Nuclear Magnetic Resonance of Phosphorus Compounds. II. The Relative Signs of the Spin–Spin Couplings in Dimethylphosphine and Methylphosphine[1,2]

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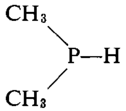
Abstract: From nmr ^{1}H–[^{1}H] decoupling experiments at 60 Mc, the P–H and P–C–H couplings in dimethylphosphine (I) and methylphosphine (II) were determined to have the same sign. Double resonance ^{1}H–[^{31}P] experiments on I at 40 and 16.2 Mc, respectively, showed that the P–C–H and H–C–P–H couplings have the same sign. Analyses of the ^{31}P nmr spectra of I and II at 24.3 Mc showed that the P–C–H, P–C–C–H, and P–H couplings in these molecules have the same relative sign. These results are discussed in light of other reported relative sign determinations of coupling constants involving ^{31}P and ^{1}H and a correlation of the absolute signs of phosphorus-31–proton couplings is presented. The relation of the magnitudes and the signs of the P–C–H couplings to the s character of the carbon and phosphorus bonding orbitals is discussed.

Although there are a number of examples of relative sign determinations for the various types of ^{1}H–^{1}H, ^{1}H–^{19}F, and ^{19}F–^{19}F nuclear magnetic resonance (nmr) coupling constants from double resonance studies,[4] spectral analyses,[5] double quantum transition spectra,[6,7] and nuclear Overhauser effects,[8,9] there is a scarcity of results for the signs of coupling constants of the types involving ^{31}P–^{1}H, ^{11}B–^{1}H, ^{31}P–^{19}F, ^{1}H–^{15}N, ^{13}C–^{19}F, and ^{13}C–^{1}H.[10]

As part of a general study of the magnitudes and relative signs of nmr coupling constants, we report here some work on dimethylphosphine (I) and methylphosphine (II) involving analyses of the ^{1}H and ^{31}P spectra and double resonance experiments which establish the relative signs of the coupling constants in these molecules. The probable absolute signs for the spin–spin coupling constants in molecules containing phosphorus are discussed.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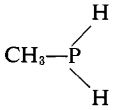
II

Experimental Section

The samples of the three methylphosphines used in this work were prepared as has been previously described[11] and were studied as the neat liquids in sealed 5-mm glass tubes containing a few per cent tetramethylsilane. Spectra were taken with a Varian A-60 spectrometer and HR spectrometers at frequencies of 24.3, 40, and 60 Mc. The field sweep ^{1}H–[^{1}H] double resonance experiments were carried out with the apparatus previously described.[4f] Frequency-sweep spectra at 60 Mc were obtained with the field-frequency lock spectrometer described elsewhere.[12]

The ^{1}H–[^{31}P] double resonance experiments were carried out at 40 and 16.2 Mc, respectively. The 16.2-Mc irradiation was obtained from a Varian V-4210A radiofrequency unit. This unit provides frequencies from 2 to 16 Mc. By reducing the value of capacitor C-102 of the V-4210A it is possible to extend the transmitter frequencies into the range 16.0–17.0 Mc. Although the short-term stability of the V-4210A was not exceptionally good by high-resolution standards (±50 cps/min), it was possible to achieve excellent stability by attachment of a simple crystal oscillator at the crystal synchronization jack.[13]

Initially the frequency of the V-4210A unit was varied without crystal control, while the 40-Mc spectrum of the methyl groups of I was recorded. The frequency range over which partial collapse occurred was found to be about 16.191000 ± 0.000500 Mc as measured by a Hewlett-Packard Model 524-C frequency counter. Two different crystals (one at 16.191033 and the other at 16.191482 Mc) were used in order to resolve any ambiguities which could have arisen as is discussed below. With the crystals employed, exceptionally stable operation was obtained (a few tenths of a cycle variation over a period of an hour after a sufficient warm-up period). Unfortunately, our initial attempts to pull the crystal frequency were unsuccessful so we resorted to the use of side bands produced

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[1] For a preliminary communication, which is paper I of this series, see S. L. Manatt, G. L. Juvinall, and D. D. Elleman, *J. Am. Chem. Soc.*, **85**, 2664 (1963).

[2] This paper represents results of one phase of research carried out at the Jet Propulsion Laboratory, California Institute of Technology, under Contract No. NAS7–100, sponsored by the National Aeronautics and Space Administration.

[3] (a) California Institute of Technology; (b) Rocketdyne, Canoga Park, Calif.

[4] See, for example, (a) R. Freeman and D. H. Whiffen, *Mol. Phys.*, 4, 321 (1961); (b) R. Freeman and D. H. Whiffen, *Proc. Phys. Soc.* (London), 79, 794 (1962); (c) S. L. Manatt and D. D. Elleman, *J. Am. Chem. Soc.*, **84**, 1305 (1962); (d) D. F. Evans, *Mol. Phys.*, **5**, 183 (1962); (e) S. L. Manatt and D. D. Elleman, *J. Am. Chem. Soc.*, **84**, 1579 (1962); (f) D. D. Elleman and S. L. Manatt, *J. Chem. Phys.*, **36**, 1945 (1962); (g) W. A. Anderson and R. Freeman, *ibid.*, **37**, 85 (1962); (h) K. A. McLaughlan, J. I. Musher, K. G. R. Packler, and R. Freeman, *Mol. Phys.*, **5**, 321 (1962); (i) D. D. Elleman and S. L. Manatt, *J. Mol. Spectry.*, **9**, 477 (1962); (j) R. Freeman and W. A. Anderson, *J. Chem. Phys.*, **37**, 2053 (1962); (k) R. Freeman and N. S. Bhacca, *ibid.*, **38**, 1088 (1963); (l) D. F. Evans, S. L. Manatt, and D. D. Elleman, *J. Am. Chem. Soc.*, **85**, 238 (1963).

[5] See, for example, (a) J. D. Swalen and C. A. Reilly, *J. Chem. Phys.*, **37**, 21 (1962), and early papers by these authors; (b) A. A. Bothner-By and C. Naar-Colin, *J. Am. Chem. Soc.*, **84**, 743 (1962); (c) P. T. Narasimhan and M. T. Rogers, *J. Chem. Phys.*, 34, 1049 (1961); (d) R. M. Lynden-Bell, *Trans. Faraday Soc.*, **57**, 888 (1961).

[6] K. A. McLaughlan and D. H. Whiffen, *Proc. Chem. Soc.*, 144 (1962).

[7] W. A. Anderson, R. Freeman, and C. A. Reilly, *J. Chem. Phys.*, **39**, 1518 (1962).

[8] K. Kuhlmann and J. D. Baldeschwieler, *J. Am. Chem. Soc.*, **85**, 1010 (1963).

[9] R. Kaiser, *J. Chem. Phys.*, **39**, 2435 (1963).

