimethylphosphine is consistent with the correlation found between the chemical shifts of the methyl protons in a methyl derivative of an element and the electronegativity of that element[39]. However, Table 1 shows that phosphonic, thiophosphonic, and phosphonium groups have a considerable deshielding effect, due primarily to the atomic contribution of the phosphorus-containing groups to the proton chemical shifts (transmissible through chemical bonds) and governed by the electron-accepting properties of such groups in comparison with the phosphinous (P^{III}) group. On the whole, estimates of the atomic contribution[25,40] are consistent with the Hammett constants, which indicate that phosphonate groups possess weak electron-accepting properties (close to those of the carboxy-group or the bromine atom). The greater deshielding effect of thiophosphonate than of phosphonate groups, in spite of the lower electronegativity of sulphur than of oxygen, definitely indicates considerable magnetic anisotropy of the P=S group.

Although in Mavel and Martin's estimation[41] the P=O group should also possess considerable magnetic anisotropy, this has not been confirmed by later work. In particular, the almost complete coincidence of the chemical shifts of the terminal protons (*cis* and *trans* with respect to phosphorus) in the spectra of derivatives of vinylphosphonic acid (Table 2),[20,24,42] and also the small difference between the chemical shifts of *cis*- and *trans*-protons in isomeric propenylphosphonates[43] and other analogous derivatives[24,44], indicate that magnetic anisotropy plays an insignificant part in the spectra of these compounds.

The Reviewers have investigated the chemical shifts of protons H_a and the methyl protons in isomeric derivatives of 2-methylbuta-1,3-dienylphosphonic acid of types



(I) (II)

($X = Cl, F, OR, NR_2, C_2H_5$), and established that the polar effect of the phosphonic group is decisive in these compounds, leading to formation of an intramolecular hydrogen bond between H_a and the phosphoryl oxygen in isomer (II).[45,46] Whereas the difference between the chemical shifts of the methyl protons in the two isomers lies in the range 0.15–0.22 ppm, the difference for the protons H_a is considerably larger (1–1.5 ppm), although the changes in the geometrical arrangement of H_a and CH_3 in the two isomers are approximately equivalent. The addition of trifluoroacetic acid, which ruptures intramolecular hydrogen bonds, halves the difference for H_a. On the whole it can be accepted as a general principle that protons located spatially closer to a phosphoryl or a thiophosphoryl group resonate at lower field. However, the situation is more complicated in cyclic esters of phosphoric and phosphonic acids[47–53] and in five-membered rings containing phosphorus[54–56]; in particular cyclic oxygen atoms evidently exert no less effect than does phosphoryl oxygen.

Table 1. Chemical shifts and spin–spin coupling constants J_{HP} in the p.m.r. spectra of organophosphorus compounds[17].

	Type of compound	ν, ppm	J, c/s
PH	PH_3	—	182.2
	P^+H	—	495—515
	P (O) H	—	490—710
	P (S) H	—	490—650
PCH	$P(CH_3)_3$	0.9	2.8
	$P^+(CH_3)_4$	2.5	14.4
	P (O) $(CH_3)_3$	1.9	13.4
	P (S) $(CH_3)_3$	1.8	13.0
PCCH	$P(CH_2CO_2)_3$	1.0	13.7
	$P^+(CH_2CH_2)_4$	1.3—1.6	18.0
	P (O) $(CH_2CH_2)_3$	1.1	16.3
	P (S) $(CH_2CH_2)_3$	1.8	11.3
	$R_2P[C\equiv C]_n H$ $n \neq 1,2$	2.6—3.0	0.3—1.5
	$R_2P[C\equiv C]_n CH_3$ $n = 1—3$	2.0—2.1	0.7—1.7
POCH	$P(OCH_3)_3$	3.6	10.5—11.5
	P (O) $(OCH_3)_3$	3.6	10.6—11.2
	P (S) $(OCH_3)_3$	3.7	13.0—13.4
	P (Se) $(OCH_3)_3$	3.7	14.1
PNCH	P $[N(CH_3)_2]_3$	2.5	8.5—9.2
	P (O) $[N(CH_3)_2]_3$	2.6	9.3—9.7
	P (S) $[N(CH_3)_2]_3$	2.6	10.8—11.1
PSCH	$P(SCH_3)_3$	2.3	9.8
	P (O) $(SCH_3)_3$	2.3	15.1—15.6
	P (S) $(SCH_3)_3$	2.4	17.5

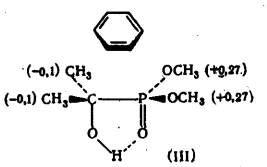
The tendency of phosphoryl compounds to form intramolecular and intermolecular hydrogen bonds is evidently the most characteristic feature distinguishing the proton resonance of these compounds. An intramolecular hydrogen bond is assumed to be the cause of the magnetic non-equivalence of the protons in compounds containing an asymmetric phosphorus atom[57,58]. The tendency of organophosphorus compounds to intermolecular hydrogen bonding has been assessed from the chemical shift of the proton in chloroform dissolved in these compounds[17]. This showed that, with compounds of the type $X_3P=O$, the tendency increases with the accumulation on the phosphorus of substituents X situated towards the end of the sequence

$$Cl < AlkS < AlkO < Alk < Alk_2N.$$

Thus the chemical shift of chloroform (7.08 and 7.28 ppm for a solution in cyclohexane and for the pure liquid)

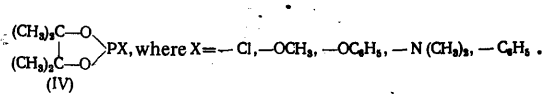
has the values 7.53, 8.00, 8.25, 8.61, and 9.11 ppm when dissolved in $Cl_3P=O$, $(CH_3S)_3P=O$, $(CH_3O)_3P=O$, $CH_3PO(OC_2H_5)_2$, and $((CH_3)_2N)_3P=O$ respectively.

The tendency to form hydrogen bonds involving the phosphoryl group determines in some measure the effect of various solvents on the proton chemical shifts. The effect of trifluoroacetic acid on the chemical shifts of protons in derivatives of 2-methylbutadienylphosphonic acid[45] has already been noted. The intramolecular hydrogen bond in dimethyl 1-hydroxyalkylphosphonates fixes the molecules in a definite conformation. When such compounds (III) are dissolved in benzene



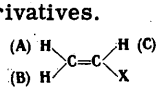
(III)

the solvent molecules are preferentially oriented in such a way that the magnetic anisotropy of the benzene ring produces shielding of methoxyl protons and deshielding of methyl protons[59]



(IV)

Table 2. Parameters δ (ppm) and J (c/s) of p.m.r. spectra of vinylphosphorus derivatives.



P-containing group X	δ_A	δ_B	δ_C	J_{AB}	J_{BC}	J_{AC}	J_{AX}	J_{BX}	J_{CX}
$POCl_2$	6.41	6.51	6.60	0.3	18.2	12.3	77.6	35.0	41.6
$PO(OCH_3)_2$	6.19	6.45	6.19	2.4	18.4	12.8	49.9	24.8	21.0
$PO(OC_2H_5)_2$	6.14	6.18	6.15	2.3	18.7	12.7	50.4	25.0	21.9
$PO[N(CH_3)_2]_2$	4.90	4.93	5.19	1.2	18.2	12.3	58.0	28.6	30.9
$PO(C_6H_5)_2$	5.10	5.10	5.35	2.3	17.9	13.2	36.3	20.4	26.3
$P(C_6H_5)_2$	—	—	—	0.05	19.0	12.8	43.8	21.7	21.2
$P(CH_3)_2C_6H_5$	—	—	—	0.4	18.6	12.8	48.5	25.3	24.0
$P(CH=CH_2)_2$	5.62	5.50	6.15	2.0	18.4	11.8	30.2	13.6	11.7

In the spectra of tetramethyldioxaphospholans of type (IV) the two pairs of methyl groups are not chemically equivalent. Dissolution in benzene increases the difference between their chemical shifts, which indicates the absence of rapid invertion relative to the phosphorus[60].

