observed in ^{1}H–[^{1}H] experiments.[3] Complete decoupling of protons leads to ^{31}P enhancements of 0.5 for $(CH_3O)_3P$ and 0.0 for $(CH_3)_3P$.

If a highly degenerate ^{1}H spectral line is irradiated in frequency-sweep experiments, as in Figure 2d, small changes (0.01 cps) in the ^{1}H frequency inside the apparent ^{1}H line width (0.15–0.30 cps) cause significant changes in ^{31}P Overhauser patterns. Systematic studies show that the ^{31}P lines with positive and negative components arise because the line widths of some ^{1}H transitions, part of a degenerate ^{1}H spectral line, are significantly less than the apparent line width. This indication of significantly different T_2's for transitions belonging to different symmetry classes of energy levels is a heretofore unrealized complicating effect to the interpretation of Overhauser experiments. This effect is not observed if the line irradiated belongs to a single symmetry class.

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Nuclear Magnetic Resonance of Phosphorus Compounds. IV. The Signs of Fluorine–Phosphorus Coupling Constants[1,2]

Sir:

Although the magnitudes of a number of fluorine–phosphorus nuclear magnetic resonance coupling constants in fluorine- and phosphorus-containing molecules have been reported,[3] only in a few instances have phosphorus–fluorine coupling-constant relative signs been established.[4] As a part of a general study of the magnitudes and signs of nuclear resonance spin–spin coupling constants and because the absolute signs of these coupling constants are intimately related to the nature of molecular wave functions,[5] we report here the signs of certain phosphorus–fluorine spin–spin coupling constants.

We have performed double-resonance studies on the compounds listed in Table I with the results indicated. The relative signs were established from transitory selective irradiation experiments,[6] tickling experiments,[7] or partial collapse of multiplet structures with larger irradiation fields[8] in the following types of double-resonance experiments: ^{31}P–[^{1}H], ^{31}P–[^{19}F], ^{19}F–[^{19}F], ^{1}H–[^{31}P], and ^{19}F–[^{31}P]. The interpretation and experimental effort were greatly reduced by simultaneous observation of the ^{31}P and ^{19}F spectra or the ^{31}P and ^{1}H spectra as described in the accompanying paper.[2] The ^{31}P frequency was always held constant and either the ^{19}F or ^{1}H frequency was changed.

Table I. The Signs of the Nuclear Magnetic Resonance Spin–Spin Coupling Constants between Phosphorus-31 and Fluorine-19 in Fluorophosphines

Compound	Type of nuclear spin–spin coupling	Sign
1. CF_3PH_2	F–C–P	+
	F–C–P–H	+
	P–H	+
2. $(CF_3)_2PH$	F–C–F	+
	F–C–P–H	+
	P–H	+
3. CF_3PF_2	F–C–P	+
	F–C–P–F	−
	P–F	−
4. $(CF_3)_2PF$	F–C–P	+
	F–C–P–F	−
	P–F	−
5. $CF_3CF_2PCl_2$	F–C–P	+
	F–C–C–P	+
	F–C–C–F	−
6. $CF_3^ACF_2^BCF_2^CPCl_2$	F–C–P	+
	F–C–C–P	+
	F–C–C–C–P	+
	F^A–C–C–F^B	−
	F–C–C–C–F	+
	F^B–C–C–F^C	?[a]
7. $(CF_3)_2P–P(CH_3)_2$	F–C–P	+
	F–C–P–P	+
	P–P	−
	H–C–P	+
	H–C–P–P	+
	F–C–P–P–C–H	+
8. $CF_3\overset{-}{P}—\overset{+}{P}(CH_3)_2$	F–C–$\overset{-}{P}$	+
	F–C–$\overset{-}{P}$–$\overset{+}{P}$	+
	$\overset{-}{P}$–$\overset{+}{P}$	−
	H–C–$\overset{+}{P}$	−
	H–C–$\overset{+}{P}$–$\overset{-}{P}$	+
	F–C–P–P–C–H	?

[a] Probably −.

The absolute signs given in Table I are based on the assumption that the sign of the directly bonded P–H coupling is absolute positive and that the signs of the F–C–C–F and F–C–C–C–F couplings are negative and positive, respectively.[9] The relation of the sign of the P–H coupling to the signs of certain proton–proton

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[2] Previous paper in this series: D. D. Elleman, S. L. Manatt, A. J. R. Bourn, and A. H. Cowley, *J. Am. Chem. Soc.*, **89**, 4542 (1967).

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[4] (a) W. Mahler, *J. Am. Chem. Soc.*, **86**, 2306 (1964); (b) R. K. Harris and C. M. Woodman, *Mol. Phys.*, **10**, 437 (1966).

[5] See M. Barfield and D. M. Grant in "Advances in Magnetic Resonance," J. S. Waugh, Ed., Academic Press Inc., New York, N. Y., 1965, pp 149–193, and references cited therein.