[10] See, however, (a) P. C. Lauterbur and R. J. Kurland, *J. Am. Chem. Soc.*, **84**, 3405 (1962); (b) G. V. D. Tiers, *ibid.*, **84**, 3972 (1962); (c) F. A. L. Anet, *ibid.*, **84**, 1053 (1962); (d) R. Freeman and W. A. Anderson, *J. Chem. Phys.*, **39**, 806 (1963); (e) G. M. Whitesides, J. L. Beauchamp, and J. D. Roberts, *J. Am. Chem. Soc.*, **85**, 2665 (1963); (f) R. K. Harris and R. G. Hayter, *Can. J. Chem.*, **42**, 2282 (1964); (g) G. Mavel and G. Martin, *J. Phys. Radium*, **24**, 108 (1963).

[11] R. I. Wagner and A. B. Burg, *J. Am. Chem. Soc.*, **75**, 3869 (1953).

[12] D. D. Elleman, S. L. Manatt, and C. D. Pearce, *J. Chem. Phys.*, **42**, 650 (1965).

[13] Very satisfactory crystals and oscillators for this purpose are available from International Crystal Manufacturing Co., Inc., Oklahoma City, Okla.

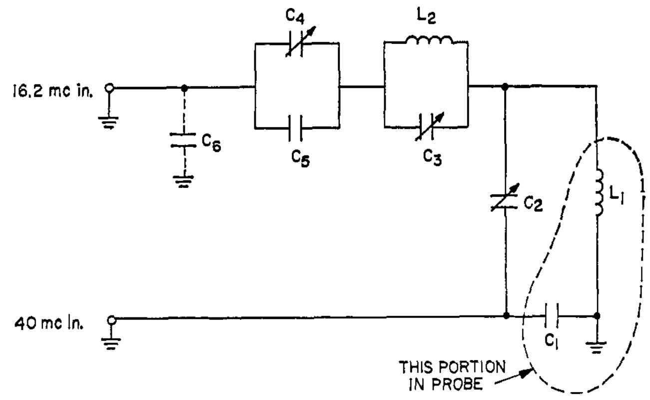

Figure 1. A coupling circuit for double tuning the transmitter coil of a Varian HR 40 nmr probe. C_6 may be necessary at some frequencies but was not at 16.2 Mc. To start with C_1 and C_2 are in the probe. C_2 was taken out and a double "coax" put on the probe. C_2 and the additional components were placed in a box attached to the probe by the double "coax." L_1, transmitter coil; C_1 and C_2, unchanged in value; L_2, 8 turns of No. 24 copper wire on a 6-mm o.d. form; C_3 and C_4, 5–50 mmμ trimer capacitors; C_5, 10 mμ.

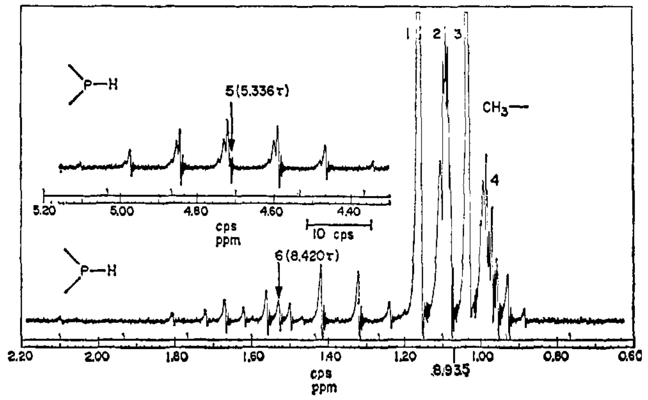

Figure 2. Proton 60-Mc spectrum of dimethylphosphine (neat liquid) recorded with an A-60 spectrometer (sweep width 100 cps and sweep time 500 sec).

by magnetic field modulation to irradiate the ^{31}P transitions. The modulation index was set by observing the proton spectrum while the 16.2-Mc radiofrequency was attenuated completely and the audio modulation was set such that the first side bands were about the same magnitude as the center band. The magnitude of the 16.2-Mc H_2 field was not calibrated. The proton portion of the spectrum was observed by looking at the center band of the 40-Mc signal. The 40-Mc probe was modified so that the transmitter coil was resonant at both 40 and 16.2 Mc. The necessary extra components to be added to a Varian probe are shown in Figure 1. This circuit was tuned for maximum 16.2-Mc output.

Spectra were calculated on an IBM 7090 using previously described computer programs.[5a,b]

Results and Interpretation

The spectrum of I, shown in Figure 2, is an A_6BX type and of such a nature that it is very easy to obtain the relative signs of the H–P and H–C–P coupling constants by ^1H-[^1H] spin decoupling. The methyl group protons show roughly a quartet structure centered at τ 8.93. Two members of the quartet (lines 1 and 3) are very sharp while the other members show complex second-order structure. The septuplet structure at τ 5.33 and the complex multiplet structure from τ 8.10 to 9.20 belong to the proton bonded to and strongly coupled to phosphorus. Measurement of the spacing in the τ 5.33 septuplet immediately gives a good approximation to the H–C–P–H coupling. From the τ 8.93 quartet structure it is obvious that the H–C–P coupling is less than the H–C–P–H coupling, and thus lines 1 and 3 should have one ^{31}P spin state and lines 2 and 4 should have the other. On irradiation of the τ 5.33 multiplet with 3–4 mgauss of power in field sweep experiments, lines 1 and 3 should be perturbed or collapse leaving lines 2 and 4 unchanged if the signs of the H–P and H–C–P couplings are the same. This is so as shown in Figure 3.

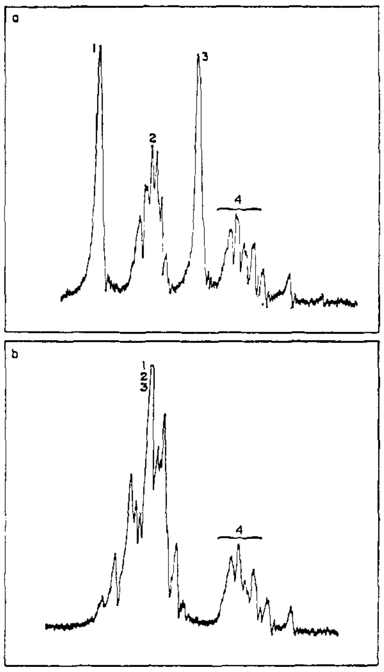

Figure 3. Proton 60-Mc spectrum of methyl group protons of dimethylphosphine recorded with a HR spectrometer: (a) normal field sweep spectrum, (b) downfield septuplet at τ 5.33 irradiated in field-sweep experiment.

It is possible to extract relative sign information directly from the spectrum without performing double resonance experiments. The spectrum of I can be analyzed as two A_6B systems, one strongly coupled and one weakly coupled, using the concept of "effective internal chemical shift."[5c] Each A_6B spin system corresponds to a particular spin state of the X nucleus or, in this case, the ^{31}P nucleus. Spectra of the A_6B type have recently been discussed in detail by Ranft.[14] For the weakly coupled A_6B system the transitions which have a particular ^{31}P spin state are the low-field (or high-frequency) members of each multiplet caused by ^{31}P coupling; this implies that the H–C–P and H–P couplings are the same sign.