Use as solvents of strong acids capable of protonating organophosphorus compounds also causes a significant change in the chemical shifts of protons in groups located close to the centre of protonation. Correlation of the change in chemical shifts with the acid function of the solvent enabled protonation constants to be determined for a series of phosphines[61], phosphonates, phosphine oxides, and andions of phosphorus acids[62-64]. In the monomethylphosphonate, which is incapable of further protonation, the proton chemical shift of the methoxyl is independent of the acidity of the solution[64].

Thus examination of proton chemical shifts of organophosphorus compounds shows that in many cases this parameter depends significantly on the state of the phosphorus atom in the molecule and on the relative positions of the proton and the phosphorus-containing group. This enables proton chemical shifts to be used to establish the structure, the geometrical configuration, and the conformational equilibria of organophosphorus compounds, as well as for physicochemical investigations. However, there are no specific differences in the chemical shifts of protons that are caused by the presence of the phosphorus-31 nucleus: the above regularities are general in character and are due to the chemical characteristics of the phosphorus-containing groups, not to the magnetic properties of the phosphorus nucleus. From this point of view the spin–spin coupling of protons and phosphorus, to be considered in the next Section, is a considerably more valuable and interesting parameter for organophosphorus compounds.

IV. SPIN–SPIN COUPLING IN ORGANOPHOSPHORUS COMPOUNDS

1. Proton–Proton Interaction Constants

Neither proton chemical shifts nor proton–proton spin–spin coupling constants are specific in character, but conform to general rules. As a consequence of the low electronegativity of phosphorus, the constants J_{HH} are of the same order of magnitude as in hydrocarbons. The geminal constant $^2J_{HH}$ between protons attached to a carbon atom bound to phosphorus is ~ 10 c/s, as also in the fragment HPH (in chloromethylphosphine $ClCH_2PH_2$ these two constants are 10.4 and 9.8 c/s, the assignment being uncertain[22]); the constant is apparently negative in both cases[65]. In vinyl derivatives of phosphorus $^2J_{HH}$ varies in the range 0.05–2.34 c/s (positive),[20,24,35,36] the lowest value corresponding to the phosphonium compound $(C_2H_5)_3P.CH:CH_2$.[36] The vicinal constant $^3J_{HH}$ between protons in an ethyl group attached to phosphorus also lies near the usual value of 7–7.5 c/s,[29,30,65] independently of the state of the phosphorus; and in ethylenic derivatives it is ~ 12.5 c/s for *cis*-protons and 18.5 to 19 c/s for *trans*-protons[20,24,35,36], an appreciable change in the values of these constants being observed only when other substituents are present at the double bond[36,43,44,66-68]. This fact has been used[69,70] for the quantitative determination of the contents of *cis*- and *trans*-enolic forms in solutions of several substituted diethyl formylmethylphosphonates of the type $R.CH(CHO).PO(OC_2H_5)_2$.

The constants $^3J_{HH}$ between *ortho*-protons in aromatic phosphine oxides also have the usual values of 8–9 c/s.[40,71,72] Values are known for the constant $^3J_{HH}$ in the H–P–P–H system which are close to the vicinal constant in a hydrocarbon fragment (10.5 and 6.8 c/s for the two vicinal constants in diphosphine H_2P-PH_2[65]). In the H–C–P–H system, however, it varies within fairly wide limits, decreasing as electron-accepting groups accumulate on the phosphorus atom[65,73]:

Compound	CH_3PH_2	$(CH_3)_3\overset{+}{P}H$	$CH_3P(O)(H)(OH)$
$^3J_{HH}$, c/s	7.98	5.48	2.0

Allenic derivatives containing phosphorus show the long-range spin–spin coupling between protons, well known with allenic systems[74], having constants $^4J_{HH}$ and

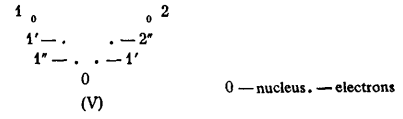
$^5J_{HH}$ of 6–7 ~ 3 c/s respectively [21,25,75–77]. Propenylphosphonic acid derivatives develop allylic spin–spin coupling between protons, with $^4J_{HH}$ being ~ 1 and ~ 1.5 c/s for *trans*- and *cis*-positions of the methyl group and the ethylenic proton [43,46,78].

The spin–spin coupling constants of protons and phosphorus are of considerably greater value for the p.m.r. investigation of organophosphorus compounds, and their intensive study during recent years has enabled the main regularities in their variation to be established. On the whole the principle rules governing magnitude and sign of the constants J_{HP} are the same as those for proton–proton spin–spin coupling, but proton–phosphorus interaction is greater in absolute magnitude and usually remains evident with a larger number of bonds separating the interacting atoms.

2. Sign of Spin–Spin Coupling Constants of Protons and Phosphorus

The relative signs of spin–spin coupling constants in molecules can be determined by analysis of complicated n.m.r. spectra, double and triple resonance, and the method of two-quanta transitions. Theoretical calculations [79] predict a positive (absolute) sign of the constant for directly bound ^{1}H and ^{13}C nuclei and for $^3J_{HH}$. During recent years new methods have been elaborated for determining the absolute signs of spin–spin coupling constants: relaxation times and saturation parameters of individual spectral lines have been shown [80] to depend on the absolute signs of the coupling constants; the dependence of the change produced by the field resulting from the action of the solvent, on the dipole moment of the test substance, has been established for the constants $^2J_{HH}$ and $^2J_{HF}$, which also enables the absolute signs of these constants to be determined [81,82]. Although the absolute signs of the constants have not been determined directly for proton–phosphorus interaction, comparison of available data on the absolute and relative signs of the constants in the spectra of various compounds enables us to elucidate for most cases the absolute signs of the spin–spin coupling constants involving ^{31}P nuclei (Table 3) [83–86].

The occurrence of particular signs of the constants (in saturated compounds) is explained theoretically [87] on the basis of Hund's multiplicity principle. In the case of two magnetic nuclei combined through two chemical bonds (V)



(V)

the Fermi contact interaction of the nuclear spins [88], which makes the chief contribution to the spin–spin coupling constant [89], can be accomplished in two ways.

(*a*) Direct overlapping of the orbitals of electrons 1′ and 2″. This leads to antiparallel pairing of the electron spins, as a result of which the nuclear spins 1 and 2, being oriented antiparallel to the electron spins, are paired together antiparallel, so that the spin–spin coupling constant between them is positive.

(*b*) Overlapping of orbitals with insertion of an intermediate atom. The spins of electrons 1′ and 1″, and independently of them the spins of electrons 2′ and 2″, are antiparallel. Since, however, 1″ and 2′ belong to the same atom, they will tend, according to Hund's rule, to be mutually parallel, the net effect of which is that electron spins 1′ and 2″, as well as nuclear spins 1 and 2, will tend to be parallel, so that the constant has a negative sign.

Table 3. Signs of spin–spin coupling constant of magnetic nuclei with phosphorus $^nJ_{PX}$.

