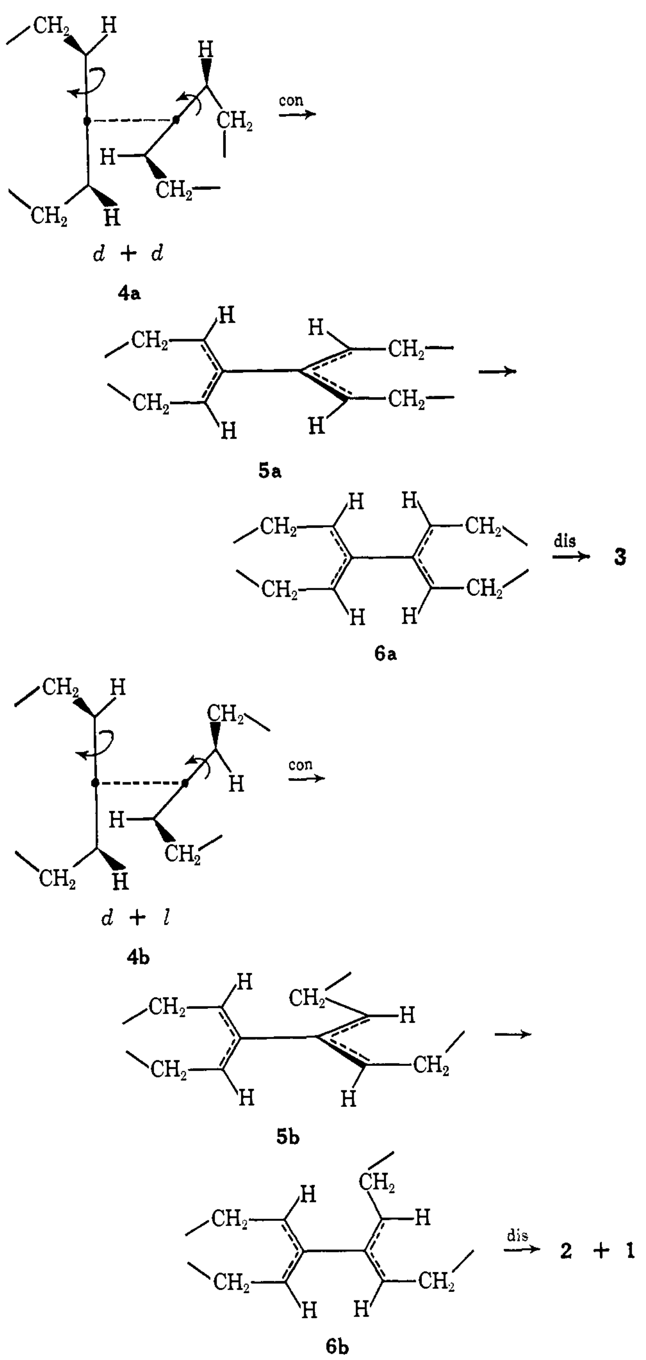
Scheme I



i.e., having a disrotatory "joining" followed by a conrotatory closure from either **5** or **6** (*e.g.*, **4a** → **5b** → **6b** → **3**), will not change the stereochemical predictions. However, the conrotatory "joining" shown in Scheme I may follow if the transition state **4** is stabilized by the equivalent of spiroconjugation.[14] While such interaction probably is very small in **5**, it could be significant in **4** if twisting is much farther advanced than bending. Disrotatory closure of **6** is predicted from orbital symmetry arguments if one assumes a singlet state for this species.

Granting that the success of the Woodward-Hoffmann predictions argues strongly for a concerted reaction in this case, we suggest that in general one must consider the possibility that intermediates both appear and react stereospecifically.

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(14) (a) H. E. Simmons and T. Fukunaga, *J. Am. Chem. Soc.*, **89**, 5208 (1967); (b) R. Hoffmann, A. Imamura, and G. D. Zeiss, *ibid.*, **89**, 5215 (1967).

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Nuclear Magnetic Resonance of Phosphorus Compounds. V. Signs of Geminal Coupling Constants between Protons on Phosphorus[1]

Sir:

We wish to report measurements of the magnitudes and multiple resonance determinations of the signs of the geminal nmr coupling constants, J_{HPH}, between protons bonded to phosphorus of different coordinations.[2] These results are important in light of the observed changes of the corresponding coupling between protons on carbon[3] and a recent approximate theoretical treatment of the latter couplings.[4]

Our results are presented in Table I.[5] The magnitudes of the J_{HPD}'s (and hence J_{HPH}'s) were obtained from the ^1H spectra. The signs of J_{HPD} relative to J_{PD} and J_{PH} were established by a variety of multiple resonance experiments. These included selective irradiation of single lines that gave rise to Overhauser effects[6] and/or splittings[7] and indor experiments where either a ^1H or ^{31}P line was continuously observed while an irradiating frequency was swept through an appropriate portion of the rest of the spectrum.[8,9]