The 60-Mc proton spectrum of methylphosphine (II) (shown in Figure 4a) is an A_3B_2X type which can also be analyzed as two A_3B_2 spectra, each corresponding to one of the ^{31}P nuclear spin states. The quartet structure, centered at τ 5.79, is the low-field member of the ^{31}P doublet for the protons bonded to phosphorus. The high-field member of this doublet lies on top of the transitions of the methyl protons (region τ 8.88–9.18). Of the two A_3B_2 spectra which should be discernible in Figure 4a, only the B_2 part of the loosely coupled one at τ 5.79 is immediately identifiable. The region τ

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(14) J. Ranft, *Ann. Physik*, **10**, 1 (1962).

8.88–9.18 is a composite of an A_3 group of a loosely coupled A_3B_2 spectrum and a strongly coupled A_3B_2 spectrum. By comparison of the spacing between the low-field quartet in Figure 4A with the spacing between line 1 (which is really a triplet) and the midpoint between lines 2 and 3 and between this same midpoint and line 5 (appearing as a triplet), all members of the loosely coupled A_3B_2 component spectrum can be identified. This was confirmed by frequency sweep double resonance experiments, one of which is shown in Figure 4b.

The complex nature of the strongly coupled A_3B_2 spectrum in II does not immediately allow any decision to be made as to the relative signs of the H–P and H–C–P coupling constants because the chemical shift position of the loosely coupled A_3 multiplet relative to that of the strongly coupled A_3 group must be determined. This certainly is not obvious from the observed spectrum. Comparison of results in a compilation of calculated A_3B_2 spectra[15] shows that in the strongly coupled A_3B_2 spectrum, the B_2 protons are downfield from the A_3 protons. It is evident from these computed spectra[15] that line 4 is precisely the chemical shift of the A_3 group of the strongly coupled A_3B_2 system and line 2 is precisely the chemical shift of the A_3 group of the weakly coupled A_3B_2. Based on spin-state arguments these assignments demonstrate that the P–H and H–C–P couplings in II are the same relative sign.[16]

A fit to the observed proton spectrum of methylphosphine (II) was made in the following manner. The separation between the troughs of the outer two members of the downfield quartet in II was determined very accurately using a field-frequency-lock spectrometer. This was done by turning up the recorder amplitude of the observing phase detector and finely adjusting its audiofrequency by hand to locate the troughs. The spacing between the two troughs was found to be 23.95 ± 0.02 cps in this manner. Dividing this separation by three gives a first-order coupling of 7.98 ± 0.01 cps. Applying a correction determined from a computed A_3B_2 spectrum yields a value of 7.99 ± 0.01 cps for the actual coupling. The 3.99 ± 0.02 cps separation of lines 2 and 4 measured as discussed above is the H–C–P coupling exactly.[15,17] It follows[15] that the chemical shift position of the B_2 proton in an A_3B_2 spectrum is exactly halfway between a particular pair of lines in the B_2 multiplet.[15] For the downfield quartet in II this point is halfway between lines 8 and 9. This position for the strongly coupled A_3B_2 system is halfway between lines 6 and 7. The spacing between these two midpoints of the two B_2 regions gives the magnitude of the H–P coupling as 187.82 ± 0.03 cps. The chemical shift location of the PH_2 protons is halfway between these points. The distance between this latter point and the midpoint between lines 2 and 4 (100.10 ± 0.05 cps) is the chemical shift between the A and B protons in II. Computation of an A_3B_2X spectrum with all the parameters measured directly from the spectrum and the relative sign of the H–C–P–H coupling either the same or different from the H–P and H–C–P couplings gave a very exact fit to the observed 60-Mc proton spectrum.

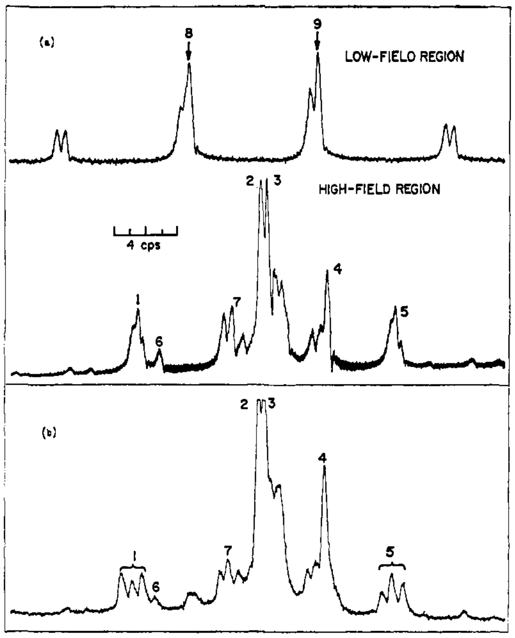

Figure 4. Proton 60-Mc frequency sweep spectrum of methylphosphine (neat liquid) recorded with nuclear-stabilized HR spectrometer: (a) normal spectrum, (b) spectrum of upfield portion with large field modulation at τ 5.79.

An exact fit of the proton spectrum of I was similarly made based on Ranft's results[14] on the A_6B system for both possible signs of the H–C–P–H coupling relative to the sign of the other couplings. Here the spacing between line 5, whose position is obscured by ring at the sweep rate shown in Figure 2, and line 6 gives the P–H coupling as 191.03 ± 0.03. The midpoint between lines 1 and 3 determines quite accurately the chemical shift position of the A_6 protons of the loosely coupled A_6B system. In the strongly coupled A_6B system the A_6 portion is made up of a number of pairs of lines which are symmetrically disposed about the chemical shift position of this A_6 grouping.[15] From highly resolved spectra of the quality shown in Figure 4a it was possible to identify a number of the symmetrical pairs, and in this way the chemical shift position of this A_6 subspectrum was measured to ±0.03 cps. The difference between the chemical shift positions for the two A_6 groups is exactly the H–C–P coupling and was measured as 3.37 ± 0.05 cps. Calculation of A_6BX spectra with these parameters and the relative sign of the H–C–P–H coupling either the same or different from the sign of the H–P and H–C–P couplings gave apparent exact fits to the observed 60-Mc proton spectrum.

Analyses of the proton spectra of I and II do not give information on the sign of the H–C–P–H coupling relative to the H–P and H–C–P couplings. We now describe some $^1H-[^{31}P]$ experiments at 40 and 16.2 Mc, respectively, which establish this relationship in I. Figure 5a shows the 40-Mc proton spectrum of the A_6 methyl groups and upfield member of the B doublet in I. The reduced chemical shift at 40 Mc has made the

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[15] P. L. Corio, *Chem. Rev.*, **60**, 363 (1960).

[16] It should be pointed out that only relative signs can be determined by the double resonance results, and the analyses presented here and any scheme of labeling the nuclear spin states will give the same relative sign results if all the spin states are reversed.