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[9] R. K. Harris (private communication) has also found the same relative signs as reported here for the couplings in $(CF_3)_2PF$. In addition, he has found in $(CF_3)_2PSCF_3$ the relative signs for the F–C–P(±), F–C–P–S–C–F(±), and F–C–S–P(±) couplings. The latter coupling is closely analogous to the F–C–P–P couplings in $(CF_3)_2P–P(CH_3)_2$ and $CF_3P–P(CH_3)_3$ and the same sign as the F–C–P coupling.

couplings has been discussed in detail elsewhere.[10] The signs of the two fluorine–fluorine couplings above have also been related directly to proton–proton couplings.[11] The P–C–F coupling was common to many of the fluorophosphine derivatives. The absolute signs given in Table I were in some cases based on the positive sign for this coupling. A careful scrutiny of the changes of the magnitude of the P–C–F coupling with the nature of the substituents in phosphines strongly suggests that no inversion of the sign of this coupling is likely for known fluorophosphines.[12] The P–F coupling is negative which is similar to the sign of the directly bonded Si–F coupling.[13,14] The results for CF_3P^{-}–$P^{+}(CH_3)_3$ and $(CF_3)_2P$–$P(CH_3)_2$ establish that the directly bonded P–P coupling constant is negative even between phosphorus nuclei of significantly different valences.[15] The F–C–P–F coupling is negative as is the analogous F–C–C–F coupling. The signs found in this study suggest that ^{31}P in general participates electronically in coupling to ^{19}F in a manner reminiscent to that of ^{1}H. Phosphorus appears to play a role similar to a carbon atom in a series of atoms in the bonding fragment between coupled nuclei.

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(14) The signs of the couplings which we refer to in this work are those for the so-called reduced coupling defined as $K_{ij} = (2\pi/\hbar\gamma_i\gamma_j)J_{ij}$. This parameter is independent of nuclear properties and reflects directly the magnitude of electronic interactions. In the case of ^{29}Si, $\gamma_{^{29}Si}$ is negative so although J_{Si-F} is positive, K_{Si-F} is negative.

(15) In support of the results presented here R. K. Harris (private communication) has recently found in double-resonance experiments on $(CH_3)_2P$–$P(CH_3)_2$ that the P–P coupling is negative relative to the directly bonded C–H coupling.

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Kinetics of *cis–trans* Isomerizations by Differential Thermal Analysis

Sir:

In the course of other investigations utilizing differential thermal analysis, we became aware of the potentialities of this technique for the determination of the kinetics and energetics of thermally induced reactions such as *cis–trans* isomerizations. We have focused our initial attention on the *cis*-to-*trans* isomerization of stilbene because this system has been extensively studied.[1-3]

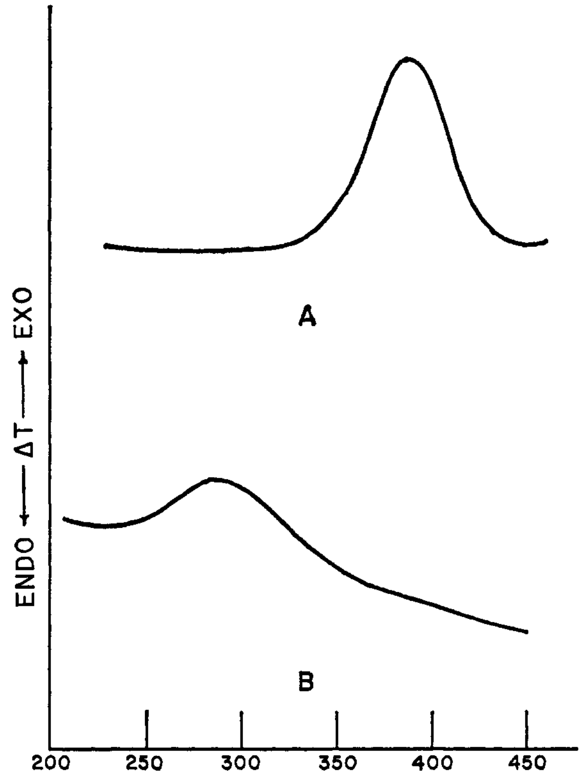

Figure 1. Thermograms for stilbene (A) and for stilbene with 10% palladium on charcoal as a catalyst (B).

While the technique of differential thermal analysis is not new, recent advances in instrumentation have greatly increased the sensitivity and reliability of the method. Review articles have discussed the instrumentation and the application of the method to inorganic, organic, and polymer systems.[4]

A number of papers have appeared which discuss the application of differential thermal analysis to the determination of kinetic parameters.[5-7] We have used the method of Piloyan, *et al.*,[7] to determine the activation energy of the spontaneous *cis*-to-*trans* isomerization of stilbene.

Whereas rate parameters are normally determined at a constant temperature, in differential thermal analysis the temperature is increased at a constant rate until eventually the equilibrium state is reached. Conversion occurs over a temperature range rather than at one temperature. Plot A of Figure 1 shows the thermogram obtained with *cis*-stilbene in a sealed cell using the Du Pont Model 900 differential thermal analyzer. Conversion to the *trans* form occurs rapidly and spontaneously once a temperature of about 300° is reached. The peak in the thermogram occurs at 385°, and the reaction is essentially completed at 440°. Only solid material could be isolated from the reaction product. This melted at 124°, the melting point of *trans*-stilbene.

The thermogram obtained when *cis*-stilbene is heated in a closed system with an equal quantity of 10% palla-

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