X	n=1	n=2	n=3	n=4	X	n=1	n=2	n=3	n=4
^{1}H ^{13}C	+ +and−	+and− +and−	+ +	+and−	^{19}F ^{31}P	− −and+	+ +	+	+

Competition between the two mechanisms may lead in the case of geminal interaction to either a positive or a negative constant. Extension of this principle to other cases leads to the conclusion that, with an odd number of chemical bonds linking the interacting magnetic nuclei, the spin–spin coupling constant should assume positive values, whereas, with an even number of bonds, it may be either positive or negative. This principle is fully consistent with experimental data on the proton–phosphorus interaction constants [90], but with heavy nuclei directly attached to phosphorus negative constants are observed, for the most part contrary to predictions. The appearance of negative constants between directly bound nuclei was explained by Pople and Santry [91] by applying the molecular orbital method to spin–spin interaction. On the other hand, negative constants may also arise if not only contact interaction but also other contributions play an appreciable part in spin–spin coupling [92–94].

3. Spin–Spin Coupling of a Directly Bound Proton with Phosphorus $^1J_{HP}$

The constant $^1J_{HP}$ varies over a very wide range—from 138 c/s in the dihydrogen phosphide anion PH_2^- [95,96] to 1092 c/s in hydrogen tetrafluorophosphate HPF_4 [97]—and is probably positive in all cases. The ease of identification in the spectra and the characteristic values of the constant $^1J_{HP}$, which vary fairly exactly with the valency state of phosphorus and the nature of the substituents, make this parameter extremely convenient both for establishing the structure and for assessing the electron distribution in phosphorus hydrides by means of proton magnetic resonance.

By analogy with the spin–spin coupling constant of directly bound ^{1}H and ^{13}C nuclei, the constant $^1J_{HP}$ has been generally recognised as depending on the *s*-character of the orbital in the H–P bond: $^1J_{HP} = 29.30 s_{PH}$, where s_{PH} is the *s*-character of the P–H bond in phosphine [67].

This relation explains satisfactorily the change in $^1J_{HP}$ on passing from three-coordinated compounds ($^1J_{HP} \simeq$ 200 c/s) to four-coordinated compounds (400–700 c/s), since in the former the P–H bonds are formed predominantly by *p*-electrons of the phosphorus with slight addition of *s*-character, whereas in four-coordinated compounds, with hybridisation of phosphorus close to sp^3,

these bonds contain 25% and more of s-character. The substantial variations in $^1J_{HP}$ within a group of compounds having the same coordination of phosphorus can be explained by the different electronegativities of the substituents: according to Bent's rule [98] the replacement of substituents on the central atom by more electronegative substituents leads to a concentration of p-character in orbitals in the direction of these electronegative substituents, with a resultant enhancement of the s-character of the coupling with hydrogen atoms. However, this approach is open to criticism.

Whereas with compounds of three-coordinated phosphorus hybridisation can vary within wide limits owing to transition of the lone pair from the s-state to sp^3-hybridisation, with phosphonium salts a significant change in hybridisation is improbable. Yet, whereas in phosphines $^1J_{HP}$ varies within comparatively narrow limits (182 to 216 c/s on passing from phosphine to diphenylphosphine [61]), phosphonium salts show a considerably larger variation (436, 506–510, and 870 c/s for $[(t\text{-}C_4H_9)_3PH]^+$, [61] $[(C_6H_5)_3PH]^+$, [61,94] and $[(C_6H_5O)_3PH]^+$ [94] respectively). The increase in $^1J_{HP}$ on passing from phosphonium salts to dialkyl hydrogen phosphites (695.5 c/s in $HO.P(CH_3O)_2$ [92,99]) and to compounds containing five-coordinated phosphorus, for which the $^1J_{HP}$ constants are especially large



730—830 c/s[100] 850—858 c/s[101] 739—780 c/s[100–104] 900 c/s[105] 1075—1092 c/s (depending on temp.) (Ref.97)

is still less explicable from this point of view. Although increase in the s-character of the bonding orbitals occurs on passing from three-coordinated to more highly coordinated phosphorus compounds, a decrease in s-character is rather to be expected in four-coordinated compounds with electronegative substituents having a lone pair of electrons (Cl, O, N) and in compounds with five-coordinated phosphorus, owing to hybridisation involving d-orbitals [106].

An explanation of this variation in $^1J_{HP}$ was given by McFarlane and White [94], who suggested, and confirmed experimentally on protonated phosphines, that, by analogy with the behaviour of $^1J_{HC}$, [107] not only the s-character of the P–H orbital but also the charge on the phosphorus atom greatly affects the magnitude of $^1J_{HP}$. It had been shown theoretically [107,108] that the spin–spin coupling constant of directly bound nuclei depends on the cube of the charge, so that small changes in the charge may have a substantial effect on the constant. This new approach opens up wide possibilities of explaining the effects of substituents on $^1J_{HP}$ and elucidating the distribution of electron density in organophosphorus molecules. Thus the effect of solvents on $^1J_{HP}$ in dimethyl hydrogen phosphite (this parameter varies from 627.9 c/s in solution in an ammoniacal buffer (pH 11.4) to 734.3 c/s in trifluoroacetic acid [99]) can be explained by a difference in solvation of the P=O group and the accompanying change in the charge on the phosphorus. The increase in $^1J_{HP}$ in the above five-coordinated phosphorus compounds is obviously due to the accumulation of electronegative substituents, which produce an increase in the positive charge on the phosphorus.

The above regularities in the spin–spin coupling of directly bound ^1H and ^{31}P atoms can be extended in considerable measure to the longer-range interaction of these nuclei, but their relative positions in space then play a considerably greater part.

4. Spin–Spin Coupling of Proton and Phosphorus in a Geminal Position $^2J_{HP}$

Geminal proton–phosphorus spin–spin coupling constants are of considerable interest both for the identification of organophosphorus compounds and for establishing general n.m.r. rules in connection with the electron distribution in them. It is usually easy to elucidate these constants in the proton spectra, and often their signs relative to $^1J_{HP}$, $^3J_{HP}$, etc. can often be determined, which facilitates the establishment of their absolute signs. The limits of variation in $^2J_{HP}$ are fairly wide, from +59.0 c/s in *cis*-propenylphosphonic dichloride [43] to between −21 and −22 c/s in compounds of the type $R.CH_2.PO(OC_2H_5)_2$, where R is an electron-accepting group having a multiple bond (C=O, C≡N, C≡C). [109,110] It is interesting that these limits exceed only slightly the known limits of variation in geminal proton–proton constants [111], but they will undoubtedly be extended for proton–phosphorus interaction.

At least three factors—the state of hybridisation at substituents on the phosphorus atom, the substituents attached to the carbon atom, and the configuration of the molecule—govern the value of $^2J_{HP}$ in the H–C–P system. In saturated four-coordinated phosphorus compounds this parameter is usually negative, varying in the vicinity of −15 to −20 c/s, [37] but it has been found recently [29] that $^2J_{HP}$ and $^3J_{HP}$ have the same signs in ethylphosphonic dichloride and difluoride, which indicates a positive absolute sign of the geminal proton–phosphorus constant $^2J_{HP}$ (+19.6 and +14.1 c/s in $C_2H_5POF_2$ and $C_2H_5POCl_2$ respectively‡). Comparison of the relative signs of the constants in ethylenic [20,24,35,36,43] and allenic [21,76,85] organophosphorus compounds shows convincingly that the geminal H–C–P constant at an unsaturated carbon atom is always positive. On the whole substituents at a carbon atom have the same effect on $^2J_{HP}$ as on the proton–proton coupling constant $^2J_{HH}$: [111] the introduction of electronegative substituents, change in the hybridisation of carbon from sp^3 to sp^2, and also the introduction of electron-donating substituents—all produce a change in $^2J_{HP}$ towards *positive values*. Substituents on the phosphorus obviously conform on the whole to the same rule in their effect on $^2J_{HP}$: electronegative substituents, capable of moving electrons to d-orbitals of phosphorus by a conjugation mechanism, produce a change in the geminal constant towards positive values.