[17] The most important source of error in determining line separations by this technique is probably the instability of the audiooscillators involved in this type of spectrometer system. For these measurements the 10-period average of the locking oscillator was recorded along with that of the observing oscillator using two Hewlett-Packard Model 524-C frequency counters.

Table I. Summary of Coupling Constants and Chemical Shifts for Phosphine, Methylphosphine, Dimethylphosphine, and Trimethylphosphine (Neat Liquids)

Compound	δ_H[a] δ_{H_P}	δ_{H_C}	δ_P[b]	J_{P-H}[c]	J_{P-C-H}[c]	$J_{H-P-C-H}$[c]	$J_{^{13}C-H}$[c,d]
PH_3	?	...	177	(+)182.2[e]	...	...	...
CH_3PH_2	158.54 ± 0.03	58.44 ± 0.05	100.79	+187.83 ± 0.03	+3.99 ± 0.02	+7.98 ± 0.01	+128.0 ± 0.5 (+0.1 ± 0.5)
$(CH_3)_2PH$	187.32 ± 0.03	63.92 ± 0.05	37.06	+191.03 ± 0.03	+3.37 ± 0.05	+7.61 ± 0.01	+128.2 ± 0.1 (+0.26 ± 0.05)
$(CH_3)_3P$	...	56.3[f]	0.00	...	(+)2.66 ± 0.01	...	+125.3 ± 0.1 (+0.7 ± 0.1)

[a] In cps downfield from TMS as an internal standard at 60 Mc. [b] In ppm relative to chemical shift of $(CH_3)_3P$ as zero; not corrected for bulk susceptibility; value for PH_3 estimated from data in ref 43. [c] In cps. [d] Isotopic chemical shifts in cps in parentheses. [e] From ref 14. [f] From ref 10e.

spectrum of one of the A_6B spin systems much more strongly coupled, but lines 1 and 3 which belong to the weakly coupled A_6B spin system are still sharp. If the low-field (or high-frequency) member of the ^{31}P doublet is irradiated, lines 1 and 2, the low-field members of each doublet caused by proton-proton coupling should be affected for like sign of the H-C-P-H and P-H couplings. On irradiation of the high-field member of the ^{31}P doublet, lines 3 and 4 should be affected. We have done both these experiments and the results, shown in Figures 5b and 5c, indicate the signs are indeed the same.

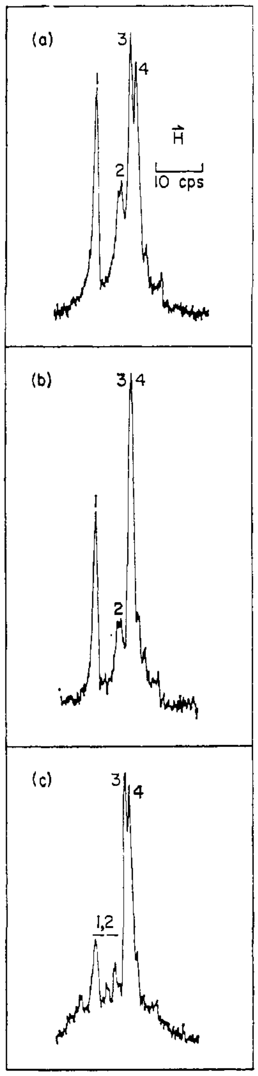

Figure 5. A_6 and upfield half of the B protons of dimethylphosphine at 40 Mc: (a) normal spectrum; (b) proton center band with 16.191033-Mc irradiation and with a field modulation of 309 cps; (c) same as b except with a field modulation of 115.5 cps.

Because we did not have a continuously variable stable 16.2-Mc radiofrequency unit available but instead a stable radiofrequency output at one frequency, we achieved strong irradiation of a particular set of ^{31}P transitions by modulating the magnetic field. One must determine which modulation side band is effective in the irradiation. In the present work two different 16.2-Mc crystals about 450 cps apart in frequency were employed. In all cases the 40-Mc center band proton spectrum was observed. With a 16.191033-Mc center band it was determined that optimum collapse of lines 1 and 2 occurred at a field modulation frequency of 309.0 ± 0.5 cps. Likewise, the optimum collapse of lines 3 and 4 occurred at a field modulation frequency of 115.5 ± 0.5 cps. With a 16.191482-Mc center band optimum collapse for lines 1 and 2 occurred at a field modulation frequency of 140 ± 1 cps and for lines 3 and 4 at 336 ± 1 cps. These results show that the downfield or high-frequency side band was effective with the lower frequency crystal, and the upfield or low-frequency side band was effective with the high-frequency crystal.

In I and II the A and B nuclei are strongly coupled to each other although weakly coupled to ^{31}P. The relative signs of the H-P and H-C-P couplings can be related to the relative sign of the H-C-P-H coupling from analyses of the ^{31}P spectra of I and II.[7] The ^{31}P spectra for the two possible choices of the relative sign of the H-C-P-H coupling were calculated and plotted for I and II. The chemical shift of ^{31}P relative to the proton spectrum was taken as about 10^6 cps in the computed spectra. As shown in Figures 6b and c, the asymmetry of the ^{31}P spectrum of II is completely reversed when the sign of the H-P-C-H coupling is changed, while the sign of the other two couplings is unchanged. The ^{31}P spectrum of II shown in Figure 6a fits exactly for the situation with all couplings the same sign. Similar analysis of the ^{31}P spectrum of I showed as in II that all the couplings are the same sign.

In Table I the final parameters for the spectra of I, II, and trimethylphosphine (III) are summarized. The ^{31}P chemical shifts of I and II relative to III were determined by a substitution side-band technique. Also included are the ^{13}C-H coupling in I, II, and III. In I the ^{13}C-satellite lines were no wider than 0.3 cps, suggesting that any long-range proton couplings of the

