

The Relative Signs of Phosphorus-Proton Nuclear Magnetic Resonance Coupling Constants

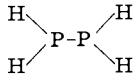
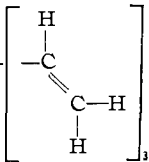



Sir:

It was suggested by Karplus¹ that an "absolute" sign determination could be made from a measurement of the sign of a nonbonded proton-X coupling constant relative to the coupling constant between a proton and a directly bonded atom X. Approximate theoretical calculations² for B-H, C¹³-H, and N-H suggest that these couplings are positive and large. Karplus' proposal has been the basis for two^{3,4} "absolute" sign determinations relating the C¹³-H coupling, which is large and taken as positive, to certain other proton-proton couplings. We would like to suggest that his proposal can be extended to the P³¹-H coupling and on this basis present a correlation of the signs of the coupling constants in some phosphorus compounds containing protons. Tiers⁵ has recently demonstrated that the C¹³-F¹⁹ coupling is a different sign from the C¹³-H coupling which demonstrates that Karplus' proposal¹ will in general probably not be valid for the coupling between directly bonded atoms X and Y (X and Y being other than hydrogen).

phosphine (III),⁸ and dimethylphosphine (IV),⁸ the recent H¹-[H¹] double resonance studies of Anderson and Freeman⁹ on trivinylphosphine (V), and our own H¹-[H¹] and H¹-[P³¹] double resonance studies on IV.¹⁰ These results are summarized in Table I.

In Table I it can be seen that the P-C-H type coupling is relatively small (except in the case of V) and this geminal coupling must be the result of near cancellation of two or more terms of different signs which could possibly include two major terms of different sign due to the Fermi contact mechanism,¹¹ spin-orbital interaction terms, and electron-dipole interaction terms. Small changes of the local electronic structure may alter the relative magnitudes of each contribution such that the sum varies. It is possible that it could vary from one sign to the other.¹² Increased alkyl substitution appears to reduce the magnitude of the H-C-P coupling in the case of the methylphosphines. We would like to suggest that in triethylphosphine (II) the sign of this coupling has been inverted relative to that of the H-C-C-P coupling by the presence of three ethyl groups on phosphorus. The results on I⁶ and V⁹ are suggestive of such an inversion of sign. We expect in ethylphosphine that the P-C-H coupling is about 1-2 c.p.s. and the

TABLE I
RELATIVE SIGNS AND MAGNITUDES OF COUPLING CONSTANTS

Compound	Ref.	Type of coupling	Relative signs	Magnitude, c.p.s.
II (CH ₃ CH ₂) ₃ P	a	P-C-H	∓	0.5
		P-C-C-H	±	13.7
		H-C-C-H	?	7.6
I 	b	P-P	∓	108.2
		H-P-P-H (<i>trans</i>)	±	10.5
		H-P-P-H (<i>cis</i>)	±	6.8
(Relative signs between group A and B indeterminate)		H-P-H	∓	12
		H-P	±	186.5
		H-P-P	±	11.9
V 	c	P-C 	±	11.74
		P-C 	±	30.21
		P-C 	±	13.62
III CH ₃ PH ₂	d	P-C-H	±	4.1
		P-H	±	186.4
		H-C-P-H	?	8.2
IV (CH ₃) ₂ PH	d	P-C-H	±	3.6
		P-H	±	191.6
		H-C-P-H	±	7.61
VII (CH ₃) ₃ P		H-C-P		2.66

^a R. M. Lynden-Bell, *Trans. Faraday Soc.*, **57**, 888 (1961). ^b T. Narasimhan and M. T. Rogers, *J. Chem. Phys.*, **34**, 1049 (1961), and J. B. Hendrickson, M. L. Maddox, J. Sims, and H. Kaesz, to be published. ^c W. A. Anderson and R. Freeman, presented at the 4th OCEANS, Mellon Institute, Pittsburgh, Pa., March 2, 1963. ^d The magnitudes of all the couplings and the relative signs of the phosphorus-proton couplings in these molecules have also been deduced from careful analyses of their proton spectra by G. M. Whitesides, J. L. Beauchamp, and J. D. Roberts, *J. Am. Chem. Soc.*, **85**, 2666 (1963).