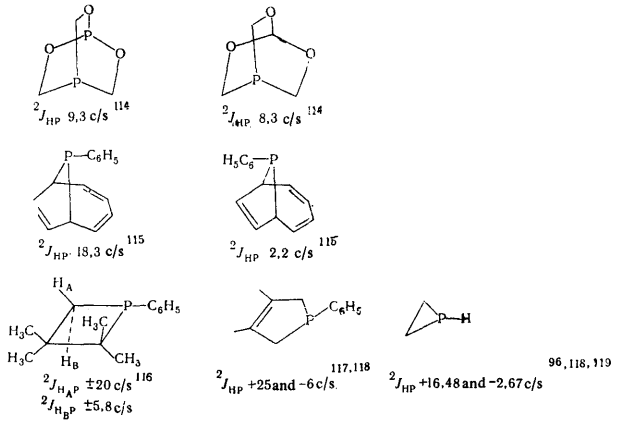
The effect of substituents on $^2J_{HP}$ is considerably smaller in three-coordinated phosphorus derivatives, although the attachment of chlorine atoms to the phosphorus or the transition from an sp^2- to an sp^3-hybridised carbon atom increases the parameter, as with the four-coordinated compounds:

Compound	$(CH_3)_3P$	$(CH_2{=}CH)_3P$	$CH_3CH_2PCl_2$
$^2J_{HP}$, c/s	+2.66[65]	+11.74[25]	+15.0§[113]

‡These results differ somewhat from the values obtained in an unpublished paper [112].

§We have adopted a positive sign for $^2J_{HP}$ in ethyldichlorophosphine on the basis that the geminal and vicinal constants in the spectrum of this compound [113] have the same sign.

In phosphines containing aliphatic and aromatic substituents $^2J_{HP}$ varies only within the narrow limits of zero to +4 c/s, but considerable departures from these limits are observed in compounds containing the phosphorus atom in a strained ring:



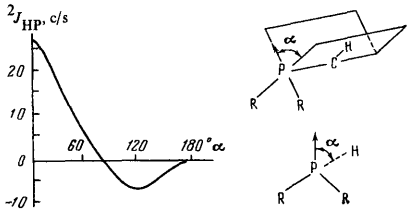
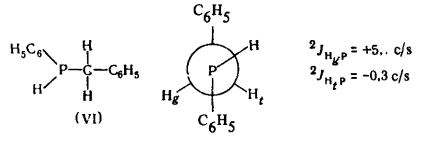


Figure 5. Angular dependence of constant $^2J_{HP}$ in phosphines.

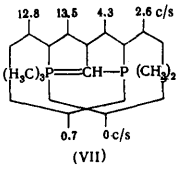
Albrand et al. [118] have analysed the above and other similar data, and have shown convincingly that the geminal constant $^2J_{HP}$ in phosphines is determined mainly by the mutual arrangement of the proton and the substituents on the phosphorus (Fig. 5). Data for compounds having a rigid configuration extend also to benzylphenylphosphine



in which the non-equivalence of the two methylene protons is due to inhibited rotation. Comparison of the proton–proton and proton–phosphorus constants enables us not only to determine the absolute signs of the latter but also to assign them to certain protons [118].

Unfortunately, so few data are available on the spin–spin coupling constants of five-coordinated phosphorus compounds that no general conclusions can be drawn.

It is interesting that the geminal constants $^2J_{HP}$ in the phosphinophosphorane



correspond exactly to the above values for three- and four-coordinated phosphorus [120].

5. Spin–Spin Coupling of Proton and Phosphorus in the Vicinal Position $^3J_{HP}$

Vicinal proton–phosphorus constants are evidently always positive, and on the whole depend on the same factors as do the geminal constants, but the mutual positioning of the interacting nuclei plays a still greater part. Analysis of vicinal constants in cyclic and unsaturated compounds [121–123], for which it is possible to estimate the dihedral angle Φ between the HC^1C^2 and C^1C^2P planes in the $H–C^1–C^2–P$ system, showed that the dependence of $^3J_{HP}$ on Φ is completely analogous to the corresponding relation for proton–proton interaction [124] (Fig. 6): (i) $^3J_{HP}$ has its maximum value at Φ = 180°; (ii) $^3J_{HP}$ has its minimum value or is zero when Φ = 90°; (iii) when Φ = 0° the constant $^3J_{HP}(0°) = (0.5–0.33)^3J_{HP}(180°)$; (iv) with other values of the angle Φ the parameter $^3J_{HP}$ assumes intermediate values.

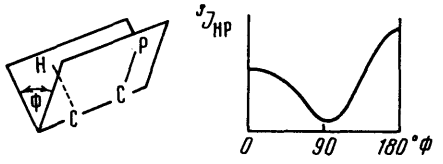
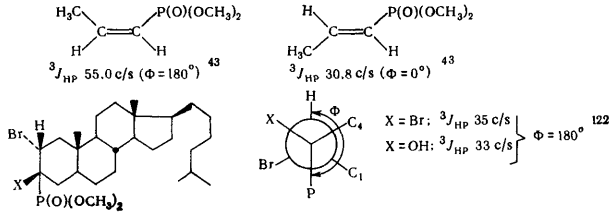
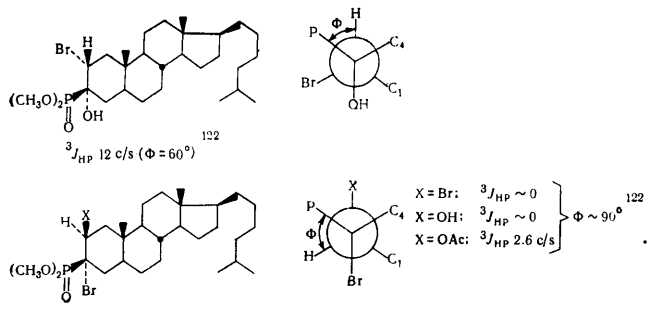


Figure 6. Angular dependence of constant $^3J_{HP}$.

The spin–spin coupling constant of the phosphorus atom in the dimethoxyphosphinyl group and a vicinal proton varies from 9 to 55 c/s with different values of Φ:





122

$^3J_{HP}$ 12 c/s ($\Phi = 60°$)

The above dependence on the dihedral angle and the considerable range of variation in $^3J_{HP}$ make elucidation of the vicinal proton–phosphorus interaction constant especially valuable in stereochemical investigations.

Substituents attached to carbon atoms have the same effect on $^3J_{HP}$ as in proton–proton interaction: electronegative substituents produce a decrease in the parameter. Thus for the bisdimethylamides of a series of vinylphosphonic acids $^3J_{HP}$ varies as follows [20,74]:



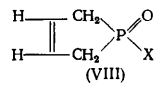
X=H	CH_3	$N(CH_3)_2$	OCH_3
$^3J_{HP} = 28.7$	18.4	14.0	10.5 c/s

On the other hand, introduction of electronegative substituents at the phosphorus atom and the change from tervalent to four-coordinated phosphorus compounds produce increases in $^3J_{HP}$, as with geminal proton–phosphorus interaction. In a series of derivatives of vinylphosphonic acid, for example, the parameter falls in the sequence [20,21,24,35,36,43–45]

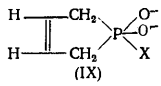
$$P(O)Cl_2 > P(O)(SC_2H_5)_2 > P(O)[N(CH_3)_2]_2 > \overset{+}{P}R_3 > P(O)R_2 > PR_2,$$

and in *cis*-prop-1-enylphosphonic dichloride the constant $^3J_{PH,trans} = 85.0$ c/s [43] assumes the maximum value known at present for constants of this type. Electronegative substituents, capable of conjugation involving vacant *d*-orbitals of phosphorus, evidently cause rehybridisation of the orbitals and enhancement of the *s*-character in the direction of the phosphorus–carbon bond. It is possible also that the variation in the parameters is associated with a change in the charge on the phosphorus. However, variation in the substituents attached to three-coordinated phosphorus in the allenic derivatives $CH_2:C:C(CH_3).PX_2$ is accompanied by variation in $^3J_{HP}$ in the opposite sequence—8.9, 7.8, and 3.4 c/s when X represents C_6H_5, $N(CH_3)_2$, and Cl respectively [21].