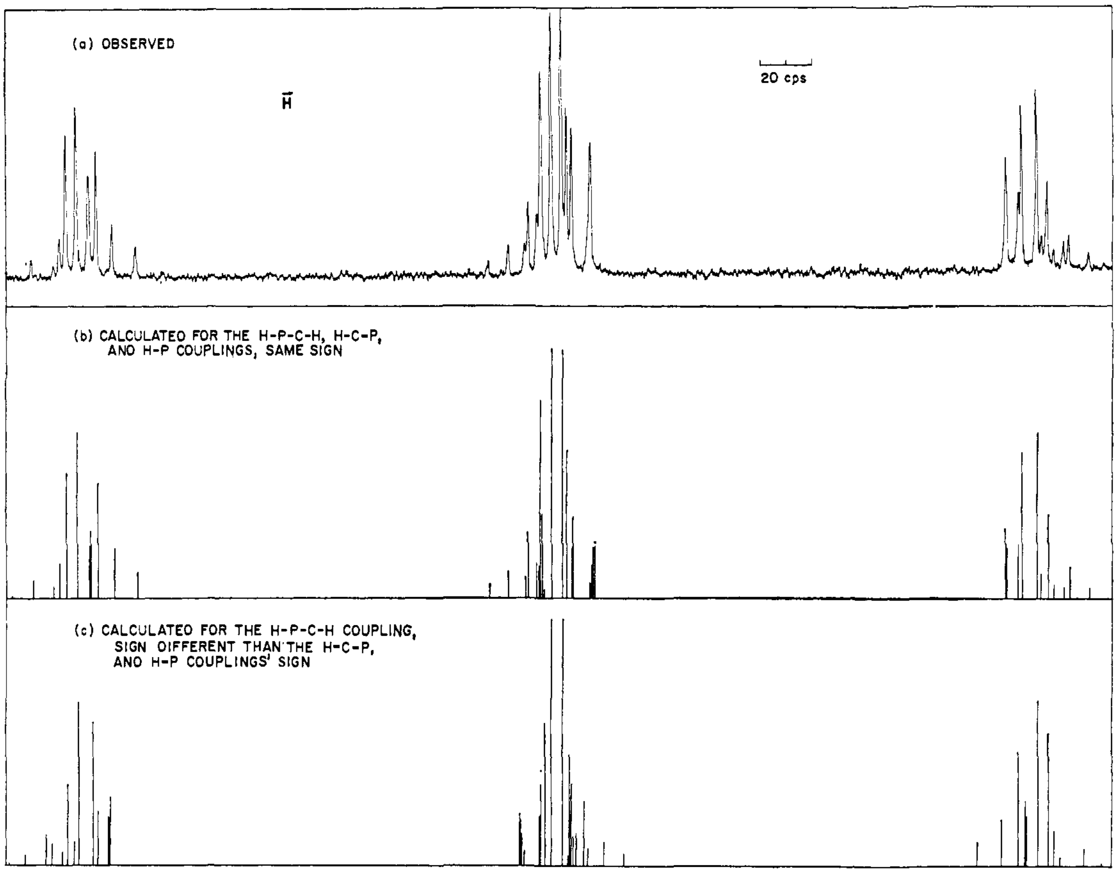

Figure 6. Phosphorus-31 spectrum of methylphosphine at 24.3 Mc.

type H–C–P–C–H are probably no greater than 0.1 cps. In III the ^{13}C-satellite lines were about 0.6–0.7 cps wide, suggesting H–C–P–C–H coupling of the order of 0.1–0.2 cps. In both cases the line widths of other single lines in the spectrum were the order of 0.2 cps.

Discussion

Because in the analyses of complex second-order spectra a knowledge of relative signs of spin coupling constants is useful and because the relative signs of nuclear spin–spin couplings are of considerable theoretical interest, we felt that it is useful to have at hand a listing of relative signs and magnitudes of the various types of couplings between phosphorus and protons. The qualitative analysis presented here attempts to do this and to suggest the factors responsible for the observed magnitudes and signs of these couplings. Table II lists a few of the results of high-resolution nmr spectral analyses for a number of ^{31}P-containing molecules from which relative sign data have been extracted and some molecules from which only the magnitudes of spin–spin couplings were obtained.

From determination of the sign of a nuclear spin–spin coupling between an atom X and a proton not bonded to X relative to the sign of the coupling between a proton and an atom X to which it is bonded Karplus[18] has suggested that "an absolute" sign determination can be made where X is carbon. His suggestion is based on the approximation, which is supported by approximate theoretical[19] calculations, that spin–spin coupling constants for the ^{13}C–^{1}H group depend principally on the Fermi contact term. Karplus' proposal has been the basis for several "absolute" sign determinations relating the ^{31}C–^{1}H coupling to certain other proton–proton couplings.[10a,b,d] We would like to suggest that his proposal can be extended to the ^{31}P–^{1}H coupling. As the discussion below indicates this assumption does not lead to any inconsistencies. The recent results of Danyluk[20] which indicate that the ^{29}Si–^{1}H reduced coupling constant[21] is positive would seem to support this situation for second-row elements. Tiers,[10b] however, has recently demonstrated that the directly bonded ^{13}C–^{19}F coupling is a different sign from the ^{13}C–^{1}H coupling. Also Danyluk[21] has shown that the reduced ^{29}Si–^{19}F coupling is negative. These results demonstrate that Karplus' proposal[18] is not valid for coupling between two directly bonded atoms, neither of which is hydrogen. Pople and Santry's[22] recent theoretical work predicts that any couplings between two directly bonded first-row elements, one of which is ^{19}F, will probably be negative.

In Table II it can be seen that the magnitude of the P–C–H coupling is relatively small in the case of the alkylphosphines. This geminal coupling is the result

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(18) M. Karplus, *J. Am. Chem. Soc.*, **84**, 2458 (1962).

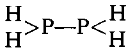
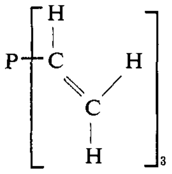
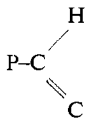
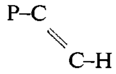
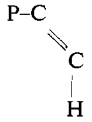
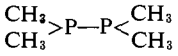
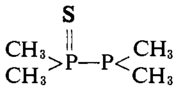
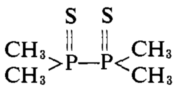
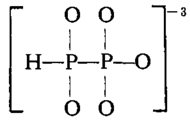
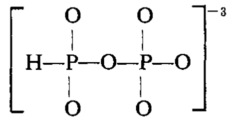
(19) (a) M. Karplus and D. M. Grant, *Proc. Natl. Acad. Sci.*, **45**, 1269 (1959); (b) N. Muller and D. E. Pritchard, *J. Chem. Phys.*, **31**, 768, 1471 (1959); (c) M. Karplus, *J. Phys. Chem.*, **64**, 1793 (1960).

(20) S. S. Danyluk, *J. Am. Chem. Soc.*, **86**, 4505 (1964).

(21) The reduced coupling constant K_{ij}, is defined as $K_{ij} = (2\pi/\hbar\gamma_i\gamma_j)J_{ij}$ where γ_i and γ_j are the nuclear magnetogyric ratios, and J_{ij} is the observed coupling. K_{ij} will be independent of nuclear magnetic properties and will reflect only the nature of the electronic mechanisms responsible for the propagation of the spin–spin coupling. See discussion in ref 22.

(22) J. A. Pople and D. P. Santry, *Mol. Phys.*, **8**, 1 (1964).