Our correlation is based on the high-resolution analyses of diposphine (I),⁶ triethylphosphine (II),⁷ methyl-

same sign as the P-C-C-H coupling. The rather com-

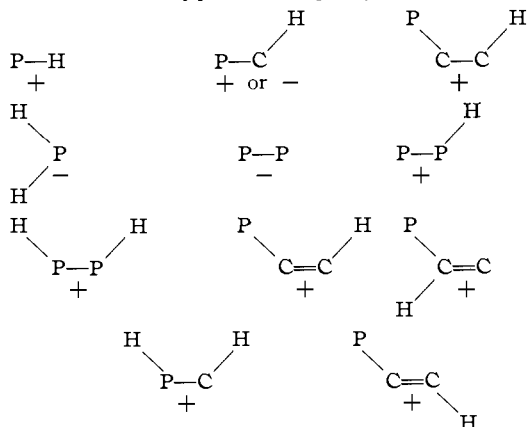
- (1) M. Karplus, *J. Am. Chem. Soc.*, **84**, 2458 (1962).
- (2) M. Karplus and D. M. Grant, *Proc. Natl. Acad. Sci. U. S. A.*, **45**, 1269 (1959); N. Muller and D. E. Pritchard, *J. Chem. Phys.*, **31**, 768, 1471 (1959); M. Karplus, *J. Phys. Chem.*, **64**, 1793 (1960).
- (3) P. C. Lauterbur and R. J. Kurland, *J. Am. Chem. Soc.*, **84**, 3405 (1962).
- (4) F. A. L. Anet, *ibid.*, **84**, 3767 (1962).
- (5) G. V. D. Tiers, *ibid.*, **84**, 3972 (1962).
- (6) R. M. Lynden-Bell, *Trans. Faraday Soc.*, **57**, 888 (1961).
- (7) P. T. Narasimhan and M. T. Rogers, *J. Chem. Phys.*, **34**, 1049 (1961); the proton spectrum of II has recently been reanalyzed by J. B. Hendrickson, M. L. Maddox, J. Sims, and H. Kaesz, who have confirmed what was originally reported for the magnitudes and relative signs of the H-C-C-P and H-C-P couplings (private communication from H. Kaesz).

- (8) G. M. Whitesides, J. L. Beauchamp, and J. D. Roberts, *J. Am. Chem. Soc.*, **85**, 2665, (1963).
- (9) W. A. Anderson and R. Freeman, presented at the 4th OCEANS, Mellon Institute, Pittsburgh, Pa., March 2, 1963.
- (10) Further details are contained in the complete paper in preparation.
- (11) S. Alexander, *J. Chem. Phys.*, **34**, 106 (1961).
- (12) A somewhat similar situation appears to exist in the case of the H-C-N and H-C-C-N couplings. The magnitudes of both these couplings are rather small (see I. D. Kuntz, P. von R. Schleyer, and A. Allerhand, *J. Chem. Phys.*, **35**, 1533 (1962)). The H-C-N coupling is zero in some cases (see J. M. Anderson, J. D. Baldeschwieler, D. C. Dittmer, and W. D. Phillips, *ibid.*, **38**, 1260 (1963)). From double resonance studies we have determined that the signs of these nitrogen-proton couplings are opposite at least in ethyl and isopropyl isonitriles (S. L. Manatt, D. D. Elleman, and J. Casanova, Jr., to be published).

plicated spectrum of this molecule is currently being investigated.

The major contributions to the H-C-C-H, H-P-C-H, and H-P-P-H couplings are expected to be similar and thus these couplings should be of the same sign. The observed magnitudes for these couplings appear to be about the same. The sign of the H-C-C-H coupling has been shown to be positive by relation to the sign of the C¹³-H coupling.^{3,4} Taking the H-P-C-H and H-P-P-H couplings as positive and reasoning from this approach, the P³¹-H coupling is positive.

Based on the data in Table I and the qualitative discussion presented above a correlation of the absolute signs of the various types of couplings can be made.



Acknowledgments.—We are indebted to Dr. Murray Geller for several discussions concerning the theoretical magnitudes of the various contributions to spin-spin coupling. We wish to thank George M. Whitesides, Jesse L. Beauchamp, and Professor John D. Roberts of the Division of Chemistry and Chemical Engineering, California Institute of Technology, for making their results available to us prior to publication.

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Relative Signs of the ³¹P-¹H and ³¹P-C-¹H Nuclear Magnetic Resonance Coupling Constants¹

Sir:

The possibility that terms other than Fermi contact interaction make significant contributions to nuclear spin-spin coupling with heavy nuclei has stimulated considerable interest in the n.m.r. spectra of compounds containing heteroatoms. In particular, relative signs and magnitudes of J_{XCH} and J_{XCCH} have been reported for ethyl derivatives of several heavy isotopes of spin $1/2$.² In order to understand better the factors responsible for spin coupling with a representative heavy nucleus, we have analyzed the spectra of $(CH_3)_3P$, $(CH_3)_2PH$, and $(CH_3)PH_2$ and have obtained relative signs and magnitudes of J_{PH} and J_{PCH} .

The proton spectrum of methylphosphine (Fig. 1) may be treated as the superposition of an A_3B_2 and an A_3X_2 spectrum, using the method of effective chemical shifts.² Inspection of the spectrum suggests that the methyl region can be separated into a triplet at lower field and a more complicated group of lines at higher field. Association of the triplet with the simpler half of

(1) Supported in part by the Office of Naval Research and the National Science Foundation.