Although no considerable spin–spin coupling in the =CH–C–P system has been detected in open-chain allyl compounds, the parameter $^3J_{HP}$ is quite large (36 to 40 c/s) in cyclic phospholens of the type



(VIII)



(IX)

and varies little with the coordination number of the phosphorus [124–126].

Considerable values of $^3J_{HP}$ are found also in systems containing a heteroatom, and depend more on the nature of the heteroatom than of the substituents attached to phosphorus [17,127–130]:

H–C–O–P	H–C–N–P	H–C–S–P
8–12 c/s	11–12 c/s	14–22 c/s

As with other vicinal constants this parameter, too, has been found to depend on the dihedral angle [48,58], and $^3J_{HCOP}$ is apparently also maximal with the interacting nuclei in the *trans*-position.

Thus the parameters $^3J_{HP}$, usually easily identifiable in the p.m.r. spectra of organophosphorus compounds, are extremely sensitive to their electronic structure and especially their geometrical structure, and can therefore be widely used in analysing the structure of compounds.

6. Long-range Proton–Phosphorus Spin–Spin Coupling $^nJ_{HP}$

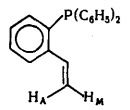
Long-range spin–spin coupling $^nJ_{HP}$ is observed in many cases through 4–8 bonds in allenic and acetylenic systems containing phosphorus atoms. A series of acetylenic phosphonates show a uniform decrease in $^nJ_{HP}$, proportional to the cube of the distance between the hydrogen and phosphorus nuclei [131], as *n* increases from 3 to 6; with $n = 6$ the constant $^6J_{HP}$ is still considerable (2.15 c/s). The long-range spin–spin coupling constant of protons and phosphorus is lower in phosphines and their oxides and sulphides than in phosphonates, but even in heptatriynyldiphenylphosphine $(C_6H_5)_2P.[C:C]_3.CH_3$ spin–spin coupling $^8J_{HP} = 0.7$ c/s is observed [132,133]. Unfortunately, the absolute signs of the constants in such systems have not been studied in detail; double resonance has shown that the constants $^4J_{HP}$ and $^1J_{FP}$ in prop-1-ynylphosphonic acid $CH_3.C:C.POF_2$ have opposite signs [134], so that the proton–phosphorus constant is positive.

Considerable spin–spin coupling $^4J_{HP}$ and $^5J_{HP}$ is observed in allenic compounds containing a three- and four-coordinated phosphorus atom [21,25,75,77]. In compounds of the type $CH_2:C:CH.POR_2$ the constants $^4J_{HP}$ vary between –10 and –18 c/s with increase in the Taft inductive constant σ_1 of the substituents (R = Alk, Ar, NAlk$_2$, OAlk, Cl). [21] In the analogous compounds containing three-coordinated phosphorus the constant $^4J_{HP}$ is proportional to the Hammett constant σ_n, and has a negative sign in all cases except when at least one of the substituents is a dimethylamino-group; this is probably due to the ability of the lone pair of the nitrogen to conjugate with vacant 3*d*-orbitals of phosphorus [21].

The constant $^5J_{HP}$ in the allenic phosphonate $(CH_3)_2C::C:CH.POX_2$ with X = Cl is +12.1 c/s, [21,135] but in compounds with other substituents attached to phosphorus it is lower (6.1, 6.3, 7.8, 9.7, and 5.4 c/s when X = $N(CH_3)_2$, C_6H_5, [21] OC_2H_5, [136] F, [77] and C_2H_5 [75] respectively). The constant may be assumed to be positive in all compounds of this type. It is interesting that, as in other cases, the proton–proton interaction parameter in this system is considerably smaller and more constant: $^5J_{HH}$ varies in the range 3.1–3.5 c/s.

The analogy between proton–phosphorus and proton–proton long-range interaction is apparent in the considerably lower long-range coupling constants in allylic and aromatic than in acetylenic and allenic systems. In $CH_3.CH:CH.POX_2$ the constants $^4J_{HP} = 0$–3.5 c/s (probably negative), the splitting being greater with methyl and phosphorus-containing groups in the *cis*-position than in the *trans*-isomers [43,45,66,137]. Derivatives of phosphonic acids with 1,3-diene substituents $CH_3XCH:CH.CH:CH.POY_2$ (*trans*, *trans*) exhibit splitting of the $C_{(3)}$ proton signal with the constant $^4J_{HP} = 1.6$–1.7 c/s. [138] The constants for the methyl protons in *o*-tolylphosphorus derivatives and for the ring *meta*-protons in various phenylphosphorus compounds lie in the range 1–4.2 c/s. [40,71,72]

However, the discovery of long-range spin–spin coupling in *o*-vinylphenyldiphenylphosphine



(X)

$^5J_{H_AP}$ 1.1 c/s

$^5J_{H_MP}$ 0.1–0.05 c/s

is quite unexpected. In this case interaction is attributed to direct overlapping of the electron clouds of the proton and phosphorus through space. Such interaction is not observed in the corresponding phosphonium iodide [139].

Long-range spin–spin coupling constants in systems containing a heteroatom are extremely small [140–144]. Nevertheless, it has been possible to establish by means of double resonance that they may have different signs depending on the substituents attached to the phosphorus [140]:

Compound	$(C_2H_5O)_3P$	$(C_2H_5O)_3P{=}O$	$(C_2H_5O)_3P{=}S$
$^4J_{HCCOP}$, c/s	−0.55	+0.84	+0.73

The variation in sign may be due to the conformational constitution of the compounds, since the above constants result from the averaging of all possible conformational structures.

In the fragment P.CO.N.CH.CH the constant $^5J_{HP}$ exceeds $^4J_{HP}$, and this serves to confirm the hypothesis of two simultaneous mechanisms of spin–spin coupling, making opposite contributions to the latter constant [144].

The above relations of the proton chemical shifts and the proton–phosphorus spin–spin coupling constants with the molecular and electronic structures of organophosphorus compounds present wide possibilities for the p.m.r. investigation of these compounds. The next Section examines the most important lines of research.

V. MAIN LINES OF THE p.m.r. INVESTIGATION OF ORGANOPHOSPHORUS COMPOUNDS

The practical application of p.m.r. spectroscopy is concerned primarily with establishing the molecular and geometrical structure of organic compounds.

Proton magnetic resonance has recently been widely used to confirm the structure of five-membered phosphorus-containing heterocycles, which result from the reaction of tervalent phosphorus derivatives with conjugated systems. As already remarked, the constants $^3J_{HP}$ are quite considerable in cyclic compounds, which enables the latter to be distinguished unambiguously from open-chain compounds [124–126,145–148]. Close attention has been paid to esters of phosphonic acids with groups, potentially capable of keto–enol tautomerism [109,149,150] or containing a mobile hydrogen atom [109,151,152], which are distinguished by a considerable $^2J_{HP}$ constant (10–21 c/s). Several esters, thioesters, and amides of phosphoric, thiophosphoric, and phosphonic acids of interest as insecticides have been identified by p.m.r. for analytical purposes [127–129].