Table II. Summary of Magnitudes and Relative Signs of Spin–Spin Couplings in Selected Phosphorus Compounds

Compound	Reference	Type of coupling	Relative sign and magnitude
PH_3	5d	P-H	182.2
		H-P-H	12
 $H_2P{-}PH_2$	5d	P-P	∓108.2
		A H-P-P-H	±10.5
		H-P-P-H	±6.8
		H-P-H	∓12
(Relative signs between group A and B indeterminate)		B P-H	±186.5
		H-P-P	±11.9
CH_3PH_2	This work, 10e	P-H	±187.83
		P-C-H	±3.99
		H-P-C-H	±7.98
$(CH_3)_3P$	This work, 10e	P-C-H	2.66
$(CH_3CH_2)_3P$	37 (30)	P-C-H	−0.06 (∓0.5)
		P-C-C-H	+13.65 (±13.7)
		H-C-C-H	+7.67 (7.6)
	7		+11.74
			+30.21
			+13.62
$(CH_3)_4\overset{\oplus}{P}\,\overset{\ominus}{I}$	30b	P-C-H	14.4
$(CH_3CH_2)_4\overset{\oplus}{P}\,\overset{\ominus}{I}$	30b	P-C-H	12.76
		P-C-C-H	17.98
		H-C-C-H	7.64
$CH_3OCH_2\overset{\oplus}{P}Ph_3\overset{\ominus}{Cl}$	30b	P-C-H	4
$CH_3\overset{\oplus}{P}Ph_3\overset{\ominus}{I}$	30b	P-C-H	13.2
$(CH_3)_3P{=}O$	30b	P-C-H	13.4
$(CH_3)_3P{=}S$	30b	P-C-H	13.0
$(CH_3CH_2)_3P{=}O$	30b	P-C-H	11.9
		P-C-C-H	16.3
		H-C-C-H	7.75
$(CH_3)_2CHP({=}S)Cl_2$	10g	P-C-H	∓9.8
		P-C-C-H	±32.1
		H-C-C-H	6.5
$(CH_3)_3\overset{\oplus}{P}H$	40	P-H	515 ± 10
		P-C-H	16.6
		H-C-P-H	5.48
 $(CH_3)_2P{-}P(CH_3)_2$	44	P-C-H	+6.9
		H-C-P-P	+7.3
		P-P	∓220
 $(CH_3)_2P({=}S){-}P(CH_3)_2$	44	H-C-P	±4.09
		H-C-P	∓12.02
		H-C-P-P	±5.84
		H-C-P-P	±17.61
 $(CH_3)_2P({=}S){-}P({=}S)(CH_3)_2$	44	H-C-P	∓12.74
		H-C-P-P	±7.26
 $[HP(O)_2{-}P(O)_3]^{-3}$	43	H-P	444 ± 10
		P-P	480 ± 10
		P-P-H	94 ± 10
 $[HP(O)_2{-}O{-}P(O)_3]^{-3}$	43	H-P	620 ± 50
		P-O-P	17
		H-P-O-P	0

of near cancellation of two or more large contributions of different signs which probably include two or more terms due to the Fermi contact mechanism.[23] There are no suitable theoretical calculations at present to indicate the signs or magnitudes to be expected for any contributions from spin-orbital or electron-dipole interaction to this geminal coupling.[24,25]

In the methylphosphine series, increased alkyl substitution appears to reduce the magnitude of the H-C-P coupling. Consideration of the changes in the angles between phosphorus bonding orbitals as indicated from the known molecular structure data for phosphine[26] and its methyl derivatives[27-29] indicates that the phosphorus bonding orbitals increase in s character with increased alkyl substitution which results in a decrease in the magnitude of the H-C-P coupling. The ^{13}C-H coupling observed for the three methylphosphines show that the carbon hybridization changes very little (see Table I). One would expect an increase in steric interactions in triethylphosphine over those in trimethylphosphine (III). Consequently, a larger C-P-C bond angle relative to that in III would result in increased s character in the phosphorus orbitals in the former. Reasoning from this hybridization change we would expect the H-C-P coupling in triethylphosphine to be smaller than that in trimethylphosphine as has been observed (|0.5| cps for the former[5c,30] and |2.66| cps for the latter). The ^{31}P hybridization changes between trimethylphosphine and triethylphosphine are small as compared with the change on going from trimethylphosphine to the tetramethylphosphine cation. In the latter the phosphorus is expected to be close to sp^3 hybridized. The H-C-P coupling in the cation is |14.4| cps. The large value of the coupling in the cation suggests an inversion of the relative sign for the H-C-P coupling relative to that in the methylphosphines. Similar inversions have been observed for other geminal couplings such as the H-C-H[31] and ^{13}C-C-H.[32] Thus, we are left with the question of whether the H-C-P coupling is positive in the methylphosphines or positive in the tetramethylphosphonium cation.

The proton-proton coupling in the H-C-C-H fragment is believed to depend, in molecular orbital language, on the proton-proton bond order, and this should be similar in the H-P-P-H and H-C-P-H fragments.[33-36] The observed magnitudes for these couplings in molecules uncluttered with substituents and where free rotation exists fall into the narrow range of 6-10 cps. All three of these couplings we have taken to be the same sign. On the basis that the H-C-C-H coupling is positive relative to the ^{13}C-H coupling,[10a,d] the H-P-P-H and H-C-P-H couplings are also positive. From the relative sign determinations described above it follows that the H-C-P and H-P couplings in the methylphosphines are positive. It would appear then that the H-C-P coupling is negative and fairly large for tetravalent phosphorus. The assumption that the H-P-P-H coupling is positive along with the results from the methylphosphines and other work[20,22] that the H-P is positive leads to the conclusion that the H-P-P coupling must be positive and the P-P and H-P-H couplings negative in biphosphine.[5d]

The sign of H-C-C-P coupling in triethylphosphine, triethylphosphine oxide, and tetraethylphosphonium cation has heretofore not been related experimentally to the sign of the H-C-C-H coupling. To establish this we can use the results of the complete analysis of the trivinylphosphine nuclear spin system in which all the spin-spin coupling are the same sign. Because the vicinal vinylic proton-proton couplings are known to be positive, the P-C-H and both P-C-C-H couplings must be positive here. The ratio of the *cis*-P-C-C-H coupling and *trans*-P-C-C-H coupling in this compound is about the same as the corresponding proton-proton case. This may reflect a similar angular dependence, and possibly the same coupling terms of the same sign as in the proton-proton case are the important ones. One would thus expect the H-C-C-P coupling to be positive even when no unsaturation exists in the bond between the coupled nuclei. Very recently we[37] have analyzed the extremely complex ^{31}P spectrum of triethylphosphine. The asymmetry of the ^{31}P spectrum was only consistent with the H-C-C-H and H-C-C-P couplings being the same sign. This result would seem to unequivocally support the qualitative arguments given above.

Based on the discussion given above the ^{31}P bonding orbitals in phosphines increase their s character on going from phosphine to dimethylphosphine. The changes are surely different for the orbitals to hydrogen than to carbon. This slight hybridization change is reflected in a gradual increase of the value of the P-H coupling from 182.2 cps[14] in phosphine to 191.03 cps in dimethylphosphine. If the Fermi contact term is the most important contribution to the P-H coupling, then there should exist an approximate linear relation between the per cent s character and the magnitude of this coupling as has been discussed for the ^{13}C-^{1}H coupling constant.[38] It can be estimated[39] using the known H-P-H bond angles that there is 6.2% s character in the phosphorus bonding orbitals in phosphine. Thus one can obtain the relation $J_{\mathrm{P-H}} = 29.30s_{\mathrm{P}}$, where s_{P}

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[23] A recent discussion of the Fermi contact contributions to the geminal H-C-H coupling has been given by M. Barfield and D. M. Grant, *J. Am. Chem. Soc.*, **85**, 1899 (1963).