Table I. Signs and Magnitudes of Geminal Proton-Proton Coupling Constants in Some Phosphorus Compounds

Compound	J_{HPD}[a]	J_{HPH}[a,b]	H-P-H bond angle, deg
CH_3PHD	−2.04	−13.4	93.4[c]
PH_2D	−2.03	−13.3	93.3[d]
C_6H_5PHD	−2.00	−13.1	. . .
CF_3PHD	−1.90	−12.5	97.4 ± 1.5[e]
PH_3D^+	<|0.2|	<|1.3|	109.47[f]
$(CH_3)_2PHD^+$	+0.51	+3.3	. . .
O_2PHD^-	+5.35	+35.1	92[g]

[a] In Hz. [b] Calculated from J_{HPD} taking $\gamma_H/\gamma_D = 6.55$. [c] E. L. Breig and C. C. Liu, *J. Chem. Phys.*, **35**, 2139 (1961). [d] C. C. Loomis and M. W. P. Standberg, *Phys. Rev.*, **81**, 798 (1951). [e] I. Y. M. Wang, C. O. Britt, A. H. Cowley, and J. E. Boggs, *J. Chem. Phys.*, **48**, 812 (1968). [f] Assumed. [g] Reference 11.

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(1) Previous paper in this series: S. L. Manatt, D. D. Elleman, A. H. Cowley, and A. B. Burg, *J. Am. Chem. Soc.*, **89**, 4544 (1967).

(2) Previous data on the sign of J_{HPH} were from the analysis of the biphosphine spectrum which could only be accommodated if J_{HPH} is the same sign as J_{PP} which is a different sign from the J_{HPPH}'s [R. M. Lynden-Bell, *Trans. Faraday Soc.*, **57**, 888 (1961)], and from preliminary analysis of the spectra of chloromethylphosphine and ethylphosphine whose spectra are best fitted if J_{HPH} and J_{HCH} are both the same sign and negative (unpublished work of S. L. Manatt).

(3) See A. A. Bothner-By, *Advan. Magnetic Resonance*, **1**, 149 (1965); R. C. Cookson, T. A. Grabb, J. J. Frankel, and J. Hudes, *Tetrahedron, Suppl.*, **7**, 355 (1966).

(4) J. A. Pople and A. A. Bothner-By, *J. Chem. Phys.*, **42**, 1339 (1965).

(5) We are grateful to Dr. W. D. White for the synthesis of C_6H_5PHD.

(6) K. Kuhlman and J. D. Baldeschwieler, *J. Am. Chem. Soc.*, **85**, 1010 (1963).

(7) R. Freeman and W. A. Anderson, *J. Chem. Phys.*, **37**, 2053 (1962).

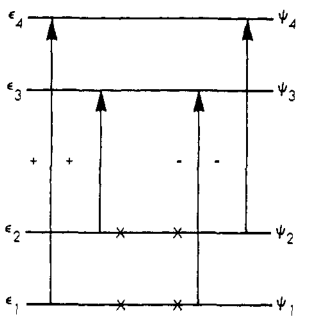

Figure 1. Molecular orbitals and excitations for the H-X-H system; sign of each contribution to contact term is given at the left of the corresponding excitation.

The most obvious features of the results in Table I is that J_{HPH} is negative for the tricoordinated phosphorus compounds and approximately zero or positive for the tetracoordinate species.[10] In the case of PH_3D^+, it was impossible to resolve the H-P-D coupling, and hence the value in Table I represents an upper limit for J_{HPD}. In the phosphorus-31 spectrum of a mixture of phosphonium and deuterated phosphonium cations all the species PH_4^+, PH_3D^+, $PH_2D_2^+$, PHD_3^+, and PD_4^+ give rise to their expected multiplets. Thus, we conclude that the unresolvable J_{HPD} is not the result of an exchange process.

Based on available structural data, it appears that opening out of the geminal H-P-H bond angle leads to an algebraic increase in the proton-proton coupling. In this sense J_{HPH} resembles J_{HCH} where increasing the H-C-H angle from tetrahedral to trigonal increases J_{HCH} from -12.5 to $+2.4$ Hz.[3] It is also apparent that the variation of the H-P-H angle is not the only significant factor because the anion O_2PHD^- has the largest J_{HPH}, yet the H-P-H angle is only about 92°.[11] At this point it is not clear whether the formal negative charge or the electronegative substituents contribute the most to increasing J_{HPH} in this anion. In the $-CH_2-$ fragment neighboring oxygen increases J_{HCH} algebraically by both inductive and lone-pair conjugative effects.[3,4]