Widespread use is made of p.m.r. for the easy establishment of the geometrical structure of organophosphorus compounds, especially ethylenic derivatives. In effect only this method has provided an approach to the problem of the *cis–trans* isomerism of ethylenic phosphonates [43,66,68,121–123]; establishment of the *trans*-structure of 2-cyanovinylphosphonic esters necessitated reconsideration of the mechanism of their formation [153].

Application of this method enabled a study to be made of the aldo-*cis–trans*-enol tautomerism of substituted formylmethylphosphonates in solution [69,70].

Extremely interesting results have been obtained on the conformations of open-chain organophosphorus compounds, made possible by the phenomenon of molecular asymmetry and governed by the difference in the chemical shifts and the spin–spin coupling constants for protons in the various conformations [118,154–156]. Study of the effects of temperature and the solvent on the spectra provides additional opportunities for investigating the problem [157]. Development of research on these lines includes the question of the pseudorotation of systems that are stable at ordinary temperatures [158,159].

The appearance of the p.m.r. method gave a sharp impetus to the development of research on interactions such as hydrogen bonding and intermolecular association. The Reviewers established the presence of an intramolecular hydrogen bond in derivatives of 2-methylbutadienylphosphonic acid [45,46]; an intramolecular hydrogen bond explains the molecular association effect in the spectrum of 2,4-dichlorophenyl methyl isopropylphosphoramidate [160]; an intermolecular hydrogen bond affects the chemical shift of the proton of chloroform dissolved in organophosphorus compounds [17]. This aspect is closely connected with the problem of chemical exchange in complexes with organophosphorus ligands [161]. The investigation of complexes of organophosphorus compounds with metals is inherently a fairly complicated problem, solution of which requires the application not only of p.m.r. but also of other types of nuclear resonance spectroscopy [161–166].

We note in conclusion that the p.m.r. method has found a valuable application for studying the protonation of organophosphorus compounds by strong acids [61–64,94]. In individual cases it is possible to determine the lifetime of molecules in the protonated state [167].

REFERENCES

1. H. S. Gutowsky, D. W. McCall, and C. P. Slichter, Phys. Rev., 84, 589 (1951).
2. J. R. Van Wazer, C. F. Callis, J. N. Shoolery, and R. C. Jones, J. Amer. Chem. Soc., 78, 5715 (1956).
3. J. D. Baldeswieler and E. W. Randall, Chem. Rev., 63, 81 (1963).
4. T. I. Zykova, Candidate's Thesis, Kazan State University, 1967.
5. Yu. Yu. Samitov, Doctoral Thesis, Kazan State University, 1968.
6. H. Finegold, Ann. New York Acad. Sci., 70, 875 (1958).
7. J. F. Nixon and R. Schmutzler, Spectrochim. Acta, 20, 1835 (1964).
8. M. L. Nielsen, J. V. Pustinger, and J. Strobel, J. Chem. and Eng. Data, 9, 167 (1964).
9. M. L. Nielsen and J. V. Pustinger, J. Phys. Chem., 68, 152 (1964).
10. B. I. Ionin and B. A. Ershov, "YaMR-spektroskopiya v Organicheskoi Khimii" (Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry), Khimiya, Leningrad, 1967, Chapter 2.
11. V. Mark, C. H. Dungan, M. M. Crutchfield, and J. R. Van Wazer, "Topics in Phosphorus Chemistry", 1967, Vol. 5, p. 229.
12. C. J. Jameson and H. S. Gutowsky, J. Chem. Phys., 40, 1714 (1964).

13. J. H. Letcher and J. R. Van Wazer, J. Chem. Phys., 44, 815 (1966).
14. H. S. Gutowsky and J. Larmann, J. Amer. Chem. Soc., 87, 3815 (1965).
15. B. I. Ionin, Zhur. Obshch. Khim., 38, 1659 (1968).
16. G. Mavel, "Progress in NMR", Pergamon Press, Oxford, 1966, Vol. 1.
17. G. Mavel, "Composés organiques du Phosphore", Coll. nat. Centre nat. Res. sci., Toulouse, 1965, (publ. 1966).
18. J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High-Resolution Nuclear Magnetic Resonance Spectra" (Translated into Russian), Inostr. Lit., 1962.
19. P. T. Narasimhan and M. T. Rogers, J. Chem. Phys., 34, 1049 (1961).
20. T. N. Timofeeva, B. V. Semakov, and B. I. Ionin, Zhur. Obshch. Khim., 40, 1169 (1970).
21. M.-P. Simmonin and C. Charrier, "Organic Magnetic Resonance", 1969, Vol. 1, p. 27.
22. H. Goldwhite and D. G. Rowsell, J. Phys. Chem., 72, 2666 (1968).
23. T. N. Timofeeva, B. I. Ionin, Yu. L. Kleiman, N. V. Morkovin, and A. A. Petrov, Zhur. Obshch. Khim., 38, 1255 (1968).
24. M. P. Williamson, S. Castellano, and C. E. Griffin, J. Phys. Chem., 72, 175 (1968).
25. B. I. Ionin, V. M. Ignat'ev, and V. B. Lebedev, Zhur. Obshch. Khim., 37, 1863 (1967).
26. P. L. Corio, Chem. Rev., 60, 363 (1960).
27. J. W. Emsley, J. Feeney, and L. H. Sutcliffe, "High-resolution Nuclear Magnetic Resonance Spectroscopy" (Translated into Russian), Mir, Moscow, 1968.
28. T. N. Timofeeva and B. I. Ionin, Zhur. Org. Khim., 5, 764 (1969).
29. T. N. Timofeeva, Yu. L. Kleiman, and B. I. Ionin, Zhur. Obshch. Khim., 40, 1046 (1970).
30. J. B. Hendrickson, M. L. Maddox, J. J. Sims, and H. D. Kaesz, Tetrahedron, 20, 449 (1964).
31. R. K. Harris, Canad. J. Chem., 42, 2275 (1964).
32. R. K. Harris and R. G. Hayter, Canad. J. Chem., 42, 2282 (1964).
33. R. K. Harris and C. M. Woodman, Mol. Phys., 10, 437 (1966).
34. D. M. Grant, R. C. Hirst, and H. S. Gutowsky, J. Chem. Phys., 38, 470 (1963).
35. W. A. Anderson, R. Freeman, and C. A. Reilly, J. Chem. Phys., 39, 1518 (1963).
36. J. E. Lancaster, Spectrochim. Acta, 23A, 1449 (1967).
37. W. McFarlane, Chem. Comm., 58 (1967).
38. L. Pauling, "The Nature of the Chemical Bond" (Translated into Russian), Goskhimizdat, Moscow–Leningrad, 1947, p. 67.
39. R. G. Kostyanovskii, I. I. Chervin, V. V. Yakshin, and A. U. Stepanyants, Izv. Akad. Nauk SSSR, Ser. Khim., 1629 (1967).
40. C. E. Griffin, Tetrahedron, 20, 2399 (1964).
41. G. Mavel and G. Martin, J. Chim. phys., 59, 762 (1962).
42. J. E. Lancaster, Spectrochim. acta, 23A, 1449 (1967).
43. T. N. Timofeeva, V. M. Ignat'ev, B. I. Ionin, and A. A. Petrov, Zhur. Obshch. Khim., 39, 2446 (1969).
44. R.-H. Lequan and M.-P. Simonnin, Compt. rend., 268, 1400 (1969).
45. T. N. Timofeeva, I. N. Mashlyakovskii, B. I. Ionin, and A. A. Petrov, Zhur. Obshch. Khim., 39, 1048 (1969).
46. T. N. Timofeeva, B. I. Ionin, and A. A. Petrov, Zhur. Obshch. Khim., 39, 354 (1969).
47. D. W. White, G. K. McEwen, and J. G. Verkade, Tetrahedron Letters, 5369 (1968).
48. J. H. Hargis and W. G. Bentrude, Tetrahedron Letters, 5365 (1968).
49. K. D. Bartle, R. S. Edmundson, and D. W. Jones, Tetrahedron, 23, 1701 (1967).
50. D. Gagnaire and J. B. Robert, Bull. Soc. chim. France, 2240 (1967).
51. D. Z. Denney and D. B. Denney, J. Amer. Chem. Soc., 88, 1830 (1966).
52. G. Alsnes, R. Eriksen, and K. Mellinyer, Acta Chem. Scand., 21, 1028 (1968).
53. E. E. Nifat'ev, I. S. Nasonovskii, and A. A. Borisenko, Zhur. Obshch. Khim., 40, 1248 (1970).
54. H. Goldwhite, Chem. and Ind., 494 (1964).
55. F. Ramirez, Pure Appl. Chem., 9, 337 (1964).
56. N. A. Razumova and F. V. Bagrov, Zhur. Obshch. Khim., 40, 1241 (1970).
57. A. W. Garrison, L. H. Keith, and A. L. Alford, Spectrochim. Acta, 25A, 77 (1969).
58. L. S. Frankel, H. Koppler, and J. Cargioli, J. Phys. Chem., 73, 91 (1969).
59. C. Benezra and G. Ourisson, Bull. Soc. chim. France, 2270 (1966).
60. B. Fontal and H. Goldwhite, Tetrahedron, 22, 3275 (1966).
61. G. A. Olah and C. W. McFarlane, J. Org. Chem., 34, 1832 (1969).
62. P. Haake, R. D. Cook, and G. H. Hurst, J. Amer. Chem. Soc., 89, 2650 (1967).
63. P. Haake and G. Hurst, J. Amer. Chem. Soc., 88, 2544 (1966).
64. E. L. Uhlenhopp, J. A. Glasel, and A. I. Krasna, J. Org. Chem., 34, 2237 (1969).
65. S. L. Mannat, G. L. Juvinall, R. I. Wagner, and D. D. Elleman, J. Amer. Chem. Soc., 88, 2689 (1966).
66. A. A. Petrov, B. I. Ionin, and V. M. Ignatyev, Tetrahedron Letters, 15 (1968).
67. A. N. Pudovik, G. E. Yastrebova, V. I. Nikitina, and Yu. Yu. Samitov, Zhur. Obshch. Khim., 38, 294 (1968).
68. W. M. Daniewski, M. Gordon, and C. E. Griffin, J. Org. Chem., 31, 2083 (1966).
69. S. T. Ioffe, K. V. Vatsuro, P. V. Petrovskii, E. I. Fedin, and M. I. Kabachnik, Izv. Akad. Nauk SSSR, Ser. Khim., 1504 (1970).
70. S. T. Ioffe, K. V. Vatsuro, P. V. Petrovskii, and M. I. Kabachnik, Izv. Akad. Nauk SSSR, Ser. Khim., 731 (1971).
71. R. Obritcky and C. E. Griffin, J. Org. Chem., 33, 632 (1968).
72. C. E. Griffin, R. B. Davidson, and M. Gordon, Tetrahedron, 22, 561 (1966).
73. B. Fontal, H. Goldwhite, and D. G. Rowsell, J. Org. Chem., 31, 2424 (1966).
74. S. Sternhell, Rev. Pure Appl. Chem., 14, 15 (1964).
75. V. M. Ignat'ev, T. N. Timofeeva, B. I. Ionin, and A. A. Petrov, Zhur. Obshch. Khim., 39, 2439 (1969).
76. M.-P. Simmonin and C. Charrier, Compt. rend., C267, 550 (1968).
77. V. M. Ignat'ev, Candidate's Thesis, Leningrad Institute of Technology, 1968.
78. F. J. Welch and H. J. Paxton, J. Polymer Sci., 3, 3439 (1965).
79. M. Barfield and D. M. Grant, Adv. Magnetic Resonance, 1, 149 (1965).
80. H. Shimizu, J. Chem. Phys., 40, 3357 (1964).
81. S. L. Smith and R. H. Cox, J. Chem. Phys., 45, 2848 (1966).