(2) For a summary and references, see G. Klose, *Ann. Physik*, **9**, 262 (1962); P. T. Narasimhan and M. T. Rogers, *J. Chem. Phys.*, **34**, 1049 (1961).

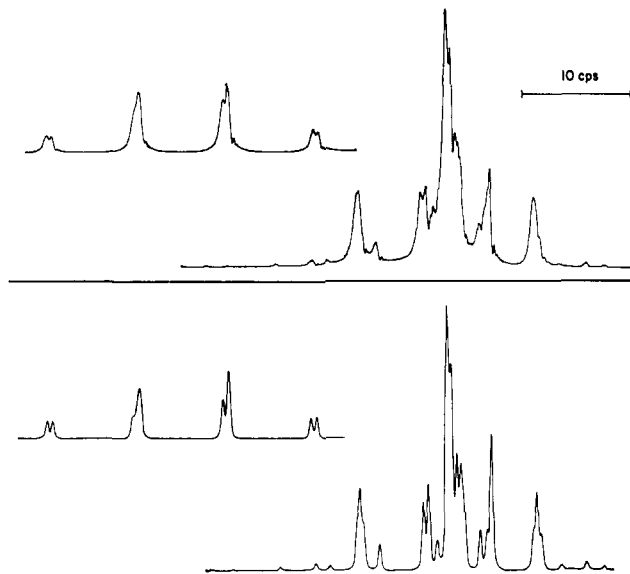


Fig. 1.—Observed (upper) and calculated (lower) proton n.m.r. spectra of methylphosphine at 60 Mc.p.s. The spectral parameters used in the calculated spectrum are given in Table I. The P-H spectrum, also occurring as the lower field part, immediately suggests that J_{PH} and J_{PCH} have the same sign. The spectrum observed for CH_3PH_2 and the spectrum calculated using the parameters in the table are shown in Fig. 1. In both methyl- and dimethylphosphine J_{PH} and J_{PCH} have the same sign; double-resonance experiments performed by Drs. G. Juvinal and S. L. Manatt of the Jet Propulsion Laboratory confirm this conclusion.

TABLE I^a
CHEMICAL SHIFTS AND COUPLING CONSTANTS FOR PHOSPHINE DERIVATIVES

Compound	J_{PH}	J_{PCH}	J_{HCPH}	ν_H	ν_{CH_3}
PH_3^b	182.2				
CH_3PH_2	± 186.4	± 4.1	8.2	157.7	58.5
$(CH_3)_2PH$	± 191.6	± 3.6	7.7	187.7	63.8
$(CH_3)_3P$		2.7			56.3

^a Chemical shifts and coupling constants were moderately temperature dependent; the values reported are for 33°. Chemical shifts are given in c.p.s. at 60 Mc.p.s. from tetramethylsilane as internal standard. ^b R. M. Lynden-Bell, *Trans. Faraday Soc.*, **57**, 888 (1961).

Anet³ has recently demonstrated by double-resonance experiments that $J^{13}CH$ and J_{HCH} have opposite sign in $H_2D^{13}COH$; Lynden-Bell and Sheppard⁴ have reached the same conclusion for $J^{13}CH$ and $J^{13}CCH$ in $H_3-^{13}C^{13}CH_3$ by analysis of the high resolution spectrum.⁴ In contrast, J_{CH} and J_{PCH} have the same sign. Theoretical treatments have indicated that contact interaction will dominate the coupling of directly bonded atoms⁵; more approximate treatments of HCH⁶ and ^{13}CCH ⁷ lead to the same conclusion.

The observed difference in relative sign of J_{XH} and J_{XCH} for X = ¹H, ¹³C and for X = ³¹P suggests that some mechanism other than the usual σ -bond interactions contribute to spin-spin coupling with phosphorus. Spin-orbital and electron-dipole interaction would be expected to be relatively more important in

(3) F. A. L. Anet, *J. Am. Chem. Soc.*, **84**, 3767 (1962).

(4) R. M. Lynden-Bell and N. Sheppard, *Proc. Roy. Soc. (London)*, **A269**, 385 (1962).

(5) M. Karplus and D. M. Grant, *Proc. Natl. Acad. Sci. U.S.A.*, **45**, 1269 (1959); N. Muller and D. E. Pritchard, *J. Chem. Phys.*, **31**, 768, 1471 (1959); J. N. Shoolery, *ibid.*, **31**, 1421 (1959).

(6) H. S. Gutowsky, M. Karplus, and D. M. Grant, *J. Chem. Phys.*, **31**, 1278 (1959), and references therein.

(7) G. T. Karabatsos, J. D. Graham, and F. Vane, *J. Phys. Chem.*, **65**, 1657 (1961).