Our results for this series of molecules may also be understood qualitatively in terms of the Pople and Bothner-By molecular orbital treatment of geminal H-X-H couplings.[4] In this model two bonding (ψ_1 and ψ_2) and two antibonding (ψ_3 and ψ_4) molecular orbitals are constructed from two H(1s) atomic orbitals and two sp hybrid orbitals centered on atom X. The excitations $\psi_1 \rightarrow \psi_4$ (see Figure 1) and $\psi_2 \rightarrow \psi_3$ lead to positive contributions to the contact term while the excitations $\psi_1 \rightarrow \psi_3$ and $\psi_2 \rightarrow \psi_4$ lead to negative contributions. The single most dominant term is $\psi_2 \rightarrow \psi_3$ because the excitation energies appear in the denominator of the contact coupling expression. As nitrogen is replaced by phosphorus in this treatment, it would be anticipated that the separation between the bonding and antibonding levels would decrease. Thus, the positive contribution from the $\psi_2 \rightarrow \psi_3$ excitation should become more important, making J_{HXH} more positive for phosphorus compounds than for nitrogen compounds.[12] This may explain why J_{HPH} is very small in the phosphonium cation [or slightly positive in $(CH_3)_2PH_2^+$] while J_{HNH} is negative in ammonium cation.[13] A similar variation in the energies of ψ_2 and ψ_3 may explain the sign inversion on changing the coordination number of phosphorus from three to four.

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(8) E. B. Baker, *J. Chem. Phys.*, **37**, 911 (1962).

(9) Performed with a modified HA-100 spectrometer whose 100- and 40.4-MHz frequencies were derived from the same source; details to be published.

(10) Our results are based on the assumption that J_{PH} and J_{PD} are always positive for both tri- and tetracoordinate phosphorus. This assumption has been discussed previously in detail [S. L. Manatt, G. L. Juvinall, R. I. Wagner, and D. D. Elleman, *J. Am. Chem. Soc.*, **88**, 2689 (1966)]; more recently it has been confirmed by double resonance studies on compounds with various coordination of phosphorus [W. McFarlane, *J. Chem. Soc., A*, 1148 (1967); S. L. Manatt, M. T. Bowers, and H. Goldwhite, unpublished work.

(11) In ammonium hypophosphite the H-P-H angle is 92°: W. H. Zachariasen and R. C. L. Mooney, *J. Chem. Phys.*, **2**, 34 (1934); M. L. Huggins, *Phys. Rev.*, **21**, 719 (1923).

(12) Similar arguments have been presented by H. Dreeschamp and C. Schumann, *Chem. Phys. Letters*, **1**, 555 (1968), to explain why the J_{HXH} couplings algebraically increase in the order X = Sn > Ge > Si > C.

(13) The sign of J_{HND} in deuterated ammonium ions has been determined to be opposite to the J_{ND} and J_{NH} couplings by W. McFarlane and R. R. Dean, *J. Chem. Soc., A*, 1535 (1968). There is good reason to believe that J_{ND} and J_{NH} are always positive; see J. A. Pople and D. P. Santry, *Mol. Phys.*, **8**, 1 (1964).

(14) NRC Resident Research Associate, Jet Propulsion Laboratory, 1967-1968.

(15) Supported under Contract No. NAS 7-100 by the National Aeronautics and Space Administration.

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Isolation of μ_4-Oxo-penta-μ-acetato-μ-trichloroacetato-tetraberyllium, $Be_4O(CH_3CO_2)_5(CCl_3CO_2)$

Sir:

We have been unable to find an adequately documented report of the isolation of a pure metal mixed carboxylate. Perhaps this is because in many instances rapid ligand exchange would prevent the isolation of a compound containing a given mixed carboxylate ratio. In instances where ligand exchange would be slow, similar solubilities of compounds with varying ratios of different carboxylate groups would militate against the isolation of one member in a series. A number of attempts to prepare mixed basic beryllium carboxylates have been made. Tanatar and Kurowski[1] claimed to have prepared specific mixed carboxylates, *e.g.*, $Be_4O(CH_3CO_2)_3(C_2H_5CO_2)_3$. However, Marvel[2] and Hardt[3] have demonstrated that the "compounds" were actually mixtures of intramolecular mixed carboxylate compounds of the general formula $Be_4(RCO_2)_x(R'CO_2)_{6-x}$ where $0 < x < 6$. A claim for the existence of acetate-monochloroacetate mixed carboxylates has been made by other workers[4] based on phase diagrams. For reasons presented below we do not believe pure compounds were present in the latter study.

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(1) S. Tanatar and E. Kurowski, *J. Russ. Phys.-Chem. Soc.*, **39**, 936 (1907); *Chem. Zentr.*, 791 (1908).

(2) C. S. Marvel and M. M. Martin, *J. Am. Chem. Soc.*, **80**, 619 (1958).

(3) H. Hardt, *Z. Anorg. Allgem. Chem.*, **314**, 210 (1962).

(4) A. V. Novoselenova and K. N. Semenenko, *Zh. Neorg. Khim.*, **1**, 2344 (1956).