82. S. L. Smith and A. M. Ihrig, J. Chem. Phys., **46**, 1181 (1967).
83. R. K. Harris and E. G. Finger, Bull. Soc. chim. France, 2805 (1968).
84. W. McFarlane, Proc. Roy. Soc., **306**, 185 (1968).
85. B. I. Ionin, V. B. Lebedev, and A. A. Petrov, Zhur. Obshch. Khim., **37**, 1174 (1967).
86. S. L. Mannatt, L. Juvinall, and D. D. Elleman, J. Amer. Chem. Soc., **85**, 2664 (1963).
87. S. Koide and E. Duval, J. Chem. Phys., **41**, 315 (1964).
88. N. F. Ramsey, Phys. Rev., **91**, 303 (1953).
89. H. M. McConnell, J. Chem. Phys., **24**, 460 (1956).
90. G. Mavel and R. Mankowski-Favelier, J. Phys. chim., 64, 1808 (1967).
91. J. A. Pople and D. P. Santry, Mol. Phys., 8, 1 (1964).
92. W. McFarlane, J. Chem. Soc. (A), 1148 (1967).
93. G. M. Whitesides, J. L. Beauchamp, and J. D. Roberts, J. Amer. Chem. Soc., **85**, 2665 (1963).
94. W. McFarlane and R. F. M. White, Chem. Comm., 744 (1969).
95. E. A. V. Ebsworth and G. M. Sheldrick, Eighth Congress on Molecular Spectroscopy, Copenhagen, (August 1965), see Ref. 96.
96. R. I. Wagner, L.-V. D. Freeman, H. Goldwhite, and D. G. Rowsell, J. Amer. Chem. Soc., 89, 1102 (1967).
97. R. Holmes and R. Storey, Inorg. Chem., 5, 2146 (1965).
98. H. A. Bent, J. Inorg. Nuclear Chem., 19, 43 (1961).
99. Yu. L. Kleiman, N. V. Morkovin, and B. I. Ionin, Zhur. Obshch. Khim., **37**, 2791 (1967).
100. M. Sancher, R. Wolf, R. Burgada, and F. Mathis, Bull. Soc. chim. France, 773 (1968).
101. G. I. Drozd, S. Z. Ivin, V. N. Kulakova, and V. V. Sheluchenko, Zhur. Obshch. Khim., **38**, 576 (1968).
102. G. I. Drozd, S. Z. Ivin, V. V. Sheluchenko, V. I. Tetel'baum, G. M. Luchanskii, and A. D. Varshavskii, Zhur. Obshch. Khim., **37**, 1631 (1967).
103. G. I. Drozd, S. Z. Ivin, V. V. Sheluchenko, and B. I. Tetel'baum, Zhur. Obshch. Khim., 37, 957 (1967).
104. G. I. Drozd, S. Z. Ivin, and V. V. Sheluchenko, Zhur. Obshch. Khim., 38, 1655 (1968).
105. E. L. Muetterties, W. Mahler, K. Packer, and R. Schmutzler, Inorg. Chem., 3, 1298 (1964).
106. J. R. van Wazer, "Phosphorus and its Compounds" (Translated into Russian), Inostr. Lit., Moscow, 1962, Chapters 1–3.
107. D. M. Grant and W. M. Litchman, J. Amer. Chem. Soc., 87, 3994 (1965).
108. J. N. Shoolery, J. Chem. Phys., **31**, 1427 (1959).
109. A. N. Pudovik, R. D. Gareeva, and L. E. Kazakova, Zhur. Obshch. Khim., **39**, 1239 (1969).
110. B. I. Ionin and A. A. Petrov, Zhur. Obshch. Khim., **33**, 2863 (1963).
111. J. A. Pople and A. A. Bothner-By, J. Chem. Phys., **31**, 1427 (1959).
112. J. Feeney and L. H. Sutcliffe; see J. W. Emsley, J. Feeney, and L. H. Sutcliffe, "High-resolution Nuclear Magnetic Resonance Spectroscopy" (Translated into Russian), Mir, Moscow, 1969, Vol. 2, Chapter 12, p. 372
113. H.-J. Köhler, Z. phys. Chem. (Leipzig), **226**, 283 (1964).
114. K. J. Coskran and J. C. Verkade, Inorg. Chem., 4, 1655 (1965).
115. T. J. Katz, C. R. Nicholson, and C. A. Reilly, J. Amer. Chem. Soc., 88, 3832 (1966).
116. S. E. Cremer, and R. J. Chorvant, J. Org. Chem., **32**, 4066 (1967).
117. D. Gagnaire, J. B. Robert, and J. Verrier, Chem. Comm., 819 (1967).
118. J. P. Albrand, D. Gagnaire, J. Martin, and J. B. Robert, Bull. Soc. chim. France, 40 (1969).
119. M. Bowers, H. Goldwhite, and S. L. Manatt, personal communications, see Ref. 118.
120. H. Schmidbaur and W. Tronich, Chem. Ber., **101**, 3545 (1968).
121. G. L. Kenyon and F. H. Westheimer, J. Amer. Chem. Soc., 88, 3557 (1966).
122. C. Benezra and G. Ourisson, Bull. Soc. chim. France, 1825 (1966).
123. G. Pattenden and B. J. Walker, J. Chem. Soc. (C), 531 (1969).
124. B. A. Arbuzov, A. O. Vizel', Yu. Yu. Samitov, and Yu. F. Tarenko, Izv. Akad. Nauk SSSR, Ser. Khim., 672 (1967).
125. Zh. L. Evtikhov, N. A. Razumova, and A. A. Petrov, Zhur. Obshch. Khim., 39, 465 (1969).
126. N. A. Razumova, Zh. L. Evtikhov, A. Kh. Voznesenskaya, and A. A. Petrov, Zhur. Obshch. Khim., 39, 176 (1969).
127. R. K. Harris, A. R. Katritzky, and S. Musieraugh, J. Chem. Soc. (A), 37 (1967).
128. H. Babad and W. Herbert, Analyt. Chem., 41, 259 (1968).
129. L. H. Kleith and A. L. Alford, Analyt. Chim. Acta, 44, 447 (1969).
130. M. P. Williamson and C. E. Griffin, J. Phys. Chem., 72, 4043 (1968).
131. B. I. Ionin, V. B. Lebedev, and A. A. Petrov, Dokl. Akad. Nauk SSSR, 152, 1354 (1963).
132. C. Carrier, M.-P. Simonnin, W. Chodkiewicz, and P. Cadiot, Compt. rend., 258, 1537 (1964).
133. C. Carrier, W. Chodkiewicz, and P. Cadiot, Bull. Soc. chim. France, 1002 (1966).
134. V. B. Lebedev and B. I. Ionin, Izv. Vys. Ucheb. Zaved., Priborostroenie, 10, No. 2, 29 (1967).
135. V. M. Ignat'ev, B. I. Ionin, and A. A. Petrov, Zhur. Obshch. Khim., **36**, 1505 (1966).
136. B. I. Ionin, Candidate's Thesis, Leningrad Institute of Technology, 1964.
137. L. N. Mashlyakovskii, B. I. Ionin, I. S. Okhrimenko, and A. A. Petrov, Zhur. Obshch. Khim., 37, 1307 (1967).
138. G. S. Vasil'ev, E. N. Prilezhaeva, V. F. Bystrov, and M. F. Shostakovskii, Zhur. Obshch. Khim., 35, 1350 (1965).
139. A. G. Moritz, J. D. Saxby, and S. Sternhell, Austral. J. Chem., 21, 2565 (1968).
140. E. Duval and E. A. C. Lucken, Mol. Phys., 10, 499 (1966).
141. G. Miyazima, K. Takahashi, and T. Yamasaki, Bull. Chem. Soc. Japan, 40, 1540 (1967).
142. C. E. Griffin and S. K. Kundu, J. Org. Chem., 34, 1532 (1969).
143. K. Takahashi, T. Yamasaki, and G. Miyazima, Bull. Chem. Soc. Japan, 39, 2787 (1966).
144. T. H. Siddall and W. E. Stewart, Spectrochim. Acta, 24A, 81 (1968).
145. Zh. L. Evtikhov, N. A. Razumova, and A. A. Petrov, Dokl. Akad. Nauk SSSR, 181, 877 (1968).
146. B. A. Arbuzov, N. A. Polezhaeva, V. S. Vinogradova, and Yu. Yu. Samitov, Dokl. Akad. Nauk SSSR, 173, 93 (1967).
147. B. A. Arbuzov, O. D. Zolova, V. S. Vinogradova, and Yu. Yu. Samitov, Dokl. Akad. Nauk SSSR, 173, 335 (1967).