[24] Three attempts to estimate these contributions to couplings in other molecules than hydrogen are given by G. A. Williams and H. S. Gutowsky, *J. Chem. Phys.*, 30, 717 (1959); J. A. Pople, *Mol. Phys.*, **1**, 216 (1958); and J. V. Hatton, W. G. Schneider, and W. Siebrand, *J. Chem. Phys.*, **39**, 1330 (1963).

[25] However, see ref 22 as regards these contributions to directly bonded couplings.

[26] C. C. Loomis and M. W. P. Standberg, *Phys. Rev.*, **81**, 798 (1951).

[27] For methyl phosphine, see E. L. Breig and C. C. Liu, *J. Chem. Phys.*, **35**, 2139 (1961).

[28] For dimethylphosphine, see R. Nelson, *ibid.*, **39**, 2382 (1963).

[29] For trimethylphosphine see D. R. Lide, Jr., and D. E. Mann, *ibid.*, **28**, 572 (1958).

[30] (a) P. T. Narasimhan and M. T. Rogers, *ibid.*, 34, 1049 (1961); (b) J. B. Hendrickson, M. L. Maddox, J. J. Sims, and H. D. Kaesz, *Tetrahedron*, **20**, 449 (1964).

[31] In aliphatic methylene groups this coupling has been shown to be negative relative to the ^{13}C-H (see ref 10a,b,d) while for oxiranes it has been shown to be positive (see ref 4i).

[32] See, for example, ref 10d, and R. M. Lynden-Bell and N. Sheppard, *Proc. Roy. Soc.* (London), **A269**, 385 (1962).

[33] M. Karplus, *J. Chem. Phys.*, **36**, 11 (1959).

[34] H. Conroy, *Advan. Org. Chem.*, **2**, 265 (1960).

[35] E. Hiroihi, *J. Phys. Soc. Japan*, **15**, 270 (1960).

[36] J. Ranft, *Anal. Phys.*, **8**, 322 (1961); **9**, 124 (1962).

[37] S. L. Manatt and C. A. Reilly, unpublished work. As is noted in Table II we find slightly different parameters then previously reported (ref 30) for this molecule. Our results are based on frequency sweep 100-Mc spectra which were fitted iteratively.

[38] See, for example, C. Juan and H. S. Gutowsky, *J. Chem. Phys.*, **37**, 2198 (1962).

[39] Using the treatment given by L. Pauling in "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960, Chapter 4.

is the per cent s character of a phosphorus orbital to hydrogen. From this relation it is calculated that the s character values of the phosphorus bonding orbitals to a proton in methyl- and dimethylphosphine are 6.4 and 6.5%, respectively. These are indeed very small changes in hybridization. With this formula the value of the unreported P–H coupling in the phosphonium cation, where s_P should be 25%, is estimated as 740 cps. This is significantly more than that observed for the trimethylphosphonium cation where is it 515 cps.[40] Part of this discrepancy is surely due to the approximate treatment but part could be attributed to the possibility that steric interactions between the methyl groups open the C–P–C angles in this cation, thus preempting some of the s character from the P–H bond. In $H(OH)_2PO$, $H(CH_3O)PO$, and $H(C_2H_5O)_2PO$ the P–H coupling are reported as 707, 710, and 701 cps, respectively.[41] These systems would be expected to have larger P–H couplings than the P^+H_4 cation based on Bend's recent arguments concerning rehydridization occurring about an atom when one group is replaced by another more electronegative group.[42] Bend's arguments suggest that of the orbitals about an atom there will be more p character present in those orbitals to the more electronegative groups.

It appears that a good linear relation between the ^{31}P–^{1}H coupling and s character does not exist as in the case of ^{13}C–^{1}H couplings. However, the qualitative aspects of this relation may be useful. The only exception appears to be the diphosphite anion[43] where the H–P coupling is reported to be only 441 ± 50 cps. Because the phosphorus spectrum for this anion appears to be rather strongly coupled, perhaps the analysis should be reconsidered in light of the fact that the H–P–P coupling may be negative in this anion as is the H–C–P coupling when the terminal ^{31}P atom is close to sp^3 hybridized.

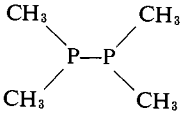
The geminal H–C–P coupling in trivinylphosphine has been shown to be positive.[7] In this compound it is expected that steric crowding should open up the C–P–C angle with parallel increase of s character in the phosphorus bonding orbitals possibly to a degree similar to that for triethylphosphine. This should cause the negative contribution to the H–C–P coupling to increase in magnitude and possibly to approach in magnitude that in triethylphosphine. The fact that the observed H–C–P coupling is positive we interpret as showing that in the fragment H–C–P, if the hybridization of the carbon atom orbitals increases in s character, a contribution to the H–C–P coupling, which is absolutely positive in magnitude, increases significantly. This same trend is borne out from comparison of the H–C–P coupling for[30b] the cations

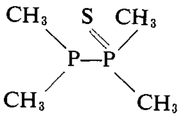
$$CH_3\overset{+}{P}(C_6H_5)_3I^- \qquad CH_3OCH_2\overset{+}{P}(C_6H_5)_3I^-$$

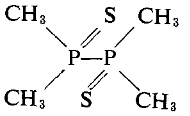
$$J_{H-C-P} = |13.2|\ \text{cps} \qquad |4|\ \text{cps}$$

In the first cation the large H–C–P coupling is most certainly negative and is not much different from the |14.4| cps for the tetramethylphosphonium cation.[30b] Substituting oxygen for one of the protons of the methyl groups causes the carbon atom to rehybridize such that the carbon bonding orbitals to the methylene protons and to the phosphorus have increased s character.

The recent relative sign results of Harris and Hayter[44] on tetramethyldiphosphine (IV), tetramethyldiphosphine sulfide (V), and tetramethyldiphosphine disulfide (VI) deserve some comment. The H–C–P coupling in IV is +6.9 cps, which is significantly greater than that of +3.37 cps for dimethylphosphine (I). This large difference is surely a composite of effects reflecting the difference between H– and $(CH_3)_2P$– as substituents and certainly is not simple describable in terms only of changes in phosphorus orbital s character. *A priori*, the hybridization of the phosphorus bonding orbitals to carbon in IV would be expected to be close to that in I because hydrogen and phosphorus have nearly the same electronegativities. Perhaps the increase in the H–C–P coupling in IV of 3.5 cps over that in I can be ascribed as due to transmission mechanism not linked to hybridization changes of the phosphorus bonding orbitals to carbon. The most useful comparison are made within the set IV, V, and VI. In IV and V the H–C–P coupling involving trivalent phosphorus should be positive while that in V and VI can all be taken positive with some confidence.