148. F. Ramirez, Pure Appl. Chem., 9, 337 (1964).
149. R. G. Kostyanovskii, V. V. Yakshin, S. L. Zimont, and I. I. Chervin, Izv. Akad. Nauk SSSR, Ser. Khim., 190 (1968).
150. L. I. Petrovskaya, M. V. Proskurina, Z. S. Novikova, and I. F. Lutsenko, Izv. Akad. Nauk SSSR, Ser. Khim., 1277 (1968).
151. V. N. Setkina, T. Ya. Medved', and M. I. Kabachnik, Izv. Akad. Nauk SSSR, Ser. Khim., 1339 (1967).
152. M. I. Kabachnik, T. Ya. Medved', P. V. Petrovskii, E. I. Fedin, and K. S. Yudina, Izv. Akad. Nauk SSSR, Ser. Khim., 419 (1968).
153. A. N. Pudovik, T. E. Yastrebova, V. I. Nikitina, and Yu. Yu. Samitov, Zhur. Obshch. Khim., 38, 294 (1968).
154. M. Tsuboi, F. Kuriyagana, K. Matsuo, and Y. Kyogoko, Bull. Chem. Soc. Japan, 40, 1813 (1967).
155. D. G. Rowsell, J. Mol. Spectroscopy, 23, 32 (1967).
156. J. P. Albrand, D. Gagnaire, and J. B. Robert, J. Mol. Spectroscopy, 27, 428 (1968).
157. L. C. Frankel, H. Klapper, and J. Cargioli, J. Phys. Chem., 73, 91 (1969).
158. D. Hellwinkel, Chimia, 22, 488 (1968).
159. D. Houlla, R. Wolf, D. Gagnaire, and J. B. Robert, Chem. Comm., 443 (1969).
160. A. W. Garrison, L. H. Keith, and A. L. Alford, Spectrochim. Acta, A25, 77 (1969).
161. J. P. Fackler, J. A. Fetchin, J. Mayhew, W. C. Siedel, T. J. Swift, and M. Weeks, J. Amer. Chem. Soc., 91, 1941 (1969).
162. R. H. Fischer and W. D. Horrocks, Inorg. Chem., 7, 2659 (1968).
163. R. G. Goodfellow, Chem. Comm., 114 (1968).
164. R. Mathieu and R. Poilblanc, Compt. rend., C265, 388 (1967).
165. J. F. Nixon, J. Chem. Soc. (A), 1136 (1967).
166. J. F. Nixon and A. Pidcock, Ann. Rev. n.m.p. Spectroscopy, 2 (1969).
167. S. O. Grim and W. McFarlane, Canad. J. Chem., 46, 2071 (1968).

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