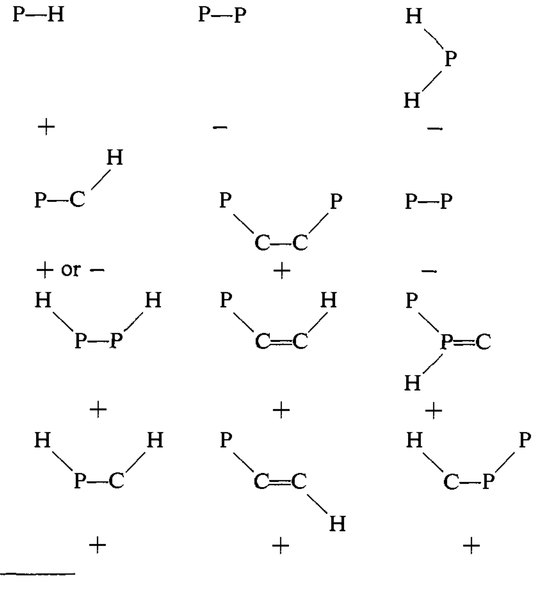

IV


V


VI

Conclusion

The qualitative analysis presented above was given in order to arrive at a description of some of the important structural factors contributing to the nuclear spin-spin coupling in the phosphorus-containing molecules. The following coupling constant absolute signs prevail.



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[40] B. Silver and Z. Luz, *J. Am. Chem. Soc.*, **83**, 786 (1961).

[41] See J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High-Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959.

[42] H. A. Bend, *Chem. Rev.*, **61**, 275 (1961).

[43] C. F. Callis, J. R. Van Wazer, J. N. Shoolery, and W. A. Anderson, *J. Am. Chem. Soc.*, **79**, 2719 (1957).

[44] R. K. Harris and R. G. Hayter, *Can. J. Chem.*, **42**, 2282 (1964).

It is possible that the following types of couplings also have the signs indicated.

H—C—N—P　　　H—C—O—P
　　+　　　　　　　+

The available data concerning the signs and magnitude of the H–C–P coupling have caused some confusion. The changes of this coupling seem to be well described by the following two rules: (1) in the H–C–P fragment the geminal coupling becomes either less positive or more negative as the s character of the phosphorus atom bonding orbitals to carbon increases; (2) in the H–C–P fragment the geminal coupling becomes either more positive or less negative as the s character of the carbon atom bonding orbital to phosphorus increases.

We take the trends described by these rules as evidence that these couplings involving phosphorus and protons result primarily from at least two large Fermi contact contributions which nearly cancel. Such a situation appears to prevail also in the cases of the H–C–H and ^{13}C–C–^{1}H couplings. The proton-phosphorus couplings between nuclei separated by three bonds appear to be positive, and the multiplicity of coupling contributions existing for the geminal coupling do not seem evident for these vicinal couplings. All the results discussed here are consistent with the ^{31}P–^{1}H coupling being positive, and the changes of this coupling with phosphorus orbital s character are qualitatively in the same absolute direction as those observed for changes of the ^{13}C–^{1}H coupling with carbon orbital s character changes.

A General Method for Relating the Absolute Configurations of Octahedral Chelate Complexes[1]

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Contribution from the Department of Chemistry, University of Pittsburgh, Pittsburgh, Pennsylvania 15213. *Received January 17, 1966*

Abstract: A ring-pairing method is proposed for relating the absolute configurations of octahedral chelate complexes of different symmetries. The method utilizes pairs of chelate rings as they occur in *cis*-$[Co(en)_2X_2]^{n+}$. The method is demonstrated for several complexes, and it is shown to be consistent with spectroscopic (circular dichroism) data.

Confusion has arisen in the designation of the absolute configurations of optically active chelate complexes of different symmetries, *e.g.*, $[Co(en)_3]^{3+}$ and $[Co(EDTA)]^-$, because of the lack of a common basis for relating their chiralities. Absolute configurations of cobalt(III) chelate complexes have been related through optical rotatory dispersion[2] (ORD) and circular dichroism (CD) spectra[3-6] to optically active $[Co(en)_3]^{3+}$ for which the absolute configuation is known.[7] It has been suggested that the most intense CD band (or Cotton effect curve) found in the $A_{1g} \rightarrow T_{1g}$ region (16,000 to 21,000 cm^{-1} for Co(III) complexes)[8] of a given enantiomorph should have the same sign as the dominant E_a (T_{1g} parentage) transition found for the configurationally related enantiomorph of $[Co(en)_3]^{3+}$.[6] The dominant CD band has been assigned E_a parentage even when an inversion of states occurs. Such inversions resulting from changes in the crystal field strengths of the ligands sometimes are observable in CD spectra even though obscured in ORD spectra.[9]

Reference Axis

The configurations of many chelate complexes can be related to the helix described by the chelate ligands of $[Co(en)_3]^{3+}$ about the major axis, C_3. This so-called chirality is left-handed for $(+)_{589}$-$[Co(en)_3]^{3+}$, and the isomer is designated Λ (Δ is used for the mirror image isomer) using Piper's convention,[10] Figure 1. Complexes with $\mathbf{C_3}$ symmetry are much less common than those with $\mathbf{C_2}$ symmetry, *e.g.*, *cis*-$[Co(en)_2X_2]^{n+}$. The configuration of such a $\mathbf{C_2}$ complex can be designated using the pseudo-C_3 axis (X's connected by imaginary line) to relate it to $[Co(en)_3]^{3+}$, or the helix can be designated using the C_2 axis. Changing the reference axis from C_3 to C_2 changes the handedness of the helix described by the chelate rings. For example, the enantiomorph of $[Co(en)_3]^{3+}$ shown in Figure 1 could be designated $\Lambda(C_3)$ or $\Delta(C_2)$, depending on whether the reference axis is C_3 or C_2.[6,11]

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(1) This work was supported by a research grant (GM10829-08) from the Division of General Medical Studies, Public Health Service.

(2) T. E. MacDermott and A. M. Sargeson, *Australian J. Chem.*, **16**, 334 (1963).

(3) B. E. Douglas and S. Yamada, *Inorg. Chem.*, **4**, 1561 (1965).

(4) R. A. Haines and B. E. Douglas, *ibid.*, **4**, 452 (1965), and other papers in this series.

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(8) T. M. Dunn in "Modern Coordination Chemistry," J. Lewis and R. G. Wilkins, Ed., Interscience Publishers, Inc., New York, N. Y., 1960, p 291.

(9) K. Garbett and R. D. Gillard, *Chem. Commun.*, 76 (1965).

(10) T. S. Piper, *J. Am. Chem. Soc.*, **83**, 3908 (1961).

(11) Before his untimely death, Piper suggested using notation such as Δ_2 or $\Delta(C_2)$ to remove the ambiguity regarding the choice of axis when it is not the major axis. The IUPAC nomenclature commission has yet to make a recommendation concerning the symbols to be used to describe the chirality, *i.e.*, Δ and Λ or P and M. Any notation system adopted can be used for the designation of configurations by the method proposed here.